Development of sugarcane activated carbon as a low-cost absorbent for the removal of arsenic from drinking water

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To the millions of Mexicans who dare to dream of a better future and to those who tirelessly work to build a Mexico with more social justice and less inequities.

Abstract

Arsenic contamination is an issue of special concern for middle and low income countries (MLICs) with widespread arsenic contamination of drinking water supplies. The economical, political and cultural circumstances in some of these countries challenge implementation of successful mitigation programmes. Some of these issues were investigated with a self-administered survey to professionals working in arsenic mitigation in MLICs. The survey had a low response rate and a high proportion of answers related to Bangladesh. Results suggested that arsenic mitigation progress in Bangladesh has been modest. The main issues affecting arsenic mitigation are: achieving a balance between economical sustainability of programmes and accessibility; bridging the knowledge-behaviour gap; the low priority given to mitigation; independent evaluation of programmes; and monitoring of arsenic-safe options. Although arsenic removal technologies have low user acceptability, their use may be necessary when there is no access to piped water supply and when surface water and groundwater are contaminated with arsenic.

A sugarcane activated carbon (SCAC) was developed in this research for arsenic adsorption with a view to deployment in MLICs. A 2^3 factorial experimental design was successfully applied to optimise the preparation conditions that maximised arsenic(V) and arsenic(III) adsorption, with a resulting carbonisation temperature of 700 °C and activation temperature of 900 °C. The surface area and micropore/pore volume ratio of SCAC samples were strongly correlated ($p < 0.050$) with arsenic(V) and arsenic(III) adsorption.

The arsenic adsorption capacity of one of the prepared SCAC samples (SC07) and a commercial activated carbon (CAC; lignite granular activated carbon type Darco® 12x20) was investigated in batch experiments. Adsorption was faster with SC07 than with CAC, and adsorption of arsenic(V) was faster than arsenic(III). Adsorption was more sensitive to the initial pH condition for SC07 than for CAC, but higher adsorption was achieved with SC07. The optimal pH for arsenic removal with SC07 was between 5 and 9, and is therefore in the range of most natural waters. The Langmuir isotherm was found to fit the SC07 adsorption data, with monolayer adsorption capacities (Q_m) of 481-653 $\mu g\ g^{-1}$ and b parameters of 1.40-4.82 $L\ mg^{-1}$.

In comparing the cost of removing 1 g of arsenic using SC07 with removing 1 g using a commercial product such as Alcan activated alumina, it is concluded that SC07 has the potential to be economically cheaper than conventional treatments. However, the production cost of SCAC may vary from one geographical region to another depending on factors such as the availability of the raw material, transportation costs and marketing costs.

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Acronyms and abbreviations

AC	Activated carbon
ANOVA	Analysis of variance
BEC-LU	Bengal Engineering College and Lehigh University
BET	Brunauer-Emmett-Teller
BGS	British Geological Survey
BSCS	British Soil Classification System
BUET	Bangladesh University of Engineering Technology
CAC	The lignite granular commercial activated carbon type Darco® 12x20 from Sigma-Aldrich
CCT	Collision cell technology
CIM	Composite iron matrix
cps	Counts per second
DANIDA	Danish International Development Assistance
DFID	United Kingdom Department for International Development
DR	Dubinin-Radushkevich
DWQ	Drinking Water Quality
EPA	US Environmental Protection Agency
ETV-AM	Environmental Technology Verification Arsenic Mitigation Programme
FAST	Fixed-bed Adsorption Simulation Tool
GoB	Government of Bangladesh
HICs	High income countries

HSDM	Homogeneous surface diffusion model
ICP-MS	Inductively coupled plasma mass spectrometry
IDL	Instrument detection limit
IUPAC	International Union of Pure and Applied Chemistry
MDL	Method detection limit
MIT	Massachusetts Institute of Technology
MLICs	Middle and low income countries
NGOs	Non-governmental organisations
NL-DFT	Non-linear density functional theory
O&M	Operation and maintenance
RAHLART	Rapid Assessment of Household Level Arsenic Removal Technologies
SCAC	Sugarcane activated carbon
SEM	Scanning electron microscopy
TCLP	Toxicity Characteristic Leaching Procedure
UN	United Nations
WHO	World Health Organisation

Nomenclature

ϵ	Random error term in the 2^3 factorial model equation
%As(III).R	Per cent arsenic(III) removal
%As(V).R	Per cent arsenic(V) removal
%As.R	Arsenic removal percentage
%yield	Yield of activated carbon
ΔpH	change in pH
$1/n$	Freundlich dimensionless parameter related to the energy of adsorption
As_0	Initial arsenic(V) or arsenic(III) concentration in $\mu g\ L^{-1}$
As_f	Final arsenic(V) or arsenic(III) concentration in $\mu g\ L^{-1}$
As_t	Arsenic concentration at time t in $\mu g\ L^{-1}$
AT	Activation temperature in °C
At	Activation time in minutes
b	Langmuir's parameter related to the energy of adsorption
c	Constant in the BET equation that determines the shape of the knee on the isotherm plot
C_e	Arsenic concentration in the aqueous phase at equilibrium in $\mu g\ L^{-1}$
C_i	Parameters in the 2^3 factorial model equation
CT	Carbonisation temperature in ºC
Ct	Carbonisation time in minutes
Eh	Redox potential
HR	Heating rate in °C min^{-1}

I	Ionic strength in mol L^{-1}
K	Freundlich relative sorption capacity in $(\mu g\ g^{-1})\ (\mu g\ L^{-1})^{-1/n}$
k_1	Pseudo first-order adsorption rate constant in min^{-1}
k_2	Pseudo-second order adsorption rate constant in g $\mu g^{-1}\ min^{-1}$
m	mass of adsorbent used in adsorption experiments in g
P	Adsorption pressure
P_0	Saturation vapour pressure
pH_0	Initial pH
pH_e	pH at equilibrium
pH_f	Final pH
pH_{ZC}	pH of zero charge
q_1	Adsorption capacity at equilibrium of the pseudo-first order kinetic model in $\mu g\ g^{-1}$
q_2	Adsorption capacity at equilibrium of the pseudo-second order kinetic model in $\mu g\ g^{-1}$
q_e	Arsenic adsorption capacity at equilibrium in $\mu g\ g^{-1}$
q_{exp}	Experimental arsenic adsorption capacity
Q_m	Langmuir monolayer adsorption capacity
q_t	Adsorption capacity at time t in units of $\mu g\ L^{-1}$ or mg L^{-1}
T	Temperature in °C
t	statistical thickness of the adsorbed film on gas sorption isotherms
V	Volume of arsenic solution used in adsorption experiments in L
V_i	Variance of models (F test)
W	Weight of adsorbate sorbed on gas sorption isotherms

x_1	Variable representing factor A in the 2^3 factorial model equation
x_2	Variable representing factor B in the 2^3 factorial model equation
x_3	Variable representing factor C in the 2^3 factorial model equation
Y	Response in the 2^3 factorial model equation
$w_{\text{activated adsorbent}}$	Weight of the activated adsorbent
$w_{\text{raw material}}$	Weight of the raw material
β	Affinity coefficient in gas sorption isotherms, it is a measure of the relative affinity of adsorbate molecules for a surface

1. Introduction

1.1 Access to drinking water

Access to clean water has been in the spotlight of national and international policy forums for more than three decades (UN 2010; WHO 2006). In 1977, the Water Supply and Sanitation Decade from 1981 to 1990 was declared at the World Water Conference in Argentina. In 1978, access to water was recognised as part of primary health care in the International Conference on Primary Health Care in Kazakhstan. In 2000, the United Nations (UN) General Assembly adopted the Millennium Development Goals which included halving the proportion of people without sustainable access to safe drinking water by 2015. In 2002, The Johannesburg World Summit for Sustainable Development saw the recognition of unfit drinking water and poor sanitation as responsible for 2.2 million deaths per year. The UN declared 2005-2015 as the “Water for life, international decade for action”. In July 2010, access to clean water was officially declared a human right by the UN.

Microbiological contamination continues to be the main hazard for drinking water not only in middle and low income countries (MLIC), but also in high income countries (WHO 2006). Only three chemicals are responsible for large-scale health effects through drinking water: fluoride, arsenic and nitrate (WHO 2006). Fluoride and arsenic occur naturally in water; though arsenic contamination may be the result of human activities in some cases. Nitrates reach drinking water as a consequence of agricultural activities, wastewater treatment, and oxidation of nitrogenous waste products in human and animal excreta (WHO 2007).

1.2 Arsenic

Arsenic contamination of drinking water supplies is of special concern due to the high toxicity of this element. Health effects of chronic arsenic poisoning include cancer of the skin, bladder and lungs (Mandal et al., 2002). The World Health Organization (WHO) guideline for arsenic in drinking water is set at 10 $\mu g\ L^{-1}$, and an estimated 137 million people worldwide are exposed to higher concentrations (Ravenscroft et al., 2009). In some MLIC, the population is exposed to arsenic in concentration ranges of hundreds or thousands of $\mu g\ L^{-1}$ (Chakraborti et al., 2002).

In regions of the world with decentralised water distribution systems, removal of microbiological and chemical contamination relies on the water users. The adoption and sustained use of water treatment systems depends on continuously engaging water users in health awareness programmes, which is very expensive. Although centralised water treatment and piped water distribution systems could be more cost-effective in the long-term for some rural populations, the high capital investment and the low ability of poor people to pay the full cost of operation and maintenance have halted expansion of piped water.

1.3 Low-cost technologies

Low-cost technologies are one possibility to provide the much needed short-term alternatives for arsenic removal. This research explores the use of activated carbon (AC) for low-cost arsenic adsorption from drinking water. Use of AC in water treatment is widespread. AC is used to remove organic contaminants, dissolved organic matter, taste, odour and colour (Karanfil 2006).

The main disadvantages of AC are its relatively high cost and low arsenic adsorption capacity. Agricultural by-products, like sugarcane bagasse (by-product of the sugar refinery industry), are a possible low-cost source for AC. Gasification processes, which can simultaneously produce energy and AC, are an attractive option for sugarcane growing regions. These processes may add a source of income in generally deprived areas and add to a more efficient use of sugarcane bagasse. The production parameters of AC, such as carbonisation and activation temperature, can be optimised for removal of specific elements and/or compounds.

1.4 Aims and objectives

1.4.1 Aims

- To evaluate the feasibility of using sugarcane based activated carbon as a low-cost arsenic adsorbent for water treatment.
- To investigate some of the issues affecting implementation of arsenic mitigation programmes in MLICs.

1.4.2 Objectives

- To optimise the preparation parameters of sugarcane activated carbon (SCAC) for maximum arsenic(V) and arsenic(III) adsorption.
- To characterise the physical and chemical properties of SCAC relevant to arsenic adsorption.
- To conduct batch arsenic(V) and arsenic(III) adsorption experiments to determine the adsorption capacity of SCAC under different experimental settings.
- To conduct a survey among professionals with experience on arsenic mitigation in MLICs to investigate some of the issues affecting arsenic mitigation.

1.5 Thesis structure

Chapter 2 is a comprehensive literature review of arsenic contamination. The issues covered are: arsenic occurrence in the environment, acute and chronic health effects, remediation technologies at laboratory and field scale level, and policy issues related to arsenic contamination. Arsenic contamination in Bangladesh, a recurrent topic in this thesis, is introduced in this chapter.

Chapter 3 explores the issue of arsenic mitigation in MLICs. A survey was applied to professionals with experience of arsenic mitigation in these countries. The survey explores arsenic mitigation policies or programmes, barriers to arsenic mitigation, and performance of arsenic removal technologies. The latter includes operation and maintenance issues of various technologies and the production of potentially toxic wastes by these technologies.

Chapters 4 to *7* present the experimental laboratory work for the development and testing of the SCAC. *Chapter 4* focuses on the general methods used throughout the development of the laboratory work; these are analysis of total arsenic in aqueous samples, preparation of adsorbents, and the experimental settings of batch adsorption experiments. *Chapter 5* centres on the methodology used for the optimisation of the preparation conditions of SCAC for arsenic(V) and arsenic(III) adsorption. *Chapter 6* presents the physical and chemical characterisation of adsorbents; pH of zero charge, scanning electron microscopy, surface area, pore size distribution, and particle size distribution. *Chapter 7* focuses on arsenic(V) and arsenic(III) batch adsorption experiments. Adsorption experiments investigated the kinetics of arsenic adsorption, and the effect of pH, temperature (sorption isotherms at 25 and 35 °C), and competing ions (Cl^-, SO_4^{2-}, PO_4^{3-}, Mn^{2+}, Si) on arsenic adsorption.

Chapter 8 brings together the two parts of the thesis; the survey on arsenic mitigation in middle and low income countries and laboratory work for the development of the low-cost adsorbent. Results from *Chapters 5* to *7* are discussed in the light of results from *Chapter 3*. Main conclusions from the research are drawn and recommendations for future work are presented in *Chapter 9*.

2. Arsenic contamination review: arsenic in the environment, health effects, remediation, and policy issues

The importance of water of adequate quality and sufficient quantity for human development can hardly be contested. Access to water is related to health, economic and recreational human activities. Water scarcity and natural and anthropogenic contamination are issues of global significance. Arsenic contamination of drinking water supplies is a worldwide problem.

The literature review presented here covers a wide range of topics regarding arsenic contamination; from laboratory development of arsenic removal media to technological and non-technological issues of arsenic mitigation. The latter is discussed in more detail in *Chapter 3* (*Expert survey: arsenic mitigation in middle and low income countries*).

First, *Section 2.1* presents a global panorama of arsenic contamination. Then, health effects associated with chronic exposure to arsenic in drinking water are introduced in *Section 2.2*. A review of the basic processes for arsenic removal, low cost removal technologies, and the use of activated carbon (AC) for arsenic removal is introduced in *Section 2.3*. Finally, the relationship between environment and policy is approached in *Section 2.4*; especially with regard to arsenic mitigation in middle and low income countries (MLICs). This was done by means of discussing the current state of arsenic mitigation in Bangladesh and by comparing arsenic mitigation programmes with other programmes implemented in Bangladesh.

2.1 Arsenic in the environment

Arsenic is naturally present in air, soils, rocks, water and dust. The main exposure pathway for humans is natural water with atypically high arsenic concentrations. Also, intake of arsenic through foodstuffs has recently arisen as an important exposition pathway. Arsenic can be integrated in the food chain if water with high arsenic content is used for irrigation of crops and/or for cooking (Kaufmann et al., 2002). Also, seafood may contain high quantities of organic arsenic (Petrusevski et al., 2007).

More than 230 arsenic occurrences in 70 countries have been documented; an estimated 57 million people are drinking water with more than 50 µg L^{-1} and 137 million are drinking water with more than 10 µg L^{-1} (Ravenscroft et al., 2009). Arsenic contamination is mostly localised in groundwater environments. Argentina, Chile, Mexico, China, Hungary, West Bengal (India) and Bangladesh are widely known cases of natural groundwater arsenic contamination. In some cases arsenic pollution may occur as a result of the mining industry and geothermal activity. Sources of air- and soil-borne arsenic contamination are localised; two examples are smelters and volcanoes.

Figure 2.1 presents a map of the worldwide documented arsenic occurrences according to the maximum concentration (Ravenscroft et al., 2009). In Figure 2.2 the number of people exposed to arsenic concentrations higher than 50 µg L^{-1} in drinking water is presented (Ravenscroft et al., 2009). The estimates for India, Myanmar, Pakistan and Mexico are uncertain; in the case of India people exposed could be either over- or under-estimated and in Myanmar, Pakistan and Mexico is believed to be under-estimated.

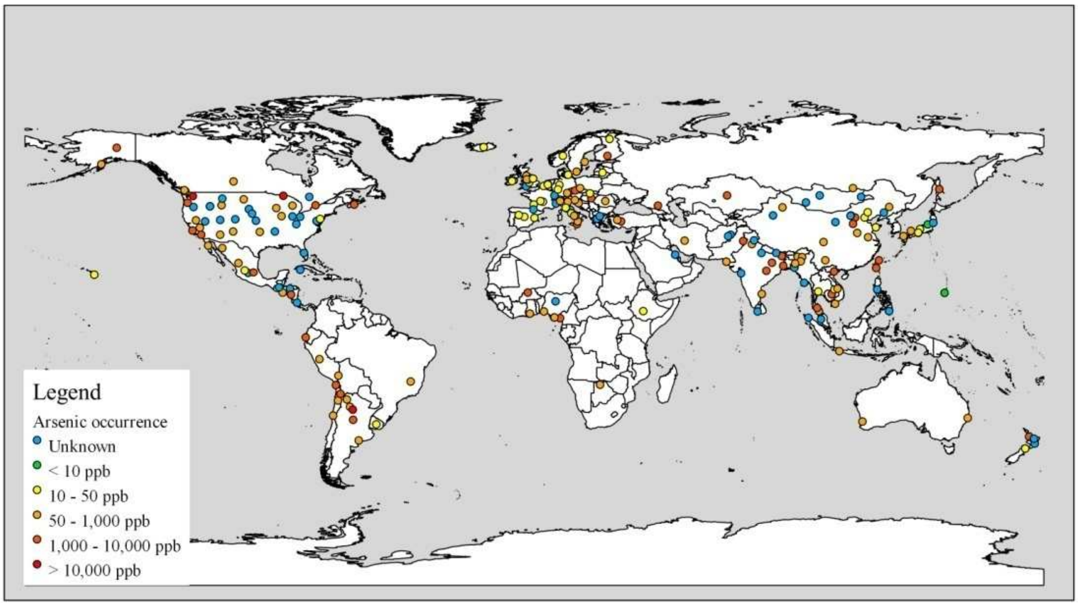


Figure 2.1 Maximum arsenic concentration documented in natural waters (Ravenscroft et al., 2009). Symbols correspond to the approximate location where contamination has been found.

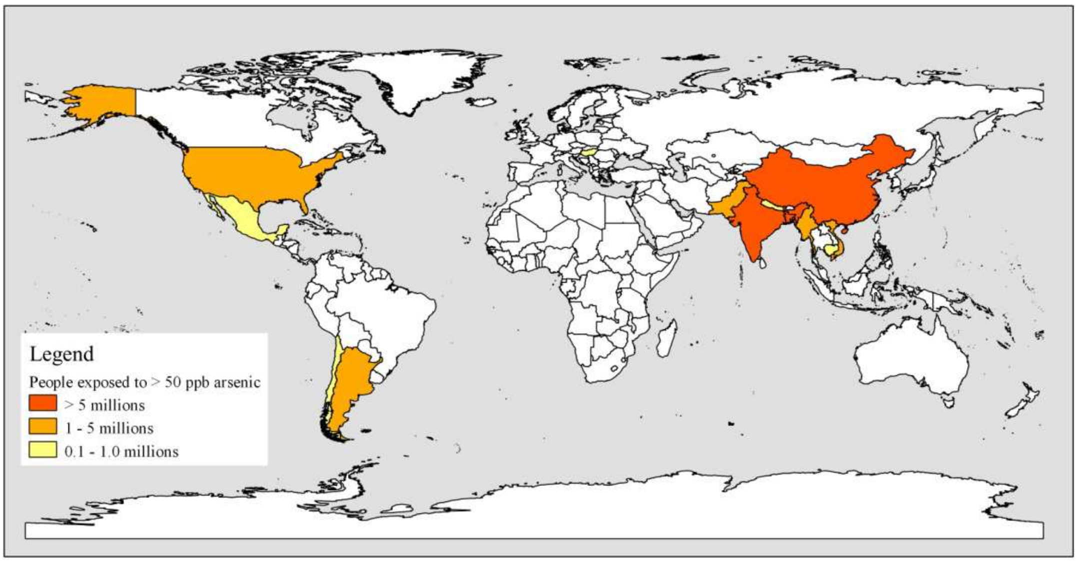


Figure 2.2 Estimates of people exposed to arsenic concentrations > 50 µg L^{-1} (ppb) in drinking water (Ravenscroft et al., 2009).

A wide range in arsenic concentrations is found in groundwaters; from 0.5 to 5,000 µg L^{-1}. Fortunately, arsenic is well below 10 µg L^{-1} in most aquifers (Smedley et al., 2002). Arsenic contamination is not correlated to arsenic content in source rocks in aquifers (Smedley et al., 2002). Arsenic mobilisation depends on the geochemical environment and hydrogeology.

Redox potential (Eh)-pH diagrams are useful to determine speciation of ions in the aqueous phase and the stability of solids (Lu et al., 2010). In contrast with most trace metals arsenic is relatively mobile under a wide range of redox conditions (Smedley et al., 2002). A few Eh-pH diagrams have been produced for arsenic systems, yet there is no consensus on the boundaries of arsenic(III) species. Differences in Eh-pH diagrams are due to uncertainty in thermodynamic properties, arsenic species included in the calculation, and definition of the system studied (Lu et al., 2010). Figure 2.3 presents two Eh-pH diagrams for the system As-O-H at a temperature of 25 °C and pressure of 1 atm.

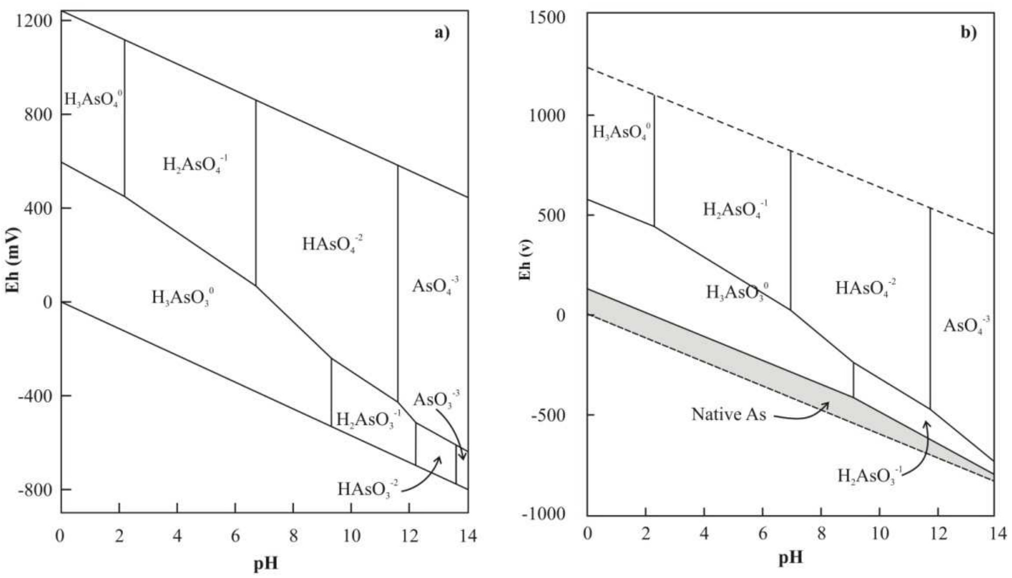


Figure 2.3 Eh pH diagrams for the system As-O-H at 25 °C and 1 atm. a) Smedley *et al.* 2002 and b) Lu *et al.* 2010.

A number of mechanisms have been proposed for mobilisation of arsenic. Table 2.1 presents a summary of these mechanisms compiled by Smedley *et al.* (2002). The release of arsenic to the environment is insufficient for contamination problems to arise; in addition arsenic must not be flushed away or diluted. Groundwater environments in which arsenic contamination occurs are reducing environments (Bangladesh, West Bengal, Taiwan, Northern China, Vietnam, Hungary and Romania), arid oxidising environments (Mexico, Chile and Argentina), mixed oxidised and reducing environments (South West USA), geothermal areas and sulphide mineralisation and mining areas (Thailand, Ghana, USA, Mexico) (Smedley et al., 2005).

Table 2.1 Arsenic mobilization mechanisms in groundwater (Adapted from Smedley *et al.* 2002).

Mechanism	Description
Desorption at high pH under oxidising conditions	Under anaerobic and acid to neutral pH conditions arsenic(V) ions are strongly adsorbed to oxide surfaces. The increase of pH, above 8.5, may cause arsenic desorption. The pH may increase due to proton uptake, ion exchange reactions and/or evaporation (in arid or semi-arid regions).
Desorption and dissolution due to a change in reducing conditions	Development of reducing conditions may favour the reaction As(V) → As(III). Arsenic(III) is less strongly adsorbed than arsenic(V). Reducing conditions may be caused by the rapid accumulation and burial of sediments. Reducing conditions are sustained if diffusion and convection of oxidants (O_2, NO_3^-, SO_4^{2-}) is slower than consumption.
Reduction in surface area of oxide minerals	Ageing of iron oxides causes a reduction in their surface area; decreasing the amount of arsenic adsorbed on a weight basis. Also, modification in the surface structure may cause a change in the binding affinity of arsenic(V) ions.
Mineral dissolution	Iron oxides dissolve under strongly acidic or strongly reducing conditions. This process partially explains arsenic contamination in mining sites and strongly reducing groundwater. However, reductive dissolution cannot explain the occurrence of high arsenic oxidising groundwater.

2.2 Health problems from chronic arsenic exposure

There are two levels of toxicity; acute and chronic. Acute toxicity refers to the health effects produced shortly after the exposure to a single and large dose; acute toxicity could result in death. Chronic toxicity is the health effects of prolonged or repeated exposure to a substance over a long period of time. Chronic arsenic toxicity may depend on the oxidation state and chemical form of arsenic (Mandal et al., 2002). Generally arsenic(III) is considered more toxic than arsenic(V) and inorganic arsenic compounds are considered more toxic than organic compounds (Jain et al., 2000). However, analytical methods for speciation in arsenic metabolites are very recent; hence epidemiological studies investigating the specific health effects of arsenic(III) and arsenic(V) are scarce (Mandal et al., 2002).

Carcinogenic and non-carcinogenic health effects of arsenic chronic exposure in drinking water at concentrations in the order of hundreds of µg L^{-1} are well established. These include respiratory, pulmonary, cardiovascular, gastrointestinal, haematological, hepatic, renal, dermal (melanosis, keratosis and hyperkeratosis), neurological, developmental, reproductive, immunologic, genotoxic, mutagenetic, biochemical, diabetes mellitus and cancers of the skin, lung, bladder, liver and kidneys (Mandal et al., 2002). However health effects at low concentrations, in the order of tens of µg L^{-1}, are contested to a great extent.

The strict drinking water standard in high income countries (HICs), ≤ 10 µg L^{-1}, is based on studies conducted in regions with atypically high arsenic concentrations such as Taiwan, Chile and Argentina; and in data from toxicological experiments using animal models. However, these studies have a number of limitations; for instance synergistic effects (or confounding factors) are not accounted for, use of animal data in carcinogens risk assessments for humans, and lack of data from exposure to low arsenic concentrations in a sufficiently large human population for a period of years (Smith et al., 2002). Confounding factors to be considered may include tobacco use, level of nourishment, genetic susceptibility and unaccounted arsenic ingested through food (Smith et al., 2004).

The importance of synergistic factors was realised relatively recently. High arsenic concentrations, up to 1,810 µg L^{-1}, were believed to be the origin of black foot disease in Taiwan. This is a cardiovascular illness which eventually results in dry gangrene of the limbs (Kaufmann et al., 2002). The first cases were documented in 1954; by 1986 the incidence was estimated in 8.9 cases per 1,000 inhabitants (Brown et al., 2002). Later, Lu *et al.* (1990) suggested that the combined effect of high arsenic concentration and humic acid in well water was the cause of the disease in Taiwan.

Risk assessments for carcinogen substances are still a matter of debate among scholars and drinking water regulators. Carcinogenic risk can be evaluated with various models; the most widely used approaches are the threshold model and linear extrapolation model. The threshold model supposes that nil risk exists for exposition up to a certain concentration level (Brown et al., 2002). In the extrapolation approach carcinogenic risk is estimated with a linear extrapolation from high to low concentrations. The latter, which was adopted by the US Environmental Protection

Agency (EPA) and the World Health Organisation (WHO), results in stricter drinking water regulations. Although it is true that evidence for carcinogenic effects at low arsenic concentrations in humans is weak; it is also true that the lack of high quality human data neither proves nor disproves the detrimental health effects of arsenic at low concentrations.

2.3 Arsenic removal from drinking water

In 2001, EPA published a list of candidates for the best available technologies for arsenic removal (EPA 2005). Far from recommending a specific removal method EPA clearly remarks that technology selection should be made in a case by case basis. The technologies listed by EPA will be presented below because most research is based on adaptation of common water treatments for MLIC settings (Alaerts et al., 2004).

Pre-treatment

Some technologies are more sensitive to arsenic speciation or pH during treatment. From pH 4 to 10, arsenic(V) species are negatively charged whereas arsenic(III) species have a neutral charge. Pre-treatment, such as pre-oxidation or pH adjustment, may be necessary to achieve optimum arsenic removal. Arsenic(III) is effectively oxidised to arsenic(V) with chlorine, permanganate, ozone and manganese dioxide (EPA 2005).

Ion exchange

In this technology, contaminated water is passed through a solid resin. Dissolved ions in solution are exchanged for ions in the resin (Johnston et al., 2001). Ion exchange is ineffective for arsenic(III) removal (EPA 2005). Sulphate ions can reduce the efficiency of ion exchangers (Choong et al., 2007).

Activated alumina

This is a porous aluminium oxide ($Al_2O_3.nH_2O$) with high surface area (Thomas et al., 1998). Activated alumina is ineffective for arsenic(III) removal and requires pH adjustment ($pH < 6.5$) for effective arsenic(V) removal (EPA 2005).

Reverse osmosis

This is a pressure driven membrane process. Apart from arsenic this technology removes others constituents from drinking water. It is not sensitive to pH (EPA 2005). Although it is a highly sophisticated technology, recent advances have made it less expensive and have allowed for lower operation pressures (Johnston et al., 2001).

Enhanced lime softening

This is normally used in hard waters to remove calcium and magnesium ions. After treatment, water has basic pH values; from 10 to 12. When lime ($Ca(OH)_2$) is added to water, it hydrolyses and combines with carbonic acid forming calcium carbonate (Singh 2007). Then, arsenic is removed with calcium carbonate.

Enhanced coagulation-filtration

Coagulation-filtration is a traditional water technology that has been optimised for arsenic removal. Iron and aluminium salts are the most common coagulants used. This technology is very sensitive to arsenic oxidation state (arsenic(III) is ineffectively removed), coagulant dosage and pH values (EPA 2005). Arsenic is removed by precipitation, co-precipitation and adsorption (Johnston et al., 2001).

Oxidation-filtration

In this process naturally occurring iron and manganese are removed from drinking water by oxidation and filtration. Soluble iron and manganese are oxidised to insoluble forms and then removed by filtration. Arsenic(V) is adsorbed onto iron hydroxides precipitates. The process is extremely dependent on the iron-arsenic ratio; pH; and high levels of naturally occurring organic matter, orthophosphates and silicates (EPA 2005).

2.3.1 Low-cost technologies and arsenic removal

Household and low cost technologies are not exclusively used in the field of arsenic removal; these technologies have been used for more than 20 years in removal of bacteria and pathogens from drinking water. However, the effectiveness of bacteria removal by household technologies is still debatable (McCann 2007). Sustained use of technologies depends on continuous awareness and hygiene education programmes. Nevertheless, the high investments necessary to create demand for household technologies through educational campaigns are not economically feasible and need to be subsided (Heierli 2008).

This section will be based mostly on low-cost technology research for implementation in Bangladesh; which is one of the MLICs where more research has been conducted with respect to arsenic contamination and remediation. The UK Department for International Development funded the Rapid Assessment of Household Level Arsenic Removal Technologies (RAHLART) programme in Bangladesh. The RAHLART programme concluded that the main causes of concern for household technologies were faecal contamination, low flow rates, use of chemicals, treatment time and high maintenance (Sutherland et al., 2001).

The RAHLART programme was run from November 2000 to March 2001 by the Bangladesh Arsenic Mitigation Water Supply Project (Sutherland et al., 2001). Nine technologies were assessed for a maximum period of 30 days. All technologies were assessed under idealised field water conditions. Additionally, three of these technologies were tested under normal household operating conditions. Of the technologies evaluated 7 removed arsenic below 50 $\mu g\ L^{-1}$ and 8 were found to have bacteriological contamination problems. The RAHLART concluded that Alcan, Tetrahedron, Sono and Stevens were the most acceptable technologies in terms of arsenic removal, bacteriological water quality and user acceptability. It was recommended to increase bacteriological quality of water and acceptability by technology’s users.

The Environmental Technology Verification Arsenic Mitigation Programme (ETV-AM) was run by the Bangladesh Council of Scientific and Industrial Research to assess the arsenic removal technologies that are used or proposed for use in Bangladesh (BCSIR 2003). Technologies were assessed in laboratory conditions and field tested on five different hydro-chemical regions in Bangladesh. Technologies were operated for up to 40 days. Under the ETV-AM four technologies have been approved for distribution/commercialisation in Bangladesh: MAGC/Alcan, Read-F, SONO and Sidko. Tetrahedron, which was considered by the RAHLART programme among the most efficient technologies, was not approved by the ETV-AM programme for distribution in Bangladesh. The media used by tetrahedron required regeneration every 5-12 days.

Activated alumina technologies

Two activated alumina technologies were assessed by RAHLART programme; community Alcan technology and household Bangladesh University of Engineering technology (BUET). Alcan is an arsenic removal proprietary media developed by Alcan Speciality Aluminas®. Both technologies are ineffective for arsenic(III) removal (ASA 2008; Jalil et al., 2001). BUET technology uses chlorine for arsenic(III) oxidation (Jalil et al., 2001). Sulphate, phosphate and iron have negative effects on arsenic removal with BUET technology. Also, residual aluminium, (80 µg L^{-1}) in drinking water has been linked to Alzheimer's disease (Yadav et al., 2006).

Danida two-bucket technology

Danida's technology is based in coagulation/flocculation processes for arsenic removal (Sutherland et al., 2001). Danida's technology consists of two buckets placed in series. In the upper bucket drinking water is mixed with a package of chemicals (200 mg L^{-1} aluminium sulphate and 2 mg L^{-1} of potassium permanganate). The mixture has to be allowed to settle for two hours. Then, water is passed through the lower bucket which contains a sand filter.

In a field test of various technologies in Narayangonj Bangladesh Danida's technology had very poor performance (Jalil et al., 2001). The average arsenic concentration of three units was consistently above 50 µg L^{-1}; initial arsenic concentration was 332 µg L^{-1}. Danida's technology had a poor performance in the RAHLART programme too (Sutherland et al., 2001). The technology removed arsenic below 50 µg L^{-1} only in groundwater with initial arsenic concentration below 120 µg L^{-1}. Effluent water had manganese and aluminium concentrations above the Bangladesh guideline standards. Bacteriological contamination in effluent water was found. In the positive side, the technology had fairly good household acceptance.

Read-F

Read-F is a technology that uses an adsorbent produced by Shin Nihon Salt Co. Ltd Japan. Read-F adsorbent is an ethylene vinyl alcohol copolymer-borne in which hydrous cerium oxide (CeO_2•n H_2O) is loaded. The Read-F technology had a good performance during the ETV-AM programme (BCSIR 2003). Read-F could treat water for a period ranging from 172 to 435 days; depending on the composition of groundwater. The technology's performance could be affected if iron exceeds 10 mg L^{-1}, phosphate exceeds 4 mg L^{-1} or pH exceeds 7.5.

AdsorpAs®

AdsorpAs®, a community based technology, is designed to serve 50 families or to treat 2,250 litres of water per day. The adsorbent, granular ferric hydroxide, for this technology was developed in a cooperation of M/S Harbauer GmbH Berlin and the Technical University of Berlin. During the ETV-AM programme the technology was capable of removing arsenic below 50 µg L^{-1} for 12 to 56 days (BCSIR 2003). The ETV-AM found that high pH values (> 7.5) and high phosphate concentrations (> 7.8 mg L^{-1}) have a negative impact on technology's performance.

Stevens Institute Technology

This technology removes arsenic by coagulation and co-precipitation with ferrous sulphate ($FeSO_4$) (Cheng et al., 2004). Water is treated in batches of 20 L with a package of chemicals; which contain 1.5 g of industrial $FeSO_4$ and 0.5 g of calcium hypochlorite ($Ca(OCl)_2$). Flocs are formed and then removed with a sand filter. High concentrations of bicarbonate (HCO_3^-) have a negative impact whereas calcium and magnesium have a positive impact on arsenic removal (Sutherland et al., 2002). In a four-month trial five out of six units removed arsenic below 50 µg L^{-1}. However, arsenic removal showed variability with time and among different units (Cheng et al., 2004).

Tetrahedron technology

This technology uses an ion exchange resin to remove arsenic. Sodium hypochlorite (NaOCl) is used for arsenic(III) oxidation. Liquid wastes from resin regeneration need treatment before disposal. Seven units of tetrahedron technology were field tested by the ETV-AM programme. Performance of these units was variable and regeneration of the resin was needed very frequently, from 5 to 12 days (BCSIR 2003).

Sono technology

Sono is probably the most widely known arsenic removal technology. Design of this filter has continuously evolved since its invention in 1997. This filter won the *2007 Grainger Challenge Prize Gold Award* by the National Academy of Engineering. The first design of the Sono filter consisted of three pitchers. The top pitcher contained cast iron turnings and sand, the middle pitcher contained wood charcoal and sand, and the bottom pitcher was the collecting vessel. The overall design of the current Sono filter is very similar to the previously described. The main difference is the arsenic removal media. The latest version uses a proprietary media named composite iron matrix (CIM); to produce this adsorbent is necessary to have a licensing agreement (Hussam et al., 2007). A diagram of this arsenic removal technology is presented in Figure 2.4.

Performance tests of the Sono filter are very encouraging overall (BCSIR 2003; Munir et al., 2001). Approximately 30,000 units had been deployed in Bangladesh until 2007 (Hussam et al; 2007). According to the manufacturer the oldest unit has been running continuously for five years with minimum maintenance. On the other hand ETV-AM found that high levels of phosphate (11.5 mg L^{-1}), silicate (24.3 mg L^{-1}) and pH > 7.5 seriously impaired arsenic removal of Sono 45-25 (BCSIR 2003). Also, a water supply programme in Bangladesh found that Sono users were discouraged from using the technology due to injuries made during cleaning of the media and due to solidification of the media (Hoque et al., 2004). Ten out of 1,411 participating families choose the Sono filter to obtain arsenic free water. All families using household technologies abandoned them after a few weeks.

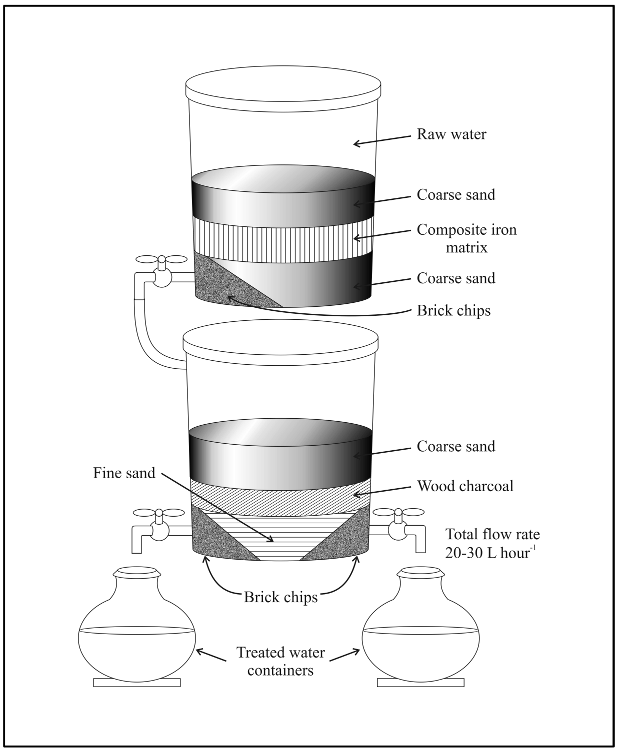


Figure 2.4 Diagram of the latest version of the SONO filter (not to scale) (Hussam et al., 2007).

Kanchan technology

The Kanchan technology has been developed by the Massachusetts Institute of Technology (MIT) Nepal Water Project for at least six years. The filter is made of a plastic bucket with a pipe attached for water collection. Gravel, coarse sand, fine sand, iron nails and brick chips are layered from the bottom to the top of the filter (Ngai et al., 2006). Fresh ferric hydroxide (iron rust) formed on the iron nails is the arsenic removal media. In addition pathogens are removed in the sand layers. Maintenance is required from once a month to once every six months. Two field studies, one by MIT-Nepali Environment and Public Health Organisation and the other by Kathmandu University-United States Peace Corps, showed 85-95 per cent of arsenic removal (Ngai et al., 2006).

A field test of the Kanchan filter in Cambodia found that pathogen and arsenic removal were variable. Chiew *et al.* (2009) attributed the poor performance of the filter to the low reactivity of the iron nails used, short retention times on the iron nails layer, and a combination of high phosphate concentration (> 0.5 mg L^{-1}) and low iron concentration (< 5 mg L^{-1}).

The contradictory results from the Kanchan filter in Nepal and in Cambodia support the opinion of some scholars that scaling up of household technologies is anticipated (Noubactep 2009; Schmidt et al., 2009). Arsenic removal technologies with iron removal media have proven to be efficient in removing arsenic (EPA 2005). However, it seems that optimum arsenic removal depends on water composition; especially on the iron-arsenic ratio, pH and phosphate concentration (BCSIR 2003). Arsenic removal with iron based adsorbents may be expected to be low in waters with low iron-arsenic ratio (< 20) (EPA 2005).

Well-head community removal units from Bengal Engineering College and Lehigh University

From 1997 to 2008 over 175 well-head community removal units, from Bengal Engineering College and Lehigh University (BEC-LU units), have been installed in India (Sarkar et al., 2008; Hossain et al., 2005; Sarkar et al., 2005). The arsenic removal media in the units is an activated alumina produced by Oxide India Ltd in Durgapur in West Bengal or the hybrid anion exchanger ArsenX. The unit contains 100 litres of adsorbent and requires a fifteen-minute-backwash every day and constant regeneration. According to a self-evaluation report the performance of this technology is good. Ten units placed in different field sites in India with arsenic groundwater concentration of 60-363 $\mu g\ L^{-1}$ were capable of removing arsenic to 18-60 $\mu g\ L^{-1}$. Dissolved oxygen, iron content and arsenic oxidation state influenced arsenic removal capacity of the technology.

An independent two-year assessment of 18 arsenic removal units from 11 manufacturers, including three BEC-LU units, was carried out in West Bengal India (Hossain et al., 2005). Although the mean arsenic concentration for the three BEC-LU units ranged from 5 to 40 $\mu g\ L^{-1}$, arsenic concentration of treated water was as high as 401 $\mu g\ L^{-1}$ after backwashing for one unit. One unit had to be closed down due to a sand gushing problem of the tube well. Users from the 11 different types of technologies complained about getting injured when the hand pump rebounds due to high pressure, and malodorous and/or yellow/red water. Only 3 of the 18 units were operating at the end of the evaluation period; no information is provided of which units were these.

Although some negative issues arouse in the independent evaluation of this technology; the BEC-LU projects shows that that implementation of arsenic removal units in rural environments is possible when certain conditions are met. Unfortunately, there is no information provided on the logistics of the programme, the type and degree of support that is given to the communities, and the economic arrangements for technology installation and operation costs.

2.3.2 Activated carbon and removal of metals

The use of AC in drinking water treatment has many advantages. First, AC is well known for its high removal capacity for organic compounds, taste, odour, and dissolved natural organic matter (Karanfil 2006). Secondly, recent research has shown promising results for metal removal (Dias et al., 2007). Thirdly, since AC is a known oxidising agent for arsenic(III), pre-oxidation of arsenic(III) may be unnecessary for arsenic removal (Bissen et al., 2003). Budinova *et al.* (2009) measured arsenic(III) oxidation from 10 to 30 per cent at initial arsenic concentrations from 5 to 10 mg L^{-1}.

AC produced from a variety of agricultural by-products and also from coal (commercial brands) has been used for removal of various metals. AC can be used untreated or pre-treated; pre-treatment may include acid washing and/or loading with metals. Performance of adsorbents is usually assessed with the uptake capacity (µg or mg of contaminant adsorbed per gram of adsorbent) or percentage of contaminant removed or adsorbed.

Adsorption of metal ions onto AC is controlled by speciation of metal ions; pH of the solution; adsorbent’s point of zero charge, surface area, porosity, and surface composition; and the size of adsorbing species (Dias et al., 2007). Solution’s pH and temperature are the more widely studied effects in metal removal. Adsorption of divalent metals ions seems to be enhanced with increments in pH. Removal of copper(II), lead(II), nickel(II) and zinc(II) with 14 different brands of AC increased from 70 per cent at near neutral pH to 100 per cent at basic pH values (Corapcioglu et al., 1987). Similar trends were found for copper, cadmium, nickel and zinc with Darco ® 12-20 AC; complete removal was achieved at pH 6.5 for copper and at pH 7 for nickel (Seco et al., 1997).

Mohan *et al.* (2002) investigated removal of cadmium, zinc and copper with a sugarcane activated carbon (SCAC). The same trend was found with this agricultural waste based AC; removal increased with pH increments. Complete removal was achieved at pH values higher than 8. For chromium(VI) the opposite trend was found for cornelian cherry, apricot stone, almond shell, and coal based AC. Removal decreased with increments in pH values; optimum pH for chromium removal was 1 (Wu et al., 2008; Dermibas et al., 2004).

The temperature effect on metal removal with AC is still debatable. Absorption is almost always an exothermic phenomenon. Theoretically, increments in temperature should lead to a reduction in metal removal. However, experimentation has produced inconclusive results in this regard (Di Natale et al., 2008). For instance, Seco *et al.* (1997) found that temperature had a positive effect on copper, cadmium, nickel and zinc removal; Mohan *et al.* (2002) found similar results for cadmium, zinc and copper. Mohan *et al.* (2008) found that removal of iron, manganese and lead were inhibited by temperature increments for coconut shell fibre, coconut shell and rice husk AC. However, zinc removal was inhibited with temperature increments for coconut shell AC but enhanced with rice husk and coconut shell fibre AC (Mohan et al., 2008).

Finally, Johns *et al.* (1998) found that adsorption of organic compounds was comparable with Calgon GRC ® AC and an agricultural waste based AC; but simultaneous metal removal (lead(II), copper(II), zinc(II) and nickel(II)) with agricultural waste based AC was from 1.6 to 2.1 times higher than with Calgon GRC® AC.

2.4 Activated carbon and removal of arsenic

Most pieces of research investigate exclusively arsenic(V) removal, few investigate arsenic(III) removal and even fewer investigate both removal of arsenic(V) and arsenic(III). This may be in part because the negatively charged arsenic(V) compounds are easier to remove by adsorption than the neutrally charged arsenic(III) compounds. Adsorption of both arsenic(III) and arsenic(V) highly depends on pH. Performance of various AC samples is summarised in Table 2.2-2.4.

The effect of pH has been widely studied for various types of commercial and agricultural based AC samples. It seems that the effect of pH on arsenic removal depends on the adsorbent, the oxidation state of arsenic and other experimental conditions. Arsenic(V) removal with coconut shell AC was investigated by Lorenzen *et al.* (1995). Removal increased from pH 2 to 6 for copper impregnated AC and from pH 2 to 5 for untreated AC, then further increments in pH diminished arsenic(V) removal (Lorenzen et al., 1995). For arsenic(V) and Aquacarb 207EA ® AC a similar trend was found; arsenic adsorption constantly increased from pH 2 to 8 and then from pH 8 to 11 it decreased (Di Natale et al., 2008). A study by Chuang *et al.* (2005) found that arsenic(V) removal with oat hull AC decreased from pH 5 to 9, at pH 9 removal was negligible.

The percent of arsenic removal with copper impregnated coconut husk carbon constantly increased from pH 2 to 12 (Manju et al., 1998). Arsenic(III) removal with a coal based activated carbon increased from pH 1 to 7; then at pH higher than 7 removal dropped (Wu et al., 2008). Arsenic(III) removal with bean pod AC increased from pH 3 to 7; then removal decreased from pH 7 to 12 (Budinova et al., 2009). Ansari *et al.* (2007) investigated arsenic(III) and arsenic(V) removal with granular and powdered AC. Contrary to the expected, arsenic(III) removal was higher than arsenic(V) removal. The optimum pH for removal depended on the oxidation state for arsenic; for arsenic(III) was pH 12 and for arsenic(V) was pH 3.

Table 2.2 Langmuir parameters for various types of AC as published in the literature. Symbols: As_0 is the initial arsenic concentration, pH_0 is the initial pH, T is the temperature at which the experiment was conducted, Q_m is the monolayer adsorption capacity estimated from Langmuir's equation, and *b* is the Langmuir's parameter related to the energy of adsorption.

Adsorbent type	As_0	pH_0	Adsorbent dose	T_0	Q_m	*b*	Reference
			g L^{-1}	°C	mg g^{-1}	L mg^{-1}	
Cu-coconut husk AC	50-150 mg L^{-1} As(III)	12	2	30	146.3	2.4×10^{-2}	Manju et al., 1998
		12	2	40	150.8	3.1×10^{-2}	
		12	2	50	154.2	4.4×10^{-2}	
		12	2	60	158.7	6.43×10^{-2}	
Oat hull AC	25-200 µg L^{-1} As(V)	5	0.015		3.1	40.5	Chuang et al., 2005
		6	0.015		2.5	39.6	
		7	0.015		2.0	44.2	
		8	0.015		1.6	43.0	
AC	0-30 mg L^{-1}As	4.7			0.04		Gu at al., 2005
Fe-AC		4.7			3.0		
Fe-AC (O_2)		4.7			1.9		
Fe-AC (H_2O_2)		4.7			3.9		
Fe-AC (NaClO)		4.7			6.6		
Fe-AC		5		25	74.4	2.7×10-2	Zhang et al., 2007
AC		5		25	60.4	7.8×10-3	
Fe-AC	22 mg L^{-1} As(V)	6		20	51.3	0.2	Chen et al., 2007
	22 mg L^{-1} As(III)	6		20	38.8	0.3	
	22 mg L^{-1} As(V)	8		20	43.6	0.2	
	22 mg L^{-1} As(III)	8		20	39.2	0.3	

Table 2.3 Freundlich parameters for various types of AC as published in the literature. Symbols: As_0 is the initial arsenic concentration, pH_0 is the initial pH, K is the Freundlich relative sorption capacity, and $1/n$ is the Freundlich dimensionless parameter related to the energy of adsorption.

Adsorbent type	As_0	pH_0	Adsorbent dose g L^{-1}	K ($\mu g\ g^{-1}$)($\mu g\ L^{-1}$)$^{-1/n}$	$1/n$	Reference
Fe-AC (Mn1)	120 $\mu g\ L^{-1}$ As(V)	6.4	0.004-1.25	263.6	0.4	Hristovski et al., 2009
Fe-AC (Mn4)		6.4		247.2	0.5	
Fe-AC (Mn1)		8.3		31.5	0.6	
Fe-AC (Mn4)		8.3		47.3	0.6	
Fe-AC (M7)		6.4		37.9	0.5	
Fe-AC (M10)		6.4		48.9	0.6	
Fe-AC (M7)		8.3		2.0×10^{-4}	2.6	
Fe-AC (M10)		8.3		5.0×10^{-2}	1.7	

Table 2.4 Experimental arsenic adsorption capacity (q_{exp}) and removal percentage (As.R) for various types of AC as published in the literature. Symbols: As_0 is the initial arsenic concentration, pH_0 is the initial pH, and T is the temperature at which the experiment was conducted.

Adsorbent type	As_0	pH_0	Adsorbent dose g L^{-1}	T °C	q_{exp} mg g^{-1}	As.R %	Reference
Fly ash char AC	709 mg L^{-1} As(III)	2.2			89.24	63	Pattanayack et al., 2000
Graphite rods AC	157 mg L^{-1} As(V)	7.5			30.48	97	
$CaCl_2$-rice husk AC	1000 µg L^{-1} As(III)	10.8	40		0.0183		Mondal P. et al., 2007
rice husk AC					2.2		
AC	0.5-10 mg L^{-1} As(V)	8	2-20	55	2.5		Di Natale et al., 2008
		8		20	1.5		
		6.5		20	0.7		
Fe-AC (Fe 11% 80 °C)	3 mg L^{-1} As(III)	8	0.1	20	1		Jang et al., 2008
Fe-AC (Fe 11% 80 °C)	3 mg L^{-1} As(V)	8	0.1	20	6		
Fe-AC (Fe 7.5% 60 °C)	3 mg L^{-1} As(III)	8	0.1	20	9		
Fe-AC (Fe 7.5% 60 °C)	3 mg L^{-1} As(V)	8	0.1	20	9		
Bean pod- AC	5-20 mg L^{-1} As(III)		10		1.01	20-80	Budinova et al., 2009
Fe-AC	311.5 µg L^{-1}		8	25	<0.008-0.028		Fierro et al., 2009

Di Natale *et al.* (2008) and Wu *et al.* (2008) studied the effect of temperature on arsenic removal. For arsenic(III) removal with a coal based AC the direction of the effect of temperature was not consistent; arsenic(III) removal follows the order 25 °C > 20 °C > 40 °C > 35 °C > 30 °C (Wu et al., 2008). Increments in temperature from 10 to 55 °C had a positive effect on arsenic(V) removal with AC Aquacarb

207EA®; temperature effect is more important from pH 7 to 9 (Di Natale et al., 2008).

Arsenic removal with AC pre-treated with metal salts has been studied with various metals. The performance of coconut shell carbon improved with copper loading; uptake capacity of untreated carbon was 4.91 mg g^{-1} and of Cu pre-treated carbon was 5.79 mg g^{-1} (Lorenzen et al., 1995). Ansari *et al.* (2007) found that arsenic(III) removal was enhanced by pre-treatment with copper, silver and sulphur salts and inhibited by pre-treatment with iron(II) and iron(III) salts. On the other hand, arsenic(V) removal with this AC was enhanced by iron(III), copper(II) and silver, and slightly inhibited by sulphur pre-treatment.

Loading of iron onto AC has been extensively studied for arsenic removal. In general, iron loaded AC (Fe-AC) would be expected to have higher arsenic uptake than the untreated AC. However, the amount of iron in AC is not always directly proportional to arsenic uptake capacity of adsorbents. It is clear that the positive effect of iron loading is extremely sensitive to the iron source and the loading methodology used; these two factors affect the distribution and morphology of iron particles loaded onto the carbon (Hristovski et al., 2009).

Arsenic removal with Fe-AC is sensitive to pH, temperature and the amount of iron loaded into the AC. It seems that the effect of pH is specific to each adsorbent. Vaughan *et al.* (2005) found that at Fe-AC dose of 144 mg L^{-1} removal of arsenic(V) decreased continuously with pH; and a Fe-AC dose of 266 mg L^{-1} removal remained constant at approximately 100 per cent from pH 4.4 to 7.5 and at pH > 7.5 dropped rapidly. Chen *et al.* (2007) studied arsenic(III) and arsenic(V) removal with spiked natural water; arsenic(III) removal was around 80 per cent at pH 6 and 8; whereas arsenic(V) removal was around 100 per cent at pH 6 and 90 per cent at pH 8. Mondal *et al.* (2007) compared arsenic(III) and arsenic(V) removal with un-treated AC and iron(III)-AC; arsenic(V) uptake was higher that arsenic(III) uptake for both adsorbents, optimum pH for arsenic(III) removal was 9-11 and for arsenic(V) removal was 5-7 for both adsorbents.

For a nano zero valent iron supported on activated carbon arsenic(V) removal was higher than arsenic(III) removal from pH 2 to 4.5, but at pH > 4.5 arsenic(III) removal was higher than arsenic(V) (Zhu et al., 2009). From pH 3 to 7 arsenic(III) removal constantly increased, and at pH > 9 arsenic(III) removal percentage drastically decreased (Zhu et al., 2009). Arsenic(V) removal decreased continuously from pH 3 to 12 (Zhu et al., 2009).

On the other hand, it seems that there is a trend regarding iron content on AC and arsenic removal. Removal increases with iron content until it reaches a maximum; then further increments in iron content cause a fall in arsenic removal. Gu *et al.* (2005) found that arsenic(V) removal significantly increased with Fe-AC with iron content between 1 and 7 per cent; but higher iron content caused a drop in arsenic removal. A similar trend appeared in two further studies; Hristovski *et al.* (2009) found that arsenic(V) removal at a pH > 7.5 with Fe-AC with 2.8 and 10.4 per cent iron was higher than 90 per cent; but arsenic(V) removal drastically dropped for samples with 15.9 per cent iron. Fierro *et al.* (2009) found that arsenic(V) uptake increased from 4 to 28 $\mu g\ g^{-1}$ when iron content was increased from 0.02 to 2.2 per cent; but when iron content was increased to 9.4 per cent arsenic(V) uptake dropped to 8 $\mu g\ g^{-1}$. Vaughan *et al.* (2005) obtained arsenic(V) removal percentages from 0 to 20 for Fe-AC with 0.62 per cent iron and from 0 to 100 with Fe-AC with 7.0 per cent iron content.

Mondal *et al.* (2007) found that increment in temperature has a negative effect on arsenic(V) and arsenic(III) removal with a iron(III)-AC and with untreated AC. The temperature effect is more significant for arsenic(V) removal with untreated AC from 30 to 35 °C; arsenic(V) removal at 30 °C is approximately 70 per cent and at 35 °C it drops to approximately 55 per cent. Arsenic removal drops less than 5 per cent for Fe-AC from 30 to 60 °C.

Gu *et al.* (2005) studied the effect of ionic strength and interfering ions for arsenic(V) removal with a Fe-AC. Ionic strength from 0.01 to 0.1 M sodium nitrate ($NaNO_3$) did not have a significant effect on arsenic removal. At pH < 7.0 sulphates (100 mg L^{-1}), phosphates (50 mg L^{-1}), silicates (50 mg L^{-1}), chloride (100 mg L^{-1}) and fluoride (1 mg L^{-1}) did not have a significant effect on arsenic(V) removal, but at pH > 9 only 20 per cent of arsenic(V) was adsorbed when phosphate and silicate were present. Zhu *et al.* (2009) found that silicate, phosphate and humic acid have a negative effect on arsenic(III) and arsenic(V) removal with nano zero valent iron supported on AC; and magnesium(II), calcium(II) and iron(II) have a positive effect on arsenic(V) removal. Positive and negative effects are more important at pH > 6.5; at pH 3.5 and 6.5 iron(II) impairs arsenic(III) removal.

2.5 Sugarcane activated carbon for arsenic removal

Disadvantages of commercial available AC for arsenic removal are its high cost and its relatively low affinity for arsenic (Juang et al., 2002; Mohan et al., 2002). The use of alternative sources has been extensively studied for production of cheaper AC. The use of agricultural by-products, including sugarcane bagasse, for AC production is attractive because of their availability and low cost (Ioannidou et al., 2007). Also, production of AC from agricultural by-products presents the additional advantages of adding value to a waste product and reducing the amount of waste going to landfills.

Sugarcane bagasse, a by-product from sugar refineries, is the residual cane pulp and pitch after sugar extraction (Mohan et al., 2002). The approximate composition of sugarcane in percentage is 50 cellulose, 25 hemicellulose and 25 lignin (Pandey et al., 2000). Cane or beet sugar is produced in 130 countries. Worldwide production of sugar was 143 million tonnes in 2002, from which 60-70 per cent was produced from sugarcane (FAO 2003). In 2005, 1,018 million tonnes of sugarcane were grown by the top 10 producing countries (FAO 2005). For each 10 tonnes of sugarcane crushed 3 tonnes of wet bagasse (40-50 per cent moisture) are produced approximately. Currently, sugarcane bagasse is extensively used for electricity generation in sugar refineries. However, burning sugarcane bagasse in boilers to produce steam and generate electricity is not energetically effective (Manahan et al., 2007).

The rapid development of bio-energy may make economically favourable the production of AC from agricultural by-products. Biomass by-products can be transformed in high grade fuel (hydrogen), AC and synthesised gas through gasification (Manahan et al., 2007). A project to evaluate gasification of sugarcane bagasse in Mexico is being run by the National University of Mexico, ChemChar Research Inc USA, and the Mexican Sugarcane Chamber.

It is estimated that gasification of biomass by-products could add income and employment to rural sugarcane production regions in Mexico and elsewhere (Manahan et al., 2007). Although gasification of sugarcane bagasse is a very promising option it is still in development and its application could be difficult to implement in some regions because training of skilled professionals is necessary to coordinate the process and capital investment could be high.

Encouraging results have been obtained for the use of SCAC for removal of cadmium, zinc, copper, lead, chromium, dyes and phenol (Giraldo-Gutierrez et al., 2008; Tseng et al., 2006; Juang et al., 2002; Mohan et al., 2002; Tsai et al., 2001). A SCAC experimental adsorption capacity at pH 5 for chromium(VI) and lead(II) was measured at 25 and 5 mg g^{-1} (Giraldo-Gutierrez et al., 2008). Potassium hydroxide (KOH) sugarcane husk AC had a Langmuir monolayer adsorption capacity of 540-608 mg g^{-1} for methylene blue dye, of 340-606 mg g^{-1} for acid blue-74 dye and of 195-239 mg g^{-1} for phenol (Tseng et al., 2006). Steam-activated sugarcane carbon adsorbed 273-674 mg g^{-1} of acid blue-25 dye, 270-942 mg g^{-1} of basic red-22 dye, and 250-308 mg $g^{-1}$of phenol (Juang et al., 2002). Zinc chloride ($ZnCl_2$) activated SCAC had a Langmuir monolayer adsorption capacity of 2.34-5.78 mg g^{-1} for acid orange-10 dye (Tsai et al., 2001).

Current production cost of agricultural by-products based activated carbon

The cost of coal based AC for general applications and for metal sequestering is around US$ 3.30 and US$ 20 per kg respectively. The cost of AC based on agricultural by-products has been estimated to be US$ 2.42 kg^{-1} for steam-activated pecan shells AC, US$ 3.12 kg^{-1} for steam activated sugarcane bagasse, US$ 2.89 kg^{-1} for phosphoric acid pecan shells AC, and from US$ 2.45 to 2.82 kg^{-1} for acid activated almond shells (Table 2.5). These costs were calculated assuming that agricultural by-products based ACs were produced with similar technologies to commercial activated carbon.

Table 2.5 Estimations for the cost of production of AC based on agricultural waste (Ng et al., 2003; Toles et al., 2000)

Raw material	Pecan shells	Sugarcane	Pecan shells	Almond shells
Activation method	Steam	Steam	Phosphoric acid	Acid
Production (kg day^{-1})	1,400	1,940	3,000	5,000
Operation (days year^{-1})	320	320	320	320
Staff (hours day^{-1})	144	144	144	
Staff cost (US$ hour^{-1})	18	18	18	
Capital investment (US$ millions)	2.12	4.32	6.32	
Annual operating cost (US$ millions)	1.22	1.94	2.78	
Product cost (US$ kg^{-1})	**2.72**	**3.12**	**2.89**	**2.45-2.82**

2.6 Policy and environment

Social sciences engaged early in the study of different aspects of environmental systems; some of the environmental social theories include ecological anthropology, political ecology, environmental and ecological economy, and environmental sociology. Some of the aspects that are of interest of social sciences are the study of environmental movements, the processes of scientific enquiry, the social and political construction of environmental problems, the public and policy responses to environmental issues, the bearing of the consequences of environmental conditions by different social groups, the agency of different social groups on environmental policy-making, and the construction of environmental discourses among others (Scoones 1999).

Since the 1970s the presence of environmental problems in the media and political arenas has become widespread. However, not all environmental conditions acquire this status. Natural sciences influence greatly the identification of potential environmental problems; which are then shaped by social, cultural and political processes (Hannigan 2006). Governments play a major role in implementing responses to environmental problems (Kraft 2011).

Scientific knowledge about the natural world is always incomplete; the uncertainties around science allow for different interpretations of environmental conditions. Nevertheless, the prejudice that solutions to environmental problems can be found through science and technology prevails. The identification of a potential threat to public health or to the environment is not enough to mount a response to it. It is necessary to assess if the risk posed by the environmental condition requires action, which kind of action, at which level, and who would implement it (Kraft 2011).

Environmental policy does not move linearly from decision-making to policy implementation; usually policies are contested, reshaped and could be postponed or disregarded (Keeley et al., 2003). Policy-making is delivered through regulation, taxation, subsidisation, use of market incentives, funding of research, provision of information or education among others. Policies can be implemented at local, regional or international level.

Policy-makers use science to validate judgements through environmental risk assessments, cost-benefit analysis, environmental auditing, life-cycle analysis, and risk management among other tools (Hannigan 2006). Beliefs about public needs, and the effects of policies on society and on the economic system are embedded in policy-making (Kraft 2011). Usually, the magnitudes of the risk are perceived differently by environmental agencies and by common citizens.

To some extent, science has developed a symbiotic relationship with policy-making processes. Politicians and environmental agencies have an increasing demand for science to legitimise environmental policies, and science has a growing dependency on policy-makers for funding resources (Weingart et al., 1999; Jasanoff 1992). The role of scientists as government or industry advisers has challenged the traditional perception of science as a source of objective knowledge without political or economical values attached. For instance, meta-analyses of drug trials have demonstrated that drug trials funded by industry are more likely to produce statistically significant results in favour of the pharmaceutical industry (Bhandari et al., 2004).

Governments have a limited budget; some environmental problems conveying considerable risk to the public health or the environment could be disregarded if solutions are too costly or unmanageable to implement. Currently, there is considerable discussion on the process used to determine the priority of environmental issues, and the cost-effectiveness of the policies to be implemented.

2.7 The case of arsenic in drinking water

The implementation of the arsenic rule in USA illustrates the intricate environmental policy-making process. In January 2001, at the end of the Clinton administration, the arsenic standard in drinking water was lowered from 50 to 10 $\mu g\ L^{-1}$. Three months later, at the beginning of the Bush administration, the EPA postponed the implementation of the arsenic rule in favour of revaluating science and cost issues.

The arsenic rule divided academic and political communities in the USA. Some politicians and scholars considered that the evidence did not support the application of a stricter drinking water standard. The validity of the assumptions and methodology used in the cost-benefit analysis of the arsenic rule, which EPA has to conduct by law, were intensely contested. One of the main issues was the weak evidence of carcinogenic effects of arsenic at low concentrations and the lack of epidemiological data in USA population (Heinzerling 2002).

Contradictory and equally justifiable assumptions could modify drastically the results of cost-benefit analysis for carcinogens (Sustain 2001). For instance, the benefits of lowering the drinking water standard from 50 to 10 $\mu g\ L^{-1}$ were estimated from zero to more than half a billion dollars (Heinzerling 2002). Also, it is difficult to estimate an economic value for the so called “unquantifiable benefits”, such as quality of life. Furthermore, cost-benefit analysis does not identify which sector of society would be affected and which would be benefited by environmental regulations (Sustain 2001). Finally, in October 2001 EPA set the standard for arsenic in drinking water at 10 $\mu g\ L^{-1}$.

On the other hand, scarcity of economic resources and political constrains associated with MLICs limit the capacity of these countries to effectively legislate and enforce environmental policies (Mumme et al., 1988). Also, MLICs with widespread occurrence of arsenic in drinking water supplies, with concentrations in the order of hundreds or thousands of $\mu g\ L^{-1}$, require efficient programmes that could be implemented in a short-term scale with limited technological and economical resources (Smith et al., 2004). Paradoxically these short-term solutions have proven to be extremely difficult to implement and to sustain.

Even though arsenic contamination in MLICs has been legitimised by international NGOs and institutions (Water Aid, The World Bank and UNICEF), it has failed in gaining the status of a global environmental crisis and in capturing the attention of politicians and citizens in HICs. The following factors may contribute to that effect:

- Powerful counter claims amplified by the controversy of the arsenic rule in USA.
- The lack of popularisation of arsenic science; especially with the affected population in MLICs.
- Mitigation responses require substantial changes in the affected groups' lifestyle.
- The latency period for chronic arsenic poisoning is 5-20 years.
- The agency of the affected groups is low.
- Media coverage of arsenic contamination has been low. However, there has been plenty of dramatisation in the press and scientific journals. Example titles are "Georgia's 'secret' arsenic village" (BBC News 2011), "Bangladesh: 77m poisoned by arsenic in drinking water" (BBC News 2010), "Arsenic calamity in the Indian subcontinent: What lessons have been learned?" (Chakraborti et al., 2002), "Arsenic contamination in Bangladesh groundwater: a major environmental and social disaster" (Alam et al., 2002), and "The arsenic crisis in Bangladesh and human rights issues" (Mannan 2006) to name a few. Powerful photographs of people suffering from chronic arsenic poisoning accompany some of these.
- The economical benefits of mitigation programmes are obscured by the uncertainties of science.
- Lack of water infrastructure in affected countries and/or low capacity of the affected groups to pay full market cost of water infrastructure which makes them unattractive for investment by water companies.

2.8 Arsenic mitigation in Bangladesh

Discussion in academic forums regarding arsenic contamination in Bangladesh is very contentious. Affairs such as establishing who (if any) is responsible for this environmental problem; the type of policies necessary to provide safe drinking water to the overall population; delimiting responsibilities for policy implementation; the appropriateness (and origin) of the technology to be used; the issues that require further research are some examples. For instance, despite arsenic being of natural origin UNICEF, the British Geological Survey (BGS), and the Government of Bangladesh have been blamed for lack of duty of care to Bangladeshis.

UNICEF initially funded and then actively promoted the drilling of tube-wells across Bangladesh. In 2001, the UK Natural Environment Research Council (parent agency of the BGS) was sued by two Bangladeshis who claimed that that the agency was negligent in not testing for the presence of arsenic in groundwater while carrying out research in Bangladesh in 1992. In 2006 the House of Lords dismissed the case on the grounds that BGS had no control over or responsibility for the provision of safe drinking water to the citizens of Bangladesh (House of Lords 2006). Both UNICEF and the BGS argued that at the time there was no reason to suspect arsenic as a possible contaminant in that region.

Bangladesh history and political, economical and social background

At the end of the 17th century and during 18th century the Bengal region was under British rule. In 1947 India and Pakistan (West and East) obtained independence from the British. West and East Pakistan were separated by 1,600 km of Indian Territory. Linguistic, cultural, and ethnic differences led to the independence of East Pakistan and the creation of People's Republic of Bangladesh in 1971 (US DoS 2010). Bangladesh was under military rule from 1971 until 1990 (Belal et al., 2001). Since then the country held democratic elections in 1991, 1996, 2001 and 2008. Political stability in Bangladesh is weak; political oppression by the ruling party is common and the opposition exploits political rights with frequent general strikes that paralyse the country for days (Belal el al., 2001).

Bangladesh is one of the most densely populated countries. It is an agrarian country; 75 per cent of the population live in rural areas and 45 per cent of the population is employed in agriculture (CIA 2010). Eighty five per cent of the population practices Islam (Brouwer et al., 2007). Literacy rates are 54.0 per cent for males and 41.4 per cent for females (CIA 2010). Infant mortality rates are 53.23 deaths/1,000 live births for males and 48.13 deaths/1,000 live births for females (CIA 2010).

Bangladesh is one of the poorest countries. The gross domestic product of the country is composed by 18.4 per cent by agriculture, 28.7 per cent by industry and 52.9 per cent by services (CIA 2010). Transportation, communication and power supply infrastructures are poorly developed. The country’s dependence in foreign aid has lead to the blooming of non-governmental organisations (NGOs) across the country. NGOs have presence in 78 per cent of villages (White 1999). Since independence Bangladesh has received US$ 30 billion in grant aid and loan commitments from foreign donors (US DoS 2010).

Bangladeshi society is highly hierarchical and has high family values, powerful elite groups and endemic corruption (Belal et al., 2001). The country occupied the 139/180 rank in the Transparency International corruption perception index in 2009 (TI 2009). Other issues that plague the political landscape are the lack of integrity and efficiency of the administrative institutions; politicisation of the civil bureaucracy; growing presence of influential business individuals in government decision-making processes; an outdated legal system; and an inefficient and unaccountable justice system (Quadir et al., 2008).

The country is exposed to various natural and manmade environmental disasters. Bangladesh is prone to floods, droughts, cyclones, tornadoes, earthquakes and natural arsenic contamination of drinking water (Gain 1998). The main manmade environmental problems include deforestation for energy generation, destruction of mangrove environment for shrimp cultivation, contamination of the coastal environment due to the ship breaking industry, air and water pollution due to development of the industry sector, and bacteriological contamination of surface water due to poor sanitation practices (Gain 1998).

Current state of arsenic mitigation in Bangladesh

The state of arsenic mitigation in Bangladesh can be estimated comparing the 1998-1999 survey conducted by the BGS, United Kingdom Department for International Development (DFID) and the Government of Bangladesh (GoB) (BGS/DFID/GoB survey) (BGS 2001) with the 2009 Drinking Water Quality Survey by the Bangladesh Bureau of Statistics and UNICEF (DWQ survey) (BBS 2011, BGS 2001). The 1998 BGS/DFID/GoB survey measured the actual arsenic concentration in water sources when few mitigation options were implemented; and the 2009 DWQ survey measured arsenic concentration in household drinking water.

In the 1998 BGS/DFID/GoB survey the percentage of samples exceeding the Bangladeshi drinking water standard was 27 (n=3,534) and 28-35 million people were estimated to be exposed to arsenic concentrations higher than 50 $\mu g\ L^{-1}$. The highest estimate averages arsenic concentration by sub-district (or upazila), and the lowest estimate by 5 km grids (BGS 2001). The latter is believed to be more accurate. In the 2009 DWQ survey 13.4 per cent of samples (n=15,000) exceeded 50 $\mu g\ L^{-1}$ and 22 million people were estimated to be exposed to arsenic; assuming that in average 15 persons use each tube well (BBS 2011).

Considering the fall in the percentage of arsenic contaminated samples, from 27 to 13.4 per cent, it could be said that considerable progress has been made. However, the estimates of people exposed to arsenic (from 28-35 million in 1998 to 22 million in 2009) show a more modest progress. In a very simplistic way, in 16 years the population exposed to arsenic in drinking water has fallen only between 12 and 38 per cent. The 2009 DWQ survey found that arsenic was found in samples from all water sources; deep tube-wells, dug wells, surface water, piped supplies, public taps/standpipes and springs (BBS 2011).

This type of comparison is helpful to obtain an indication of the past and current state of arsenic mitigation. One of the problems with this approach is that it does not identify if the population is actively participating in arsenic mitigation and the arsenic mitigation options that households are adopting (if any).

Comparison of arsenic mitigation with other programmes

This section presents and discusses two programmes that have been implemented in Bangladesh. The purpose of this section is to highlight the similarities of these programmes with arsenic mitigation and to compare the effectiveness of these programmes in terms of adoption rates and compliance with their initial aims. The programmes selected were rural sanitation and rural mobile phone use. Background information for both programmes is summarised at the beginning of each subsection.

Sanitation programmes

Arsenic mitigation and sanitation share many characteristics. Arsenic mitigation clearly fits within access to safe drinking water. Both sanitation and safe drinking water access are included in the United Nations Millennium Developing Goals (UN 2011). In many cases health education, sanitation and drinking water programmes are run in parallel. Both programmes could involve the understanding of abstract concepts; germ theory in sanitation and arsenic occurrence and health effects in arsenic mitigation. Sanitation and drinking water programmes involve behaviour change and may involve the adoption of some sort of technology.

Latrine coverage in Bangladesh has dramatically improved; it went from 1 per cent in 1971 to 73 per cent in 2008 (Galway et al., 2000). The *Community led total sanitation* programme has had a big impact in sanitation; when the programme started in 2001 sanitation coverage was stagnated at 33 per cent (WAB 2011). In Bangladesh, mortality (the number of deaths within a particular society and within a particular period of time) of children under 5 years old from diarrhoea decreased 86 per cent from 1971 to 2004 (Unicef 2007). However, diarrhoea's morbidity (the relative incidence of a particular disease) has not decreased as drastically as mortality rates; children in Bangladesh suffer from 2 to 5 diarrhoea episodes per year (Unicef 2007). The reduction in mortality rates but not in morbidity rates could be explained by confounding factors such as oral rehydration therapy, hand washing and water supply programmes.

The effect of sanitation on reducing mortality and morbidity due to diarrhoea is highly controversial. Studies investigating exclusively the effect of sanitation are rare; four Chinese studies reported effects ranging from 8 to 63 per cent reduction in morbidity (Cairncross et al., 2010). A meta-analysis of 144 water supply and/or sanitation studies found a 26 per cent reduction in diarrhoea morbidity due to adequate access to sanitation (Esrey et al., 1991).

Another similarity between sanitation and arsenic mitigation programmes is the tendency to report effectiveness in terms of delivery of hardware; latrines, wells, arsenic removal units, etc. This is especially relevant for water access in Bangladesh. Although physical access to a water source may be possible for a household; water rights in Bangladesh are not secure and they depend on government, religious and/or customary laws that regulate who may get access to what source and for what purpose (Sultana 2006).

In contrast to arsenic mitigation, delivery of sanitation hardware since the 1990s has been mostly in the hands of the private sector as a commercial enterprise (Galway 2000). Sanitation programmes within *Community led total sanitation* have adopted the premise that subsidies to hardware slow and inhibit the universal adoption of sanitation (Kar et al., 2006). Interestingly, since this policy was implemented latrine coverage sharply increased.

Households benefiting from sanitation programmes could sense the comfort and social status benefits of latrine adoption. In contrast, some arsenic mitigation programmes actually involve a loss in comfort (since more time and effort are required to collect water) or in social status (given that owners of private wells marked as arsenic contaminated could face social issues).

Poverty reduction through expansion of mobile phone use in rural Bangladesh

Although it may not seem apparent, mobile phone use in Bangladesh is an interesting comparison to arsenic mitigation. For some of the mitigation programmes households require to use a water treatment system to obtain safe water. Water treatment programmes usually have very low adoption rates; which are then explained in terms of low literacy of users and the relatively high cost of technologies. However, neither of those barriers has limited widespread adoption of mobile phone in rural Bangladesh.

In 2000, there were 0.26-0.3 fixed telephone lines per 100 inhabitants (Richardson et al., 2000). By 2007, one in seven Bangladeshis owned a phone (Shaffer 2007). Mobile telephones contributed in great extent to the improvement in telephone density (Hoque et al., 2005).

In 1997, the Grameen Phone’s programme for income generation was launched. The programme is exclusively open to Grameen Bank members; which are mostly women. Grammen Bank’s members, fulfilling certain criteria, are eligible to obtain a loan to buy a mobile phone. The village phone operators generate a profit by reselling mobile air time to their fellow villagers. The profits generated are used to repay the loan and to supplement household income.

In theory, mobile phones would enhance productivity and social welfare, and would create new sources of income in rural communities through telecommunication access. However, the village phone programme generates a small portion of Grameen Phone revenues and it relies on subsidies from urban mobile users (Falkenberg et al., 2009; Cohen et al., 2001). Evidence on economical benefits for mobile phone users is anecdotal (de Silva et al., 2008). Although some villagers use mobile phone to obtain access to the price of commodities and get a fairer price from middleman, most customers use the phone to keep in touch with relatives or to arrange delivery of remittances from expatriates (Selinger 2008).

Income generated by village phone operators has sharply decreased. The average income of a village phone operator fell from US$ 300 in 2000 to US$ 70 in 2006 (Shaffer 2007; Richardson et al., 2000). This effect is related to the increased ownership of mobile phone and the increased number of phone operators per village. On the positive side, increased ownership of mobile phones created 238,000 jobs in one year in Bangladesh (Shaffer 2007).

Although economic benefits for mobile phone users have been small and substantial economic motivations are gone for village phone operators; the programme has had in overall a positive impact on the livelihoods of rural Bangladeshis. This programme also shows that illiteracy and relatively high cost of technology are not a barrier when users can easily recognise the benefits that they could obtain from a technology.

2.9 Summary

Contamination of drinking water supplies with arsenic in concentrations higher than the WHO guideline value affects millions of people worldwide. Health effects of chronic arsenic poisoning include cancer of the skin, lung and bladder to name a few. Arsenic contamination is of special concern in MLICs with widespread contamination of drinking water supplies. These countries require effective, simple and cost-effective mitigation strategies that could be implemented in a short period of time. However, some MLICs have political, economical and infrastructure systems in which implementation of mitigation programmes is complex.

Construction and use of conventional arsenic removal technologies is unfeasible in some MLICs. Low-cost technologies, which have been applied for a number of years in removal of bacteria and microorganisms from drinking water, have emerged as one possibility to reduce exposition to arsenic in MLICs. Various household and community level technologies have been tested for arsenic removal in laboratory settings, but very few have been field tested in ideal household conditions, and even fewer have been run at pilot level. Among the latter are the Sono and the Kanchan filters.

Some discrepancies in the effectiveness of technologies have arisen in field trials; which support the view that widespread implementation of low-cost technologies is not yet appropriate. Variation in the performance of low-cost technologies is related to the chemical composition and pH of water. Also, quality control of units and differences between user procedures may play a role.

AC is extensively used in water treatment for removal of organic compounds, taste, odour and dissolved organic matter. The use of AC for metal removal has been extensively investigated. The main limitations of AC are its relatively low arsenic adsorption capacity and its high cost. The preparation process of AC can be optimised to maximise arsenic adsorption. Use of agricultural by-products for production of AC is one alternative to lower its cost. Other advantages of the use of agricultural by-products are the production of a value added commodity and reduction of the amount of wastes going to landfills. In addition, gasification of agricultural wastes could be used to simultaneously produce energy and AC. The cost of conventional AC varies between US$3.30 (general use) and US$ 20 (metal sequestration) per kg; while the cost of agricultural based AC has been estimated between US$ 2.42 and 3.12 per kg.

Non-technological aspects of arsenic contamination are important for implementing successful mitigation strategies. These non technological issues include the way in which the political, cultural and social environments shape the perception of environmental problems, the selection of possible solutions, and the way in which these are implemented. Technologists and social scientists need to collaborate to develop solutions that are technologicaly sound and politically and culturally acceptable.

3. Expert survey: arsenic mitigation in middle and low income countries

This chapter presents the *Expert survey: arsenic mitigation in middle and low income countries* with the purpose of investigating some of the non-technological problems related to arsenic mitigation in middle and low income countries (MLICs). The survey is by no means an exhaustive investigation of arsenic mitigation problems; and the results of the survey are limited by the low response rate achieved and the academic profile of most of the respondents. The discussion of the survey results, based on the comments of the respondents, includes consideration of all arsenic-safe water options.

3.1 Survey aim

The specific objective of the survey was to get a deeper understanding of the factors surrounding arsenic mitigation and implementation of low-cost technologies in MLICs. The survey aimed to collect the opinion of respondents regarding the effectiveness of programmes that have been implemented in MLIC, the effectiveness of different technologies used for arsenic removal, and issues affecting arsenic mitigation in MLIC.

The survey was directed to three types of professionals with expertise on arsenic mitigation in MLIC; academics, policy-makers, and development practitioners. In this chapter, survey results are contextualised with the support of literature available on academic journals, development agencies and governmental reports. Later, in *Chapter 8*, the survey results are integrated with the experimental research of the thesis.

3.2 Survey methodology

The survey was delivered by e-mail as a self-administered questionnaire. Respondents received an e-mail inviting them to take part in the survey. The e-mail contained general information about the research programme, and instructions to complete and return the survey. Three attached files were sent; the survey instrument, explanatory notes for the survey, and the informed consent form. These three documents are contained in *Appendix A*. Completed surveys and informed consents forms were collected by e-mail.

The survey was first tested on January 2009 with the supervisory team and with two additional persons unrelated to the research. Then, this version was tested with one respondent on March 2009 and some minor modifications were made. Finally, the survey was sent to all respondents on April 2009. Remainders for the survey were sent after two and four weeks of the initial contact. Information linking individual surveys and names of respondents was destroyed. Analysis of results for most of the questions was made in Excel 2007 and for some questions SPSS version 14.0 was used to run statistical analysis.

3.3 Characteristics of respondents

Potential respondents were identified in academic journals, web sites specialised on arsenic issues, and public reports from non-governmental organisations, international organizations and governments. Potential respondents were selected with base on their experience on arsenic issues because the survey was highly specialised. The survey was sent to 82 potential respondents. Twenty-two questionnaires were returned of which one was excluded from the analysis because most questions were unanswered.

Table 3.1 shows information on gender, nationality, highest qualification and job sector of respondents. Of the respondents 18 (86 per cent) were male, 9 (43 per cent) were of Bangladeshi nationality, 16 (76 per cent) had a PhD qualification and 15 (71 per cent) worked in academia. Six respondents were males of Bangladeshi nationality with a PhD degree working in the academic sector.

Table 3.1 Number of respondents by gender, nationality, highest qualification and job sector. Symbols: No. Number of respondents.

Gender	No.	Nationality	No.	Qualification	No.	Job sector	No.
Male	18	Bangladeshi	9	PhD	16	Academic	15
Female	3	American	2	Masters	3	Development practitioner	4
		British	2	First degree	2		
		Indian	2			Other	2
		Australian	1				
		British/American	1				
		Canadian	1				
		Dutch	1				
		Japanese	1				
		Swedish	1				

The professional expertise and background of respondents was investigated through several questions. Respondents had to describe their experience on arsenic related issues selecting one of the following options: expert, intermediate, some, and little. Sixteen respondents classed their experience as *expert*, two as *intermediate*, two as *some*, and one as *little*. Fieldwork experience of respondents on arsenic related issues was also investigated. To ensure homogeneity respondents were provided with the following definition for fieldwork:

> *"Fieldwork is considered as any kind of practical activity that is carried out (at least in part) away from laboratories and offices"*

All respondents reported having fieldwork experience on arsenic related issues. Countries where respondents mentioned to have fieldwork experience were Argentina, Bangladesh, Bolivia, Cambodia, Chile, China, Costa Rica, India, Lao, Myanmar, Nepal, Thailand and Vietnam. Of the respondents, 19 (91 per cent) have conducted fieldwork on arsenic related issues in Bangladesh; 12 (57 per cent) only in Bangladesh and 7 (33 per cent) in more than one country.

Respondents selected the areas on which they have experience from a list of options. Table 3.2 presents areas of experience by number and percentage of respondents. More than 90 per cent of respondents have experience in more than one area. The areas in which more respondents had experience were in testing drinking water for arsenic, and arsenic awareness programmes. The percentage of respondents with experience on technology related issues and social related issues were very similar; 76 and 86 per cent respectively. Also, 62 per cent of respondents had experience in both areas.

Table 3.2. Arsenic related areas of experience by number and percentage of respondents.

Area of experience	Number of respondents	Percentage of respondents
Testing drinking water for arsenic	15	71
Arsenic awareness programmes	14	67
Identification of alternative arsenic-free water sources	12	57
Elaboration of national policies for arsenic mitigation	11	52
Design or implementation of arsenic removal technologies for drinking water	10	48
Arsenic studies in food, soil or air	9	43
Hydrochemical surveys	7	33
Identification of arsenic patients	7	33
Social care for arsenic patients and their families	6	29
Arsenic toxicity studies	6	29
Other arsenic-related issues	6	29
Health care for arsenic patients	5	24
Epidemiological surveys	5	24
Mental health care for arsenic patients and their families	0	0

3.4 Survey results

3.4.1 Arsenic mitigation in middle and low income countries

Three issues were mainly investigated in the survey, arsenic mitigation policies or programmes, barriers to arsenic mitigation, and performance of arsenic removal technologies. Respondents were asked to consider the following definition for arsenic mitigation:

> *“Set of actions that are performed with the objective to lessen population’s exposure to arsenic and to improve quality life of persons that have been affected by arsenic in any way”*

3.4.2 Arsenic mitigation programmes

The efficiency of arsenic mitigation policies and programmes was investigated with the question presented in Figure 3.1. Answers were post-coded and analysed by country and by type of programme. Although the number of respondents for the survey was 21, the number of responses for this question was 67. Since each respondent could list up to 6 programmes or policies, the number of expected responses was greater than the number of respondents.

Figure 3.1 Format of the question used to investigate the efficiency of arsenic mitigation policies and programmes.

<table>
<tr><td colspan="3">In the right column, list a maximum of six policies or programmes undertaken in middle or low income countries to mitigate arsenic. In the middle column, write the name of the country where these programmes were undertaken. In the right column, rate each of these programmes or policies from 10 (very efficient) to 0 (very inefficient).</td></tr>
<tr><td>Policies or programmes
1)</td><td>Country</td><td>Rate</td></tr>
</table>

Ten countries were mentioned by respondents: Argentina, Bangladesh, Cambodia, Chile, China, Hungary, India, Lao, Nepal and Unites States of America. The latter was excluded from the analysis because is a high income country and hence falls outside the survey remit. Of all responses, 46 refer to Bangladesh, 9 to India, 4 to Nepal, 2 to Cambodia and 1 to Argentina, Chile, Lao, Hungary and China. Respondents from Bangladesh provided 37 per cent of all responses. Considering responses only for Bangladesh, 52 per cent were given by Bangladeshis. Table 3.3 shows the frequency distribution for rates of efficiency of mitigation programmes for countries with more than one response.

Table 3.3 Frequency distribution of efficiency rates for arsenic mitigation programmes in Bangladesh, India, Nepal and Cambodia.

Country	Frequency											
	0	1	2	3	4	5	6	7	8	9	10	Total
Bangladesh	3	7	2	6	5	8	4	2	6	1	2	46
India	2	1	0	0	2	1	0	0	2	0	1	9
Nepal	1	0	1	0	0	0	0	1	0	1	0	4
Cambodia	0	0	0	0	1	0	1	0	0	0	0	2

Efficiency of programmes among countries was compared using the median non-parametric test. Statistic tests were performed with the software SPSS version 14.0. A non-parametric test was used for two main reasons. Firstly, parametric tests assume that the variable is of interval type. In this case, efficiency of programmes is an ordinal variable. Secondly, the frequency distribution seems not to be normally distributed. Non-parametric tests do not make assumptions about the distribution of variables and hence are most appropriate in this case. According to the median test there is no significant difference between the medians of efficiency of programmes in Bangladesh, India, Nepal and Cambodia; χ^2 = 0.095, p-value of 0.992 and programme efficiency median of 4.0/10.

Bangladesh was the only country with sufficient answers to analyse the differences among types of programmes. Arsenic mitigation policies and programmes were classified into four categories; governmental-university or non-governmental organisation (NGO) programmes, arsenic removal technologies, alternative water sources, and other (Table 3.4). Identification and treatment of arsenicosis patients and investigation of arsenic content in food crops programmes were included in the "others" category because the small number of responses.

Table 3.4 Classification outline of arsenic mitigation programmes and policies implemented in Bangladesh.

Programme category	Programme outline
Governmental-university or NGO programmes	Programmes conducted by government, international or local NGOs and universities. For example, the National Arsenic Mitigation Programme and the Bangladesh Environmental Technology Verification Arsenic Mitigation Programme (ETV-AM)
Arsenic removal technologies	Arsenic removal filters and research on arsenic removal
Alternative water sources	Alternative arsenic-safe water sources such as rain water, deep tube wells, dug wells, surface water, bottled water and piped water
Other	Identification and treatment of arsenicosis patients and investigation of arsenic content in food crops

Table 3.5 presents the frequency distribution of responses by type of programme in Bangladesh. Programme category *alternative water sources,* obtained the highest number of responses. All types of programmes were rated by respondents with a wide range of efficiency rates.

Table 3.5 Frequency distribution for efficiency rates of arsenic mitigation programmes by type of programme in Bangladesh.

Programme	Frequency											
	0	1	2	3	4	5	6	7	8	9	10	Total
Governmental-university or NGO programmes	0	1	1	0	2	2	1	1	2	0	0	10
Arsenic removal technologies	2	0	0	0	0	0	2	0	1	1	0	6
Alternative water sources	0	5	1	4	2	5	1	1	3	0	2	24
Other	1	1	0	2	1	1	0	0	0	0	0	6

Efficiency among programmes in Bangladesh was compared with the median non-parametric test. The reasons for using a non-parametric test are explained previously in this section. According to the median test there is no significant statistical difference among the medians of efficiency of different type of programmes in

Bangladesh; χ^2 = 3.733, p-value of 0.292 and programme efficiency median of 4.5/10.

3.4.3 Performance of arsenic removal technologies

The opinion of respondents about general performance of arsenic removal technologies was explored in the survey. Technology types included in the survey were selected from academic journals and specialised websites on arsenic mitigation. Evaluation of actual performance of technologies is beyond the reach of the survey. Respondents answered a set of multi-choice questions regarding chemical quality of water; bacteriological quality of water; cost-effectiveness; and operation and maintenance problems for different types of arsenic removal technologies. Additionally, respondents could comment on performance of technologies and name other technologies that were excluded from the survey.

The set of questions used to investigate the general performance of technologies is presented in Table 3.6. Possible answers to these questions were *yes*, *no* and *don't know*. For each technology type the following procedure was followed. First, the total number of answers was calculated by adding the number of *yes*, *no* and *don't know* answers. Then for Q1, Q2 and Q3, *yes* answers were assigned a value of *+1*, *no* answers were assigned a value of *-1* and *don't know* answers were assigned a value of *0*. For Q4, *yes* answers were assigned a value of *-1*, *no* answers were assigned a value of *+1* and *don't know* answers were assigned a value of *0*. In the case of Q1, Q2 and Q3, *yes* answers reflect good technology performance whereas in Q4, *no* answers reflect good technology performance.

Table 3.6 Questions used to explore the opinion of respondents about performance of types of arsenic removal technologies.

Symbol	Question
Q1	Do you consider it chemically safe?
Q2	Do you consider it bacteriologically safe?
Q3	Do you consider it cost- effective?
Q4	Do you consider it to have operation and maintenance problems?

Next, *yes*, *no* and *don't know* answers were added and then divided between the total number of answers. The results of this mathematical operation were called Q1, Q2, Q3 and Q4 depending on the question. To calculate the overall performance of technologies the values obtained for Q1, Q2, Q3 and Q4 were added and the result was named ΣQ.

Table 3.7 presents the number of total answers and the values obtained for Q1, Q2, Q3, Q4 and ΣQ for each technology type. The maximum and minimum possible values for Q1, Q2, Q3 and Q4 were *+1* and *-1* and for ΣQ were *+4* and *-4*. The respondents' perception of good technology performance is reflected by larger positive values. It is important to remark that these results reflect the opinion of experts regarding technology performance and not actual performance of technologies and that the opinion of respondents may be biased due to more familiarity with certain technologies than others.

Table 3.7 Number of total responses and values obtained for Q1, Q2, Q3, Q4 and ΣQ for each technology type. Technologies are in descending order of overall performance (ΣQ). Symbols: Q1 chemically safety; Q2 bacteriological safety, Q3 cost-effectiveness, Q4 operation and maintenance problems and ΣQ overall technology performance.

	Technology type	Total responses	Q1	Q2	Q3	Q4	ΣQ
1	Composite iron matrix technologies (e.g. Sono filter)	17	+0.9	+0.2	+0.8	-0.7	+1.2
2	Granular ferric hydroxide technologies (e.g. Sidko ADSORPAS)	13	+0.9	+0.4	-0.4	-0.4	+0.5
3	Co-polymer adsorbent technologies (e.g. Read-F)	10	+0.8	0	-0.1	-0.6	+0.1
4	Coagulation-flocculation processes with iron salts (e.g. Steven’s Institute of Technology)	13	+0.4	-0.2	+0.2	-0.4	+0.0
5	Ion exchange technologies (e.g. Tetrahedron)	10	+0.1	0	-0.3	-0.1	-0.3
6	Household technologies using locally produced activated alumina (e.g. BUET in Bangladesh)	16	+0.3	-0.2	-0.1	-0.6	-0.6
7	Coagulation-flocculation processes with aluminium salts (e.g. DANIDA bucket)	14	-0.3	0	0	-0.5	-0.8
8	Household technologies using imported activated alumina (e.g. Alcan)	17	+0.4	-0.3	-0.5	-0.5	-0.9

The results presented in Table 3.7 allow comparisons among technology types. Household technologies using imported activated alumina (technology type 8), household technologies using locally produced activated alumina (technology type 6) and composite iron matrix technologies (technology type 1) obtained the highest number of responses. None of the technology types obtained positive values for all factors investigated.

Technology types with more negative values were household technologies using imported activated alumina (technology type 8) and household technologies using locally produced activated alumina (technology type 6). On the contrary, the technology type with the greatest number of positive values was composite iron matrix technologies (technology type 1) followed by granular ferric hydroxide technologies (technology type 2) and coagulation-flocculation processes with iron salts (technology type 4). Composite iron matrix technologies (technology type 1) and granular ferric hydroxide technologies (technology type 2) obtained the highest positive values for overall technology performance (ΣQ).

Additionally, respondents commented on performance of technology types. Some responses mentioned the difficulties of estimating the time for reactivation or replacement of removal media for technologies. For example, one respondent commented:

> *"If users do not perform arsenic analysis it [sic] is hard to find out whether the device has reached breakthrough or not. Most of the time users think water from the filter is safe, however it has reached breakthrough and is not treating arsenic any longer."*

Also, respondents commented about operation and maintenance (O&M) issues. An example comment was:

> *"In our project we had experts who examined this sort of approach. In theory it worked but in practice it did not because it was not maintained properly by the householders."*

Cost of O&M, handling of potentially harmful materials by technology users, and complex and time consuming O&M procedures were mentioned as current issues for most technologies. Also, initial cost was identified as a limitation for some technologies.

Composite iron matrix technologies (technology type 1) obtained relatively high positive values for most of the issues investigated, with the exception of O&M performance (Q4). This technology also obtained positive comments about performance. However, issues such as monitoring of performance of technologies and production of potentially toxic wastes were mentioned as potential constraints for this technology type.

Other technologies that were mentioned by respondents were Pal-Trokner and Amul in West Bengal, Kanchan arsenic filter, PuR, Lifestraw, SORAS, Hybrid Ion Exchange, activated alumina, Shapla filter, Asia Arsenic Network filter and CAWST Bio-Sand filter.

3.4.4 Operation and maintenance problems of arsenic removal technologies and generation of toxic wastes by technologies

Respondents were asked to consider technologies that were chemically and bacteriologically safe and comment on how O&M problems could be overcome. Respondents' answers were post-coded in eight categories (Figure 3.2): maintenance problems, support to users, water quality, technology design, cost of O&M, community participation, wastes, and others.

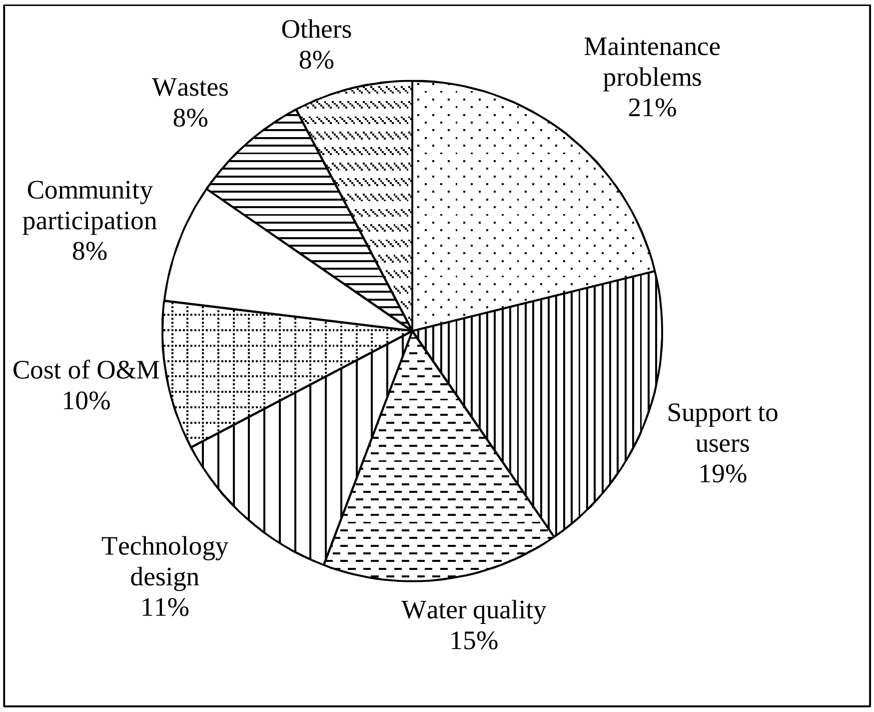


Figure 3.2 Operation and maintenance problems on arsenic removal technologies identified by respondents.

Maintenance problems obtained the highest number of responses, 21 per cent, with responses mentioning availability of spare parts for technologies; and easiness and frequency of maintenance of technologies where classed in this category. *Support to users* obtained the second highest percentage of responses. This category included issues such as adequate training to users to operate and maintain technologies; support for monitoring of chemical and bacteriological quality of water treated; support for media regeneration or replacement; and implementation of arsenic and health awareness programmes. A respondent highlighted the importance of awareness programmes for technology adopters:

> *"Technology alone cannot save people and their lives. It must be accompanied by awareness/building/raising activities to ensure behavioural changes in their water fetching pattern."*

The *water quality* category obtained the third highest percentage of responses. Responses in this category included mentions to actual chemical and bacteriological quality of treated water, and the need to monitor the chemical and bacteriological quality of treated water. One respondent commented:

> *"None of the above mentioned technologies are able to produce safe water in terms of chemically and biologically jointly."*

Regarding generation of wastes by arsenic removal technologies, respondents were asked if, in their opinion, wastes produced by arsenic removal technologies were a potential contamination source. Of the respondents, 67 per cent answered *yes*, 19 per cent answered *no,* and 10 per cent answered *don't know*.

3.4.5 Routine use of arsenic removal technologies

In an open question respondents were asked to comment on the factors that may be affecting the routine use of arsenic removal technologies in households in rural communities. Answers were post-coded in the following categories: O&M problems, economical issues, social issues, accessibility, follow up issues, and others (Figure 3.3).

O&M problems obtained the highest percentage of responses, 50 per cent. In this category easiness of technology operation; amount of treated water available; time required for water treatment; frequency and easiness of maintenance; replacement of spare parts, water quality issues and drawbacks of technology design were included. *Financial issues* and *social issues* obtained the second highest percentage of responses, 16 per cent each. *Financial issues* included responses concerning the economic cost of obtaining a technology for a household; the cost of operating a technology on a daily basis; and the cost of maintaining a technology. *Social issues* contained responses concerning awareness of health effects of arsenic; user's motivation to use a technology on a daily basis; and low education profile of potential users. A respondent commented:

> *"The major problem is long-term motivation when there other pressures on the time of household members"*

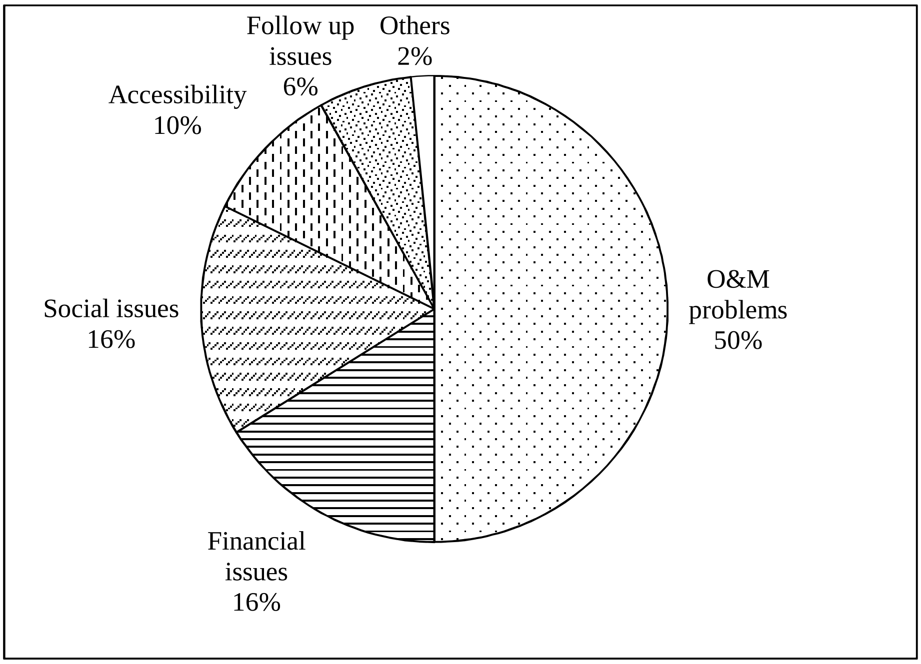


Figure 3.3 Factors affecting the routine use of arsenic removal technologies in households in rural communities according to respondents.

3.4.6 Factors affecting arsenic mitigation

Factors that may be affecting arsenic mitigation programmes were investigated in two questions. Firstly, a closed question investigated whether or not there are some problems affecting arsenic mitigation in the opinion of respondents. When asked if they considered that there are some problems affecting arsenic mitigation in MLIC 86 per cent of respondents answered *yes*, 5 per cent answered *no* and 5 per cent answered *don't know*. Secondly, in an open question respondents listed these problems. Responses were post-coded in the following categories (Figure 3.4): political issues, technological issues, economical issues, awareness issues, health issues, quality issues, and other.

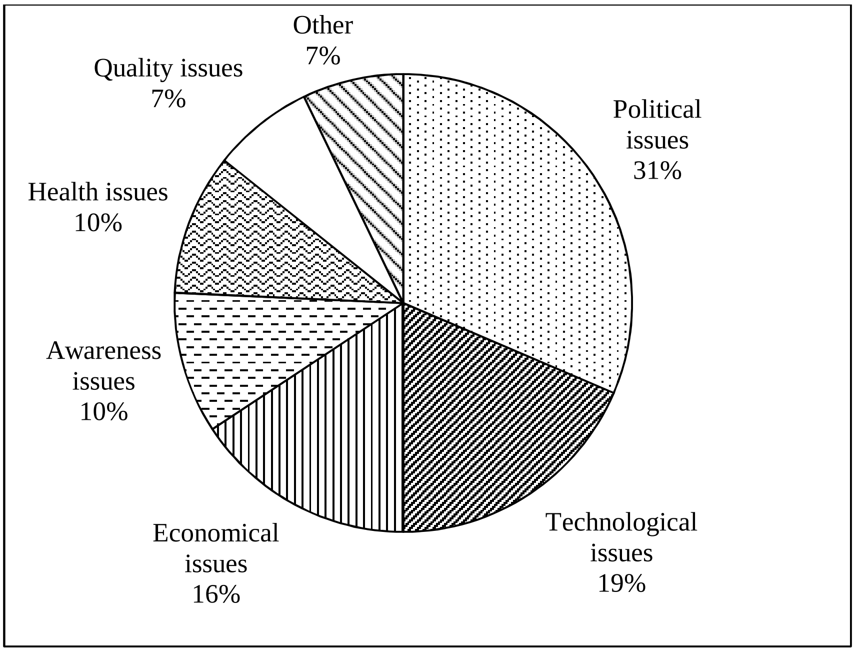


Figure 3.4 Factors that may be affecting arsenic mitigation strategies in middle and low income countries.

Political issues obtained the highest number of responses, 31 per cent. This category included responses concerning the role of government and NGOs on implementation, administration and follow up of mitigation strategies; sustainability of mitigation strategies; and coordination of mitigation actions among NGOs, government and public. Two example comments are:

> *"The over-reliance on NGOs which [sic] are becoming more a profit-making [sic] organizations. NGOs are becoming big business in underdeveloped countries. The filters mentioned above are distributed by NGO's. None of them are commercial products in poor countries."*

> *"No follow-up action or monitoring/surveillance of the technologies introduced in rural areas. Hence while targets are met on paper, there are no beneficiaries at the ground level."*

Technological issues obtained the second highest number of responses, 19 per cent. This category includes responses concerning the availability of arsenic-safe options (apart from arsenic removal technologies) to affected people. One respondent commented:

> *"Suitable region-specific [sic] water options are yet to be available for all the arsenic affected areas."*

Economical issues category obtained 16 per cent of responses. In this category two types of economical aspects were included; economic aspects at country level and at household level. Country level covers economic aspects of arsenic mitigation programmes for country's governments. Household level covers the affordability of arsenic mitigation options to individual households. A respondent commented:

> *"The arsenic in drinking water and the potability of drinking water are massive issues in terms of magnitude and cost. Low income countries do not have the means to solve this issue alone. For example, just to provide filters to rural poor would cost more than $150 million in Bangladesh. The solution is the development of local-appropriate technologies through development of local expertise and capacity. None of overseas experts are interested in this..."*

The *quality issues* category had the smaller percentage of responses, apart from *other* category. Provision of hardware of adequate quality is important because constant breakdowns may discourage villagers to use the technology. Also, low quality hardware may cause contamination of the environment in the long run. Two interesting comments provided in this category are as follows:

> *"A solid water device will supply safe water of good quality for a long period, but I have seen many pond sand filters abandoned since they were poorly designed/constructed probably to cut down the cost and produced unsafe or smelly water."*

> *""Short cut" attitude probably due to inadequate fund in addition to lack of knowledge and skills. For example, it is well understood that in installing a deep tube well the annular space must be sealed, but in many cases sealing has been neglected, causing another arsenic contamination in deeper aquifers. Another example: in selecting an appropriate water device in one particular place, a hydro-geological survey is required to find a most suitable one, but it is neglected, causing the abandonment of many installed devices."*

3.5 Discussion

This section discusses the main results from the survey. In the light of the proportion of survey results referring to Bangladesh and the information available in the literature regarding arsenic mitigation in Bangladesh, discussion will be based on this country unless specified otherwise. Relevant information about arsenic mitigation available in the literature is presented along with the discussion of the survey results.

The section is structured as follows: arsenic contamination in Bangladesh, characteristics of respondents, arsenic mitigation programmes, arsenic-safe water alternatives and factors affecting arsenic mitigation programmes. Although arsenic-removal technologies were the only alternative water source investigated in the survey, discussion of other alternative safe water sources is included in this section due to their importance in arsenic mitigation.

3.5.1 Arsenic contamination in Bangladesh

In Bangladesh surface water was the main source of drinking water until the early 1970s. Typical drinking water sources for a household included shallow hand-dug wells, ponds and rivers (Kaufmann et al., 2002). During the 1970s the Bangladesh government supported by international organisations promoted a shift from surface water to groundwater to reduce high mortality rates in children caused by microbiological contamination of surface water (Caldwell et al., 2003). Since then millions of tube wells have been installed for groundwater extraction for household use. The current number of tube wells in Bangladesh is estimated in11 million (BBS 2011). It is considered that the main driver for installation of tube wells in Bangladesh was the convenience of having a water source within the household rather than health considerations (Caldwell et al., 2003).

In 1976 arsenic was found in wells in West Bengal India (Atkins et al., 2007). Then, in 1983 health ailments of inhabitants of West Bengal were attributed to arsenic contamination in tube well (Chakraborti et al; 2002). In 1984 patients with similar symptoms were identified in Bangladesh. But, it was until 1998-1999 that the first national survey was launched to investigate the scale of arsenic contamination in Bangladesh (Atkins et al., 2007). This was the 1998-1999 British Geological Survey/ United Kingdom Department for International Development/Government of

Bangladesh (BGS/DFID/GoB) survey, used in *Chapter 2* of this thesis as baseline for arsenic contamination in Bangladesh. In total 3,534 well water samples were collected throughout the country. Of the shallow tube wells (< 150 m deep), 27 per cent exceeded 50 μg L^{-1} of arsenic and 46 per cent exceeded 10 μg L^{-1} (BGS 2001). Only, 5 per cent of deep tube wells (> 150 m deep) exceeded 50 μg L^{-1} and 1 per cent exceeded 10 μg L^{-1} (BGS 2001). According to this survey, an estimated 28-35 million people were exposed to health treating arsenic in the concentrations. The areas more affected by arsenic contamination in Bangladesh are in the south and southeast.

3.5.2 Characteristics of respondents

The survey attempted to reach a large number of professionals with a variety of expertise and backgrounds related to arsenic mitigation. However, the total number of respondents was relatively small (21), more than half of respondents had conducted field work only in Bangladesh, and almost three quarters of respondents work in academia. Such a small response rate, 26 per cent, is typical of this type of surveys. Acknowledging these limitations is not possible to make generalisations of arsenic mitigation programmes in MLICs with the data collected.

3.5.3 Arsenic mitigation programmes

Several mitigation programmes have been implemented in Bangladesh since arsenic was found (BGS 2001). The Bangladesh Department of Public Health and Engineering is responsible for providing safe water supply, environmental sanitation and hygiene education throughout Bangladesh (SDNP 2010). However, many arsenic mitigation actions have been taken over by NGOs and foreign donor agencies (Atkins et al., 2007). Arsenic mitigation has mainly focused on hydro-chemical surveys; investigation of arsenic removal methods and provision of alternative water sources. However, training of health workers for identification and treatment of arsenic-related health effects; and arsenic and health awareness programmes have only been partially covered. Some of the major programmes implemented in Bangladesh are (Atkins et al; 2007):

- Bangladesh Arsenic Mitigation Water Supply (1997).
- British Geologic Survey; Phases I and II (1998-2000).

- Rapid Assessment of Household Level Arsenic Removal Technologies (RAHLART) (2001).
- Environmental Technology Verification Arsenic Mitigation Project (2000-2003).
- Danish International Development Assistance (DANIDA) Arsenic Mitigation Pilot Project (2001-2005).
- Arsenic Mitigation and Measurement Project (2001-2005).
- National Project for Arsenic Mitigation (2004).
- Bangladesh Water Supply Programme Project (2004-2010).

Survey responses for the efficiency rates of arsenic mitigation programmes in Bangladesh, Cambodia, India and Nepal were analysed using a measure of central tendency; the median. According to the median non-parametric test there was no statistical difference in the medians of efficiency rates in programmes in Bangladesh, Cambodia, India and Nepal, with the median being 4.0/10.0. However, due to the different number of responses for each country, from 2 to 46, this result must be interpreted with caution.

On the other hand, no statistical difference was found either on the median of different types of arsenic mitigation programmes in Bangladesh, with the median being 4.5/10.0. Hence, according to survey responses arsenic mitigation programmes are perceived as little efficient. On literature, the impact of arsenic mitigation programmes in Bangladesh have been regarded as low (Atkins et al., 2007, Caldwell et al., 2005; Alaerts et al., 2004; Kaufmann et al., 2002).

Kaufmann *et al.* (2002) attributed the slow progress of the Bangladesh Arsenic Mitigation Water Supply Project to the lack of a national policy and of lack of coordination of the mitigation actions by the government of Bangladesh. On the Implementation Plan for Arsenic Mitigation published by the government of Bangladesh the limited success of provision of arsenic-safe drinking water was attributed to *"the uncertainties of effectiveness of the alternative water supply technology options, inappropriate institutional arrangements, and confusion over the service delivery mechanism"* (BAMWSP 2004).

3.5.4 Arsenic-safe water alternatives

There are various sources from which arsenic-safe water can be obtained. However, all arsenic-safe water options have strengths and weakness on different cultural, economical and hydro-geochemical settings. Survey respondents considered important to provide a variety of mitigation options for individual households. In *Section 3.4.2* alternative water sources was the category with the highest number of responses. In *Section 3.4.6* some respondents commented that it was necessary to offer to households various arsenic-safe water options. Arsenic-safe water sources mentioned by survey respondents include arsenic-safe wells, pond water, rain water harvesting, community or household arsenic removal technologies, bottled water, and piped water. These arsenic-safe water options will be discussed in the following subsections.

Arsenic-safe wells

Some evidence suggest that hand pump tube wells (8-14 m deep), deep tube wells (> 150 m deep) and hand-dug wells (< 10 m deep) tend to have arsenic concentrations below 50 µg L^{-1} (BGS 2001). However, the most recent drinking water quality survey (2009 Drinking Water Quality (DWQ) survey in *Chapter 2*) found high arsenic concentrations in all water sources (BBS 2011). These findings could mean that arsenic contamination is spreading to other water sources or that information provided by households was inaccurate.

Since hand tube wells are extensively used in Bangladesh and the proportion of contaminated tube wells is moderate in some regions, tube well switching is regarded by some as the simplest and most efficient alternative for provision of arsenic-safe drinking water (Ahmed et al., 2006). In tube well switching households, drinking water from an arsenic-unsafe well would have to switch to an arsenic-safe well located on the vicinity of their households. Tube wells with arsenic concentrations below 50 µg L^{-1} are marked with green paint, whereas tube wells with arsenic concentrations above 50 µg L^{-1} are marked with red paint.

Tube well switching may not be applicable in some circumstances. Firstly, although at country level there is a distinct pattern for arsenic contamination in Bangladesh, arsenic concentrations vary from well to well at village scale and with time on individual wells (BGS 2001). Hence, it is necessary to test periodically each well to ensure water is arsenic-safe (Smedley et al., 2002). It is estimated that only 4.95 million wells have been tested for first time for arsenic (Atkins et al., 2007; Alaerts et al., 2004). Secondly, in villages with a high proportion of red-painted tube wells, switching may be not feasible. Thirdly, educational programmes may be needed to ensure the red-green colour code for marking tube wells is understood among households. Studies have reported confusion with this colour code among people in Bangladesh (Hanchett et al., 2002). Finally, it is important to consider that even if access to a water source is possible in terms of proximity, there are other issues affecting access to water sources (*Section 2.4.2*). In addition, most Bangladeshi women observe strict purdah; hence water collection outside of the house compound and especially in public places is inappropriate.

Besides the technological challenges of tube well switching, social problems arising for this practice need consideration also (Sultana et al., 2007). The increased demand on arsenic-safe wells is causing problems between tube well owners/caretakers and water users. On one hand, owners of arsenic-safe tube wells complain of losing privacy at their household; bearing the cost of O&M; and enduring arguments between neighbours on their property. On the other hand, tube well users complain about being forced to maintain good relationships with tube well owners/caretakers; paying occasional fees; and feeling humiliated to use someone else’s well (Sultana et al., 2007). Also, there is a widespread belief that arsenic-safe water may run out if too much water is withdrawn from individual tube wells (Sultana et al., 2007). Furthermore, there are cases in which people with visible symptoms of arsenicosis are not allowed access to arsenic-safe wells (Hassan et al., 2005).

Dug wells and deep tube wells are regarded as arsenic-safe drinking water alternatives in Bangladesh. Shallow aquifers (< 10 m deep) and deep aquifers (> 150 m deep) have arsenic concentrations mostly below 50 $\mu g\ L^{-1}$ (BGS 2001). However these types of wells have other limitations. Hand-dug wells are prone to bacteriological contamination. Water extracted from dug wells may need treatment to remove microorganisms.

Deep tube wells are more difficult and expensive to install and operate. Also, deep tube wells need a diesel pump for water abstraction (Ahmed et al., 2006; Alam et al., 2002). The use of deep groundwater at a large scale requires additional research. First, it is necessary to screen the chemical composition of deep groundwater at a national level (BGS 2001). Although the proportion of deep tube wells contaminated by arsenic is very low, sampled deep tube wells may be unrepresentative of the national deep groundwater quality. For instance, on the survey conducted by the BGS, most deep tube wells sampled were from the south coastal area of Bangladesh. Secondly, it is necessary to consider the impact of large scale abstraction of deep groundwater on water quality (BGS 2001).

An additional complication regarding testing of tube wells is the cost and laboratory requirements of the most sensitive and precise techniques for arsenic analysis in water; hydride generation atomic absorption spectrometry and inductively coupled plasma mass spectrometry (ICP-MS). In terms of cost and analysis time, field test kits are an alternative to these laboratory techniques (Kinniburgh et al., 2002). However, field test kits have disadvantages compared to laboratory analyses. First, the detection limit for some field test kits is 100 $\mu g\ L^{-1}$. There are field test kits with detection limits below 10 $\mu g\ L^{-1}$ but they are significantly more expensive (Kinniburgh et al., 2002). Secondly, some studies have shown underestimation of arsenic concentration determination with field test kits compared to laboratory methods (Petrusevski at al., 2007). Finally, sample analysis is prone to errors if methodologies are not accurately followed.

The 2009 DWQ survey in Bangladesh used both field and laboratory techniques to analyse water samples (BBS 2011). In total 14,442 samples were analysed in the field with a digital arsenator (Wagtech model WE-10500) and 1,925 samples were analysed in the field and also in a Canadian laboratory by ICP-MS. Correlation between laboratory data and field data was reasonable; with a correlation coefficient (R^2) of 0.91 and a slope of 1.03. The good match between these samples is an indication that if methodologies are strictly followed, good quality data can be obtained from field analysis.

Pond water

Overall, microbiological and chemical quality of pond water is poor (Rahman et al., 2003). The microbiological quality of pond water could improve with sand filtration, but sand filters do not remove chemicals. Furthermore, adoption of sand filters by water users is difficult to achieve and sustain. Ponds are used for a variety of activities that affect their water quality. Pond use includes economical activities such as fish culture and washing of livestock, activities related with household chores (washing clothes and dishes) and personal hygiene (bathing). Also some latrines are directly drained to ponds (Johnston et al., 2001). If ponds are to be used as drinking water supply they cannot be used for any of the activities mentioned above (Jakariya et al., 2003). The exclusive use of ponds for drinking water supplies is difficult to achieve because other pond uses are important for households too.

Rain water harvesting

In general rain water is arsenic-safe and has good bacteriological and chemical quality. However, rain water harvesting requires a suitable roof, gutters and storage tank. Also, rain water is subject to bacteriological contamination during collection and storage. Rain water harvesting is limited to the rain season (Johnston et al., 2001).

Piped and bottled water

Although household preference for piped water supply has been documented, only 10 per cent of the population in Bangladesh is served by a piped water network (Barkat et al., 2008; Ahmed et al., 2006; Hoque et al., 2004). According to the World Bank, the long-term cost of piped water in Bangladesh for villages with more than 250 households is less than the cost of home base treatments (Atkins et al., 2007). However, there are economical and non-economical factors that prohibit widespread installation of piped water supplies. The high installation cost of piped water infrastructure is prohibitive for most MLICs. Also, piped water networks require trained professional operators and rigorous quality controls that may be scarce in MLICs (Johnston et al., 2001). On the other hand, bottled water is expensive and not widely available in rural Bangladesh (Crow et al., 2002). Hence, its use is restricted to emergencies.

3.5.5 Community or household arsenic removal technologies

Throughout the survey special attention was given to arsenic removal technologies for their importance on arsenic mitigation and for their link with the experimental work of this research. The efficiency of arsenic removal technologies, as perceived by survey respondents, was investigated in two different sections. In *Section 3.4.2*, arsenic mitigation programmes, arsenic removal technologies were mentioned only a few times. This result was unexpected due to the abundance on research on arsenic removal and arsenic removal technologies. This could be possibly related to the very few field trials of arsenic removal technologies (Aguirre et al., 2006).

Section 3.4.3 focused on the perception of survey respondents on technology performance. *Section 2.3.1* provides a brief description of the technologies included in the survey. The aspects of technology performance examined were chemical and bacteriological quality of water, cost-effectiveness, and O&M problems. The survey results showed that a greater proportion of respondents considered technologies to be chemically safe than to be bacteriologically safe. Also, very few respondents considered technologies to be free of O&M problems.

A high number of respondents considered that composite iron matrix technologies (e.g. Sono filter) were cost-effective. Respondents commented on technology drawbacks mentioned elsewhere such as correct O&M of technologies, cost of O&M, and problems in forecasting how long technologies will remove arsenic under specific groundwater compositions. An issue less commonly mentioned in the literature and which was revised by survey respondents was the necessity to regularly monitor the efficiency of technologies through arsenic and bacteriological water tests.

Overall, the survey results agree with the findings from the two programmes assessing performance of household technologies in Bangladesh; the RAHLART and ETV-AM programmes (described in *Section 2.3.1*). Alcan technology, approved by both programmes, was perceived by survey respondents to have problems with bacteriological quality of water, cost-efficiency and operation and maintenance. Survey respondents considered Sono filters (approved by RAHLART and ETV-AM) and Sidko technology (approved by ETV-AM) as chemically safe, bacteriologically safe and cost-effective. Survey respondents considered that both technologies have O&M problems. A high proportion of survey respondents considered Tetrahedron technology (approved by RAHLART but unapproved by ETV-AM) to be not bacteriologically safe, not cost-effective and to have problems with O&M.

There are two widely know examples of implementation of arsenic removal technologies; the Kanchan filter in Nepal and the Sono filter in Bangladesh. The differences found in the literature regarding performance of technologies, which are described in *Section 2.3.1*, illustrate perfectly the lack of conclusive evidence on technology efficiency and the effect of groundwater composition on arsenic removal.

These examples also support the respondents' opinion of the requirement to constantly monitor arsenic concentration of effluent water from technologies (and other alternative safe water sources). On the other hand, there are advocates of promoting an exclusive type of mitigation programme (i.e. tube well switching or an specific arsenic removal unit) (Barkat et al., 2008; Ahmed et al., 2006). However, it is the general point of view that blanket approaches have proven to be ineffective on providing sustainable arsenic-safe drinking water options (Atkins et al., 2007).

O&M problems of arsenic removal technologies as perceived by survey respondents were investigated in *Section 3.4.4*. According with survey responses, O&M problems are the main issue affecting the routine use of arsenic removal technologies (*Section 3.4.5*). Of the issues affecting the routine use of technologies listed by survey respondents, 50 per cent is related to O&M problems. Of the O&M problems mentioned by survey respondents, more than 50 per cent are related to availability of spare parts for technologies, easiness and frequency of maintenance, monitoring arsenic removal, support for media regeneration or replacement, water quality, and awareness of arsenic. With exception of awareness of arsenic, which is common to all mitigation programmes, these issues will be discussed on the following paragraphs.

The importance of availability of spare parts has been identified earlier in non-arsenic related rural water programmes. The World Bank considers that in order to be sustainable, a rural water project requires a reliable source for spare parts (WB 2002). In this regard a contradiction arises. On one hand the rural population is scattered in settlements with a small population, while on the other hand a variety of options with spare part availability at all times have to be offered to communities with arsenic problems. At first hand this does not seem to be economically feasible.

Some survey respondents considered that household acceptance for removal technologies could be improved by reducing the frequency and difficulty of maintenance tasks (replacing filter media, backwashing). The importance of easiness of maintenance procedures can be illustrated with an example from Hoque *et al.* (2004); the use of iron fillings technologies (Sono filter) in Srinagar (rural

Bangladesh) was discontinued because householders were usually hurt when replacing iron fillings.

Survey respondents identified both water quality and perception of water quality by households as important. In this respect water quality pre- and post-treatment is important. Chemicals present in the water to be treated may affect the performance of arsenic removal technologies in at least two ways; they may significantly reduce the time that a technology can efficiently remove arsenic or they may affect arsenic removal to a point in which the technology does not remove arsenic to a safe level at all (BCSIR 2003). Hence, technologies need to be periodically monitored to verify that they remove arsenic to the target level. Apart from arsenic-safe concentrations, water treated by technologies must have good chemical and bacteriological quality. On the other hand, changes in water taste, smell or temperature may lead to rejection of chemically and bacteriologically safe water by households (Rainey et al., 2005).

3.5.6 Factors affecting arsenic mitigation programmes

In the literature there is agreement that arsenic mitigation programmes have had limited success in providing arsenic-safe water to affected populations (and especially to rural populations) in Bangladesh. However, the factors that affect the efficiency of these programmes are not totally understood (Atkins et al., 2007). Assessment of many of the programmes implemented in Bangladesh is difficult since in the beginning mitigation efforts were highly uncoordinated and isolated from water management policies.

Most survey respondents (86 per cent) agree that there are a number of problems affecting arsenic mitigation in MLICs. The current state of arsenic mitigation in Bangladesh is assessed in *Section 2.4.2* by means of comparing the 1998 BGS/DFID/GoB survey and the 2009 DWQ survey. According to this comparison, the population exposed to an arsenic concentration higher than 50 $\mu g\ L^{-1}$ has fallen between 12 and 38 per cent; which represents modest progress.

Political issues

Almost a third of the survey responses related to factors affecting arsenic mitigation programmes were post-coded to the political issues category. The *Position paper on the Bangladesh response to arsenic contamination of groundwater* summarises the actions that have been taken by different stakeholders in Bangladesh (APSU 2008). The paper observes that the degree of achievement in mitigation in Bangladesh is obscured due to the low diffusion of mitigation actions in academic papers and international forums. Although it is true that the paper list many mitigation actions, it does not mention whether arsenic and other water programmes have been independently evaluated, and if a census of the functionality state and usage of arsenic mitigation options has been conducted.

Survey responses reproduce some of the political issues that have arisen recently in the literature. For instance, the role of NGOs in arsenic mitigation, coordination of mitigation actions among stakeholders (government, NGOs, aid donors, and water users), follow-up of arsenic mitigation programmes, and influence of political events on arsenic mitigation programmes. Atkins *et al.* (2007) reflects on the role of the Bangladeshi government in the poor performance of arsenic mitigation programmes.

In regard to NGOs, the comment of a survey respondent in *Section 3.4.6* exemplifies the criticisms that are now more frequently found in the development aid literature. Haque *et al.* (2002) analysed the role of NGOs in governance issues in Bangladesh. The main conclusions of Haque *et al.* (2002) are as follows:

- The political and economical power of NGOs has increased in relation to the government.
- Foreign donors have contributed to this situation by limiting financial support to the government and increasing it to NGOs.
- NGOs are more accountable to donors than to their members.
- NGOs have replaced the government in the provision of some of the basic services (such as health, sanitation and education).

These issues are relevant for arsenic mitigation because NGOs play an important role in arsenic mitigation in some MLICs. Some NGOs have been delivering mitigation actions with funds from foreign donors. In this respect, there have been serious criticisms to the way aid programmes are delivered, evaluated and monitored (Easterly 2006; Cooke et al., 2001; Johnson et al; 2001). These criticisms include the low sustainability of programmes, the use of participatory approaches as a mean of persuasion towards already established agendas, and lack of independent evaluation of programmes among others.

Sustainability

There is not a globally accepted definition for sustainability in arsenic mitigation. A simplified definition of sustainability that is frequently used in water related and sanitation programmes is that a project is sustainable if the community can continue on its own without external support (McConville 2008). In the case of arsenic mitigation there have been limited attempts to measure sustainability of programmes. Two examples are below.

A statistically representative sample of 1,060 alternative water supplies was surveyed in Bangladesh in 2005 (Kabir et al., 2007). Of the water supplies surveyed, 8 per cent could not been localised, 59 per cent were functioning and 33 per cent were not functioning at the time of the survey. It was found that deep tube wells were most likely to be functioning and that arsenic and iron removal plants were most likely to not be functioning at the time of the survey. Only 59 per cent of the water supplies installed were maintained regularly and 0.7 per cent had a caretaker. The main causes for most water supplies to be not functioning were breakdown problems and insufficient water. In this study, community contribution for installation was found to be important for the functional status of water supplies.

A mitigation programme based on demand and community participation was implemented in rural Bangladesh from 1999 to 2003 (Hoque et al., 2004). After implementation, households drinking water with arsenic concentrations higher than 50 $\mu g\ L^{-1}$ dropped from 84 to 54 per cent. This study found that preferred alternatives for drinking water were deep tube wells and piped water supplies. Households considered the daily use of household arsenic removal technologies as inconvenient but acknowledged that they could be used in emergencies. Pond sand filters were not installed because owners did not agree to use ponds exclusively for drinking water. The smell and taste of water from dug wells was unacceptable.

Although the percentage of households exposed to arsenic dropped after the intervention, this programme excluded communities that were not able to contribute with the 30 per cent of the installation cost and 100 per cent of O&M cost. Hence, the most vulnerable communities were excluded. However, there is evidence suggesting that subsidisation of hardware can be detrimental to water related programmes (*Section 2.4.2*).

Economics

Survey responses referred to economics of arsenic mitigation in terms of household economics, and also in terms of country economics. Frequently, arsenic mitigation literature refers to economic aspects in terms of financial cost of arsenic-safe water sources and in terms of cost-benefit analysis compared to other development interventions (Kemper 2004). However, detailed economic studies are difficult to conduct due to knowledge gaps in arsenic health effects, safe arsenic thresholds for different populations, synergistic effects of malnutrition and smoking in arsenic poisoning, the actual cost of different water alternatives in specific hydro-chemical conditions, the effect of long-term irrigation with water with high arsenic content, the benefits of arsenic mitigation compared to other development interventions, and social effects of chronic arsenic poisoning (Kemper 2004; Smith el at., 2004; BCSIR 2003; Kaufmann et al., 2002).

It is important to consider, as it was observed in *Section 2.4.1*, that MLIC have a limited budget and arsenic contamination is just another issue on the development agenda. On one hand, on ethical grounds arsenic mitigation actions should not be entirely decided on the basis of economic analysis. On the other hand, arsenic mitigation programmes with high impact should be prioritised considering the financial limitations of countries.

Other aspects indirectly related to economics of arsenic mitigation are the quality of interventions and the quality of alternative water supplies (*Section 3.4.6*). For instance, in the field of household arsenic removal technologies, researchers have noticed that the cost of technologies must not compromise the robustness of technologies or the capacity of technologies to remove arsenic from water (Sutherland et al., 2001).

Awareness programmes

Effectiveness of awareness programmes was identified by survey respondents as a factor affecting arsenic mitigation programmes in MLIC. In literature, the importance of awareness campaigns has been acknowledged as a key component of mitigation strategies (Kaufmann et al., 2002). However, transmission of health messages to communities has always been challenging (Harris 2005). Some characteristics of arsenic and arsenic poisoning make it difficult to communicate and to understand the health risks associated with long-term consumption of arsenic contaminated water. First, arsenic does not alter the taste, colour and odour of water (Smith et al., 2004). Secondly, the latency period for arsenic is relatively large; from 5 to 20 years (Paul 2004). Thirdly, the extent and severity of arsenic-related health effects varies from person to person (Smith et al., 2004).

Changes in household knowledge about arsenic contamination and arsenic-safe water options have been monitored for only a few awareness programmes. The results of these monitoring campaigns are contrasting. Awareness campaigns have measured different levels of adoption of arsenic-safe drinking water sources. These may reflect a real difference in efficiency rates among campaigns or differences in monitoring methodologies.

An awareness campaign was conducted on Araihazar District where 54 per cent of wells exceed 50 $\mu g\ L^{-1}$ (Madajewicz et al., 2007). During the campaign, households were given information about arsenic and arsenic poisoning; results from an arsenic test on their well; and results from a health examination. The effect of the awareness campaign was measured after 6-12 months of implementation. Of households with arsenic concentrations > 50 $\mu g\ L^{-1}$, 60 per cent switched to an arsenic-safe drinking water well. Of those who switched wells, 24 per cent installed a new well.

Three factors may have influenced the high efficiency rate of this awareness programme. First, the elapsed time from the awareness campaign to the monitoring stage was relatively short. Second, 90 per cent of households lived within 100 m of an arsenic-safe well. Although the required time to collect water increased 15 fold, walking time to the water source increased up to 4.30 minutes for a round trip. Finally, this study considered self-reported changes on drinking water source. Usually self-reported data overestimate changes in a population’s behaviour (Schmidt et al., 2009).

Contrastingly, a follow up of a national awareness survey found a huge increase in awareness of arsenic but only small increases in adoption of arsenic-safe drinking water sources (Caldwell et al., 2005). In this study, the elapsed time between the two surveys was 3 years. The study found that knowledge of arsenic contamination of wells increased from 32.2 to 62.9 per cent amongst men and from 22.3 to 59.8 per cent amongst women. However, only 3.9 per cent of men and 3.0 per cent of women changed their water source in response to arsenic contamination. Another study found low arsenic awareness levels in 20 rural villages with low to medium levels of arsenic contamination (Paul 2004). The two variables with most influence on arsenic awareness were: living in a high arsenic risk area, and education level of the households.

The main conclusions from these studies were that households have very low awareness of their personal risk level to arsenic; households failed to recognise the potential seriousness of arsenic poisoning; and households did not know how to respond to arsenic contamination of their wells. In the last of the two examples, most households did not adopt an arsenic-safe drinking water source even though they were aware of arsenic and arsenic poisoning. This is known as the knowledge-behaviour gap in health social sciences (Johnson et al., 2001).

In general, awareness campaigns have a small measurable effect on the proportion of households switching from an arsenic-unsafe to an arsenic-safe water source. Some studies suggest that factors such as low levels of education, poverty and the relatively low prevalence of arsenicosis have a negative effect on transmitting to affected people the severity of the risk of arsenic contamination (Madajewicz et al., 2007; Sultana 2006; Paul 2004; Hanchett et al., 2002).

Community participation

Community participation was mentioned just a few times in the survey. This was unexpected due to the emphasis that has been placed on community participation techniques in NGO programmes since the 1980s (Galway 2001; Manikutty 1998). In this technique, community members are involved in decision-making processes for planning and delivery of aid programmes. This approach is supposed to empower participants and promote ownership of programmes; which should result in more sustainable programmes (McConville 2008; Singh 2007; Johnson 2001).

Strong criticisms have been raised about participatory approaches. Firstly, after more than 20 years of participatory approaches on rural water systems, there is little evidence of sustainability (McCann 2007). One quarter of rural water systems is out of order in MLICs and arsenic removal systems are frequently abandoned after a few weeks of installation (Hoque et al., 2004; Johnston 2001). Secondly, it has been argued that participatory approaches are used in some cases to lessen local opposition to investments and in some cases to persuade households to follow an already decided policy (Atkins et al., 2007; Cooke et al., 2001).

A study of indigenous water management practices in rural Bangladesh found evidence that contradicts the general belief that rural people in Bangladesh do not participate actively in water management. Some of the relevant findings of that study for arsenic mitigation are (Duyne 1998): people in rural Bangladesh are not passive recipients of water development programmes; they have the material, technical and organisational capacity to collect, administer and make optimal usage of large amounts of financial resources; and they have a maintenance culture. However, some of these initiatives are conducted by influential individuals or groups of individuals and therefore some people have limited or no rights to access them (Duyne 1998).

Toxic wastes

Most arsenic removal technologies generate wastes. Depending on the technology type the waste can be liquid or solid. Adequate and safe disposal of hazardous liquids is more problematic than that of solids. The hazardous character of wastes is generally determined with the United States Environmental Protection Agency Toxicity Characteristic Leaching Procedure (TCLP). However, there are some concerns regarding underestimation of arsenic leaching from solid wastes with the TCLP in landfill conditions.

Only 19 per cent of survey respondents considered that wastes generated by arsenic removal technologies do not represent a potential contamination source. According to Ghosh *et al.* (2004) the TCLP reproduce poorly the conditions at which arsenic wastes will be subject in a mature landfill. Wastes from household and small scale community technologies are especially subject to inadequate disposal. A procedure for waste management should be in place before promoting or installing arsenic removal technologies (Ravenscroft et al., 2009). Various methods for disposal of arsenic wastes have been proposed in the literature. For instance, the Kanchan filter recommends disposing of the water used to clean the filter in a dug hole with fresh cow dung (Ngai 2006). Some studies suggests that bio-methylation in cow-dung may led to significant reduction of arsenic (Shrestha 2011).

3.6 Summary

This chapter investigated some of the non-technological issues involved in arsenic mitigation in MLICs. These non-technological aspects involve various fields of study; i.e. political, social, health and behaviour change sciences. The survey presented in this chapter aimed to gain a deeper understanding of some of these issues. However, the low response rate and the background of respondents meant that most of the analysis and discussion was centred on Bangladesh.

In general respondents considered that arsenic mitigation programmes have had limited effect in Bangladesh. This is also the most common point of view in the literature. However, a position paper from the Bangladeshi government argues that the low efficiency of mitigation programmes is a misconception arising from the low diffusion of mitigation actions in international forums. There is a tendency in water related programmes to measure the efficiency of programmes in terms of the infrastructure that has been delivered. This practice can be misleading due to differences in delivery and actual usage of hardware.

Survey responses and data from the literature review (*Section 2.4.1*) suggest that modest advances have been made in reducing exposure for people to chronic arsenic poisoning. Nevertheless, there is little evidence on the type of programmes that have been successful and little information on the follow up of programmes once the implementation phase has been finished. Efficiency of arsenic mitigation programmes was investigated in the survey by asking respondents to list up to six programmes implemented in MLICs and rating them according to their efficiency. The survey did not identify a type programme that was particularly efficient.

All types of arsenic removal technologies investigated in the survey had problems with operation and maintenance. According to the survey, maintenance problems are the main issue affecting the implementation of arsenic removal units (*Section 3.4.4* and *3.4.5*); especially availability of spare parts, and easy and frequency of maintenance tasks. Only two technology types were considered to be cost-effective; composite iron matrix technologies (Sono filter) and coagulation-flocculation processes with iron salts (Steven’s Institute of Technology). The microbiological quality of water was an issue of concern for most technologies.

On the other hand, it seems apparent that arsenic mitigation programmes are affected by the low priority given to arsenic mitigation by households. This can partially explain why technologies such as pond sand filters, rain water harvesters or arsenic removal technologies are not fixed when they breakdown. However, some mitigation options are very acceptable in terms of social status or comfort and hence they are very likely to be accepted by households, and this is the case for deep tube wells or piped water.

It is apparent that arsenic mitigation is not considered any longer an exclusively technology problem. According to the responses in the survey, the main issues affecting arsenic mitigation programmes are political, technological and economical. The many uncertainties around arsenic hydro-geochemistry, health effects and remediation complicate planning and implementation of arsenic mitigation programmes. However, it is generally agreed that the use of blanket approaches is ineffective and that a variety of alternative safe drinking water options in parallel with awareness programmes must be offered to households. In the particular case of Bangladesh, arsenic mitigation is affected by the complicated political arena, customary and religion norms, and the economical circumstances.

4. General methods: analysis of total arsenic in aqueous samples, preparation of adsorbents and batch adsorption experiments

This chapter presents the methods that were continuously used in the laboratory work of this thesis. These include sample analysis for measurement of total arsenic in aqueous samples, the preparation of adsorbents and the experimental conditions for adsorption experiments. The development of the method took a long time in part due to an unidentified interference and in part due to a series of breakdowns of the inductively coupled plasma mass spectrometer (ICP-MS) in the School of Environmental Sciences at the University of East Anglia. The preliminary adsorption experiments are included in this chapter because they were used as a means to develop the method for analysis of arsenic concentrations and to establish the experimental settings for adsorption experiments with sugarcane activated carbon (SCAC).

4.1 Analysis of total arsenic in aqueous samples from adsorption experiments

The concentration of total arsenic in aqueous samples was measured with an ICP-MS. The samples analysed were collected from adsorption experiments with iron and activated carbon (AC) based adsorbents. This section presents the basic principles of mass spectrometry, the overall operation conditions for ICP-MS, and the method development for measurement of the samples studied in this thesis.

4.1.1 Inductively coupled plasma mass spectrometry

An ICP-MS model X5 Series I from Thermo Electron Corporation was used for analysis of total arsenic in aqueous samples from adsorption experiments. In MS the molecules or atoms in a sample are transformed to gas phase ions, separated according to their mass-to-charge ratio (m/z) (in which m is the mass in unified atomic mass units and z is the number of charges on the ion) and measured according to their relative abundance in the sample (Robinson et al., 2005). The ICP-MS has four main components; a sample introduction system, an ionization source, a mass selective analyser, and an ion detector. A diagram of a typical ICP-MS system is presented in Figure 4.1.

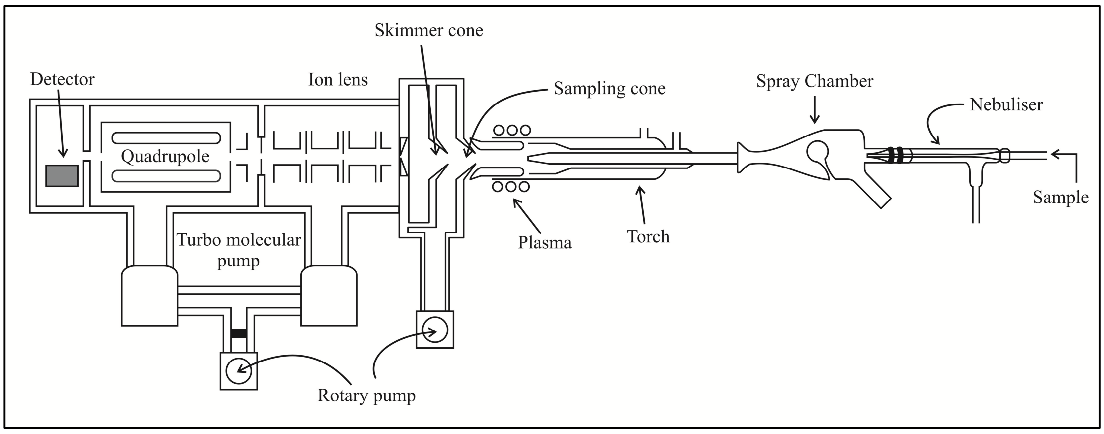


Figure 4.1 Diagram of the ICP-MS (not to scale).

Liquid samples are passed through a nebuliser in which a stream of high purity argon is used to transform the sample into aerosol droplets. Then, the finest droplets (< 10 µm) are introduced into the plasma; the temperature in the plasma can reach 10,000 K. In the plasma the sample is vaporised, atomised and finally ionized. An advantage of argon ICP is that most of the elements form mainly singly-charged positive ions which generate relatively simple mass spectrums.

Ions are then extracted from the plasma to the first vacuum stages of the MS. The interface between the plasma and the MS is the sampler and the skimmer cones. The stream of ions passes through an orifice of 1 mm in the sampler cone; most of the argon carrier gas is removed at this stage. The pressure is around 2 mbar for this stage. Then, the sample coming from the central part of the plasma (the most ionised) is passed through an orifice of 0.70-0.75 mm in the skimmer cone. The skimmer cone separates the neutral ions from the stream of ions and reduces the gas flow into the MS. The region behind the skimmer cone is at a pressure of 10^{-4} mbar.

In the next stage, ion lenses focus the sample for introduction into the quadrupole mass analyser. The positively charged ions are separated from neutrally and negatively charged ions by the use of potentials applied to several lenses placed within the chamber. The ICP-MS model X5 Series I can be used in standard mode or in collision cell technology (CCT) mode. In CCT mode the sample is passed through the dynamic reaction cell, a chamber placed before the quadrupole. In the cell a collision gas is used to attenuate interferences caused by the carrier gas argon. Then, the quadrupole filters out ions of a specific mass-to-charge ratio. Finally, ions transmitted through the quadrupole are counted (or detected). The analyser pressure is between 10^{-6} and 10^{-7} mbar. The ICP-MS model X5 Series I is fully controlled by the software Plasma Lab from Thermo Electron Corporation.

ICP-MS is susceptible to a number of interferences (Table 4.1). In the case of arsenic the most common interference is caused by the ion $^{40}Ar^{35}Cl^{+}$. This ion has the same mass-to-charge ratio as arsenic, 75. This interference was avoided by using nitric acid instead of hydrochloric acid for sample acidification and by the use of CCT. In one case, an adsorption experiment required the use of a compound containing the ion Cl^{-} (*Section 7.4*). For that experiment, the $^{40}Ar^{35}Cl^{+}$ interference was monitored, reduced as much as possible, and accounted for in data analysis.

Table 4.1 Common interferences in ICP-MS (adapted from EPA 1994).

Interference	Description
Isobaric elemental ion	Caused by isotopes of different elements which form singly or doubly charged ions of the same mass-to-charge ratio than the analyte.
Isobaric polyatomic ion	Caused by ions consisting of more than one atom which have the same mass-to-charge ratio than the analyte.
Physical	Caused by the physical processes in the transport of the sample to the plasma, processes into the plasma, and transmission of ions through the plasma-mass spectrometer interface.
Memory	Occurs when isotopes of elements in a previous sample contribute to the signals measured in a new sample.

4.1.2 Method development

ICP-MS tuning

In each analysis run the instrument was first tuned to operate in the standard mode and then tuned to operate in the CCT mode. The standard mode was tuned with a solution containing cerium, indium, lithium, and uranium at 10 µg L^{-1} each. The tuning solution was acidified at 2 per cent with nitric acid (HNO_3). The multi-element tune solution A from Thermo Electron Corporation (barium, beryllium, bismuth, cerium, cobalt, indium, lithium, nickel, lead and uranium at 10 mg L^{-1}) was used to prepare the tuning solution. The passing criterion for this tune is shown in Table 4.2.

Table 4.2 Passing criteria for the standard mode tune for the ICP-MS.

Isotope	% stability	Counts per second
^{7}Li	2	> 1,000
^{115}In	2	> 100
^{220}Bkg		< 1
^{238}U	2	> 100
^{7}Li / ^{5}Bkg		> 20,000
^{115}In / ^{101}Bkg		> 100,000
^{238}U / ^{220}Bkg		> 100,000
^{156}CeO/ ^{140}Ce		< 0.02

The CCT tune was carried out with a 10 µg L^{-1} cobalt solution with no vanadium and acidified with high purity hydrochloric acid (HCl) at a concentration of 2 per cent. This solution was prepared with the multi-tune A solution from Thermo Electron Corporation. The solution was chosen in accordance with the collision gas used, ammonia (NH_3). The passing criteria for the tune was an intensity of < 200 counts per second (cps) for vanadium and intensity > 1,000 cps for cobalt and a standard deviation < 2 per cent for cobalt. Typical instrument conditions and some method parameters are shown in Table 4.3.

Table 4.3 Typical instrumental conditions and method parameters for ICP-MS.

RF power	1200 Watts	Analysis time (total)	216 s
Plasma gas flow	15 L min^{-1}	Detector mode	Standard resolution
Auxiliary gas flow	0.9 L min^{-1}	Sampler/skimmer cones	nickel
Nebuliser gas flow (micro mist)	0.88-0.4 mL min^{-1}	Dwell time	30ms
Solution pump rate	16 rpm	Number of sweeps/reading	1,000
Sample introduction system	Concentric flow	Number of readings/replicate	1
Rinse time	100 s	Number of replicates	3
Equilibration time	70 s	Total acquisition time	6.43 min

ICP-MS calibration

Two calibration methods were tested for sample analysis, the working calibration curve method and the standard addition method. In the working calibration curve method standards are analysed to produce a calibration curve, the sample concentration is determined by comparison against the calibration curve. The addition of an internal standard can be used to improve the precision of the method.

An internal standard is a substance that is added in the same quantity to the calibration standards, samples, and blanks. The internal standard is used to measure the relative response of the analyte (EPA 1994). The internal standard is chosen according to the first ionisation potential of the analyte. In this case the internal standard used was rhodium (Rh) at a concentration of 10 μg L^{-1}. The first ionisation potential of rhodium and arsenic are 7.460 and 9.810 Volts respectively.

The standard addition method is used to eliminate rotational matrix effects in sample analysis (Ellison et al., 2008). The rotational matrix effect occurs when different analytical signals are produced for the same analyte concentration in different sample matrices. This effect could occur when the matrix of the standards is different from the matrix of the samples to be analysed or when samples with different matrices are to be analysed. The standard addition method consists in analysing the responses of several aliquots of the unknown sample with additions of increasing amounts of a stock solution of the analyte. The concentration of the unknown sample is determined by the extrapolation of the calibration curve to a zero response (Ellison et al., 2008).

Sample analysis

Samples from preliminary adsorption experiments were initially analysed with the working calibration curve method without an internal standard. Then an interference of unknown origin was suspected. In an attempt to control the interference the samples were analysed with the standard addition method; but the effect persisted. In a later stage the interference was identified when it was noticed that concentrations of iron and arsenic in the samples were correlated (Figure 4.2).

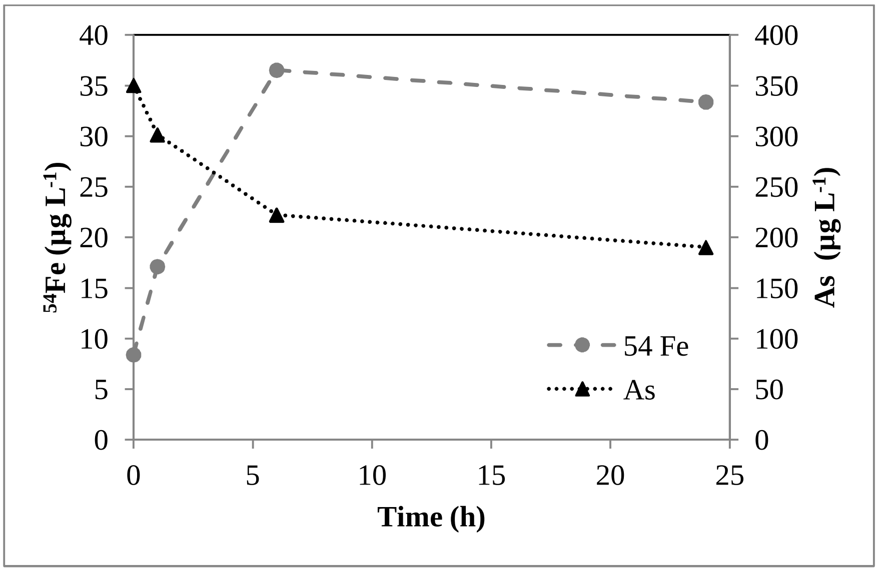


Figure 4.2 Graphic illustrating the correlation between arsenic and iron concentrations as measured with the ICP-MS in one of the absorption experiments. Samples were analysed with the standard addition method.

To test if iron was having an effect in the arsenic concentration as measured with the ICP-MS a very simple experiment was carried out. An arsenic solution of 50 µg L^{-1} was prepared and spiked with iron concentrations up to 1,500 µg L^{-1}. Then samples were analysed with the ICP-MS with the working calibration curve. A sample spiked with arsenic but not with iron was analysed too. Arsenic recovery was calculated by dividing the concentration measured with the ICP-MS by the real concentration of samples. Arsenic recovery for the sample without iron was 99 per cent, whereas arsenic recovery of samples spiked with iron varied from 16 to 104 per cent. Arsenic recovery was not linear with respect to iron concentrations. First arsenic recovery decreased when iron concentrations increased and then arsenic recovery increased when iron concentrations increased.

In another experiment, iron removal from arsenic samples was tested with the cation exchange resin Dowex 26G®. For this experiment three sets of samples were analysed. The first set of samples consisted of arsenic solutions at a concentration of 10 and 250 µg L^{-1}; this set served as control. The second and third set of samples consisted of solutions with known iron concentrations, up to 1,800 µg L^{-1}, spiked at two arsenic concentrations of 10 and 250 µg L^{-1}. Samples from sets 1 and 2 were analysed with the ICP-MS without pre-treatment and samples from set 3 were passed through a resin for iron removal before analysis with the ICP-MS. Sample analysis was done with the working calibration curve method.

The resin was activated with the following procedure. Forty mL of resin were packed in a glass column. Then, 5 L of reagent grade water were passed through the resin. Next, 120 mL of a solution of 6 per cent reagent grade HCl was passed through the resin. Finally, the resin was washed with reagent grade water. The pH of effluent water was monitored to ensure the HCl had been washed out from the resin.

The device for sample filtering consisted of 3 mL of activated resin packed in a 5 mL plastic syringe. A layer of fiberglass was placed above the resin to avoid disturbing the resin when introducing the sample. One column-syringe was used per sample. The pH of samples was not adjusted before passing them through the column.

Figure 4.3 presents the fraction of recovery for samples spiked with iron with no treatment and samples spiked with iron and passed through the resin. It is clear that arsenic recovery is not optimum. To improve recovery, the pH of samples could be modified or a more highly iron selective resin could be used. No further attempts were made to improve the recovery rates because to optimise the method would have taken considerable time and money, and because the main samples (from SCAC) of the research did not contain iron.

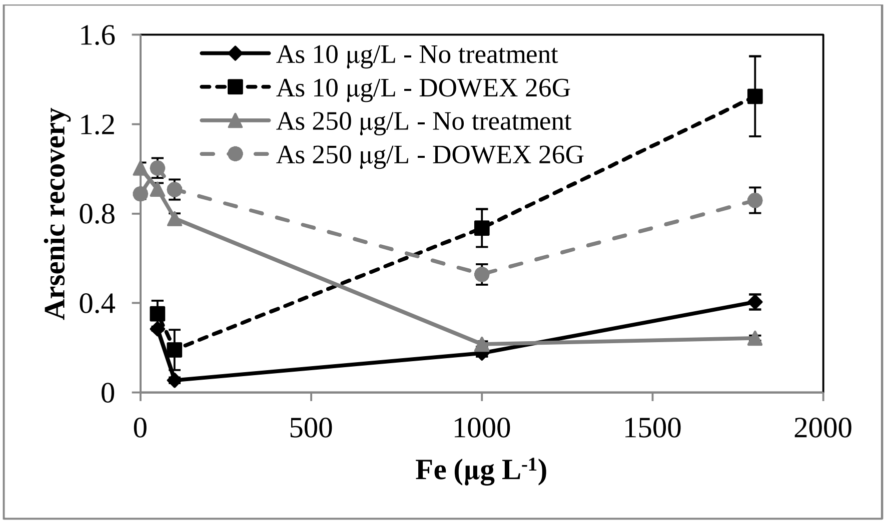


Figure 4.3 Arsenic recovery for samples spiked with iron up to 1,800 µg L^{-1}. Symbols: No treatment = arsenic samples spiked with iron and analysed without pre-treatment; DOWEX 26G® = arsenic samples spiked with iron and analysed after removal of iron with the resin.

SCAC samples were analysed with a working calibration curve method with the internal standard Rh at 10 µg L^{-1}. The single element solutions 1,000 mg L^{-1} As in 2 per cent HNO_3 and 10 mg L^{-1} Rh in 2 per cent HCl from Claritas PPT were used for the preparation of the calibration and internal standards. Drift in the signal was monitored during the analytical run with the absolute response of the internal standard. The absolute response of the internal standard must not deviate more than 65-125 per cent of the response in the calibration blank (EPA 1994). In most analysis runs the internal standard response was kept between 85 and 115 per cent.

Arsenic recovery was monitored in each run by analysing a spike every 10 samples. A spike sample is an aliquot of reagent grade water to which known quantities of the analytes are added. For each spike analysed the per cent recovery was calculated (Equation 4.1). The per cent recovery for each analyte must be within 85 and 115 per cent (EPA 1994).

Equation 4.1

$$\%\ \text{recovery} = \frac{\text{spike} - \text{blank}}{\text{s}} \times 100$$

In the equation, spike is the arsenic concentration as measured in the spike, blank is the arsenic concentration in an aliquot of reagent grade water, and s is the analyte concentration added to the spike. Memory effects were monitored by analysing an aliquot of reagent grade water every ten samples.

The instrument detection limit (IDL) and the method detection limit (MDL) were calculated. These calculations are presented with detail in *Appendix B*. The IDL was measured at 0.08 µg L^{-1}, the MDL for a concentration range of 0-350 µg L^{-1} at 0.15 µg L^{-1}, and the MDL for a concentration range of 0-3,000 µg L^{-1} at 0.80 µg L^{-1}. Finally, matrix effects were investigated for SCAC samples. Reagent grade water was added to a reactor containing the same amount of SCAC used in adsorption experiments. The reactor was shaken for 24 hours and then the content of the reactor was filtered. The filtrate was spiked with a known concentration of arsenic and analysed with the working calibration curve method with 10 µg L^{-1} Rh internal standard. The average arsenic recovery for these samples was 105 per cent (n = 2).

4.2 Preparation of adsorbents

4.2.1 Commercial activated carbon and iron filings

In all experiments involving commercial activated carbon (CAC) the lignite granular AC type Darco® 12x20 from Sigma-Aldrich was used. The only preparation that CAC required was drying overnight at 105 °C and keeping in desiccators until used. Reagent grade iron filings (Fe) were obtained from Fisher Scientific and used without pre-treatment.

4.2.2 Synthesis of iron hydroxide

The synthesis of iron hydroxide (FeOOH) was based on a method by Streat *et al.* (2008). First, a solution of 0.3M iron(III) chloride ($FeCl_3$) and a solution of 0.9M sodium hydroxide (NaOH) were prepared. Then, each solution was placed in a dropping funnel. Next, solutions were mixed in an Erlenmeyer flask. The mixture was magnetically stirred and kept at 45 °C. The flow rates of the reagents were controlled to keep the reaction at a pH of 4. Heating and stirring continued for one hour when addition of both reagents had finished. A brown precipitate was formed after suspending heating and stirring. This precipitate was left to age for four days. Then, the precipitate was washed with reagent grade water, dried in an oven at 35 °C, pulverised with pestle and mortar, and kept in a desiccators.

4.2.3 Iron impregnated commercial activated carbon

Arsenic uptake capacity of AC can be improved by loading iron onto its surface. In this case iron(II) was used for two main reasons. Firstly, higher amounts of iron are loaded on CAC with iron(II) compounds than with iron(III) compounds (Gu et al., 2005). Secondly, at pH > 3.0, iron(III) forms hydroxides that are more difficult to diffuse in the internal pores of AC (Gu et al., 2005). CAC was impregnated with iron using two different treatments, called A and B. In treatment A, iron(II) was loaded onto CAC and then oxidised to iron(III) (Gu et al., 2005). In treatment B, the surface of CAC was oxidised and then iron(II) was loaded (Chen et al., 2007).

Treatment A was based on a method by Gu *et al.* (2005). Iron(II) solutions with a concentration of 0.1M and 0.01M were prepared with iron(II) chloride tetrahydrate ($FeCl_2 \cdot 4H_2O$). Then, the CAC and the iron(II) solution were mixed in a low density polyethylene bottle; the impregnation ratio was 1 g of CAC per 15 mL of iron(II) solution. Sodium hypochlorite solution (NaClO) was added at the beginning of the reaction and then every 6 hours for 24 hours; the NaClO: $FeCl_2 \cdot 4H_2O$ ratio was 20 mL:10 g. The CAC was separated from the iron solution by filtration. Finally, iron treated CAC was washed several times with reagent grade water, dried at 105 °C, and kept in desiccators.

In treatment B, based on a method by Chen *et al.* (2007), CAC was boiled for three hours in a 25 per cent HNO_3 solution. Then, the mixture was allowed to cool and CAC was separated by filtration. Oxidised CAC was washed three times with reagent grade water, dried at 105 °C and kept in desiccators. Then, iron(II) was loaded onto the oxidised CAC. Iron(II) concentration, CAC : iron(II) solution ratio and reaction time were the same as in treatment A. The pH of the reaction was controlled between 4.5 and 5.0 with addition of 1M sodium hydroxide (NaOH) every six hours per 24 hours. Table 4.4 shows the treatment summary. Iron impregnated CAC samples were named according to the impregnation treatment and iron concentration of the solution. For instance, the name “A-0.1M Fe” represents a CAC sample impregnated with treatment A with an iron solution with a concentration of 0.1 M iron.

Table 4.4 Treatment combinations for impregnation of CAC with iron(II).

Treatment	Oxidant	Iron(II)
		M
A-0.1M Fe	NaOCl	0.1
A-0.01M Fe	NaOCl	0.01
B-0.1M Fe	HNO_3	0.1
B-0.01M Fe	HNO_3	0.01

4.2.4 Sugarcane activated carbon

All SCAC adsorbents used in the experimental part of this research were prepared with the procedure described in the following paragraphs. A horizontal tube furnace Carbolite CTF12-65-301 was used for preparation of the sugarcane adsorbents. First, raw sugarcane was squeezed with metallic rollers. Then, it was washed three times with reagent grade water. Next, sugarcane was mechanically cut and sieved. Sugarcane that passed through a 4.0 mm sieve but not through a 1.0 mm sieve was used for preparation of the AC. After sieving, sugarcane was washed three times with reagent grade water and dried overnight.

Adsorbents were prepared in a two-stage process: carbonisation and activation. For the carbonisation stage sugarcane was weighted and placed in ceramic boats (width = 4 cm, length = 10.5 cm, depth = 2 cm). Then, the boats were loaded into the furnace. Nitrogen free of oxygen (100 cm^3 min^{-1}) was continuously passed through the furnace. The temperature in the furnace was increased at a heating rate (HR) of 5 °C min^{-1} until the carbonisation temperature (CT) was reached. Then, the furnace was kept at this temperature during the carbonisation time (Ct). The carbonised material was allowed to cool inside the furnace in the nitrogen atmosphere. Next, the carbonised material was weighed and crushed with a ceramic pestle and mortar to a particle size < 180 μm. After crushing and sieving the carbonised material was weighed.

For the activation stage, the furnace was loaded with the carbonised material. Then, a nitrogen flow of 100 cm^3 min^{-1} and a HR of 5 °C min^{-1} were set. Once the activation temperature (AT) was reached the gas was switched to carbon dioxide (CO_2) at a flow rate of 100 cm^3 min^{-1}. The AT was maintained for the activation time (At). When the At elapsed the gas was switched back to nitrogen (100 cm^3 min^{-1}). The activated material was allowed to cool in the nitrogen atmosphere. Then, the activated material was weighed. Finally, each gram of AC was washed five times with 100 mL of reagent grade water, dried overnight and kept in desiccators until used. The overall preparation process for SCAC is illustrated in Figure 4.4.

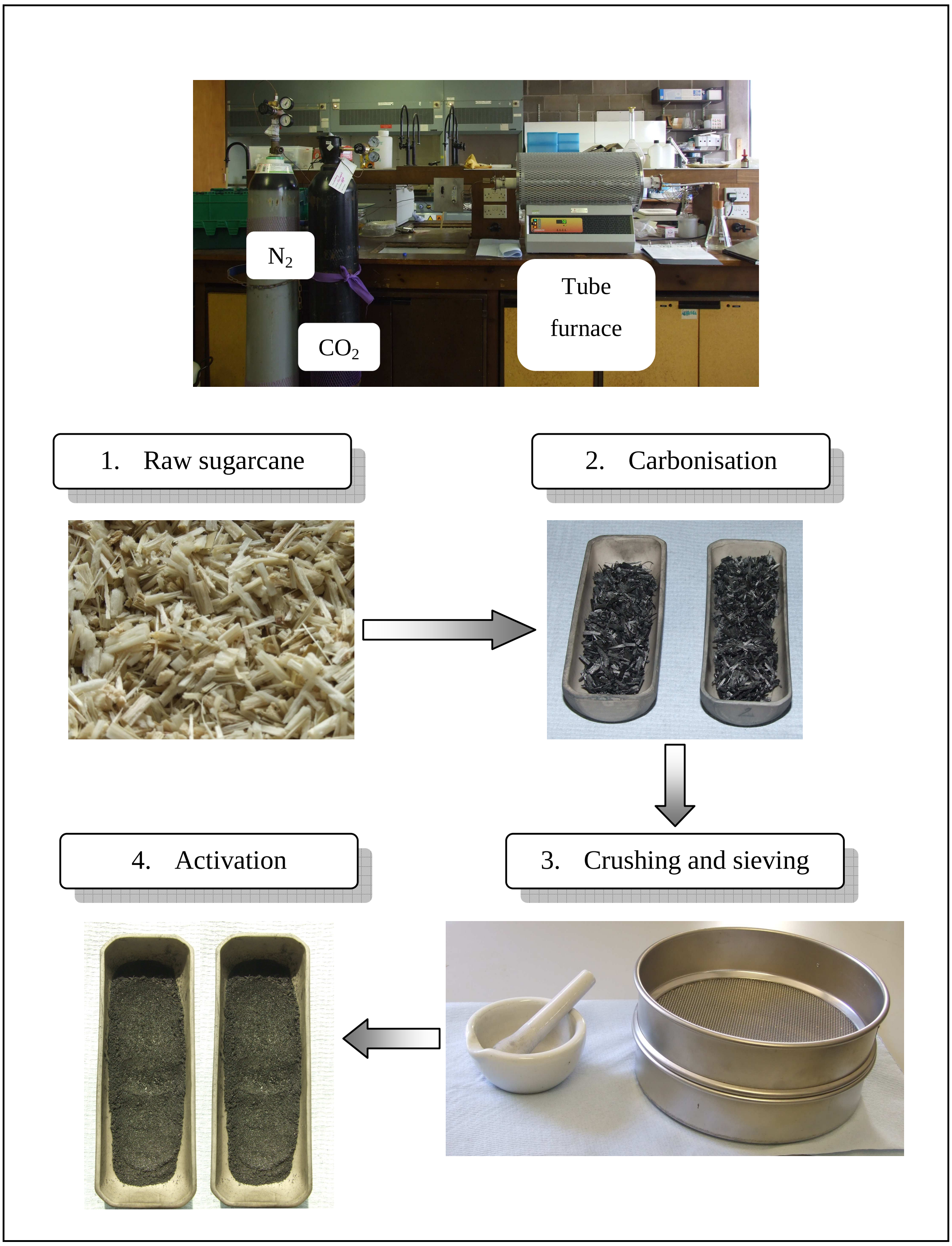


Figure 4.4 Flow diagram showing the preparation steps for SCAC. The tube furnace is used in steps 2 (carbonisation) and 4 (activation).

4.3 Experimental conditions for arsenic adsorption batch experiments

4.3.1 Materials and cleaning procedures

Chemicals used in adsorption experiments were of at least reagent grade. Nitric acid used to acidify samples or adjust the pH of solutions was of high purity. Ultrapure acid was double distilled in the university laboratory and stored in a narrow neck Teflon fluorinated ethylene propylene bottle. A pH-meter Mettler Toledo seven easy S20 and a balance Ohaus analytical plus model AP250D were used throughout the experimental work.

The following chemicals were used in adsorption experiments; sodium hydroxide (NaOH) 99.1 per cent, sodium chloride (NaCl) 99.5 per cent, disodium hydrogen phosphate ($NaHPO_4$) 99.5 per cent, potassium sulphate (K_2SO_4) 99 per cent, laboratory reagent grade manganese sulphate ($MnSO_4$), sodium silicate ($Na_2O(SiO_2)x{\cdot}xH_2O$) solution (12 per cent silicon), sodium arsenate dibasic heptahydrate ($Na_2HAsO_4{\cdot}7H_2O$) > 98 per cent, and sodium arsenite ($NaAsO_2$) > 99.0 per cent.

All plastic ware and glassware were cleaned before and after use in adsorption experiments. First, laboratory ware was rinsed three times with deionised water. Then, it was soaked for 24 hours in a 5 per cent Decon 90® bath. Decon 90® is a surface active cleaning agent for laboratory applications. Then, laboratory ware was rinsed three times with deionised water. Next, it was soaked 24 hours in a 20 per cent HNO_3 bath. Then, it was rinsed three times with reagent grade water and allowed to dry in a clean air cabinet. Finally, clean and dry laboratory ware was stored in resealable polythene bags. Acid baths were made with analytical reagent grade 70 per cent HNO_3 from Fisher Scientific. Acid and Decon 90® baths were changed at least every six months.

4.3.2 Batch adsorption experiments

A similar methodology was followed in all batch experiments. For each experiment a fresh arsenic solution of 1,000 mg L^{-1} was prepared with sodium arsenate dibasic heptahydrate ($Na_2HAsO_4{\cdot}7H_2O$) or sodium arsenite ($NaAsO_2$) depending on the experiment. The solution was then diluted to the concentration required in each experiment. Experiments involving arsenic(III) were conducted in darkness, covering reactors with black paper, to avoid oxidation of arsenic(III) to arsenic(V) (Bednar et al., 2002). Also, arsenic(III) stock solutions were acidified with HNO_3. The pH of solutions was adjusted with drop wise addition of sodium hydroxide 0.1M (NaOH) or nitric acid 2.25 M (HNO_3) when necessary.

First, the adsorbent was weighted and placed in clean glass reactors. Then, the arsenic solution was poured into the reactors. Next, reactors were placed in a bottle shaker for time t. Finally, samples were filtered through a 0.2 μm cellulose acetate filter. McCleskey *et al.* (2004) found that filter pore sizes (0.1 to 0.45 μm) did not affected preservation of arsenic samples.

Prior to sample filtration the membrane filter assembly was pre-rinsed with 10 mL of the sample to be filtered. After filtration the sample was split in two parts; one part was used for measurement of pH and the other was kept for ICP-MS analysis. Samples for ICP-MS analysis were acidified with double distilled HNO_3, 100 μL of acid per 20 mL of sample, and stored in 50 mL plastic centrifuge tubes in a refrigerator at 4 °C until analysis. Samples were analysed with the ICP-MS within a month. Used adsorbent and arsenic residual solutions were collected for adequate disposal.

4.3.3 Preliminary adsorption experiments with commercial activated carbon, iron filings, iron hydroxide, and iron impregnated commercial activated carbon

The original experimental plan only included experiments with SCAC. Initially, it was planned to prepare the AC samples in a conventional oven. However, some concerns were raised with respect to the safety of modifying the design of the oven for use with gases. Hence, it was necessary to apply for funding to get an adequate oven for the planned experiments. In the meantime preliminary adsorption experiments with arsenic(III) and arsenic(V) were run with CAC, iron filings (Fe), iron hydroxide (FeOOH) and AC impregnated with iron(II). These experiments helped not only to define the experimental conditions for the adsorption experiments with SCAC but also to develop the method for sample analysis.

Experimental conditions in this preliminary experiment were as follows: initial concentration of 185 $\mu g\ L^{-1}$ for arsenic(III) and of 247 $\mu g\ L^{-1}$ for arsenic(V), 1 g of adsorbent, 90 mL of arsenic(III) solution and room temperature. The pH was not adjusted in this experiment. Samples were collected at different times, from 60 to 1,497 minutes. The experiments were conducted in triplicate with a control and a blank. A limitation of the experimental design was that 20 mL of sample, almost a quarter of the total volume, was extracted from the reactor at each sampling time. Hence, the initial conditions of the experiment changed drastically during the experiment. Samples from the arsenic(III) experiment were analysed with the ICP-MS using the working calibration curve method and samples from the arsenic(V) experiment were analysed with the standard addition method. The method of analysis was changed because interferences were suspected.

Additional batch experiments were run with iron impregnated CAC. Adsorbents A-0.1M Fe and B-0.1M Fe were tested at two arsenic(V) initial concentrations, 100 and 472 $\mu g\ L^{-1}$. The experimental conditions were initial pH of 8, room temperature and adsorbent dose of 10 $g\ L^{-1}$. Adsorbents A-0.01M Fe and B-0.01M Fe were tested at an arsenic(V) initial concentration of 350 $\mu g\ L^{-1}$. Samples were collected at 60, 360 and 1,440 minutes. Samples were analysed with the standard addition method in the ICP-MS.

It was concluded that both methods, the working calibration curve and standard addition methods, were inappropriate for analysis of samples with an iron content. The correct procedure would be to remove iron from samples and then analyse samples with the working calibration curve method. The results from these experiments are included in this section (Figure 4.5) rather than in the results section since they contributed to the development of the method used to analyse the samples.

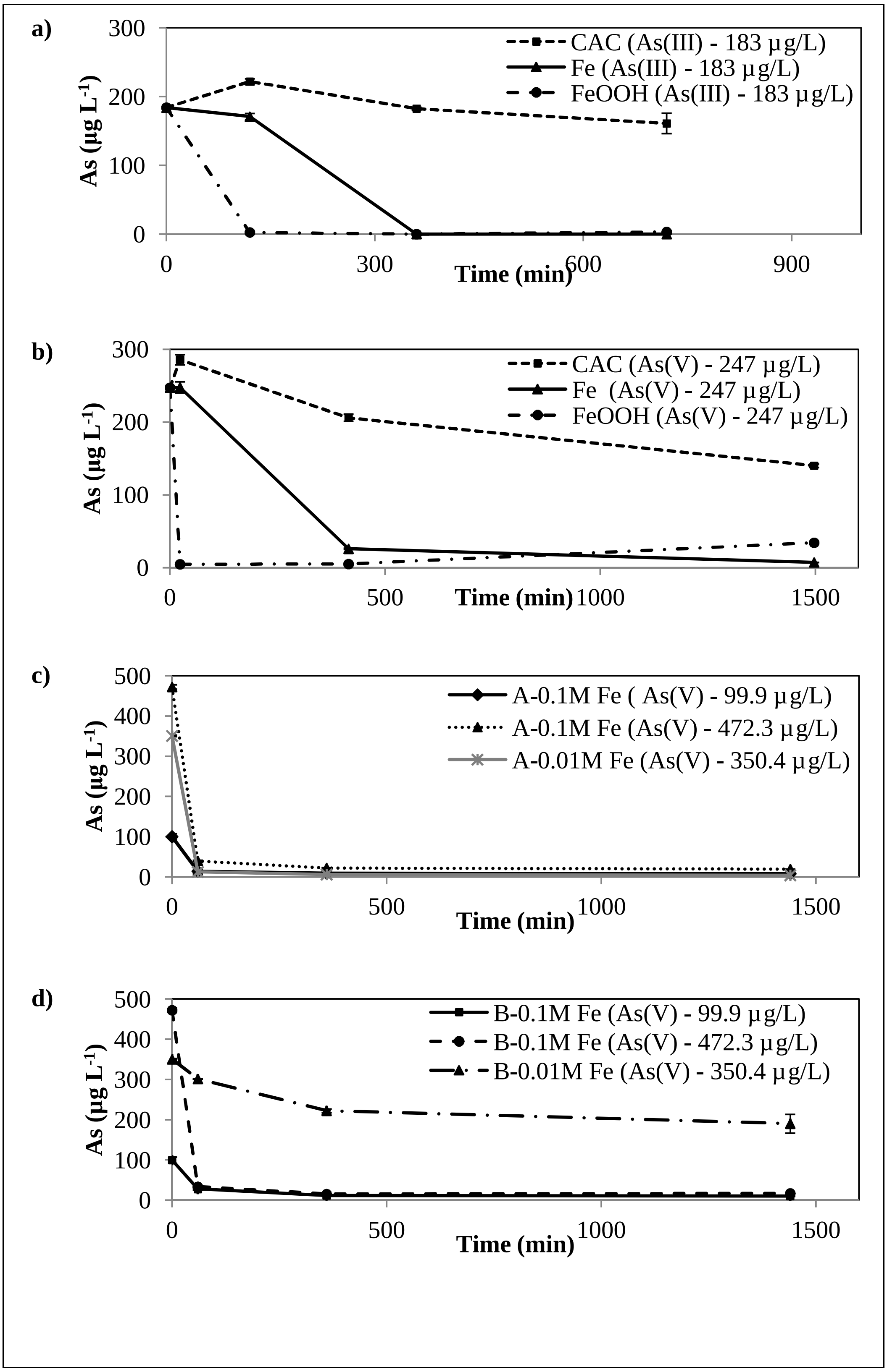


Figure 4.5 Results from preliminary adsorption experiments that served to identify interferences on sample analysis. a) arsenic(III) and adsorbents CAC, Fe and FeOOH; samples analysed with a working calibration curve; b) arsenic(V) and adsorbents CAC, Fe and FeOOH; c) arsenic(V) and adsorbents A-0.01M Fe and A-0.1M Fe; d) arsenic(V) and

adsorbent B-0.01M Fe and B-0.1M Fe. Samples from b), c) and d) were analysed with the standard addition method.

4.3.4 Batch experiments with sugarcane activated carbon

Batch experiments with SCAC were carried out in the conditions stated in *Section 4.3.2*. Experimental settings specific to batch experiments with SCAC were an adsorbent dose of 5 g L^{-1} and a total arsenic solution volume of 40 mL. Since a large amount of sample was required for ICP-MS analysis and pH measurement, reactors were sampled only once to avoid changing the initial experimental conditions. For instance, for the adsorption experiment in which the change in concentration was measured with respect to time, instead of sampling the same reactor at different times one reactor was set for each time investigated. Experiments were done in triplicate and with a control and blank.

The sampling methodology, explained in *Section 4.3.2*, was tested to verify its adequacy. Arsenic solutions were prepared at three concentrations: 50, 273 and 581 µg L^{-1}. Each solution was split into four aliquots. One aliquot was analysed to obtain the real concentration of the solution. The other three aliquots and a blank were treated like samples: filtered, acidified and stored at 4 °C. The arsenic concentration in blank samples was from 0.1 to 0.8 µg L^{-1}. Recovery was 98 ± 2.2 % in samples with 50 µg L^{-1} arsenic, 105 ± 2.5 % in samples with 273 µg L^{-1} and 102 ± 1.5 % in samples with 581 µg L^{-1}.

The analysis of samples from the first adsorption experiments with SCAC revealed that the standard deviation of triplicates was higher than expected, up to 9 per cent. To investigate this variation an experiment with a twofold objective was carried out. The first objective was to investigate if an increase in the number of replicates, from three to six, would reduce the standard deviation of replicates to below 5 per cent. The second objective was to investigate the effect of the composition of the raw sugarcane on arsenic removal. The raw material is composed by the husk and the fibre of the sugarcane that are left after extraction of the juices; this is normally referred as to bagasse. For this experiment three sets of reactors were prepared. The first set was the control; i.e. reactors with arsenic solution and no adsorbent. The second set was for the SCAC prepared with sugarcane bagasse with husk, and the third set was for SCAC prepared only with the fibre (the husk was mechanically separated from the fibre).

The SCAC for this experiment was prepared with the following parameters; CT of 700°C, Ct of 90 min, AT of 850°C and At of 180 min. Figure 4.6 presents the arsenic concentration of the liquid phase at equilibrium time for the two adsorbents tested. Even though the arsenic concentration was as low as 14 µg L^{-1}, the standard deviation for the six replicates was 2.6 per cent for SCAC made from the fibre and husk and 3.2 per cent for SCAC made from the fibre.

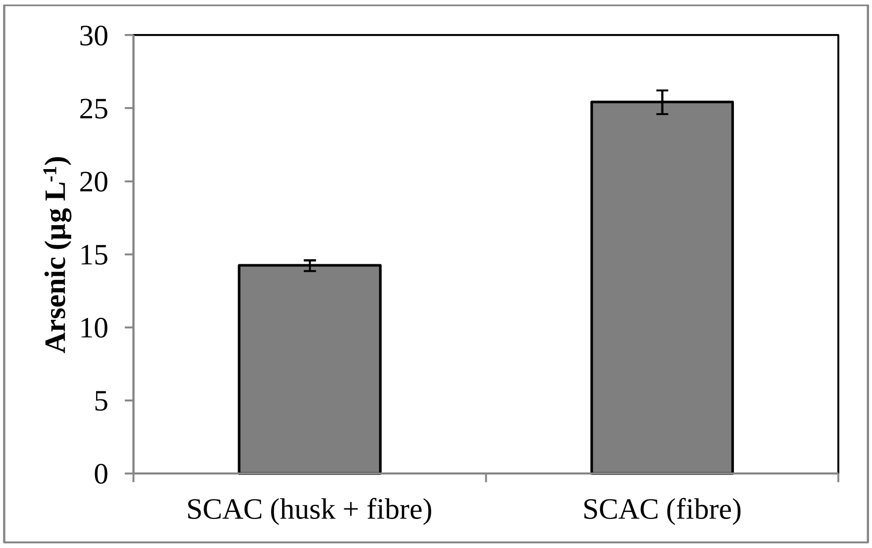


Figure 4.6 Average of arsenic concentrations for six replicas of SCAC made of bagasse and husk and SCAC made exclusively of bagasse. Standard deviation is below 5% in both cases.

This experiment confirmed that increasing the number of replicates would improve the standard deviation values. Also, it was found that husk content on SCAC had a positive effect on arsenic removal. Potentially, SCAC made exclusively of husk would remove more arsenic than SCAC made of a mixture of fibre and husk.

In spite of these findings it was decided to keep the number of replicates at three and to prepare SCAC with the mixture of fibre and husk. These decisions were taken for two main reasons. Firstly, due to the size of the tube furnace, the preparation of one gram of SCAC could take as long as six days, depending on the activation temperature. Hence, if six replicates were used instead of three replicates, the time to produce the necessary amount of SCAC would double. Secondly, production of SCAC would be impractical at a pilot or industrial scale if the fibre had to be removed.

4.4 Summary

This chapter introduced the general methods used throughout the development of the experimental work and preliminary adsorption experiments. Laboratory methods included procedures to clean plastic and glassware, preparation of adsorbents and sample analysis with the ICP-MS. Preliminary adsorption experiments with CAC, iron filings, FeOOH, and Fe-GAC were used to develop the sample analysis method and to establish the experimental conditions for SCAC adsorption experiments.

Interferences, of unknown origin, in the measurement of total arsenic using the ICP-MS with the working calibration method were detected when analysing samples from preliminary adsorption experiments. The iron content in samples was later identified as the source of the interference. A series of experiments concluded that the appropriate method for samples with iron content was removal of iron with an ion/exchange resin prior to analysis on the ICP-MS with the working calibration curve method. The resin used here, Dowex 26G, was not capable of removing 100 per cent of the iron. No further attempts were made to find a suitable resin since samples from the main adsorbent investigated (SCAC) did not contain iron.

Samples from adsorption experiments with SCAC were analysed with the working calibration method with Rh at 10 μg L^{-1} as the internal standard. Matrix effects on arsenic analysis were ruled out; the recovery rate of samples with the SCAC matrix was 105 per cent. The arsenic IDL was measured as 0.08 μg L^{-1}, the MDL for concentrations from 0-350 μg L^{-1} was 0.15 μg L^{-1}, and the MDL for concentrations from 0-3,000 μg L^{-1} was 0.80 μg L^{-1}.

An experiment suggested that SCAC made exclusively of husk could have a higher adsorption capacity for arsenic; however removal of the SC bagasse would be impractical in pilot or full scale production of SCAC. Hence, SCAC was prepared from the husk and fibre. Although standard deviation of arsenic concentration from SCAC adsorption experiments dropped from 9 to 3.2 percent when six replicates were used instead of triplicates, the latter were kept in order to keep within acceptable limits the time required to prepare the adsorbent.

5. Optimising the sugarcane activated carbon preparation conditions for the removal of arsenic

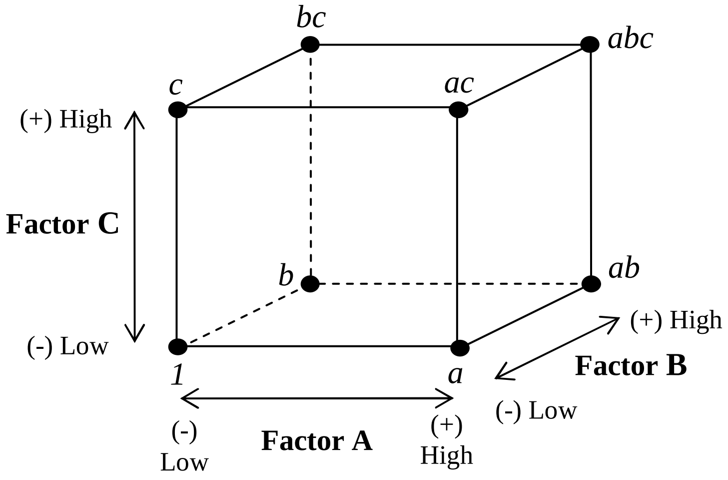
The preparation conditions of activated carbon (AC) have an effect on its physical and chemical properties and hence on its adsorption capacity. In the specific case of sugarcane activated carbon (SCAC) and arsenic removal, the amount of existing information on this subject is scarce. The settings for the preparation of SCAC used in this research were established with a combination of experimental work in the laboratory and statistical analysis. This chapter presents the experimental and statistical methods used for determining the optimum preparation parameters for arsenic adsorption.

5.1 Experimental design for establishing the preparation conditions for sugarcane activated carbon

There are two AC preparation methods, physical and chemical activation. Physical activation is a two-stage process; carbonisation of the raw material in an inert atmosphere followed by activation with water steam or carbon dioxide (CO_2). Chemical activation is a one-stage process; the raw material is mixed with chemical agents, then chemicals are rinsed out, and finally carbonisation and activation are simultaneously performed. The SCAC used in this research was produced with physical activation since chemical activation would be more problematic to implement in middle and low income country settings.

A three-factor experimental design with two levels, called a 2^3 factorial experimental design, was used to establish the values of the preparation parameters of physical activation of SCAC. This experimental design is particularly useful to investigate individual and joint effects of several factors on a response with a minimum of experimental runs when there is little information about the system studied (Montgomery et al., 2009). Two-level factorial designs assume an approximate linear response between the levels studied.

The 2^3 factorial design is defined as follows; let y_{ijkl} be the observed response when factor A is at the ith level ($i = 1, 2$), factor B is at the jth level ($j = 1, 2$) and factor C is at the kth level ($k = 1, 2$) for the lth replicate ($l = 1, 2, \ldots n$) (Montgomery et al., 2009). A graphical representation of the 2^3 factorial experimental design and a table with the treatment combinations with coded factors is presented in Figure 5.1. In the coded factorial design, low levels are assigned the value of -1 and high levels the value of +1.



Run	Factor A	Factor B	Factor C
1	-	-	-
a	+	-	-
b	-	+	-
ab	+	+	-
c	-	-	+
ac	+	-	+
bc	-	+	+
abc	+	+	+

Figure 5.1 Graphical representation and coded treatment combinations of the 2^3 factorial experimental design.

The variables investigated in the factorial experiment, were carbonisation temperature (CT), activation temperature (AT) and activation time (At). These factors were chosen due to their effect on the physical and chemical properties of AC. Carbonisation time (90 min), carbonisation and activation heating rates (5 °C min^{-1}), nitrogen flow (100 $\text{cm}^3\ \text{min}^{-1}$) and carbon dioxide flow (100 $\text{cm}^3\ \text{min}^{-1}$) were kept constant in all treatment combinations. Carbonisation and activation heating rates affect the development of the pore structure of the materials; they usually vary between 5 and 10 °C min^{-1}. However, the maximum heating rate achieved by the furnace is 5 °C min^{-1}. For this reason, it was not possible to include this parameter in the experimental design.

In addition to the factorial experiment, two more small-scale experiments were carried out; the variation of AT and pre-treatment of SCAC with acid (acid treatment is commonly used to improve adsorption of AC). In the variation of AT experiment four adsorbents were prepared at AT values from 750 to 900 °C, a CT of 700 °C and an At of 120 minutes. In the acid treatment experiment, two types of SCAC were treated with nitric acid.

Acid treated SCAC samples were prepared with the following procedure. First, SCAC samples were boiled for 30 min in a solution of 25 per cent nitric acid, at a ratio of 1 gram of AC per 15 mL of solution. Next, samples were washed with reagent grade water until the pH of the water did not change. Finally, samples were dried overnight at 105 °C and kept in a desiccator. The treatment combinations for these three experiments are shown in Table 5.1.

Table 5.1 Treatment combinations for the 2^3 factorial experiment design and the variation of activation temperature experiment.

Experiment	Adsorbent	Carbonisation temperature	Activation temperature	Activation time	Nitric acid
		°C	°C	min	
2^3 factorial	SC01	700	600	60	No
	SC02	850	600	60	No
	SC03	700	900	60	No
	SC04	850	900	60	No
	SC05	700	600	180	No
	SC06	850	600	180	No
	SC07	700	900	180	No
	SC08	850	900	180	No
Variation of activation temperature	SC09	700	750	120	No
	SC10	700	800	120	No
	SC11	700	850	120	No
	SC12	700	900	120	No
Acid treatment	SC01-A	700	600	60	Yes
	SC07-A	700	900	180	Yes

SCAC samples were tested in separate arsenic(V) and arsenic(III) adsorption experiments. For comparison a sample of the commercial activated carbon (CAC) was included in the adsorption experiment. Experiments were carried out at room temperature, at an initial arsenic concentration of ≈ 250 µg L^{-1} and at an initial pH of ≈ 8. Experiments were run in triplicate; the results presented here are the average of triplicates. The responses measured were the percent of arsenic(V) or arsenic(III) removal, and yield of SCAC samples. The percent arsenic removal and yield were calculated with Equation 5.1 and Equation 5.2 respectively:

$$\%\mathrm{As.R} = \frac{\mathrm{As_0} - \mathrm{As_f}}{\mathrm{As_0}} \times 100$$ Equation 5.1

in which %As.R is the percent of arsenic(III) or arsenic(V) removal, $\mathrm{As_0}$ is the initial arsenic(V) or arsenic(III) concentration, and $\mathrm{As_f}$ is the final arsenic(V) or arsenic(III) concentration.

$$\%\mathrm{yield} = \frac{\mathrm{w_{activated\ adsorbent}}}{\mathrm{w_{raw\ \ material}}} \times 100$$ Equation 5.2

in which $\mathrm{w_{activated\ adsorbent}}$ is the weight of the activated adsorbent and $\mathrm{w_{raw\ material}}$ is the weight of the raw material.

Data collected from the factorial experiment was statistically analysed with the SPSS software package, version 14.0. First, percent arsenic removal and yield were calculated for each treatment combination. Then, the factors were coded to facilitate mathematical operations and interpretation of the statistical test results. Next, the data were check for violations of the assumptions of parametric tests; i.e. normally distributed population with equal variance.

An analysis of variance (ANOVA) test was run to identify the factors and the factor interactions that have an effect on arsenic adsorption. Results from the ANOVA test were used to model arsenic(V) and arsenic(III) adsorption on SCAC. The general regression model for a 2^3 factorial experiment is presented in Equation 5.3.

$$Y = \mathrm{C_0} + \mathrm{C_1}x_1 + \mathrm{C_2}x_2 + \mathrm{C_3}x_3 + \mathrm{C_{12}}x_1x_2 + \mathrm{C_{13}}x_1x_3 + \mathrm{C_{23}}x_2x_3 + \mathrm{C_{123}}x_1x_2x_3 + \epsilon$$

Equation 5.3

in which Y is the response; the C terms are parameters to be determined; x_1, x_2 and x_3 are variables representing factors A, B and C respectively; x_1x_2, x_1x_3, x_2x_3, $x_1x_2x_3$ represent interactions between the factors, and ϵ is a random error term. The C terms were calculated with the least squares estimates method.

Three models were proposed for arsenic(V) and arsenic(III) adsorption. The first model included only statistically significant terms from the ANOVA test, with no consideration of fulfilling the hierarchy principle (Montgomery et al., 2009). The second model included the statistical significant terms plus additional terms to fulfil the hierarchy principle. The third model explores the quadratic effect of AT.

Finally, the adequacy of the models was verified. For each model, the predicted response with the 95 per cent confidence interval was calculated for the data used for the factorial experiment and for experimental data not included in the model (when possible). Also, surface and contour plots were produced for each model. The plots, the calculations for the predicted response of the model, and the calculation of the 95 per cent confidence interval were made with the R programming language, version 2.13.1.

5.2 Results

The effect of the preparation conditions on arsenic removal was tested initially with arsenic(V) and then with arsenic(III). Preliminary results of the arsenic(V) experiment were presented at two conferences (*Appendix F*). Analysis for these samples was initially carried out with the standard addition method. However, later it was found that this method was inadequate to analyse SCAC samples. It was not possible to reanalyse these samples with the working calibration curve method because there was not enough sample to do so. Also, sample analysis coincided with a serious breakdown of the ICP-MS.

An arsenic(V) adsorption experiment with four treatments from the factorial design was run to confirm the previous results. Samples were analysed with the working calibration curve with an internal standard (*Section 4.1.2* provides an explanation for using the working calibration method). The same trend for arsenic adsorption was observed, but higher percentages of arsenic adsorption were achieved. Due to this difference the full factorial experiment was run again. Results from this last experiment agreed with results from the partial factorial experiment. The results presented here are those from the last experiment. Results included in this chapter and *Chapter 7* were analysed with the working calibration curve method with rhodium as the internal standard.

5.2.1 Sugarcane activated carbon yield and adsorption of arsenic(V) and arsenic(III)

Results from arsenic adsorption experiments are presented in Table 5.2. The three responses measured (yield, %As(V).R and %.As(III).R) clearly vary with the preparation conditions of SCAC. Although interpretation of the factorial design is restricted to statistical tests some remarks can be made. Firstly, arsenic(V) removal is considerably higher than arsenic(III) removal with CAC. Secondly, arsenic removal is higher with CAC than with SC01, SC02, SC05, SC06 and SC09. Thirdly, results from the variation of the AT experiment suggest that AT has a strong effect on both yield and arsenic removal. Results from the acid treated adsorbents for arsenic(V) were very discouraging; adsorption dropped practically to zero per cent. Hence, arsenic(III) adsorption experiments with acid treated samples were not carried out.

Table 5.2 Percent yield, and arsenic(V) and arsenic(III) removal for the factorial, variation of activation temperature, acid treated and commercial activated carbon experiments.

Experiment	Adsorbent	Yield %	SD	Arsenic(V) % removal	SD	Arsenic(III) % removal	SD
2^3 factorial	SC01	22.7	0.8	7.3	8.7	7.6	1.2
	SC02	21.6	0.6	17.5	1.9	10.8	1.3
	SC03	16.1	2.4	78.8	1.3	78.6	1.7
	SC04	16.2	1.7	80.4	2.1	81.6	0.5
	SC05	21.6	0.7	2.8	1.4	4.8	1.1
	SC06	21.4	0.6	11.7	1.8	6.5	0.9
	SC07	13.5	1.4	87.6	0.8	90.0	0.2
	SC08	10.5	2.3	93.4	0.8	92.0	0.1
Variation of activation temperature	SC09	21.6	0.3	15.5	0.2	9.4	0.3
	SC10	20.1	0.4	34.6	2.5	25.9	1.5
	SC11	16.4	1.1	65.4	3.6	70.4	1.1
	SC12	13.0	2.0	93.4	0.8	93.0	0.1
Acid treated	SC01-A	22.7	0.8	0	0.9	-	-
	SC07-A	13.5	1.4	0.4	1.2	-	-
Commercial sample	CAC	-	-	37.0	1.3	25.2	2.3

Prior to statistical analysis the data were analysed for violations of the assumption of normal distribution for parametric tests. Since sample size was smaller than 50 the Shapiro-Wilk test was used. The test was statistically not significant ($p > 0.01$) for yield, %As(V).R and %As(III).R experiments and so all samples have an approximate normal distribution.

Then, the effect of the preparation parameters CT, AT and At on yield of SCAC was investigated with an ANOVA test for repeated measures. This test was selected because yield measurements were not independent from each other. At one time, two batches of SCAC were prepared in the same furnace run; hence variations in yield also reflect the variability within the furnace run. Results from this test suggest that CT ($p = 0.041$), AT ($p < 0.001$), At ($p = 0.001$), and the interaction between AT and At ($p = 0.001$) have an effect on SCAC yield. The ANOVA test for yield is included in Table E1 in *Appendix E*. Plots of the main factors against yield, presented from Figures E1 to E6 in *Appendix E*, indicate that AT has a strong effect on yield and that the effect of At is more important at higher values of AT and CT.

The standardised residual plots of the ANOVA tests for factorial experiments and the arsenic(V) and arsenic(III) per cent removal did not present a regular or systematic pattern. Also, with the exception of two points, residuals were equally distributed across $y = 0$. The criterion to identify outliers was a standard residual value higher than 3.3 or smaller than -3.3 (Pallant 2007). Based on this criterion, no outliers were found in the data sets. The normality probability plot presented a reasonably straight diagonal for both data sets. The Levene's test of equality of error variances was statistically significant ($p < 0.050$) for both arsenic(V) and arsenic(III) factorial experiments. This result implies that the equality of variance assumption is not fulfilled. However, the ANOVA test is robust for this type of violation if group sizes are similar; which is the case (Pallant 2007).

The plots of the effect of the main factors on %As(V).R (Figures E7 to E12 in *Appendix E*) and on %As(III).R (Figures E13 to E18 in *Appendix E*) indicate that AT and the interaction AT-At could have an effect on both arsenic(V) and arsenic(III) adsorption. According to the ANOVA test CT ($p < 0.001$), AT ($p < 0.001$), the interaction CT-AT ($p = 0.050$), and the interaction AT-At ($p < 0.001$) are statistically significant for arsenic(V) adsorption (Table E2 *Appendix E*). The factor At ($p = 0.052$) is borderline statistically significant. The ANOVA test shows that CT ($p < 0.001$), AT ($p < 0.001$), At ($p < 0.001$) and the interaction AT-At ($p < 0.001$) are statistically significant for arsenic(III) adsorption (Table E3 *Appendix E*).

The effect of CT, AT and At on arsenic(V) and arsenic(III) adsorption was modelled with the general regression equation for the 2^3 factorial experiment presented in *Section 5.1* (Equation 5.3). The general linear model function in the SPSS software was used to calculate the C terms in Equation 5.3. The plot of residuals was checked for each model; no significant abnormalities were detected. The models for arsenic(V) and arsenic(III) are presented below.

Arsenic(V) adsorption models

- Model A: first degree equation with the statistically significant terms from the ANOVA test (Equation 5.4 and Figure 5.2). Model A was derived from data from the factorial experiment (SC01-SC08). The goodness of fit value for this model was $R^2 = 0.993$. The equations and plots for all models presented in this chapter are for coded factors.

$$\%\,As(V).R = 47.454\ + (3.307 \times CT) + (37.636 \times AT) - (1.462 \times CT \times AT) + (4.000 \times AT \times At)$$

Equation 5.4

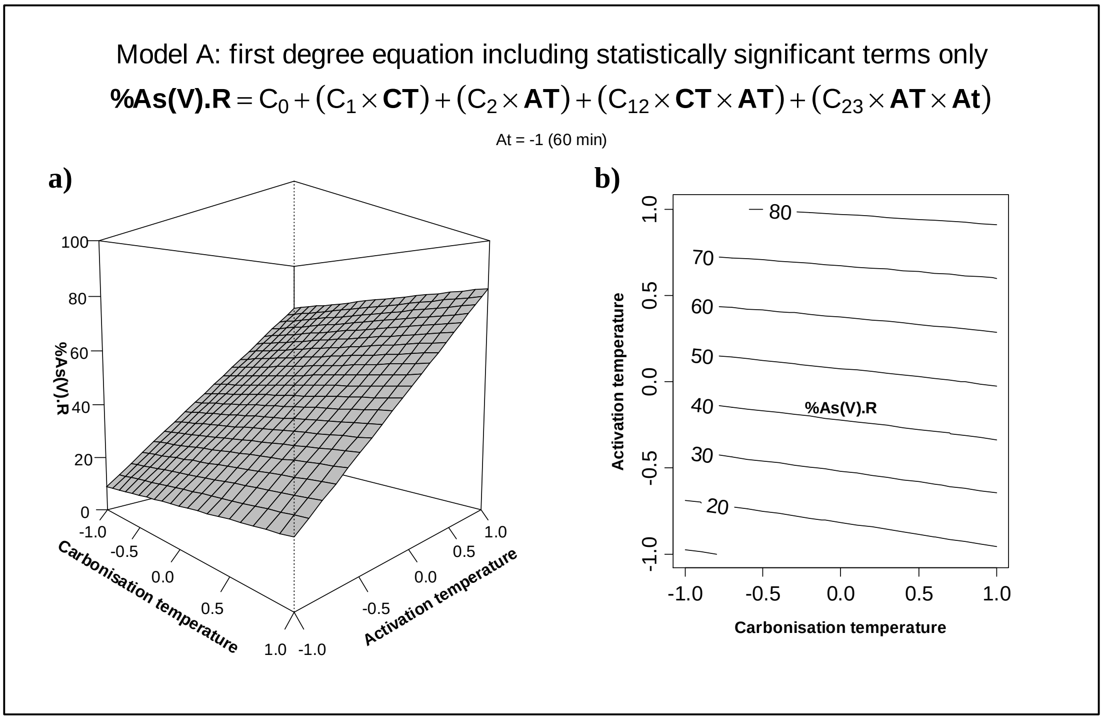


Figure 5.2 Arsenic(V) adsorption model A: first degree equation with the statistically significant terms only. a) Surface plot, and b) contour plot at an activation time of 60 min.

- Model B: a first degree equation with the statistically significant terms from the ANOVA test plus additional terms to observe the hierarchy principle (Equation 5.5 and Figure 5.3). This model was obtained using results from the factorial experiment (SC01-SC08). The goodness of fit value was $R^2 = 0.994$.

$$\%\,As(V).R = 47.454\ + (3.307 \times CT) + (37.636 \times AT) + (1.448 \times At) - (1.462 \times CT \times AT) + (4.000 \times AT \times At)$$

Equation 5.5

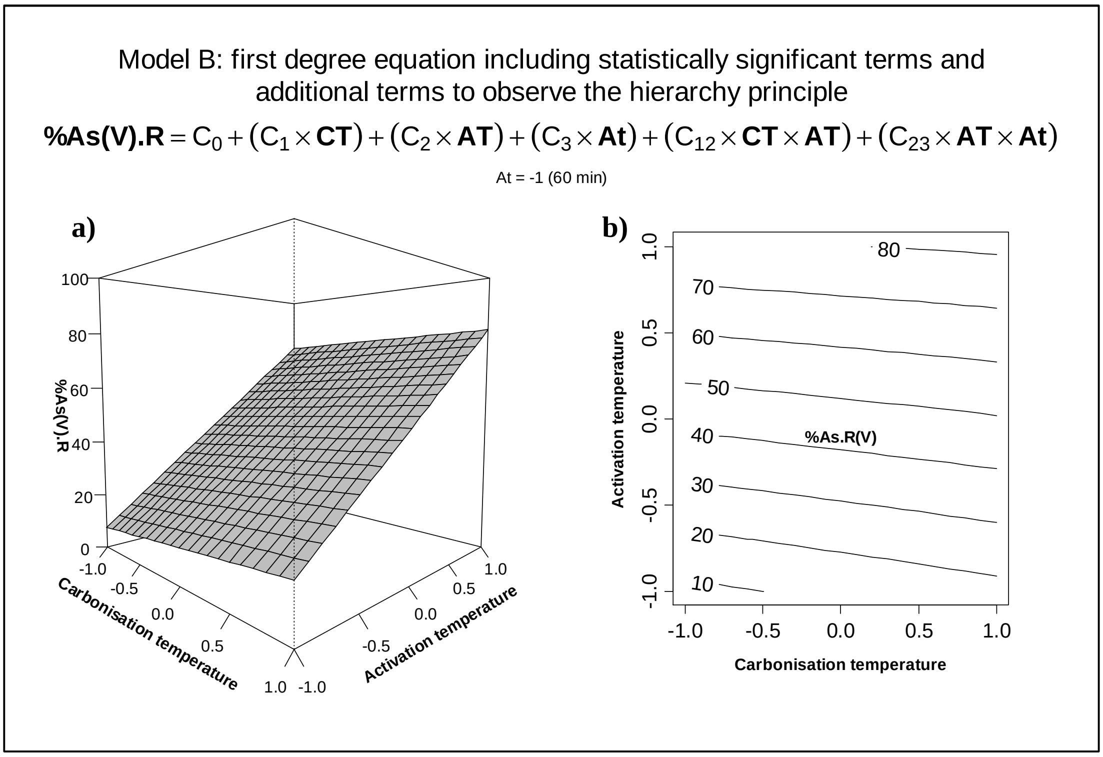


Figure 5.3 Arsenic(V) adsorption model B: first degree equation including statistically significant terms and additional terms to observe the hierarchy principle. a) Surface plot, and b) contour plot at an activation time of 60 min.

- Model C: second degree equation with respect to AT (Equation 5.6). Results from the variation of AT experiment suggested that the effect of AT on arsenic(V) removal was quadratic. The factorial experiment data (SC01-SC08) could not reproduce this quadratic relationship. Hence, this model was derived with data from the factorial experiment and data from the variation of AT experiment. Figure 5.4 shows the surface plot of the model at an At of 60 min, and contour plot at an At of 60 and 180 min. The purpose of the two contour plots is to illustrate the effect of At on arsenic(V) adsorption. The goodness of fit value for this model was $R^2 = 0.987$.

$$\%As(V).R = 48.510 + (29.982 \times CT) + (38.856 \times AT) - (2.682 \times CT \times AT) - (27.731 \times CT \times AT^2) + (4.000 \times AT \times At) + (1.448 \times AT^2 \times At)$$

Equation 5.6

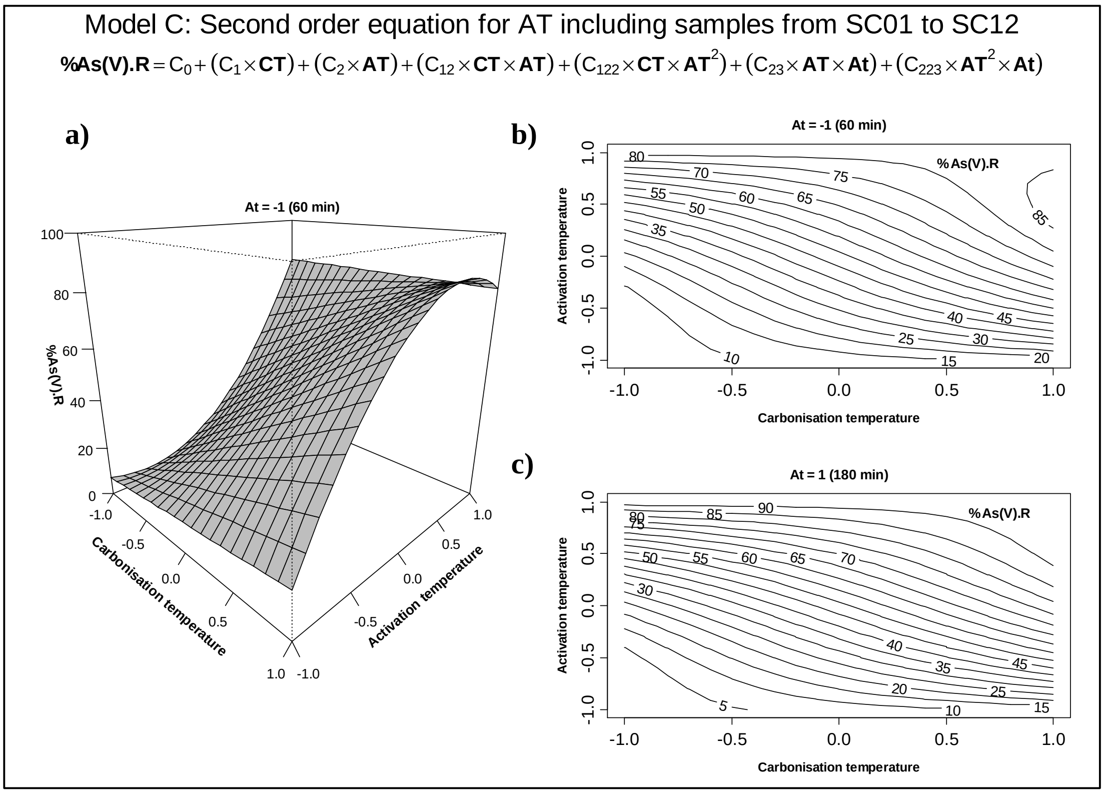


Figure 5.4 Arsenic(V) adsorption model C: second degree equation with respect to AT. a) Surface plot at an activation time of 60 min, b) contour plot at an activation time of 60 min, and c) contour plot at an activation time of 180 min.

Arsenic(III) adsorption models

- Model D: first degree equation with the statistically significant terms from the ANOVA test (Equation 5.7 and Figure 5.5). The model observes the hierarchy principle. The R^2 value is 1.000.

$$\%As(III).R = 46.471 + (1.232 \times CT) + (39.060 \times AT) + (1.833 \times At) + (3.606 \times AT \times At)$$

Equation 5.7

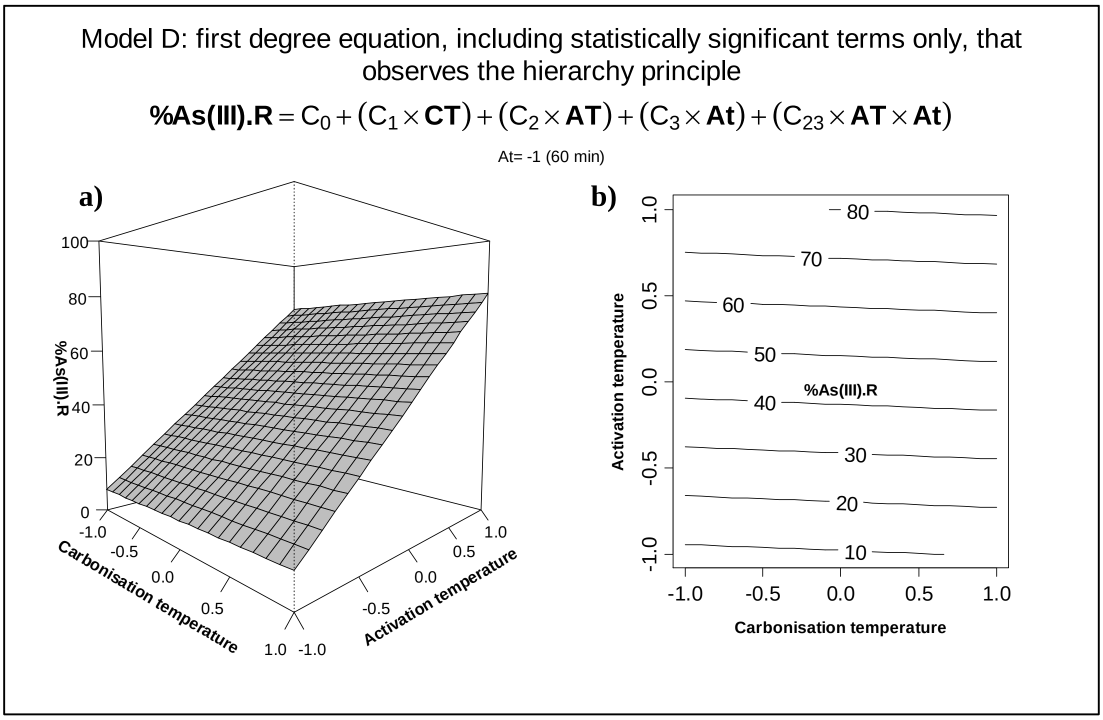


Figure 5.5 Arsenic(III) adsorption model D: first degree equation with statistically significant terms that observe the hierarchical principle. a) Surface plot, and b) contour plot at an activation time of 60 min.

- Model E: second order equation with respect to AT (Equation 5.8 and Figure 5.6). The relationship between AT and arsenic(III) adsorption appears to be quadratic; as for the case of arsenic(V) removal. The model was derived from samples SC01 to SC12. The goodness of fit value for model E is $R^2 = 0.982$.

$$\%As(III).R = 13.23 - (6.68E^{-2} \times CT) + (40.63 \times AT) + (34.54 \times AT^2) - (8.65 \times At) + (3.61 \times AT \times At) + (10.48 \times AT^2 \times At)$$

Equation 5.8

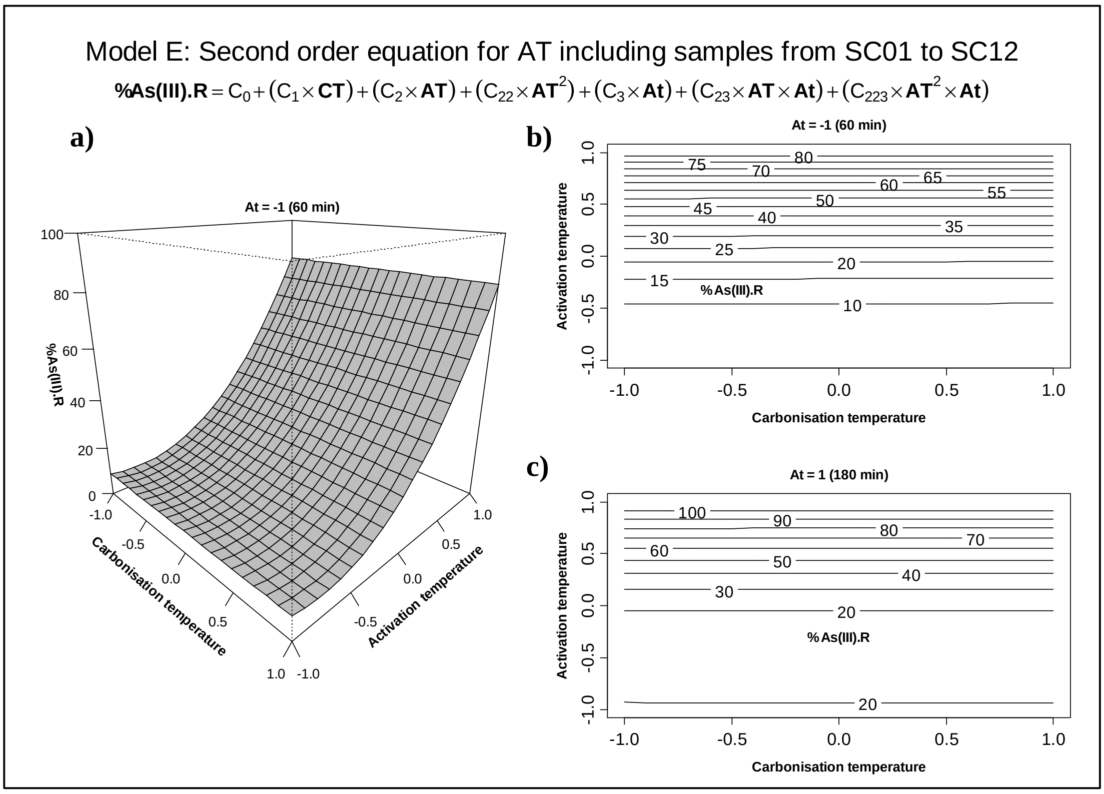


Figure 5.6 Arsenic(III) adsorption model E: second degree equation with respect to AT. a) Surface plot at an activation time of 60 min, b) contour plot at an activation time of 60 min, and c) contour plot at an activation time of 180 min.

5.2.2 Model adequacy checking

Table 5.3 presents the experimental, predicted and ± 95 per cent confidence interval for percent arsenic(V) removal for models A, B and C. For the three models, the experimental %As(V).R for samples SC01-SC08 is in good agreement with the predicted values. Also, the experimental values are within the ± 95 per cent confidence interval estimated for the models. The experimental data from the variation of the AT experiment (SC09-SC12) is poorly reproduced by models A and B. Experimental %As(V).R is within the ± 95 per cent confidence interval only for SC11. On the other hand, model C accurately reproduces %As(V) removal for these four samples.

Table 5.3 Experimental, predicted and ± 95 per cent confidence intervals for arsenic(V) per cent removal with sugarcane activated carbon for the adsorption models: A (first degree equation with the statistically significant terms only); B (first degree equation including statistically significant terms and additional terms to observe the hierarchy principle); and C (second degree equation with respect to AT).

Adsorbent	Per cent arsenic(V) removal						
	Experimental	Model A		Model B		Model C	
		Predicted	± 95 % CI (a)	Predicted	± 95 % CI (a)	Predicted	± 95 % CI (a)
SC01	7.3	9.0	8.3	7.6	7.8	7.3	10.5
SC02	17.5	18.6	8.3	17.1	7.8	17.1	10.5
SC03	78.8	79.2	8.3	77.8	7.8	82.3	10.2
SC04	80.4	82.9	8.3	81.5	7.8	81.5	10.5
SC05	2.8	1.0	8.3	2.5	7.8	2.2	10.5
SC06	11.7	10.6	8.3	12.0	7.8	12.0	10.5
SC07	87.6	87.2	8.3	88.7	7.8	93.2	10.2
SC08	93.4	90.9	8.3	92.4	7.8	92.4	10.5
SC09	15.5	44.1	7.9	44.1	7.2	18.5	10.1
SC10	34.6	57.0	7.9	57.0	7.3	35.3	9.9
SC11	65.4	70.3	8.0	70.3	7.4	58.8	9.7
SC12	93.4	83.2	8.2	83.2	7.5	87.8	5.9

(a) CI = confidence interval

Table 5.4 presents the experimental, predicted and 95 per cent confidence intervals for the arsenic(III) adsorption models. Results are similar to those for arsenic(V) adsorption. The linear model reproduces well the experimental results from the factorial experiment but poorly reproduces the data from the variation of AT experiment. The quadratic model (E) very closely reproduces experimental data from both experiments, with exception of SC11.

Table 5.4 Experimental, predicted and 95 per cent confidence intervals for arsenic(III) per cent removal with sugarcane activated carbon for the adsorption models: D (first degree equation with statistically significant terms that observes the hierarchy principle); and E (second degree equation with respect to AT).

Adsorbent	Percent arsenic(III) removal				
	Experimental	Model D		Model E	
		Predicted	± 95 % CI (a)	Predicted	± 95 % CI (a)
SC01	7.6	8.0	1.8	9.0	12.7
SC02	10.8	10.4	1.8	8.9	12.7
SC03	78.6	78.9	1.8	83.0	12.5
SC04	81.6	81.3	1.8	82.9	12.7
SC05	4.8	4.4	1.8	5.4	12.9
SC06	6.5	6.9	1.8	5.3	12.8
SC07	90	89.7	1.8	93.9	12.5
SC08	92	92.2	1.8	93.8	12.7
SC09	9.4	45.2	1.7	13.3	12.5
SC10	25.9	58.1	1.7	30.5	12.3
SC11	70.4	71.4	1.7	56.0	11.9
SC12	93	84.3	1.7	88.5	12.1

(a) CI = confidence interval

5.3 Discussion

The experimental data and statistical analysis carried out on the experimental data allowed the identification of the preparation parameters that maximise arsenic adsorption with SCAC. First, the factor and combination of factors with an effect on yield, %As(V).R and %As(III).R were identified with separate factorial experiments. Then, the effect of AT was more closely studied. Finally, the effect of nitric acid washing of SCAC on arsenic adsorption was tested.

The ANOVA test for yield agreed with the expected results; higher values of CT, AT and At reduce the yield of SCAC. The specific effect of AT on yield can be clearly observed in the variation of the AT experiment. Unfortunately, SCAC samples with high yield values are poor arsenic adsorbents, and adsorbents with higher arsenic adsorption were prepared at high AT. High yield and low AT are desired characteristics of AC; low yield may increase the cost of the AC and adsorbents with high AT require more energy input for preparation.

The ANOVA tests emphasised the differences between arsenic(V) and arsenic(III) adsorption. The factors CT, AT, AT-At were statistically significant for both arsenic(V) and arsenic(III) adsorption; but the effect of the interaction CT-AT was statistically significant only for arsenic(V) adsorption, and the effect of At was statistically significant only for arsenic(III) adsorption.

High arsenic(V) and arsenic(III) adsorption occurs for similar preparation conditions; low CT-high AT and high CT-high AT. This similarity is favourable since arsenic(V) and arsenic(III) could be removed with the same SCAC without pre-oxidation of arsenic(III). On the other hand, the CAC adsorbed more arsenic than some SCAC types. This highlights the importance of optimising preparation conditions for agriculturally based AC for the substance (or element) to be adsorbed.

Linear models, derived from the factorial experiment, do not reproduce the effect of AT on arsenic(V) or arsenic(III) removal. This disagreement between experimental data and the response predicted by the model is due to the assumption of a linear relationship between the two levels of AT. In the variation of AT experiment, it is clear that the relationship between AT and arsenic adsorption is not linear. The rate of change of %As(V).R from 800 to 850 °C AT is 1.6 times higher than from 750 to 800 °C AT for arsenic(V) and 2.5 times higher for arsenic(III) removal. On the other hand, quadratic models reproduce very closely experimental data from the factorial and variation of AT experiments. Overall, the ± 95 per cent confidence interval for the predicted responses is wider for quadratic than for linear models.

The adequacy of the quadratic models could not be completely verified since all experimental data (SC01-SC12) were used in the derivation of these models. Also, the assumption of the linear relationship between the low and high CT levels could not be verified. Although pair-wise comparisons of SCAC samples prepared at the same AT and At but at high and low CT levels revealed relatively small changes in arsenic(V) and arsenic(III) adsorption, there are no experimental points at intermediate values of CT to draw a strong conclusion about the CT effect.

Assuming that the quadratic model accurately represents arsenic(V) and arsenic(III) removal, the following conclusions can be drawn. First, at the same CT arsenic(V) adsorption is enhanced with increments in AT for most part of the experimental range. Second, %As(V).R varies significantly with relatively small changes in CT and AT. For instance, arsenic(V) removal increases by 5 per cent from AT 850 to 860 °C (CT = 700 °C and At = 60 min). Thirdly, the factor At has a relatively small effect on arsenic(V) and arsenic(III) adsorption. Arsenic(V) adsorption increases with At at high AT, and decreases with At at low AT, while arsenic(III) increases with At at high and low AT. A few percentage units in arsenic adsorption could make the difference in complying with arsenic drinking water regulations or not. Hence, the process has to be carefully monitored to ensure the right temperature is reached.

The assumption about the CT effect is less relevant for arsenic(III) adsorption than for arsenic(V) adsorption, since the interaction of the CT-AT term is not statistically significant for arsenic(III) adsorption. The CT effect on arsenic(III) removal is very small; which causes the contour %As(III).R lines to be parallel to the CT axis. The effect of AT is more important at higher AT values; the distance between contour lines is smaller at higher AT.

The uncertainties of the effect of CT on arsenic(V) removal are of little practical importance for the following reasons. Firstly, the study identified that the combination of low CT and high AT produce SCAC with high arsenic adsorption. The only combination of factors that could be of more interest is low CT and low AT; but according to the experimental data %As(V).R and %As(III).R are low for these conditions. Secondly, arsenic removal is optimal at high activation temperatures with no regard to the CT value. Further experimentation could clarify the effect of CT on arsenic removal, especially in a lower temperature range that studied here.

5.4 Summary

In this chapter, a 2^3 factorial experimental design was used to optimise the preparation conditions of SCAC for arsenic(V) and arsenic(III) removal. The factors investigated were CT at 700 and 850 °C, AT at 600 and 900 °C, and At at 60 and 180 minutes. Also, the effect of AT and pre-treatment with acid were investigated in two small-scale experiments. Arsenic removal was highest with the SCAC prepared at an AT of 900 °C. In comparison, arsenic removal was higher with CAC than with SCAC prepared at AT of 600 and 750 °C. Pre-treatment of SCAC with nitric acid reduced to negligible levels the adsorption of arsenic(V). According to the ANOVA test for the factorial experiments for yield, and arsenic(V) and arsenic(III) adsorption,

- the factors CT ($p = 0.041$), AT ($p < 0.001$), At ($p = 0.001$), and the interaction AT-At ($p = 0.001$) have a statistically significant effect on yield,
- the factors CT ($p < 0.001$), AT ($p < 0.001$), the interaction CT-AT ($p = 0.050$), and the interaction AT-At ($p < 0.001$) have a statistically significant effect on arsenic(V) adsorption, and
- the factors CT ($p < 0.001$), AT ($p < 0.001$), At ($p < 0.001$), and the interaction AT-At ($p < 0.001$) have a statistically significant effect on arsenic(III) adsorption.

Linear models for arsenic(V) and arsenic(III) adsorption did not reproduce accurately the data from the variation of AT experiment. This result was attributed to the non-linear relation between AT and per cent arsenic removal. Although quadratic models (with respect to AT) reproduced very well data from the factorial and AT experiments, it was not possible to verify the robustness of the models since all experimental data were used to derive these models.

Despite the limitations of the 2^3 factorial experimental design, such as assuming a linear relationship between the levels of the factors studied, it proved to be a useful method to optimise the preparation conditions of ACs for removal of target pollutants. The main objective of the experiment was fulfilled, to identify the region at which arsenic(V) and arsenic(III) removal are optimal, that is low CT and high AT.

6. Characterisation of sugarcane activated carbon and commercially available activated carbon

The characterisation of some of the physical and chemical properties of AC samples was made to identify some of the properties that may have an effect on arsenic adsorption. The characterisation experiments included the pH of zero charge (pH_{ZC}), scanning electron microscopy (SEM), surface area, and particle size analysis. It was not possible to characterise the 12 different samples of sugarcane activated carbon (SCAC) since the preparation of the materials would have taken a considerable amount of time. Then, two samples with low percentage of arsenic removal (SC05 and SC06), and three samples with medium to high percentage of arsenic removal (SC07, SC11 and SC12) and the commercial activated carbon (CAC) sample were selected to carry out sample characterization experiments.

6.1 Determination of the pH of zero charge

6.1.1 Importance of the pH of zero charge in adsorption

The pH_{ZC} is the pH at which the surface of the adsorbent has a net neutral charge (Hiscock, 2005). At higher pH values the surface has a net negative charge and at lower pH values the surface has a net positive charge. The pH_{ZC} is an important parameter in adsorption. In the typical pH range of natural waters, from 6.5 to 8.5, arsenate is present as $H_2AsO_4^-$ and $HAsO_4^{2-}$ (Ravenscroft et al., 2009). At pH values lower that 9.2 the arsenite ion $H_3AsO_3^0$ dominates and at higher pH values the species $H_2AsO_3^-$ and $HAsO_3^{2-}$ are also present (Ravenscroft et al., 2009). Favourable electrostatic conditions may influence adsorption of the negatively charged arsenate and arsenite ions (Johnston et al., 2001).

6.1.2 Methodology for measurement of the pH of zero charge

The pH_{ZC} of the SCAC samples and the CAC sample was determined with the immersion technique (Bourikas et al., 2003). The experimental methodology for the determination of the pH_{ZC} requires the use of free carbon dioxide (CO_2) water. Free CO_2 water was prepared by boiling reagent grade water for 15 minutes, and then cooling it quickly. The pH was measured with a Mettler Toledo seven easy S20 pH-meter. Three pH standards were used to calibrate daily the instrument; 4, 7 and 9.2. The calibration curve had always a maximum error of ± 5 per cent.

A stock solution of 0.1M sodium nitrate ($NaNO_3$) was prepared with the free CO_2 water. This stock solution was used for preparation of solutions with pH values from 2 to 11. The pH of solutions was adjusted with dropwise addition of 0.1 M sodium hydroxide (NaOH) or 2.25 M nitric acid (HNO_3). Next, activated carbon was weighed and placed in glass vials. Then, 20 mL of the pH adjusted solution were poured into the glass vials. The glass vials were sealed and placed in a bottle shaker for 48 hours. Finally, the pH of solutions was measured. For each adsorbent the experiment was done by triplicate for each pH value.

The pH_{ZC} was determined from the experimental data as follows. The change in pH of solutions ($\Delta pH = pH_{t=48hours} - pH_{t=0}$) was plotted against the initial pH ($pH_{t=0}$). The point at which $\Delta pH = 0$ is the pH_{ZC}. This procedure was tested on commercial activated carbon with two different amounts of adsorbent; 0.15 g and 0.20 g. The pH_{ZC} value determined with both tests was practically the same. For an activated carbon mass of 0.15 g the pH_{ZC} was determined as 6.83 ± 0.1, and for an activated carbon mass of 0.20 g the pH_{ZC} was 6.83 ± 0.1. Hence, following tests were done with an adsorbent mass of 0.15 g. An initial test for sugarcane activated carbon samples revealed that their pH_{ZC} was higher than 8, hence the pH_0 screened for these adsorbents was from 4 to 11. Figure 6.1 presents an example plot for sample SC07 the calculation of the pH_{ZC}.

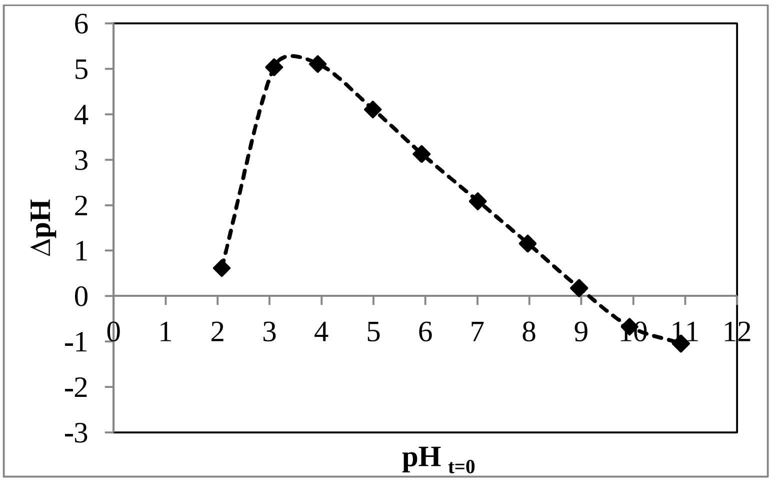


Figure 6.1 Example plot for SC07 for the calculation of the pH_{ZC} for activated carbon samples.

6.1.3 Results

Table 6.1 shows the pH_{ZC} values obtained for different activated carbon samples. The error term on the pH_{ZC} was calculated as the standard deviation of the average of the triplicates. CAC has a pH_{ZC} very close to neutrality and SCAC samples are of basic character (from pH_{ZC} 9.2 to 10.2). In terms of the pH_{ZC} arsenic(V) adsorption on SCAC is favourable across the pH range of natural waters; As(V) ions are negatively charged and the SCAC surface is positively charged. As(V) adsorption on CAC is only favourable when natural waters have a pH smaller than the pH_{ZC} of CAC.

Table 6.1 pH of zero charge (pH_{ZC}) of commercial activated carbon (CAC) and sugarcane activated carbon samples (SC05, SC06, SC07, SC11 and SC12). The preparation conditions for SCAC samples were presented in Table 5.1 in *Section 5.1*.

Adsorbent	pH_{ZC}
CAC	6.8 ± 0.1
SC05	9.2 ± 0.1
SC06	10.2 ± 0.2
SC07	9.2 ± 0.1
SC11	9.8 ± 0.1
SC12	9.7 ± 0.1

6.2 Scanning electron microscopy

6.2.1 Scanning electron microscopy theory and sample analysis methodology

Samples were studied with SEM; an application of x-ray emission spectroscopy. In this technique the sample is bombarded with electrons (the primary beam), then the sample emits other electrons (the secondary beam), this signal is then used to produce an image of the sample. In this research a JEOL JSM-5900 LV scanning electron microscope was used. This instrument was used to produce topographic contrast (secondary electron imaging) and chemical contrast (backscattered secondary electron imaging) pictures. A qualitative analysis of the sample was done with energy dispersive X-ray spectrometry (energy dispersive spectrometer).

6.2.2 Scanning electron microscopy results

Below are presented the topographic contrast pictures taken for CAC (Figure 6.2) and SCAC samples SC05 (Figure 6.3), SC06 (Figure 6.4), SC07 (Figure 6.5), SC11 (Figure 6.6) and SC12 (Figure 6.7). The qualitative composition of SCAC samples was as follows carbon (C), oxygen (O), aluminium (Al), calcium (Ca), chloride (Cl), copper (Cu), and iron (Fe). The elements carbon (C), oxygen (O), aluminium (Al), chloride (Cl), sodium (Na), sulphur (S), silicon (Si), and titanium (Ti) were identified in CAC samples.

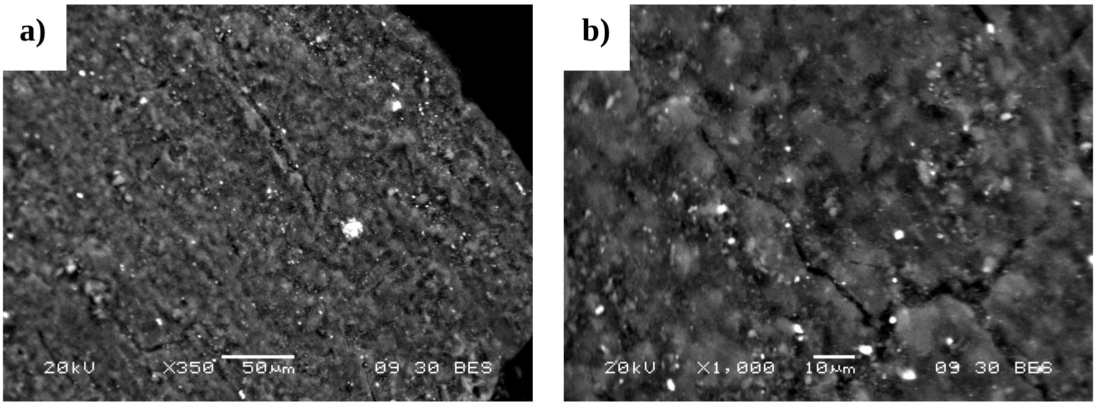


Figure 6.2 Micrographs of commercial activated carbon CAC. Micrographs were taken at a) ×350, and b) ×1000.

The SEM micrographs illustrate the assortment of topographies found on CAC and SCAC samples. SCAC samples look very different from CAC; this was expected since raw material and preparation conditions are very different for both types of adsorbents. CAC samples appear to have a more porous surface than SCAC samples. SCAC samples are mostly flakes of various sizes and irregular shapes. Some of the flakes have holes of different sizes. In some cases these holes seem to follow a pattern; e.g. Figure 6.3 d), Figure 6.4 b), Figure 6.5 d), and Figure 6.6 d). There is no apparent relation between the synthesis parameters of SCAC and development of certain type of structures.

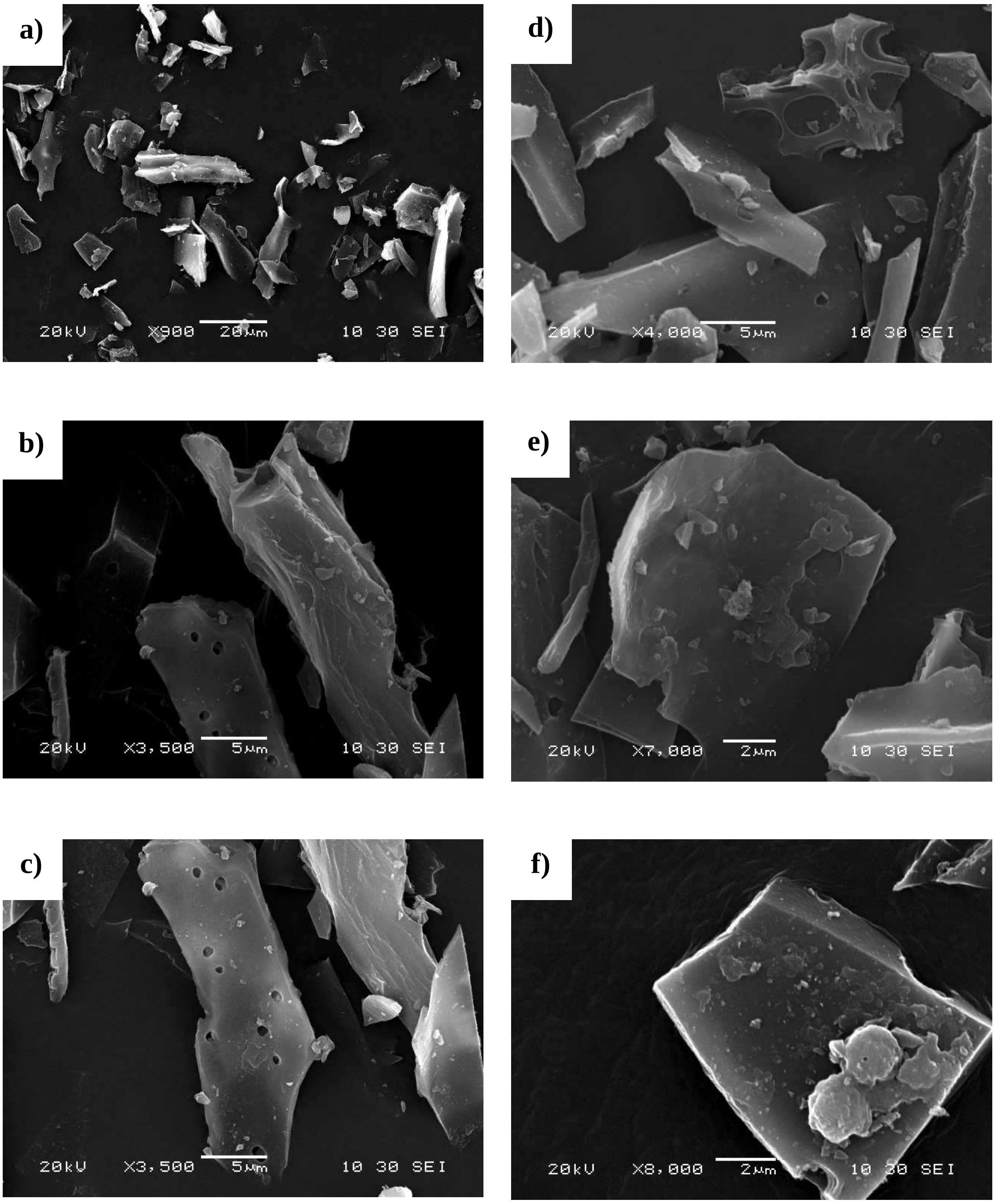


Figure 6.3 Micrographs of sugarcane activated carbon sample SC05. Micrographs were taken at a) ×900, b) and c) ×3500, d) ×4000, e) ×7000 and f) ×8000.

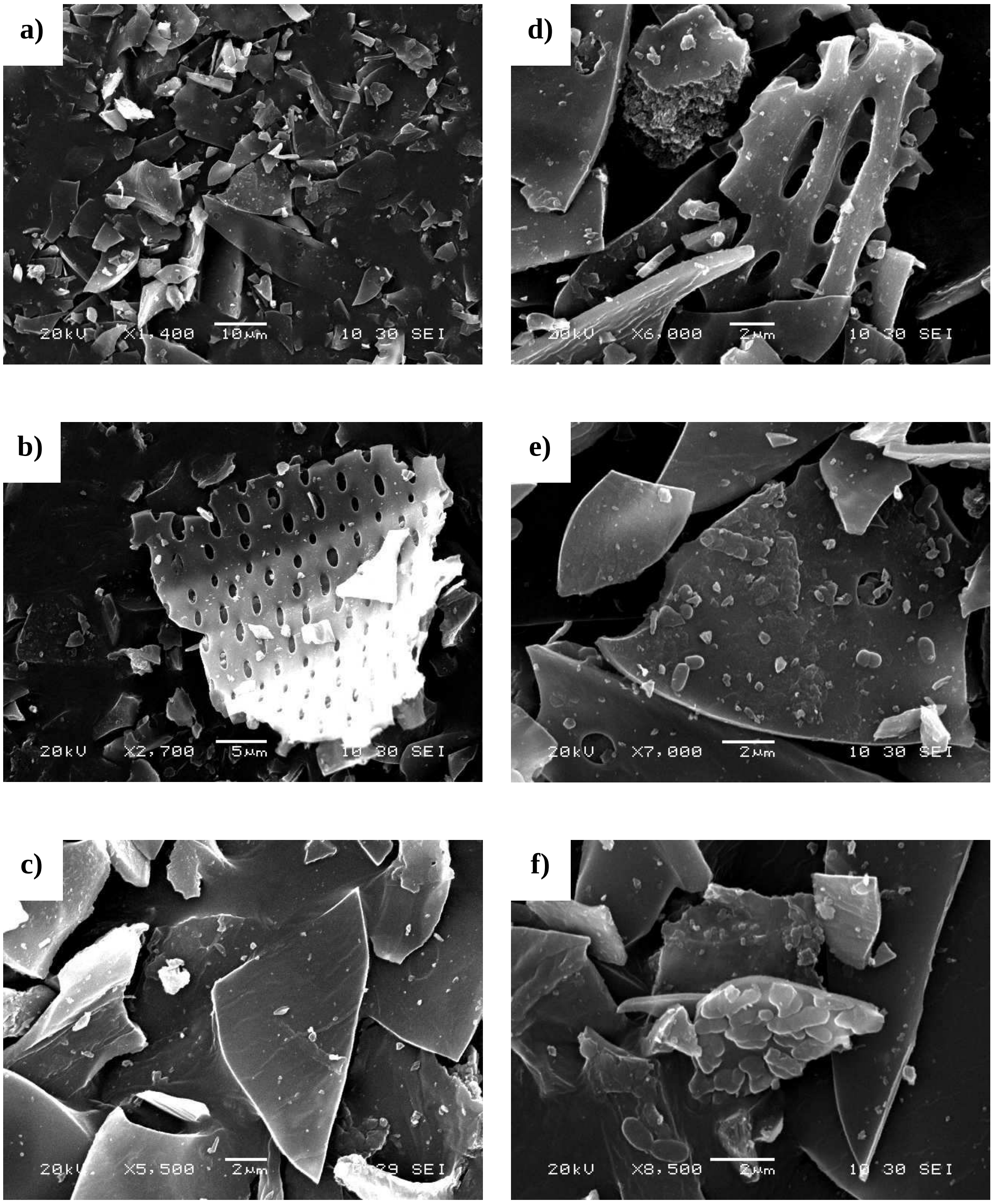


Figure 6.4 Micrographs of sugarcane activated carbon sample SC06. Micrographs were taken at a) ×1400, b) ×2700 and c) ×5500, d) ×6000 e) ×7000 and f) ×8500.

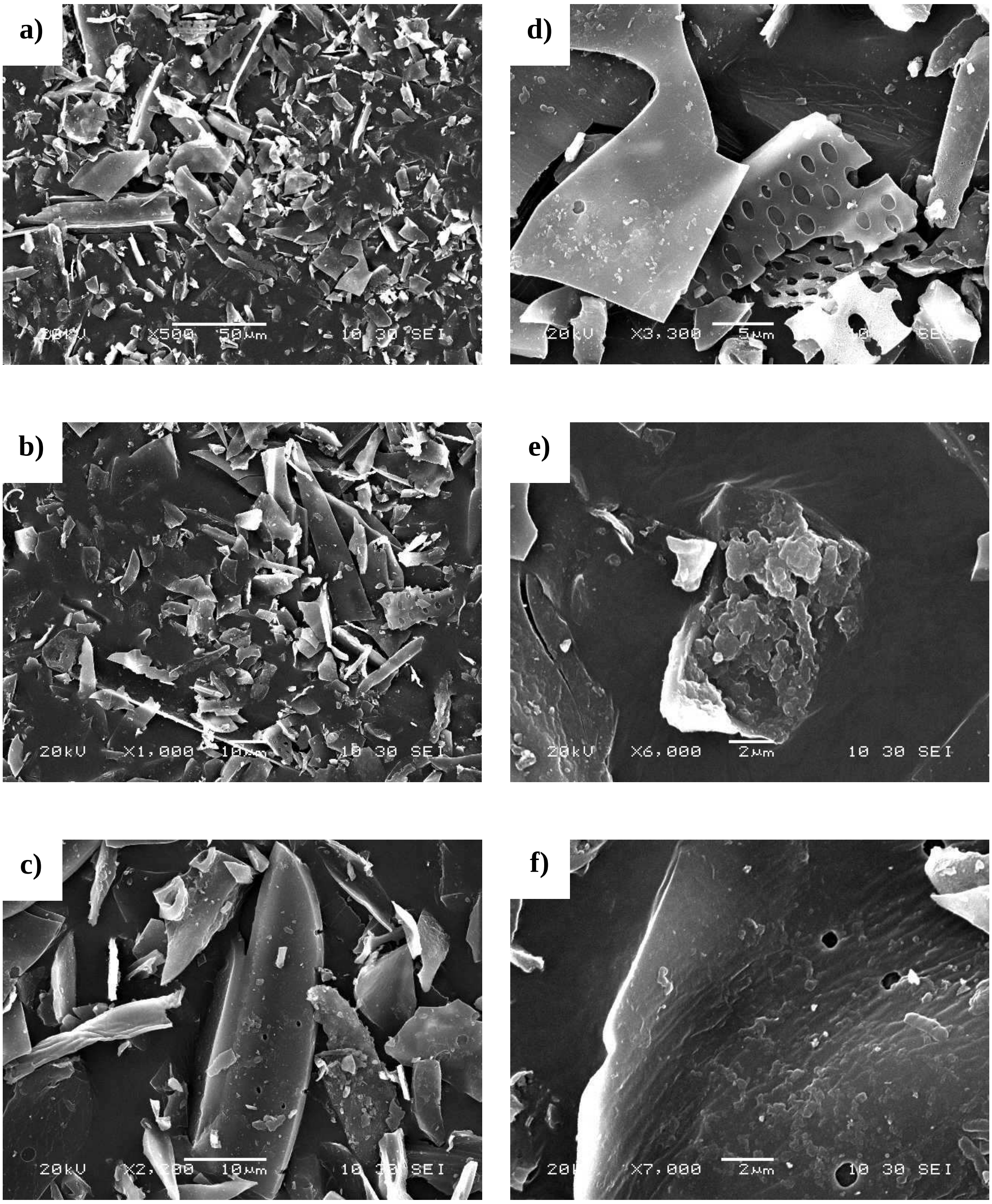


Figure 6.5 Micrographs of sugarcane activated carbon sample SC07. Micrographs were taken at a) ×500, b) ×1000, c) ×2200, d) ×3300, e) ×6000 and f) ×7000.

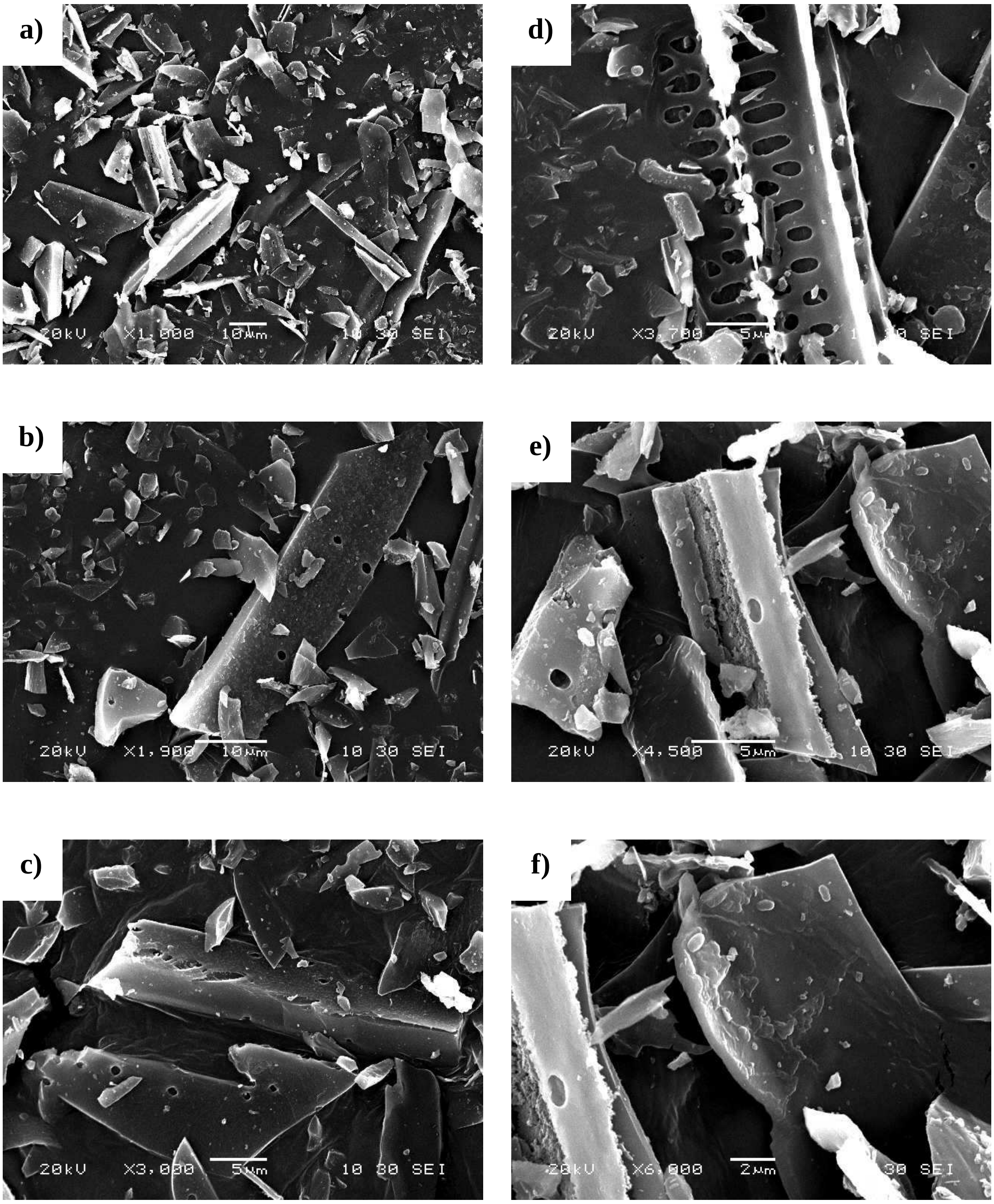


Figure 6.6 Micrographs of sugarcane activated carbon sample SC11. Micrographs were taken at a) ×1000, b) ×1900, c) ×3000, d) ×3700, e) ×4500 and f) ×6000.

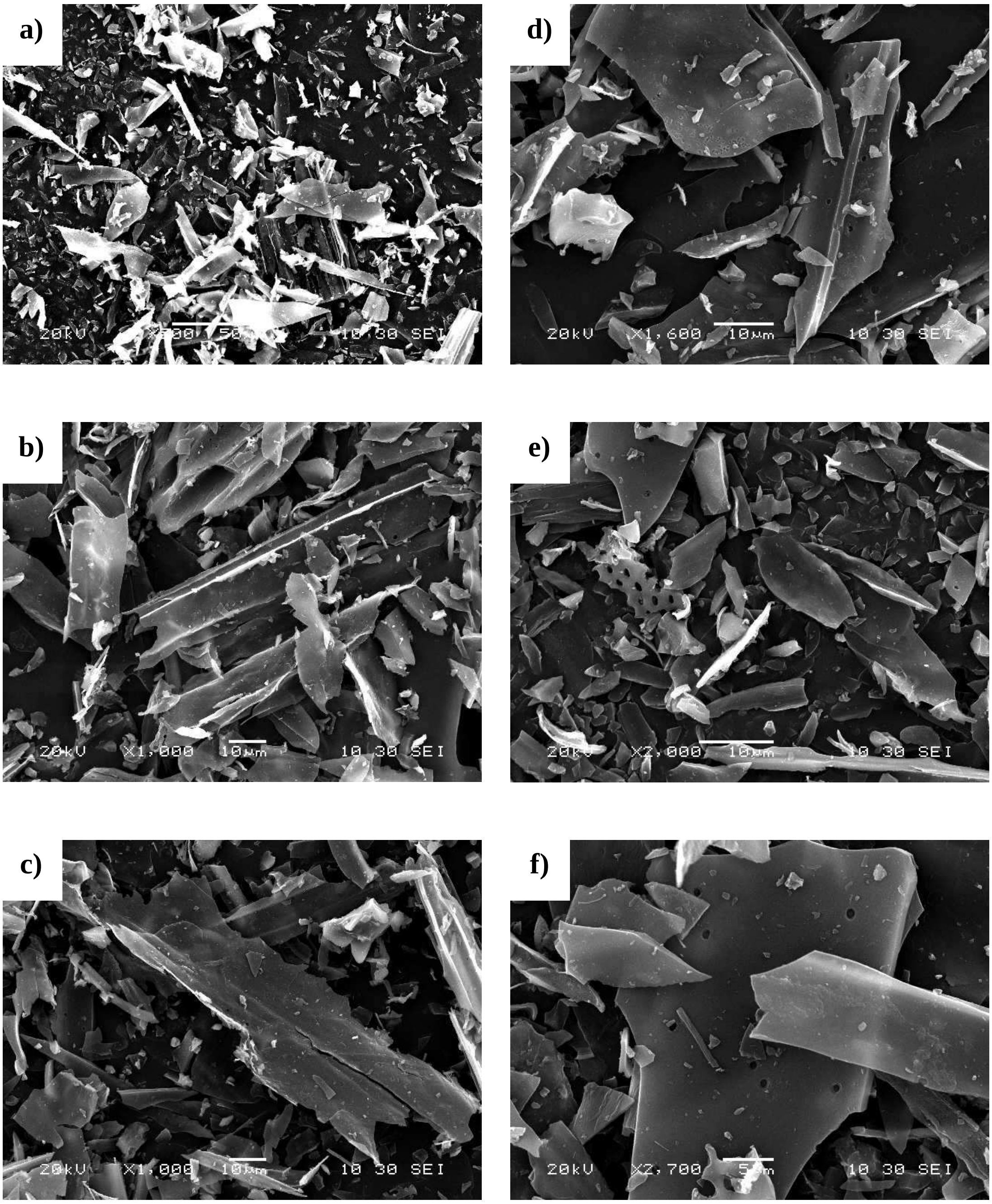


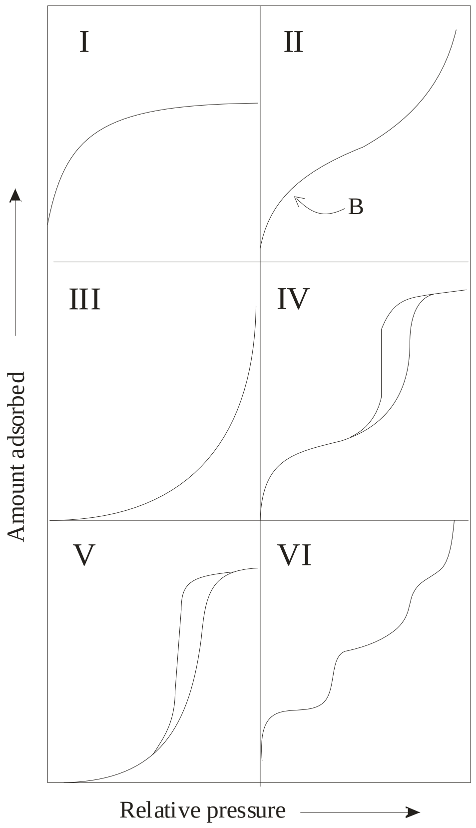
Figure 6.7 Micrographs of sugarcane activated carbon sample SC12. Micrographs were taken at a) ×500, b) and c) ×1000, d) ×1600, e) ×2000 and f) ×2700.

6.3 Specific surface area and pore width distribution

Specific surface area and pore width distribution were determined for SCAC and CAC samples. The experimental analysis was done with the gas adsorption method. Surface area and pore width distribution concepts are briefly introduced in this section. *Section 6.3.1* deals with the experimental method for sample analysis, *Section 6.3.2* with the methods for interpretation of absorption isotherms used in this research, and *Section 6.3.3* with the results.

Surface area and pore size, among other factors, affect the adsorption process and consequently the shape of sorption isotherms. The specific surface area is defined as the surface area in square metres per gram of adsorbent (m^2 g^{-1}). The International Union of Pure and Applied Chemistry (IUPAC) classes pores according to their internal pore width in micropores (< 2 nm), mesopores (2-50 nm) and macropores (> 50 nm). In micropore filling, adsorption is governed by the interactions between adsorbate molecules and the walls of the pores (Lowell et al., 2004). For mesopores the interaction between adsorbate molecules is also important; this interaction leads to capillarity condensation (Lowell et al., 2004).

The IUPAC has classed the different types of adsorption isotherms and hysteresis loops experimentally found by many researchers (Sing et al., 1985). Figure 6.8 presents the IUPAC isotherm classification. The IUPAC classification for hysteresis loops is not included here for space reasons. Hysteresis loops are formed when the adsorption and desorption branches of the isotherm differ; they are an indication that capillarity condensation is occurring.



Isotherm	Characteristics
Type I (Langmuir)	• Typical of chemisorption or physisorption of microporous adsorbents.
Type II	• Typical of non-porous or macroporous adsorbents. • The inflexion point B, is the point at which the monolayer is complete.
Type III	• Isotherm is convex to the axis P/P_0. • There is no point B. • Adsorbate-adsorbent interactions are weak. • Adsorbate-adsorbate interactions are important.
Type IV	• Typical of mesoporous adsorbents. • Hysteresis loop associated with pore condensation. • Low P/P_0 range is associated with Type II isotherm.
Type V	• Hysteresis loop. • Low P/P_0 range associated with Type III isotherms.
Type VI	• Stepwise multilayer adsorption on a uniform non-porous adsorbent.

Figure 6.8 IUPAC classification of isotherm types; graphic representation, name and characteristics (Lowell et al., 2004; Sing et al., 1985).

6.3.1 Experimental settings of sorption isotherms

The analysis was carried out in an Autosorb-1® from Quantachrome Instruments and the data were analysed with the Quantachrome AS1Win software. In general terms, the experimental procedure was as follows. First the sample was degassed at 300 °C in a high purity helium flow; this is a cleaning procedure. Then, the sample was brought to constant temperature by means of a liquid nitrogen (-195.8 °C) bath. Next, small amounts of the adsorbate gas (argon) were introduced by steps in the vacuum chamber in which the sample was kept. The adsorbed volume was measured across the relative pressure (P/P_0) range 0-1; in which P is the adsorption pressure and P_0 is the saturation vapour pressure.

6.3.2 Methods for determination of surface area with sorption isotherms

Non-porous materials, the Brunauer-Emmett-Teller equation

The Brunauer-Emmett-Teller (BET) theory is an extension of the Langmuir equation to multilayer adsorption. It was developed through the concept of an ideal localised monolayer in which it is assumed that each layer serves as a site for the adsorption of a molecule on the subsequent layer. The BET theory also assumes that adsorption sites are energetically identical and neglects the interactions between adsorbate molecules in the same layer (Gregg et al., 1982).

The BET equation has a limited applicability range which depends on the adsorbent-adsorbate system (Sing et al., 2004). The c constant in the BET equation determines the shape of the knee on the isotherm plot; the knee becomes sharper when c values become greater. The BET equation can be used to determine the specific surface area of Type II isotherms ($c > 2$) and of Type IV isotherms.

Classical approaches to adsorption in micropores

Langmuir isotherm

The Langmuir theory was the first theory applied to gas adsorption isotherms. The Langmuir model assumes monolayer adsorption onto homogeneous surfaces (Allen 1999). In the earliest studies, microporous materials with Type II isotherms were explained through the Langmuir equation; it was assumed that narrow pores could fit only one layer of adsorbate (Gregg et al., 1982). The monolayer completion was thus related to the isotherm plateau. However, since the 1980's it is accepted that Type I isotherms are related to the micropore filling mechanism; in which layer by layer adsorption turns to volume filling by a similar process to capillarity condensation (Sing et al., 2004).

Since the amount adsorbed is related to the micropore volume and not to the monolayer surface the concept of surface area for micropores is meaningless for the micropore filling mechanism. The micropore volume of microporous samples can be estimated with the t-plot and the Dubinin-Radushkevich (DR) method. The theory behind the t-plot assumes that the thickness of the adsorbed layer remains constant throughout the relative pressure range. Then, the volume of gas adsorbed may be plotted against the statistical thickness of the adsorbed film (*t*). The Boer equation is the most popular method for the calculation of *t*.

The Polanyi's potential theory explains micropore filling. Polanyi's theory assumes that below the critical temperature the adsorbate completely liquefies and the absorbed volume of the liquid can be determined from the adsorption isotherm (Allen 1999). The DR equation uses the Polanyi's theory to describe micropore filling (Hutson et al., 1997). The DR theory has been successfully used for adsorption in microporous carbonaceous adsorbents and activated carbons; DR theory is not applicable for adsorbents with a wide micropore distribution (Hutson et al., 1997). The constant β, referred to as an affinity coefficient, is a measure of the relative affinity of adsorbate molecules for a surface.

Classical approaches to adsorption in mesopores

Data analysis for Type IV isotherms (mesoporous adsorbents) is made through the application of the Kelvin equation. The Kelvin equation is used to calculate the minimum pore radius at which capillarity condensation can occur (Gregg et al., 1982). This equation makes several assumptions and hence has an applicability range; usually for pore radius from 1 to 25 nm. According to the Kelvin equation capillarity condensation should occur within a pore at pressure P, which is determined by the pore radius, smaller than the saturation pressure P_0; and the meniscus should be concave. The use of the Kelvin equation requires the assumption or knowledge of the pore shape and the angle of contact between the condensate and the adsorbate film on the pore walls.

The non-linear density functional theory

Classical methods have a narrow range of applicability; i.e. can be used to estimate either micropore or mesopore volume. Also, the accuracy of these methods is limited because they assume that the pore fluid has the same properties as the bulk fluid. The non-linear density functional theory (NL-DFT) allows a more realistic interpretation of micropore and mesopore filling. This method uses statistical mechanics to model pore fluid properties (Thommes et al., 2010).

Although software development has extended the use of NL-DFT methods for routine experiments, its use is limited because knowledge of the adsorbent bulk properties and surface structure is needed, and adsorbents with rigid pores of known shape are required (Sing 2004). Literature in the application of this method is slowly but steadily increasing.

6.3.3 Results

The sorption isotherms obtained for SCAC and CAC samples are shown in Figure 6.9. From this figure it seems that SC05, SC06 and SC11 samples are Type I isotherms; SC07 and SC12 are Type II isotherms; and CAC is a Type IV isotherm with hysteresis loop Type H3 (IUPAC classification). This hysteresis loop is characteristic of open silt-shaped capillaries with parallel walls, capillaries with very wide bodies and narrow short necks, or plate-like particles giving rise to slit-shaped pores (Allen 1999). Isotherms for all SCAC samples present a hysteresis loop too. This is open at the low relative pressure end for samples SC05 and SC06; and closed at both ends for SC07, SC11 and SC12 samples. The hysteresis loop for SCAC samples is not observable in the figure due to the scale.

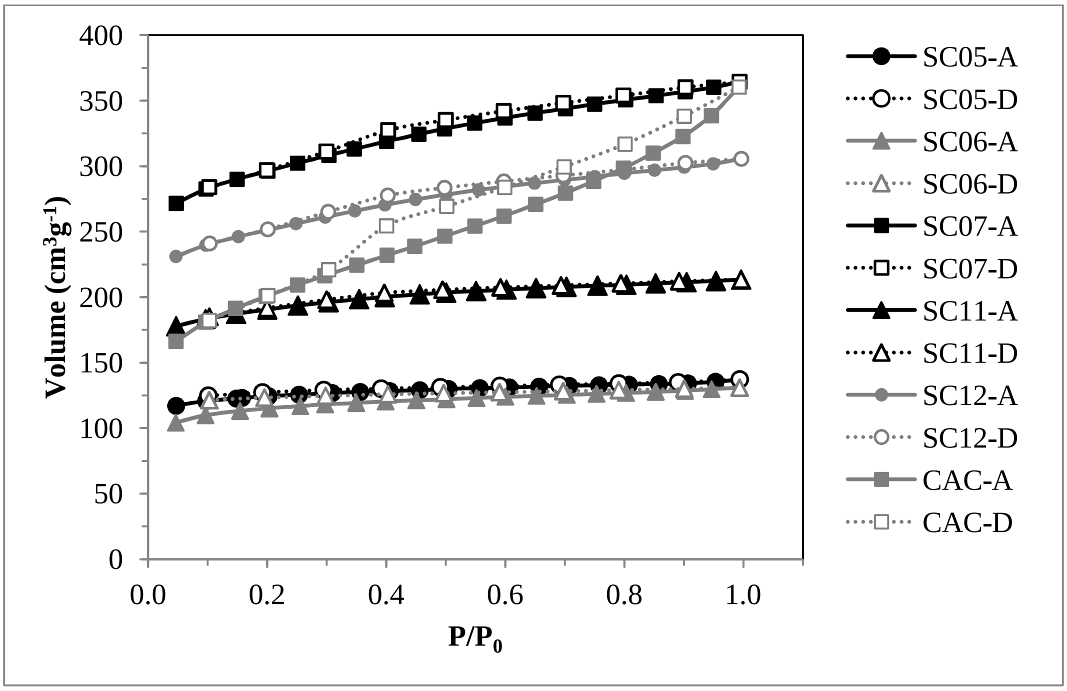


Figure 6.9 Argon isotherms at -195.8°C (nitrogen liquid bath) for SC05, SC06, SC07, SC11, SC12, and CAC samples. Symbols: (A), adsorption branch of the isotherm; (D), desorption branch of the isotherm; (P/P_0), relative pressure range; (P), adsorption pressure; and (P_0), saturation vapour pressure.

First, the presence of micropores and mesopores on samples was tested with the t-plot and DR plot. The t-plot for an exclusively nonporous material should yield a straight line passing through the origin. Figure 6.10 presents the t-plots obtained for the samples studied. The positive intercept value of the fitting curve suggests the presence of micropores. Table 6.2 summarises the main results obtained for all adsorbents.

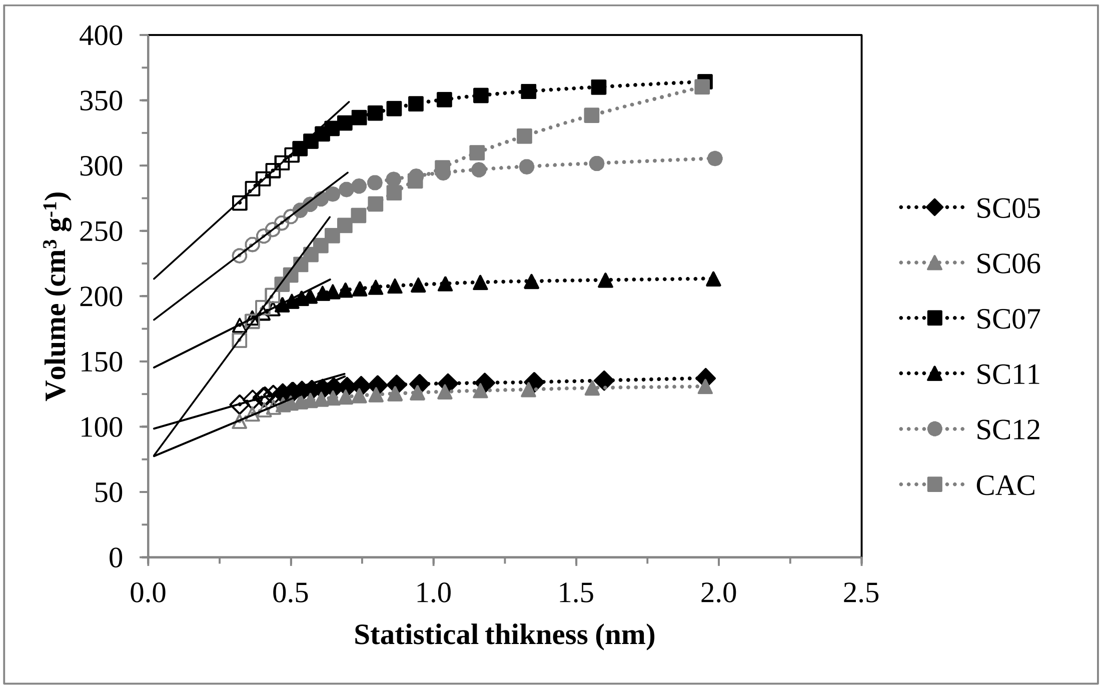


Figure 6.10 t-plot for SCAC and CAC samples. Hollow markers represent the data that were included in the calculation of the best fitting line, solid markers represent the excluded data, and solid lines are the best fitting curve for the linear region of each sample.

Table 6.2 t-plot results for SC05, SC06, SC07, SC11, SC12 and CAC.

t-plot	**SC05**	**SC06**	**SC07**	**SC11**	**SC12**	**CAC**
P_0/P	0.05–0.20	0.05–0.20	0.05–0.30	0.05–0.20	0.05–0.30	0.05–0.20
Slope	6.27	9.11	19.83	10.91	16.58	29.66
Intercept	97.31	75.76	209.20	143.20	178.68	71.91
R^2	0.9930	0.9869	0.9980	0.9982	0.9992	0.9991
Micropore volume ($cm^3\ g^{-1}$)	0.12	0.09	0.26	0.18	0.22	0.09
Micropore area ($m^2\ g^{-1}$)	285.4	224.3	621.5	421.0	531.5	250.6
External surface area + mesopores walls ($m^2\ g^{-1}$)	77.0	111.9	243.8	134.1	203.8	364.6

The DR plots for the AC samples are presented in Figure 6.11. For a microporous sample the DR plot should produce a straight line with an interception equal to the micropore volume. All samples in Figure 6.11 present an upward turn as the saturation pressure approaches; this is characteristic of samples with multilayer adsorption and capillarity condensation in mesopores. Table 6.3 presents the main results for the DR method. The t-plot and the DR method confirm that all samples have micro and mesopores.

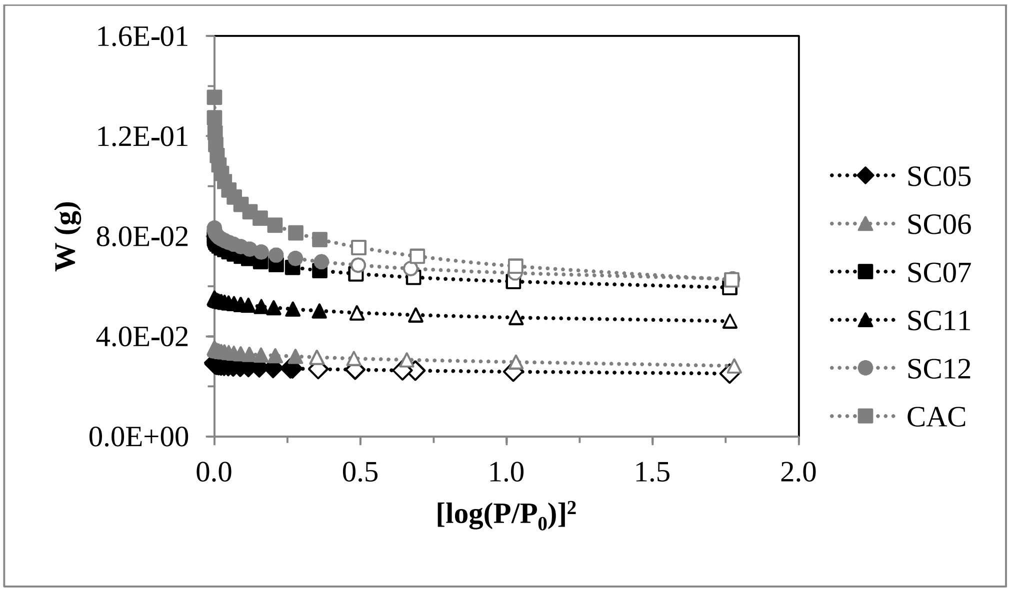


Figure 6.11 DR plot for SCAC and CAC samples. Hollow markers represent the data that was included in the calculation of the best fitting line, and solid markers represent the excluded data. Symbols: W=weight adsorbed, P/P_0=relative pressure.

Table 6.3 DR plot results for SC05, SC06, SC07, SC11, SC12 and CAC.

DR plot	**SC05**	**SC06**	**SC07**	**SC11**	**SC12**	**CAC**
P_0/P	0.05-0.25	0.05–0.25	0.05–0.20	0.05–0.20	0.05–0.20	0.05–0.20
Slope	-2.11×10^{-2}	-3.4×10^{-2}	-2.9×10^{-2}	-2.3×10^{-2}	-2.7×10^{-2}	-6.2×10^{-2}
Intercept	2.74×10^{-2}	3.2×10^{-2}	6.67×10^{-2}	5.05×10^{-2}	7.07×10^{-2}	7.99×10^{-2}
R^2	0.9917	0.9966	0.9894	0.9881	0.9871	0.9883
Affinity coefficient (β)	0.3113	0.3113	0.3113	0.3113	0.3113	0.3113
Average pore width (nm)	1.2	1.5	1.4	1.3	1.4	2.1
Adsorption energy (KJ mol^{-1})	21.58	16.93	18.50	20.79	19.00	12.63
Micropore vol.(cm^3 g^{-1})	0.16	0.15	0.37	0.24	0.32	0.26
Micropore surface area (m^2 g^{-1})	473.4	445.2	1132.1	724.1	958.1	790.5

The surface area of samples with isotherm Type I was calculated with the Langmuir equation. Figure 6.12 presents the Langmuir isotherm for these samples; at high relative pressures the experimental data deviates from the straight line. Table 6.4 shows the Langmuir surface area for these samples. The surface area for SC11 is higher than that of SC05 and SC06.

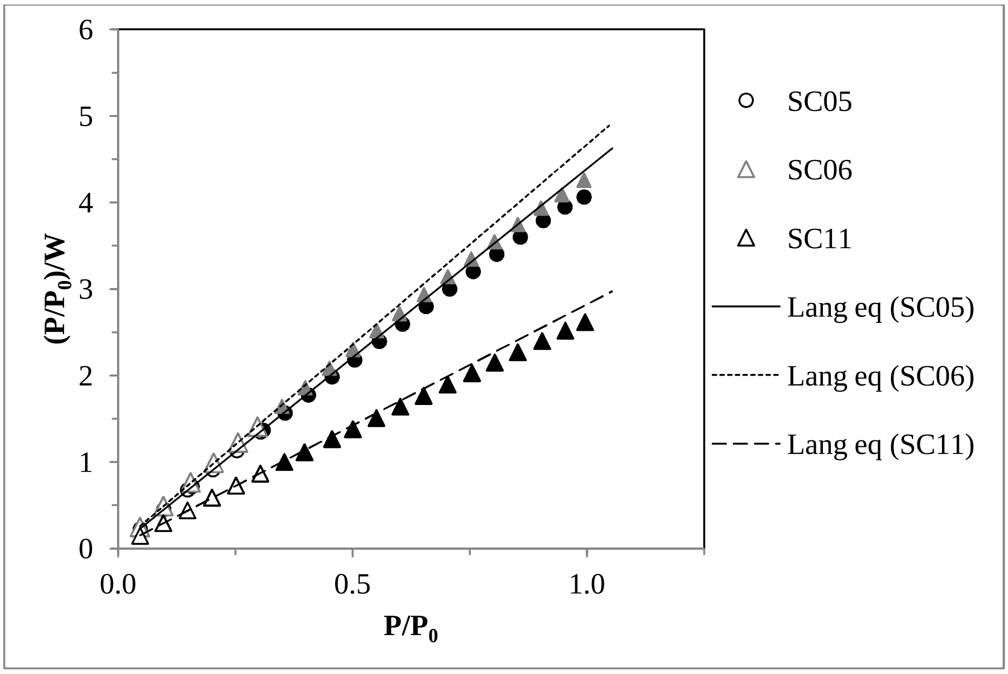


Figure 6.12 Langmuir isotherm for SCAC samples with isotherm Type I. Hollow symbols represent the adsorption data included in the analysis, and full symbols represent the adsorption data not included in the analysis. Symbols: Lang eq = Langmuir equation, Symbols: W = weight adsorbed, P/P_0 = relative pressure.

Table 6.4 Langmuir surface area for SC05, SC06 and SC11 samples.

	SC05	**SC06**	**SC11**
P_0/P	0.05-0.3	0.05-0.3	0.05-0.3
Surface area (m^2 g^{-1})	478.8	451.4	745.2

The BET isotherm was used to determine the surface area of samples for isotherms Type II and Type IV. Results from the BET isotherm for these samples are shown in Table 6.5. The *c* constant had a negative value for SC07 and SC12 samples. This is an indication that the BET theory does not represent adequately the adsorbate-adsorbent system.

Table 6.5 BET isotherm results for SC07, SC12 and CAC.

	SC07	**SC12**	**CAC**
P_0/P	0.05 – 0.20	0.05 – 0.20	0.05 – 0.15
Slope	2.43	2.86	3.39
Intercept	-1.76×10^{-2}	-2.03×10^{-2}	6.15×10^{-3}
c	-137.28	-139.87	553.18
R^2	0.9993	0.9994	1.0000
Surface area ($m^2\ g^{-1}$)	865.2	735.3	615.2

Finally, Figure 6.13 shows the pore size distribution obtained for SCAC and CAC samples from pore sizes from 1.0 to 7.0 nm obtained from the NL-DFT analysis. Pore volume in samples SC05 and SC06 is mainly microporous; whereas the proportion of mesopore volume increases in the following order SC11 < SC12 & SC07 < CAC (Table 6.6). The mode for pore width for all SCAC is within the micropore range, and for the CAC is in the mesopore range.

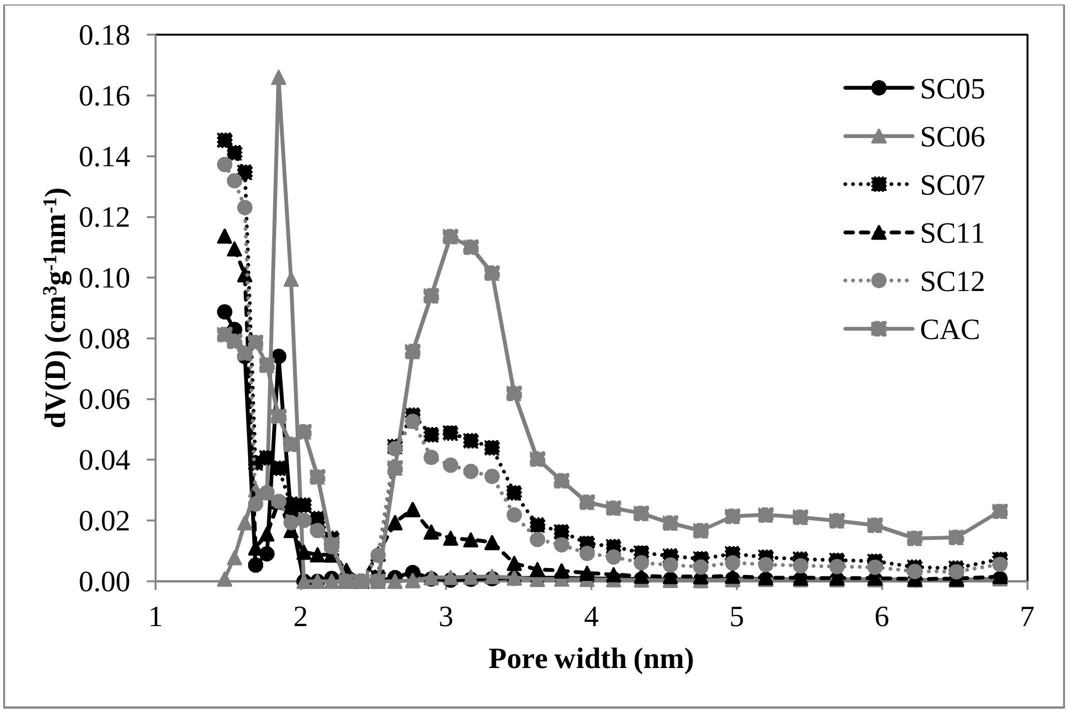


Figure 6.13 Pore width distribution from NL-DFT theory for SC05, SC07, and CAC.

Table 6.6 DFT results for SC05, SC06, SC07, SC11, SC12 and CAC.

	SC05	**SC06**	**SC07**	**SC11**	**SC12**	**CAC**
Pore volume ($cm^3\ g^{-1}$)	0.156	0.152	0.411	0.245	0.345	0.359
Micropore volume/pore volume	0.98	0.98	0.83	0.91	0.83	0.58
Lower confidence limit (nm)	1.5	1.5	1.5	1.5	1.5	1.5
Fitting error %	0.029	0.066	0.212	0.100	0.204	0.643
Pore width (mode) (nm)	1.5	1.8	1.5	1.5	1.5	3.0

6.4 Particle size analysis

6.4.1 Method background

Particle size is an important parameter for adsorbents. Properties such as the chemical reactivity and adsorbent strength may be affected by particle size. The size distribution of a material can be measured by sieving, sedimentation, microscopy, and laser diffraction methods. Sizing methods assume that particles are spheres and particle size is reported as the diameter of the equivalent sphere.

With exception of samples composed by spherical particles there may be significant disagreements among size distributions produced by different methods (MIL 2011). Thus, most particle size distributions are only comparable to those obtained with the same method. For instance, microscopy methods produce a number distribution, and laser diffraction methods a volume distribution. These distributions have a very different meaning and are incomparable.

In this research the laser diffraction method was used to obtain the particle size distribution of SCAC and CAC samples. In laser diffraction techniques the diffraction pattern produced when light is scattered by the particles in a wet or dry suspension is matched to a theoretical pattern produced by an optical model (EL 2011). Optical models are based on the Maxwell’s electromagnetic field equations; the models used are the Mie theory or the Fraunhofer approximation of the Mie theory. Table 6.7 presents a comparison of these two optical models. Modern instruments use the Mie theory but the Fraunhofer approximation is still very popular.

Table 6.7 Comparison between Mie theory and the Fraunhofer approximation of the Mie theory in laser diffraction methods for particle sizing.

Fraunhofer approximation	Mie theory
Assumptions	
Particles are opaque discs. Light is scattered at narrow angles. All particles scatter light with the same efficiency. The difference between the refractive index of the particle and the medium is infinite.	Particles are spheres. Light is scattered by one particle and detected before it interacts with other particle. Particles are homogeneous.
Advantages /disadvantages	
Particle and medium properties are not required. Inaccurate for particle sizes < 50 µm. Especially inaccurate for particle sizes < 2 µm.	In many cases it is superior to Fraunhofer approximation. Particle and medium properties need to be known.

6.4.2 Methodology for sample analysis

The instrument used was a Mastersizer 2000 with a Hydro G dispersion unit; both manufactured by Malvern Instruments Limited. Particle size resolution for this instrument is from 20 nm to 2000 µm. The particle size distribution was calculated with the Mie theory. Prior to analysis, samples were placed in a beaker, pre-wetted with the dispersant and stirred until they were introduced for sample analysis. Samples were measured in wet dispersion; the dispersant used was water (refraction index = 1.330). The refraction index for activated carbon samples was 2.420. Three different aliquots of the same sample were analysed; the results presented here are the average of these replicates.

6.4.3 Results

The particle size distribution of AC samples is presented in Figure 6.14. Particle size distributions for SCAC samples are very similar; 90 per cent of the cumulative volume for all SCAC samples is due to particles with a size smaller than 180 µm. On the other hand, the particle size distribution of CAC is very different from SCAC samples; the differences in particle size are apparent to the naked eye. The SCAC samples are flakes, according to the SEM micrographs, and the CAC particles are of granular structure.

The particle size distribution was also analysed according to the British Soil Classification System (BSCS) (Table 6.8) (Davison et al., 2010). The percentage of silt varies from 47.1 to 54.2 per cent in SCAC samples. The CAC is composed mainly by sand-size-fraction (97.1 per cent). In both types of samples, SCAC and CAC, the clay-size-fraction is below 0.3 per cent.

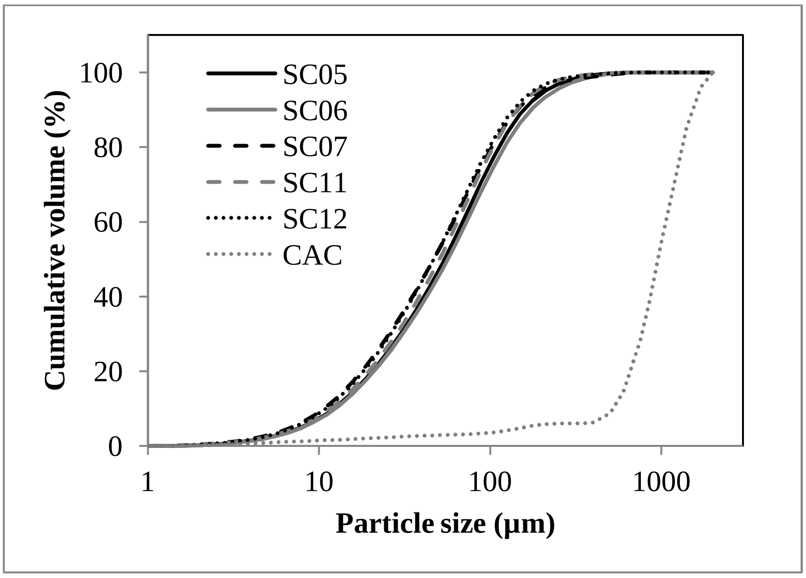


Figure 6.14 Particle size distribution of SC05, SC06, SC07, SC11, SC12 and CAC samples.

Table 6.8 Size limits for soil separates according to the British Soil Classification System (Davison et al., 2010).

Soil size fraction	Particle size μm	%Volume					
		AC05	AC06	AC07	AC11	AC12	CAC
Coarse sand	600–2,000	0.1	0.1	0.3	0.0	0.1	85.5
Medium sand	200–600	7.4	9.4	5.9	5.6	4.9	9.1
Fine sand	60–200	43.6	43.1	39.4	42.7	40.5	2.5
Coarse silt	20–60	31.2	30.0	33.3	32.8	34.0	0.9
Medium silt	6–20	15.1	14.8	17.7	15.9	17.3	1.0
Fine silt	2–6	2.5	2.4	3.1	2.7	2.9	0.8
Clay	< 2	0.2	0.2	0.3	0.3	0.3	0.1

6.5 Discussion

Adsorption of metals onto AC is a complex phenomenon and the processes involved are not yet fully understood. The influence of pH on adsorption has been observed in the literature (*Section 2.3.2* and *2.3.3*). In electrostatic terms, arsenic(V) adsorption is favoured on SCAC samples but not on CAC at the pH at which the factorial experiment was run (*Section 5.1*). However, arsenic(V) and arsenic(III) adsorption was higher with CAC than with the SCAC samples: SC05 and SC06. Also, although the pH_{ZC} of samples SC05 and SC07 is approximately equal, adsorption performance with these two samples was contrasting. Percentage of arsenic removal was much higher with SC07 than with SC05. On the other hand, arsenic(III) adsorption cannot be explained in terms of electrostatic forces since the neutrally charged ion $H_3AsO_3^0$ is predominant below pH 9.2.

The pH_{ZC} for other SCAC adsorbents has been measured at 4.7 for CO_2 activation and 3.5 for phosphoric acid (H_3PO_4) activation (Giraldo-Gutierrez et al., 2008). Preparation methodologies explain the difference observed in those materials and the SCAC samples prepared in this research. The SCAC in this research was prepared using the husk and the bagasse with no addition of chemicals, whereas the referenced materials were prepared exclusively with husk and soaked in 30 per cent nitric acid prior activation. The pH_{ZC} of other agricultural waste-based AC samples was determined at 11.90 for bean pods, 7.5 for copper impregnated coconut husk, and 6.2 for agricultural bagasse (Budinova et al., 2009; Juang et al., 2002; Manju et al., 1998).

In another study, the commercial activated carbon NC-100 from PICA France was modified with various oxidants (Muñiz et al., 2009). Arsenic removal at an initial pH of 8 followed the order $pH_{ZC} = 3.08 > 3.45 > 10.26$ (NC-100) $> 6.70 > 6.43 \approx 4.33$. For this research the initial oxidation state of arsenic is unknown. Electrostatic conditions are only favourable for arsenic(V) adsorption onto NC-100 ($pH_{ZC} = 10.26$). The effect of the pH_{ZC} on arsenic adsorption is not evident either in that research.

The surface area analysis presented in *Section 6.4.3* suggests that CAC and SCAC samples have micro and mesopores. The presence of mesopores in the SCAC materials was confirmed with the t-plot, DR plot and the NL-NDF theory. The micropore volume calculated with the DR method is from 1.3 to 3.0 times the micropore volume from the t-plot. This was expected since the micropore volume calculated from the DR plot needs correction due to absorption on mesopores at low relative pressures. The pore volume calculated with the NL-DFT theory is from 1.0 to 1.1 times the micropore volume calculated with the DR theory. Although the NL-DFT analysis is not accurate enough to establish the pore size distribution in the micropore region, it is possible to deduce that in all samples most of the pore volume comes from microporosity. Also, the samples with a higher degree of mesoporosity are SC07, SC12 and CAC.

Surfaces areas of SCAC samples range from 451 to 865 g^2 m^{-1}. Samples SC05, SC06 and SC11 have Type I isotherms; SC07 and SC12 have Type II isotherms; and CAC has a Type IV isotherm. Tsai *et al.* (2001) and Tseng *et al.* (2006) also found Type I isotherms for SCAC adsorbents. Tsai *et al.* (2001) obtained Langmuir surfaces areas from 4.86 to 790 m^2 g^{-1} for zinc chloride ($ZnCl_2$) activated SCAC and Tseng *et al.* (2006) from 391 to 2,299 m^2 g^{-1} for red sugar cane pith AC activated with potassium hydroxide (KOH). Ng *et al.* (2002) measured the surface area of sugarcane steam-activated carbon in 565 m^2 g^{-1}.

The results obtained with the particle size analysis are consistent with the preparation methods of the SCAC adsorbents and the topographic images obtained with SEM. In the case of SCAC samples the particle size may depend on the preparation procedure; carbonised samples are crushed with a pestle and mortar and passed through a 180 µm sieve. If the adsorbent were prepared at a larger scale the particle size distribution may change.

The relationship between arsenic adsorption and properties of the AC samples was analysed with a Pearson's correlation test. First, arsenic adsorption data from the factorial experiment (Table 5.2 in *Section 5.2.1*) was plotted against the pH_{ZC}, surface area, micropore/pore volume ratio and per cent sand. Per cent arsenic(V) removal data is presented in Figure 6.15 and per cent arsenic(III) removal data in Figure 6.16.

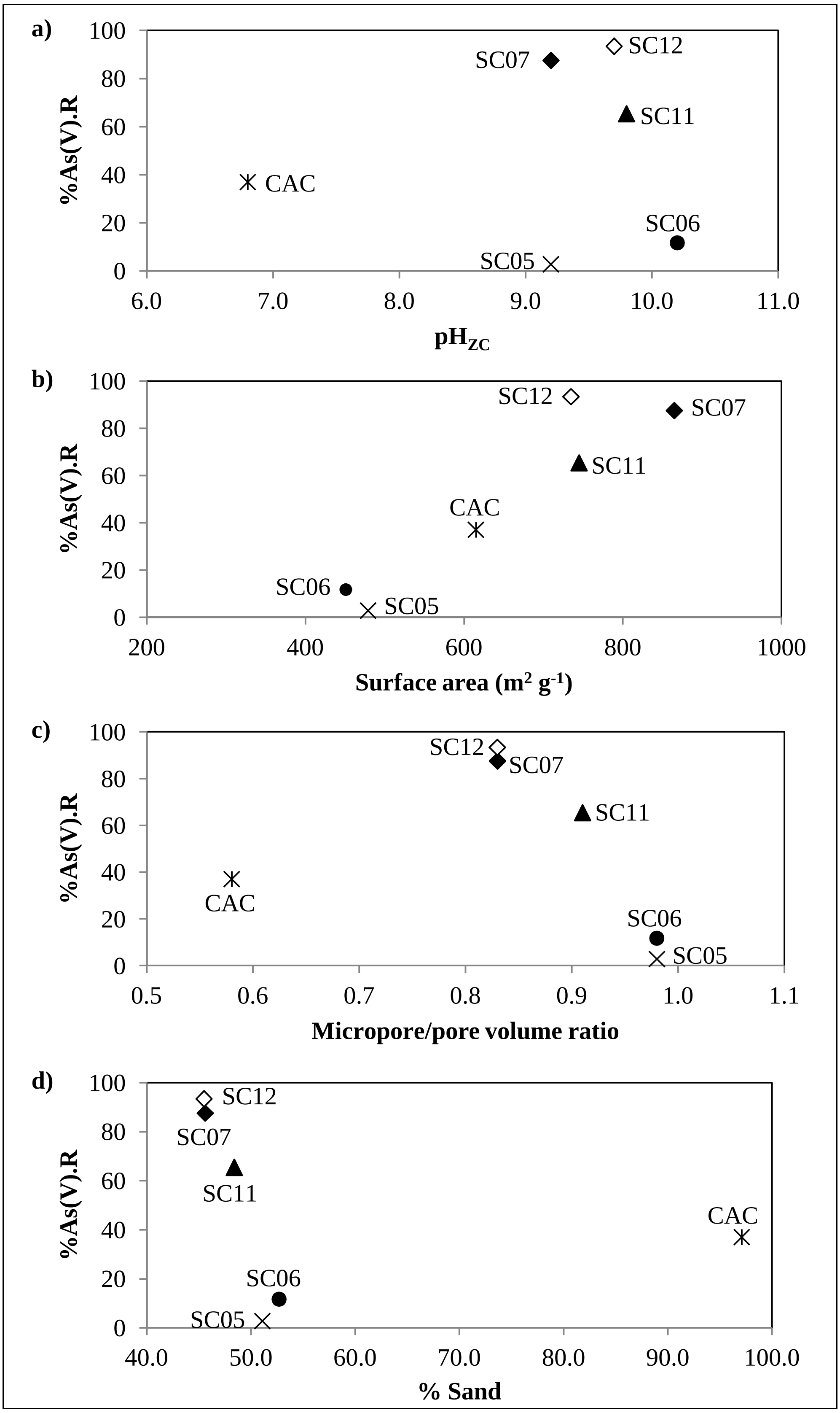


Figure 6.15 Correlation between per cent arsenic(V) removal (%As(V).R)) and a) pH of zero change (pH$_{ZC}$), b) surface area, c) micropore/pore volume ratio and d) % sand.

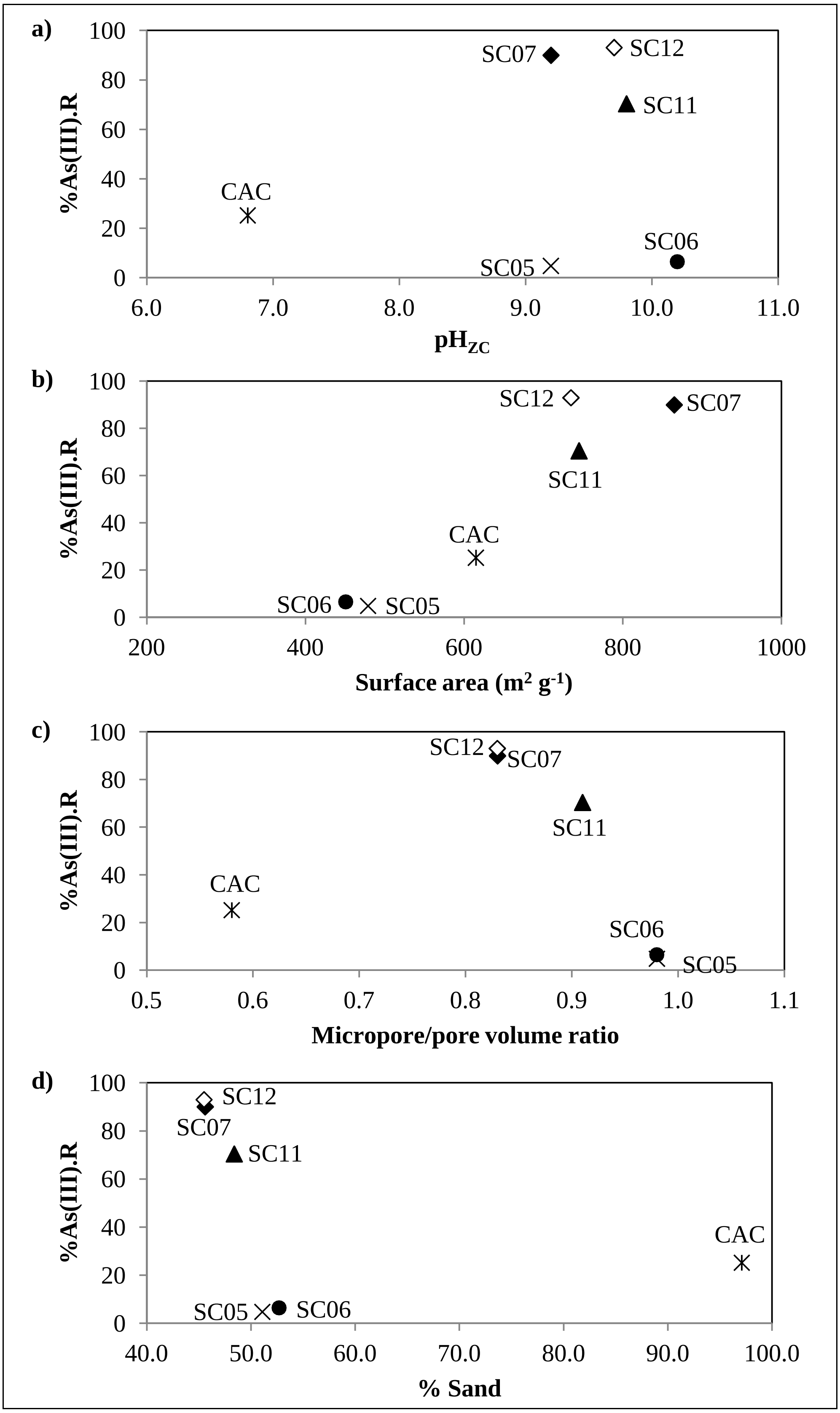


Figure 6.16 Correlation between per cent arsenic(III) removal (%As(III).R) and a) pH of zero change (pH_{ZC}), b) surface area, c) micropore/pore volume ratio and d) % sand.

The Pearson's correlation coefficient was calculated for data sets with a linear relationship; the Person's coefficient cannot be applied to non-linear data. Two separate Pearson's correlation test were run; one including only SCAC samples (Table 6.9) and other for the only set of data of SCAC samples and the CAC sample that had a linear relationship (surface area) (Table 6.10). In the test for SCAC the surface area, micropore/pore volume ratio, and percent sand were strongly correlated ($p < 0.050$) to percent arsenic(V) and arsenic(III) adsorption. The correlation is negative for micropore/pore volume ratio and percent sand, and positive for surface area. The Pearson's correlation test for surface area and the data set for SCAC samples and the CAC sample shows a strong a positive correlation for arsenic(V) and arsenic(III) per cent removal and surface area.

Table 6.9 Pearson correlation test for samples SC05, SC06, SC07, SC11 and SC12. Statistically significant terms are in bold font.

		%As(V).R	%As(III).R
pH_{ZC}	Pearson correlation	-0.165	-0.212
	Significance (2-tailed)	0.791	0.732
Surface area	Pearson correlation	**0.939**	**0.956**
	Significance (2-tailed)	**0.018**	**0.011**
Micropore/pore volume ratio	Pearson correlation	**-0.975**	**-0.968**
	Significance (2-tailed)	**0.005**	**0.007**
Pore width	Pearson correlation	-0.533	-0.590
	Significance (2-tailed)	0.355	0.295
% Sand-size-fraction	Pearson correlation	**-0.960**	**-0.966**
	Significance (2-tailed)	**0.010**	**0.007**

Table 6.10 Pearson correlation test for samples CAC, SC05, SC06, SC07, SC11 and SC12. Statistically significant terms are in bold font.

		As(V).R	As(III).R
Surface area	Pearson correlation	**0.938**	**0.942**
	Significance (2-tailed)	**0.006**	**0.005**

From the analysis of the data presented in this section some observations can be made with respect to SCAC properties and arsenic removal. It is apparent that surface area, micropore/pore volume ratio and particle size have an effect on the percentage of arsenic(V) and arsenic(III) that can be removed from solution. SCAC with a higher surface area and lower content of sand-size fraction is able to remove a higher percentage of arsenic from solution. This result is explained in terms of the well known inverse relationship between particle size and surface area. Also, samples of SCAC with lower micropore/pore volume ratios remove a higher percentage of arsenic. This suggests that arsenic adsorption on SCAC may be limited by the small pore diameter of micropores. On the other hand, surface area is the only property that has an effect on arsenic adsorption when all AC samples (SCAC samples and the CAC samples) are considered. However, the Pearson correlation test does not prove that the relationship between variables is causal.

6.6 Summary

The CAC sample, two SCAC samples with low arsenic removal capacity (SC05 and SC06), and three SCAC samples with medium to high arsenic removal capacity (SC07, SC11and SC12) were characterized with the determination of the pH_{ZC}, surface area and particle size distribution. Also, topographic analysis of samples was carried out with SEM.

The pH_{ZC}, as measured with the immersion technique, was 6.8 for CAC, 9.2 for SC05, 10.2 for SC06, 9.2 for SC07, 9.8 for SC11, and 9.7 for SC12. The pH_{ZC} was not related to the adsorption capacity of SCAC adsorbents. For instance, SC05 and SC07 had similar pH_{ZC}, but arsenic adsorption capacity of SC07 was much higher than that of SC05. According to the topographic analysis with SEM, SCAC samples were composed of flake-like particles of various sizes (< 200 µm). Some of the flakes presented holes of different sizes. No apparent relationship between the preparation conditions of SCAC and the type of structures developed was found.

The specific surface area and the pore width distribution of samples were determined with argon gas adsorption at -195.8 °C (nitrogen liquid bath). Samples SC05, SC06 and SC11 presented a Type I IUPAC isotherm, samples SC07 and SC12 a Type II isotherm, and CAC a Type IV isotherm. The t-plot, the DR plot and the NL-DFT analysis showed that micropores and mesopores were present in all samples. The surface area of samples with isotherm Type I was calculated with the Langmuir equation and the surface area of samples with isotherm Type II and IV was calculated with the BET isotherm. The Langmuir surface area in m^2 g^{-1} was 479 for SC05, 451 for SC06, and 745 for SC11. The BET surface area in m^2 g^{-1} was 865 for SC07, 735 for SC12, and 615 for CAC.

According to the NL-DFT the pore width mode was in the micropore range for SCAC samples (1.5-1.8 nm) and in the mesopore range for the CAC sample (3.0 nm). SCAC samples with the lowest arsenic adsorption capacity (SC05 and SC06) also had the lowest surface area, pore volume, and mesopore volume. SCAC samples with the highest arsenic adsorption capacity had a micropore/pore volume ratio between 0.83 and 0.91.

The particle size distribution of samples was measured with a laser diffraction method. Ninety per cent of the cumulative volume of SCAC samples was due to particles with a size < 180 µm. According to the BSCS, SCAC samples were composed by 47.1-54.2 per cent volume of silt-size fraction (2-60 µm) and less than 0.3 per cent volume of clay-size fraction (< 2 µm). The predominant soil-size-fraction in the CAC sample was the sand-size fraction (60-2,000 µm) measured at 97.1 per cent.

According to the Pearson correlation test, including only SCAC samples, surface area has a strong and positive correlation ($R = 0.939$, $p = 0.018$), micropore/pore volume ratio has a strong negative correlation ($R = -0.975$, $p = 0.005$) and per cent sand-size fraction has a strong negative correlation ($R = -0.960$, $p = 0.010$) with arsenic(V) adsorption; similar results were obtained for arsenic(III) adsorption with SCAC. The Pearson' test for SCAC samples and the CAC sample found a correlation between surface area and arsenic(V) ($R = 0.938$, $p = 0.006$) and arsenic(III) ($R = 0.942$, $p = 0.005$) per cent removal.

7. Arsenic(V) and arsenic(III) adsorption experiments with sugarcane activated carbon and commercially available carbon

The adsorption performance of adsorbents is expected to vary under different experimental conditions. Factors such as pH, time, temperature and species present in solution can have an effect on the adsorbent capability to remove specific contaminants from water. Based on the results from *Chapter 5*, the adsorbent SC07 (carbonisation temperature 700 °C, activation temperature 900 °C and activation time 3 h) was selected to conduct further experiments to investigate the adsorption kinetics (*Section 7.1*), and the effect of pH (*Section 7.2*), temperature (*Section 7.3*) and interference from the water constituents chloride, sulphate, phosphate and silicate (*Section 7.4*) on arsenic(V) and arsenic(III) adsorption. These experiments were run in parallel with adsorption experiments with the lignite granular activated carbon type Darco® 12x20 (CAC).

7.1 Kinetics of arsenic(V) and arsenic(III) adsorption

7.1.1 Experimental methodology

Separate kinetic experiments were run for SC07 and CAC; for each adsorbent the effect of the initial oxidation state of arsenic and of the initial concentration were investigated. In total four test were carried out for each adsorbent; arsenic(V) at low initial concentration (≈ 240 µg L^{-1}), arsenic(V) at high initial concentration (≈ 2,500 µg L^{-1}), arsenic(III) at low initial concentration, and arsenic(III) at high initial concentration. This concentration range was chosen because most groundwater samples would fall within this range. For instance, of the samples analysed in the 2009 Drinking Water Quality Survey in Bangladesh, 90 per cent were below 77 µg L^{-1} and the maximum concentration found was 900 µg L^{-1} (BBS et al., 2011). Experiments were carried out at an initial pH of approximately 8, an adsorbent dose of 5 g L^{-1}, and room temperature. The period of time investigated was from 15 min to 2,880 min (48 hours); the final total arsenic concentration (As_f) and final pH (pH_f) values were measured for each sample.

7.1.2 Analysis of kinetic data

Kinetic data were analysed with a pseudo-first order model and a pseudo-second order model. First, the experimental adsorption capacity (q_{exp}) of adsorbents was calculated with the following equation:

$$q_{exp} = \frac{(\mathrm{As}_0 - As_t)}{\mathrm{m}} \times \mathrm{V} \qquad \text{Equation 7.1}$$

where;

q_{exp} is the adsorption capacity in µg g^{-1} at time t,
As_0 is the initial arsenic(V) or arsenic(III) concentration in µg L^{-1},
As_t is the arsenic concentration in µg L^{-1} at a given time t,
V is the volume of arsenic solution in L,
m is the mass of adsorbent in g.

Then, the experimental data were fitted to a pseudo first-order equation (Lagergren, 1898).

$$\frac{dq_t}{dt} = k_1(\mathrm{q}_1 - q_t) \qquad \text{Equation 7.2}$$

where:

q_1 is the adsorption capacity at equilibrium in µg g^{-1},
q_t is the adsorption capacity in µg g^{-1} at time t,
k_1 is the pseudo first-order adsorption rate constant in min^{-1}.

Integration of the pseudo-first order equation with boundary conditions from t = 0 to t = t, and from $q_t = 0$ to $q_t = q_1$ gives:

$$\log(\mathrm{q}_1 - q_t) = \log(\mathrm{q}_1) - \frac{k_1}{2.303}\mathrm{t} \qquad \text{Equation 7.3}$$

For each experimental condition the experimental data were fitted to Equation 7.3 with the least-squares method. The values of q_1 and k_1 were determined from the intercept and the slope of the linear correlation, respectively. In a similar fashion, data were fitted to the pseudo second-order equation (Ho et al., 2000):

$$\frac{dq_t}{d_t} = k_2(q_2 - q_t)^2 \qquad \text{Equation 7.4}$$

where:

k_2 is the rate constant of pseudo second-order adsorption in g μg^{-1} min^{-1},

q_2 is the adsorption capacity at equilibrium in μg g^{-1}.

Integration of the pseudo-second order equation with boundary conditions from t = 0 to t = t, and from $q_t = 0$ to $q_t = q_2$ gives Equation 7.5. The experimental data were plotted with (t/q_t) on the y axis and time on the x axis. Values for the pseudo-second order equation were calculated with the least-squares method; q_2 and k_2 were determined from the slope and the interception terms, respectively.

$$\left(\frac{t}{q_t}\right) = \frac{1}{k_2 q_2{}^2} + \frac{1}{q_2}(t) \qquad \text{Equation 7.5}$$

The selection of the model that best represented the experimental data followed various criteria. First, the adsorption capacity at equilibrium (q_1 and q_2) obtained from the models was compared against experimental values (q_{exp}). Secondly, the pseudo-first and pseudo-second order models were graphically compared against the experimental kinetic data. Thirdly, the variance of each model was calculated with Equation 7.6; it was assumed that the error in the data follows a chi-square distribution (Masel 2001). The statistical significance of the difference between models was tested with the F test.

$$V_i = \frac{\sum\left[\, q_{t\,(\mathrm{exp})} - q_{t\,(\mathrm{model})}\right]^2}{(\text{samples}) - \ (\text{independent parameters in model})} \qquad \text{Equation 7.6}$$

The F test is not mathematically rigorous but provides a practical and fast approach. A rigorous approach would be to run a Cox, Bayesian maximum-likelihood or minimum-entropy algorithm (Masel, 2001). It is believed that these series of steps provide a more truthful approach compared to the “goodness of fit” by the correlation factor (R^2) of the least square method.

7.1.3 Results for kinetic experiments

Percent arsenic removal with respect to time

The percentage of arsenic removal (%As.R) with respect to time for SC07 and CAC is presented in Figure 7.1 and Figure 7.2 respectively. In all experimental conditions arsenic adsorption is higher with SC07 than with CAC. The data for arsenic(III) adsorption onto SC07 at low initial concentration contradicts expected results; the percentage of arsenic adsorption at low initial concentration was lower than at high initial concentration. These data also differ from other experimental data obtained under similar experimental conditions. For instance, in the factorial experiment (*Section 5.2.1*) arsenic removal at an initial arsenic(III) concentration of 246.3 µg L^{-1}, initial pH of 8.03, and room temperature was 90 per cent.

Adsorption onto sugarcane activated carbon (SCAC) follows the same trend at low and at high initial arsenic(V) concentrations. Adsorption occurs very rapidly during the first 15-30 minutes, and then arsenic is adsorbed very slowly. Arsenic(III) adsorption differs from arsenic(V) adsorption. At high initial arsenic(III) concentrations, arsenic removal is 39 per cent at 15 minutes and then gradually reaches 85 per cent at 2,880 minutes.

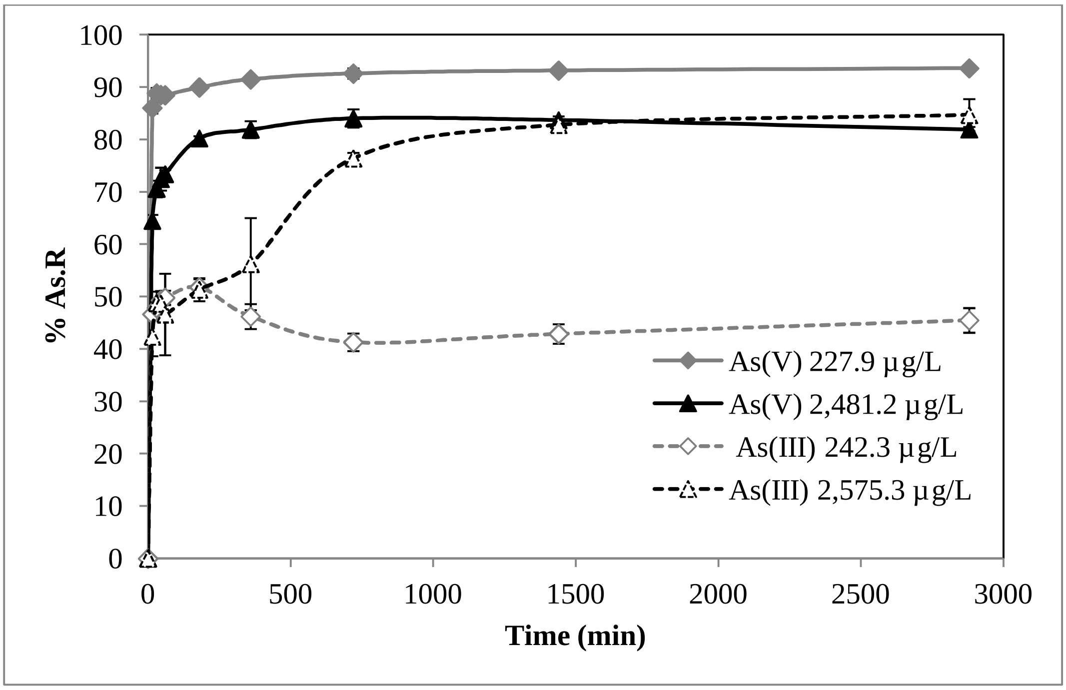


Figure 7.1 Kinetics of arsenic adsorption onto SC07. Percentage of arsenic removal (%As.R) with respect to time for two initial concentrations for arsenic(V) and arsenic(III).

Overall, arsenic adsorption onto CAC follows the same trend for the four experimental conditions investigated; %As.R gradually increases with time (Figure 7.2). Arsenic(III) adsorption at high initial concentration seems abnormally high at 15 minutes; the standard deviation of this point is relatively high (± 6 per cent). Also, arsenic(III) adsorption at high initial concentration is higher than at low initial concentration during the first 1,000 minutes.

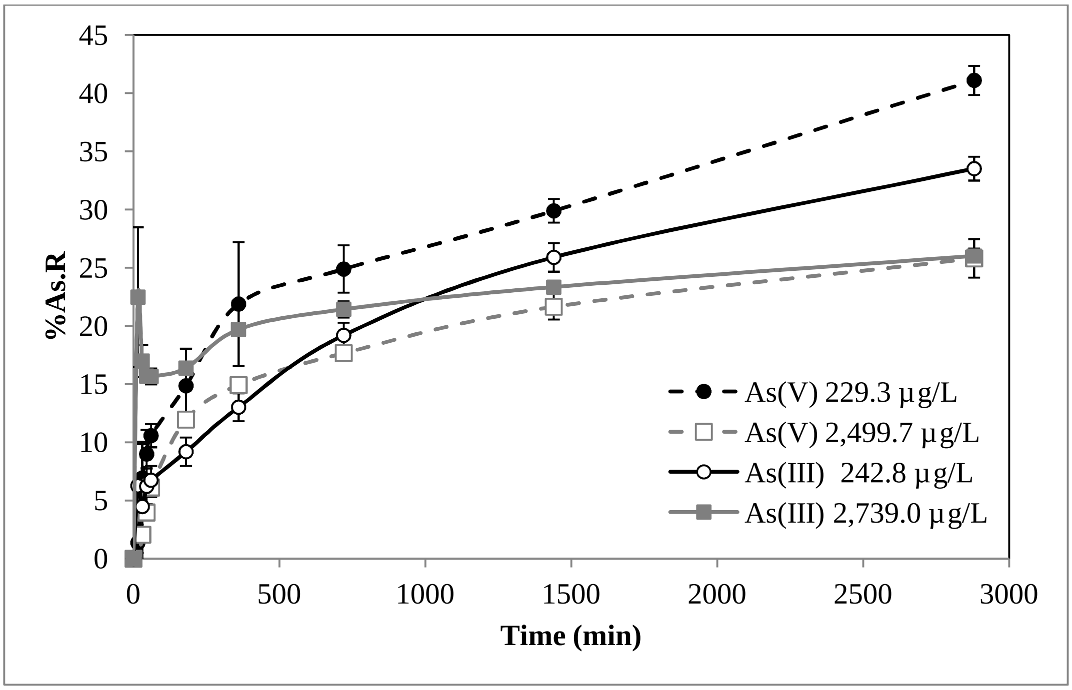


Figure 7.2 Kinetics of arsenic adsorption onto CAC. Percentage of arsenic removal (%As.R) with respect to time for two initial concentrations of arsenic(V) and arsenic(III).

pH variation with respect to time

Figure 7.3 presents the changes in pH in solution with respect to time for SC07 and CAC samples, respectively. In a similar manner to concentration, the pH of samples changes mostly during the first 15-30 minutes of the reaction. In the case of SC07, pH values at 2,880 minutes (pH_f) vary between 7.0 and 7.6. For adsorption with CAC, pH falls from $pH_0 \approx 8.0$ to values of between 6.3 and 4.8 during the first 15 minutes. No apparent relationship between changes in pH and %As.R was observed for both SC07 samples and CAC samples.

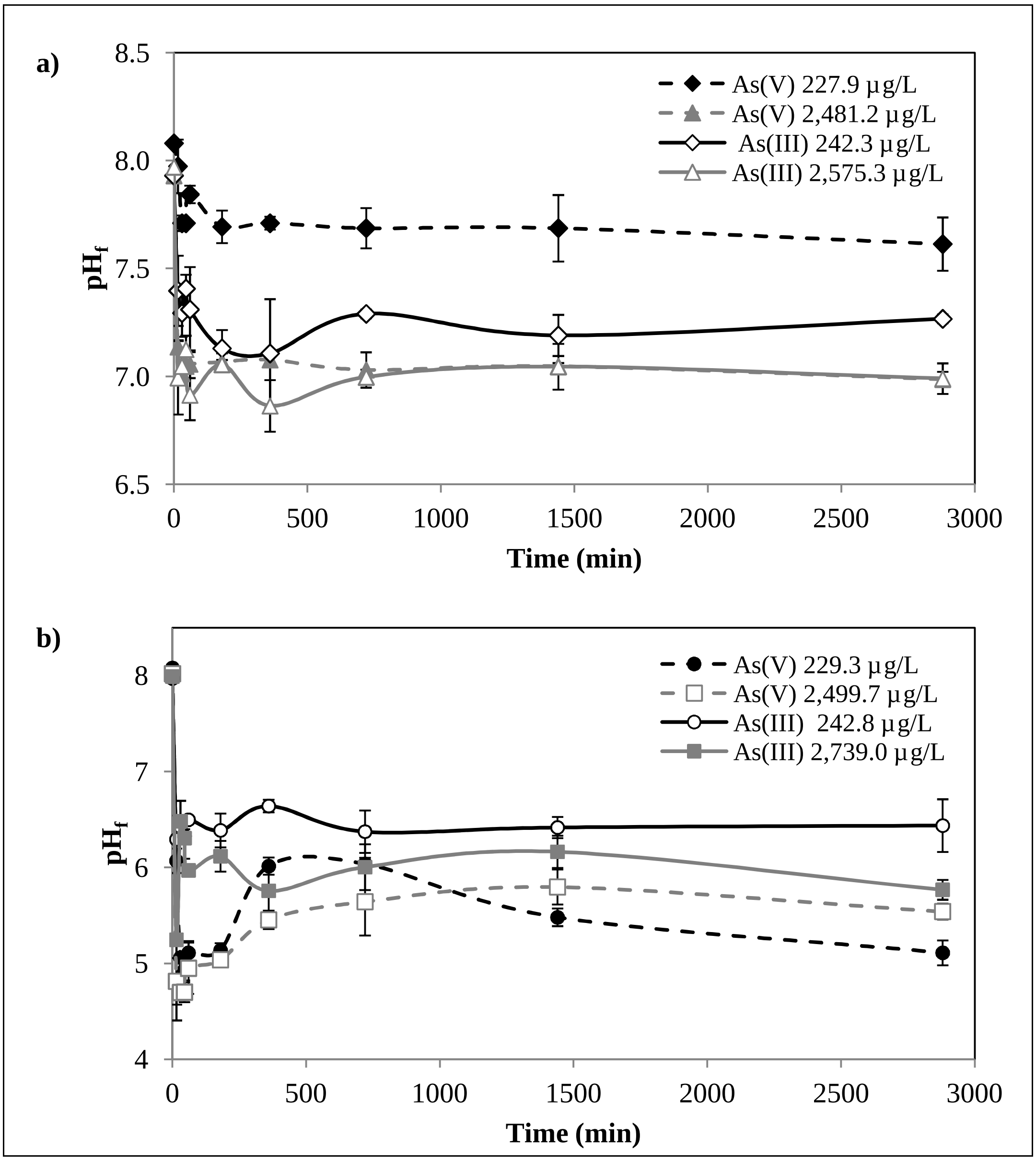


Figure 7.3 Variation of pH with respect to time for adsorption at two initial concentrations of arsenic(V) and arsenic(III): a) adsorption onto SC07; and b) adsorption onto CAC.

Kinetic models for arsenic adsorption

Adsorption capacities calculated with the pseudo-first order (q_1) and for the pseudo-second order (q_2) models are plotted against the experimental adsorption capacities for adsorption of arsenic(V) and arsenic(III) onto SC07 (Figure 7.4) and CAC (Figure 7.5). From these figures is evident, in most cases, that the pseudo-second order model reproduces better the experimental data. However, for CAC at low initial concentrations it is not possible to determine from the plots which model better fits the data. In the case of arsenic(III) adsorption at low initial concentration onto SC07, the pseudo-second order model accurately predicts the equilibrium adsorption capacity (q_e) but fails to reproduce the maximum adsorption capacity reached at 180 minutes. This cannot be observed in the graph of Figure 7.4 due to its scale.

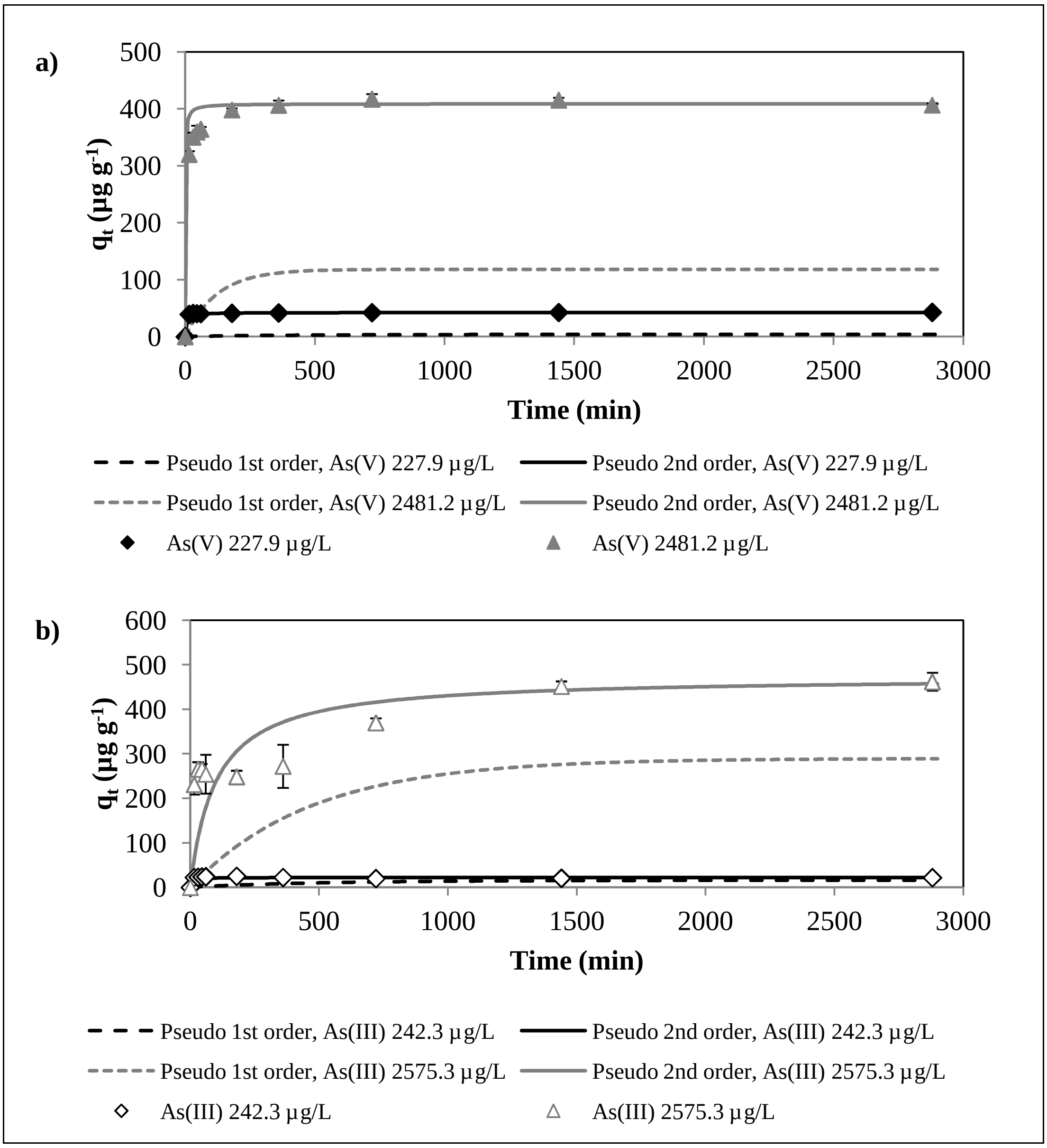


Figure 7.4 Experimental data, and pseudo-first order and pseudo-second order model data for arsenic adsorption onto SC07 for: a) initial arsenic(V) concentrations of 229.3 and 2,499.7 µg L^{-1}; and b) arsenic(III) initial concentrations of 242.3 and 2,575.3 µg L^{-1}.

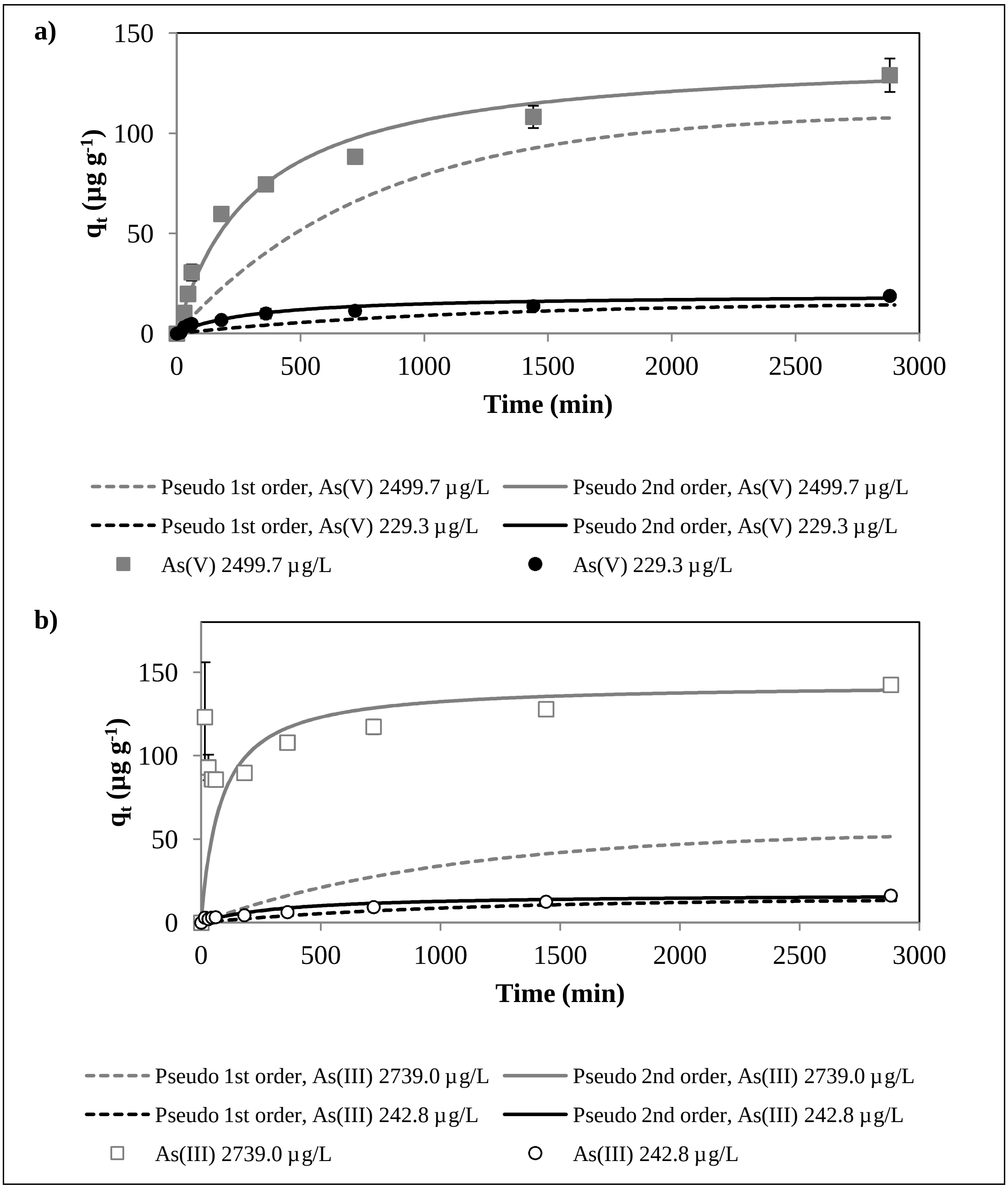


Figure 7.5 Experimental data, and pseudo-first order model and pseudo-second order model data for arsenic adsorption onto CAC for: a) arsenic(V) initial concentration of 229.3 and 2,499.7 µg L^{-1}; b) arsenic(III) initial concentration of 242.8 and 2,739.0 µg L^{-1}.

Table 7.1 presents the experimental arsenic adsorption capacity (q_{exp}), and the parameters for the pseudo-first order and pseudo-second order kinetic models for SC07 and CAC under the different experimental conditions investigated. In the case of adsorption with SC07, at low initial concentration q_{exp} for arsenic(III) is approximately half of q_{exp} for arsenic(V); but at high initial concentration q_{exp} for arsenic(III) is 14 per cent higher than q_{exp} for arsenic(V). The adsorption capacity for

SC07 increases roughly 10 times and 20 times for a tenfold increase in concentration of arsenic(V) and arsenic(III), respectively.

In most kinetic tests, the F test for the variance of models was statistically significant ($p < 0.05$) for the pseudo-second order model; the exception being adsorption of arsenic(III) at low initial concentration onto CAC ($p = 0.12$). Based on the experimental adsorption values, the model plots and the F test, the pseudo-second order model better represents arsenic adsorption onto SC07 and CAC.

Table 7.1 Experimental adsorption capacity at equilibrium (q_{exp}), pseudo-first order adsorption rate constant (k_1), pseudo-first order adsorption capacity (q_1), pseudo-second order adsorption rate constant (k_2), and pseudo-second order adsorption capacity (q_2) for arsenic(V) and arsenic(III) adsorption at two initial concentrations onto SC07 and CAC. Statistically significant terms are in bold font.

Adsorbent	Oxidation state	Initial concentration	q_{exp}	Pseudo-first order		Pseudo-second order	
				k_1	q_1	k_2	q_2
		µg L^{-1}	µg g^{-1}	min^{-1}	µg g^{-1}	g µg^{-1} min^{-1}	µg g^{-1}
SC07	As(V)	227.9	43	2.39×10^{-3}	4	$\mathbf{4.91\times10^{-3}}$	**43**
SC07	As(V)	2,481.2	407	8.15×10^{-3}	118	$\mathbf{2.66\times10^{-3}}$	**409**
CAC	As(V)	229.3	19	8.61×10^{-4}	16	$\mathbf{1.56\times10^{-4}}$	**20**
CAC	As(V)	2,499.7	129	1.26×10^{-3}	111	$\mathbf{2.30\times10^{-5}}$	**140**
SC07	As(III)	224.3	22	1.99×10^{-3}	16	$\mathbf{8.48\times10^{-3}}$	**22**
SC07	As(III)	2,575.3	462	2.13×10^{-3}	289	$\mathbf{2.14\times10^{-5}}$	**473**
CAC	As(III)	242.8	16	9.51×10^{-4}	14	1.64×10^{-4}	17
CAC	As(III)	2,739.0	142	9.63×10^{-4}	55	$\mathbf{8.51\times10^{-5}}$	**143**

7.2 Effect of pH on arsenic(V) and arsenic(III) adsorption

7.2.1 Experimental methodology

This experiment investigated the effect of the initial pH of the aqueous phase on arsenic(V) and arsenic(III) adsorption onto SC07 and CAC. All experiments were run at room temperature, an adsorbent dose of 5 g L^{-1}, and initial arsenic concentrations from 206 to 235 µg L^{-1}. Solutions of different pH values were prepared by modifying the pH of a stock solution with dropwise addition of double distilled nitric acid (HNO_3) or 0.1M sodium hydroxide (NaOH). After collection, a sample aliquot was used to measure the pH at equilibrium (pH_e) and the other aliquot was kept to analyse total arsenic in the ICP-MS.

7.2.2 Results

Percent of arsenic removal (%As.R) and pH_e are plotted against the initial pH (pH_0) for arsenic(V) and arsenic(III) adsorption onto SC07 and CAC in Figure 7.6. Experimental points for each series were joined with dashed lines to ease the reading of the plot. However, interpolation of %As.R and pH_e between experimental points is uncertain and should be undertaken with care. Overall, arsenic removal is less sensitive to changes in pH_0 with CAC than with SC07, and less sensitive to the arsenic oxidation state with SC07 than with CAC. Also, for most pH_0 values tested, %As.R is higher with SC07 than with CAC.

For arsenic(V) and arsenic(III) adsorption onto SC07 and arsenic(V) adsorption onto CAC high arsenic(V) removal occurs at pH_0 values from 5 to 9. Within this pH_0 interval the pH_e varies from 7.1 to 7.5 for SC07 and from 5.1 to 6.2 for CAC. Arsenic(III) removal with SC07 is higher than 85 per cent from pH_0 5.1 to 9.0 ($pH_e \approx$ 6.8). As(III) removal with CAC follows a very different pattern; average %As.R varies between 15 and 20 per cent from pH_0 2 to 7, then from pH_0 9 to 11 adsorption increases to 27 per cent.

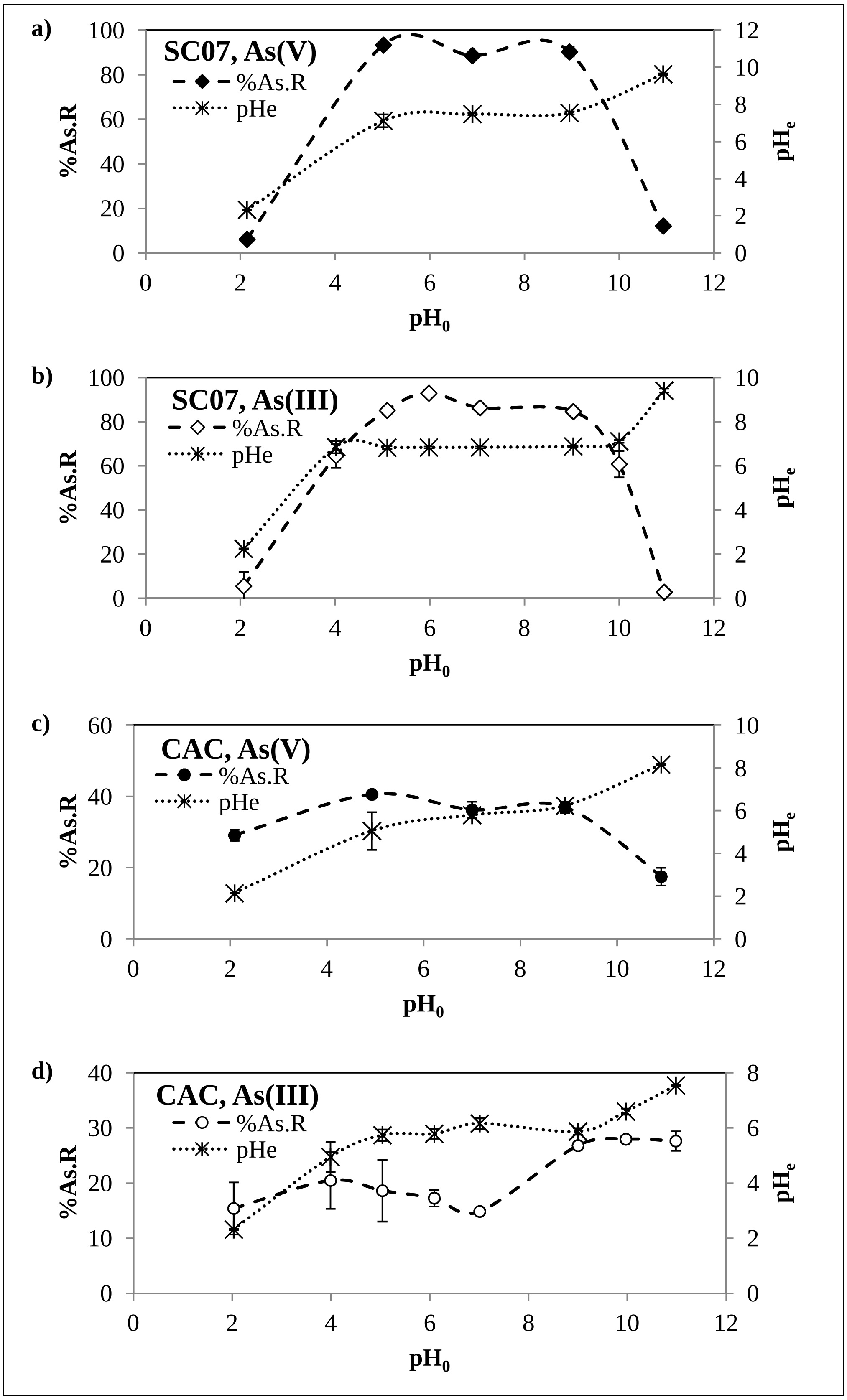


Figure 7.6 Percentage arsenic removal (%As.R) and pH at equilibrium (pH_e) plotted against initial pH (pH_0). a) arsenic(V) adsorption onto SC07, b) arsenic(III) adsorption onto SC07, c) arsenic(V) adsorption onto CAC, and d) arsenic(III) adsorption onto CAC.

7.3 Arsenic(V) and arsenic(III) isotherms at 25 and 35 °C

7.3.1 Experimental methodology

Adsorption isotherms for arsenic(V) and arsenic(III) at 25 and 35 °C were obtained for SC07 and CAC. Experiments were carried out in a bottle shaker in which the air temperature was controlled. For each series, eight arsenic solutions with concentrations ranging from 66 to 2,337 µg L^{-1} were prepared, the initial pH of each solution was adjusted to ≈ 8 with dropwise addition of ultrapure HNO_3 or 0.1M NaOH. An aliquot of the sample was used to measure the final pH, and the rest was keep for analysing total arsenic using the ICP-MS.

7.3.2 Analysis of isotherm data

The Langmuir and Freundlich equations were used to analyse the experimental isotherm data. The Langmuir equation is based on a kinetic principle in which the rate of adsorption is equal to the rate of desorption from the surface (Do et al., 2008). The Langmuir model makes three basic assumptions; the adsorption surface is homogeneous (i.e. all sites have a constant adsorption energy); adsorption occurs at definite localised sites; and each site can fit just one molecule or atom (Do et al., 2008). Equation 7.7 is the linear form of the Langmuir equation (Langmuir, 1918).

$$\frac{C_e}{q_e} = \frac{1}{Q_m b} + \frac{C_e}{Q_m} \qquad \text{Equation 7.7}$$

where;

C_e is the arsenic concentration in the aqueous phase at equilibrium in µg L^{-1},
q_e is the adsorption capacity at equilibrium in µg g^{-1},
Q_m is the monolayer adsorption capacity in µg g^{-1},
b is the Langmuir parameter related to the energy of adsorption in L µg^{-1}.

The Freundlich isotherm, of empirical origin, has actually a theoretical justification. This isotherm assumes: that the surface is heterogeneous, i.e. the surface is distributed in regions with the same adsorption energy; that the regions are independent and there is no interaction between regions; and that on each region one molecule or atom is adsorbed on only one adsorption site (Do et al., 2008). Equation 7.8 is the linear form of the Freundlich isotherm.

$$\ln \mathrm{q_e} = \ln K_F + \frac{1}{n} \ln \mathrm{C_e} \qquad \text{Equation 7.8}$$

where;

$1/n$ is the a dimensionless parameter related to the energy of adsorption and,

K_F is the relative sorption capacity in (μg g^{-1}) (L μg^{-1})$^{1/n}$.

The Langmuir and Freundlich parameters were derived with the linear forms of the equations using the least-square method. The model that best represents the experimental data was selected using a similar criterion to that used for the kinetic adsorption model (*Section 7.1*).

7.3.3 Results

Percentage Arsenic removal with respect to initial concentration at 25 and 35 °C

Figure 7.7 presents the adsorption isotherms for the SC07 and the CAC series; percentage of arsenic removal (%As.R) is plotted against the initial arsenic concentration (As_0). In general, %As.R is higher with SC07 than with CAC, and it was higher for arsenic(V) than for arsenic(III) at both temperatures 25 and 35 °C. No apparent trend was found in the effect of temperature on %As.R, also this effect is relatively small. For both adsorbents, arsenic(V) removal is similar at 25 and 35 °C. However, for SC07, %As(III).R is slightly higher at 25 °C than at 35 °C and for CAC %As(III).R is higher at 35 °C than at 25 °C. The initial oxidation state of arsenic seems to have an effect on adsorption; for SC07 and CAC, %As(V).R is higher than %As(III).R at both temperatures. The initial oxidation state effect is smaller for arsenic adsorption at high initial concentrations for CAC.

The overall trend for adsorption is that %As.R decreases as the initial arsenic concentration (As_0) increases, with the exception of arsenic(III) adsorption onto CAC at 25 °C. For this series, the %As.R slightly increases when the initial arsenic concentration increases. A decreasing trend in %As.R was expected since higher initial concentrations lead to saturation of the adsorption capacity of adsorbents. However, at the highest arsenic concentration investigated, arsenic removal with SC07 was higher than 73 per cent; which suggest that SC07 was not fully saturated. In the arsenic(V) adsorption onto CAC series and experiments at an initial arsenic concentration (As_0) of 366.2 µg L^{-1}, the percentage of arsenic removal appears to be particularly high.

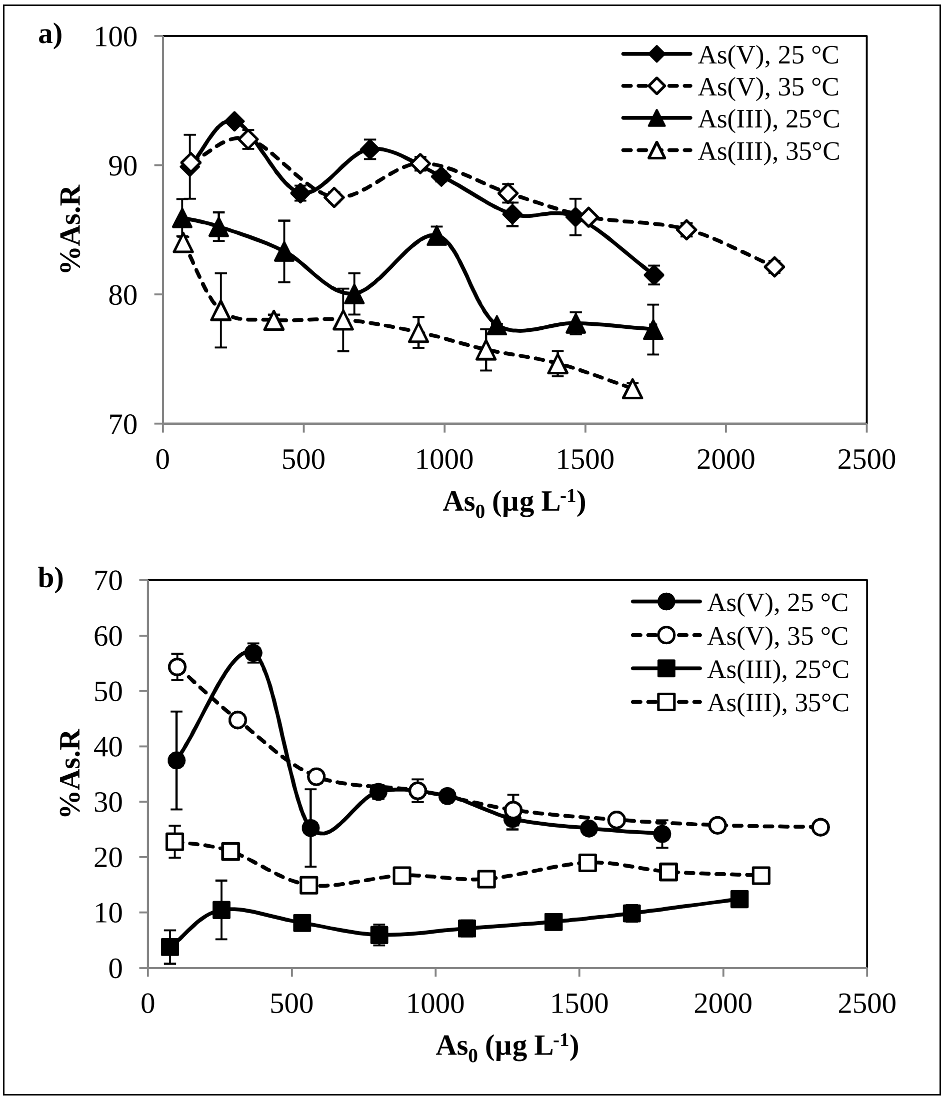


Figure 7.7 Adsorption isotherm experiments: a) arsenic(V) and arsenic(III) adsorption onto SC07 at 25 and 35 °C; and b) arsenic(V) and arsenic(III) adsorption onto CAC at 25 and 35 °C.

Variation of pH with respect to initial arsenic concentration at 25 and 35 °C

The variation of pH_e at various initial arsenic(V) and arsenic(III) initial concentrations at 25 and 35 °C is presented in Figure 7.8. In general, pH_e values are similar for the differential experimental conditions tested for each adsorbent. The pH_e values for the SC07 series vary from 6.8 to 7.6; and pH_e for the CAC series from 5.1 to 6.0.

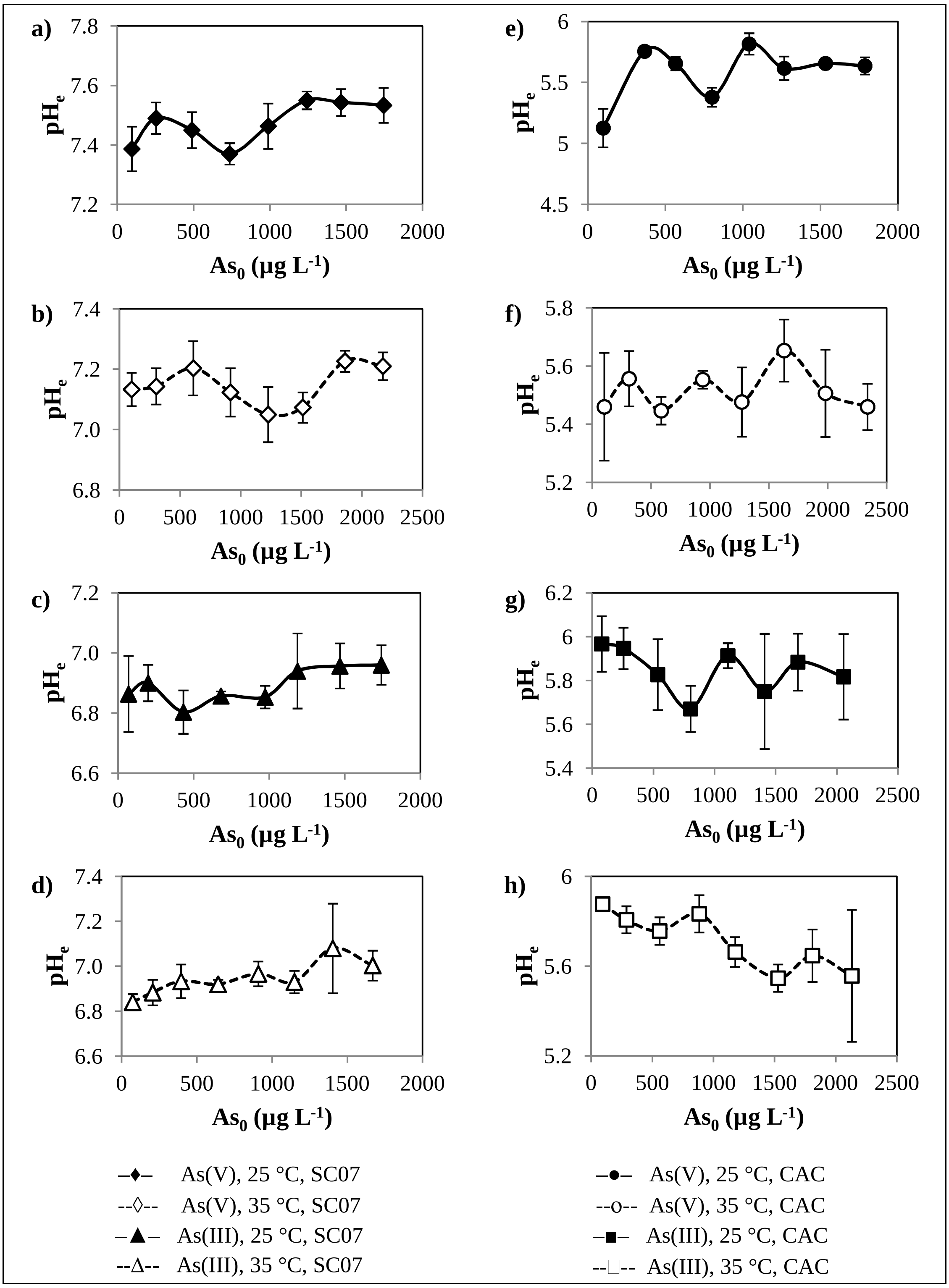


Figure 7.8 Variation of $\mathrm{pH_e}$ with respect to initial arsenic concentration ($\mathrm{As_0}$) at 25 and 35 °C. a) arsenic(V) adsorption onto SC07 at 25 °C, b) arsenic(V) adsorption onto SC07 at 35 °C, c) arsenic(III) adsorption onto SC07 at 25 °C, d) arsenic(III) adsorption onto SC07 at 35 °C, e) arsenic(V) adsorption onto CAC at 25 °C, f) arsenic(V) adsorption onto CAC at 35 °C, g) arsenic(III) adsorption onto CAC at 25 °C, and h) arsenic(III) adsorption onto CAC at 35 °C.

Langmuir and Freundlich models

The experimental adsorption capacity (q_{exp}), and the Langmuir and Freundlich models are plotted in Figure 7.9 for SC07 and in Figure 7.10 for CAC. The models were plotted using values of the parameters found with the least-squares method from Equation 7.7 and Equation 7.8.

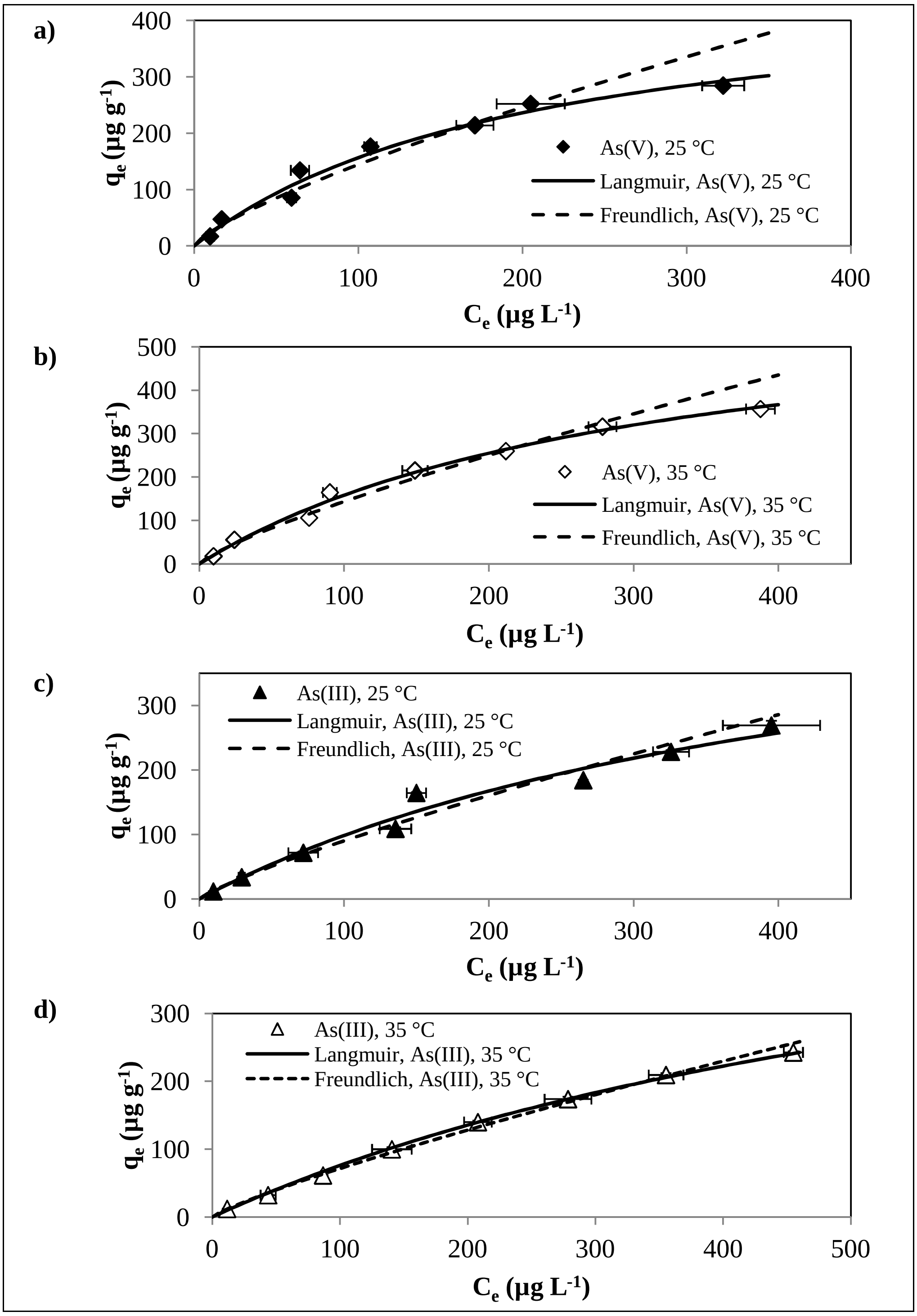


Figure 7.9 Isotherms for arsenic adsorption onto SC07. a) arsenic(V) at 25 °C, b) arsenic(V) at 35 °C, c) arsenic(III) at 25 °C, and d) arsenic(III) at 35 °C.

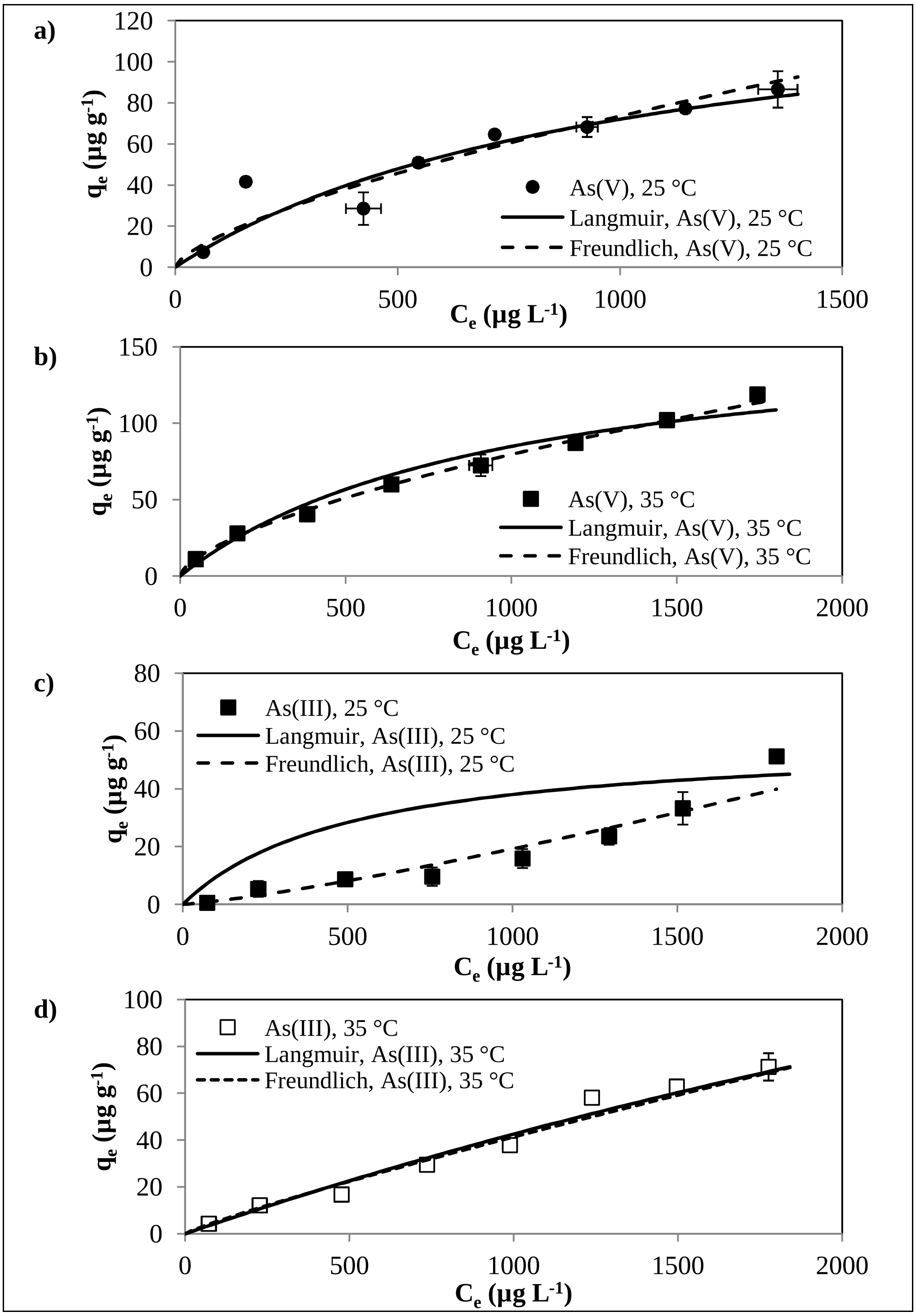


Figure 7.10 Isotherms for arsenic adsorption onto CAC. a) arsenic(V) at 25 °C, b) arsenic(V) at 35 °C, c) arsenic(III) at 25 °C, and d) arsenic(III) at 35 °C.

According to these figures, for most of the experimental runs both Langmuir and Freundlich models fit the experimental data reasonably well. The exception is the Langmuir model for adsorption of arsenic(III) onto CAC at 25 °C; this series seems to have a different trend from the rest of the data. Also, the Freundlich model overestimates q_{exp} for arsenic(V) adsorption onto SC07 at high arsenic equilibrium concentrations (C_e).

Table 7.2 presents the Langmuir monolayer adsorption capacity (Q_m), the Langmuir parameter related to the energy of adsorption (b), the Freundlich relative adsorption capacity (K_F), the Freundlich parameter related to the energy of adsorption ($1/n$), and the goodness of fit value (R^2) for the Langmuir and Freundlich models for all experimental runs. The F test was run for each series to identify the model with the least variance with respect to the experimental data; these models ($p < 0.050$) are in bold font.

Table 7.2 Langmuir monolayer adsorption capacity (Q_m), Langmuir parameter related to the energy of adsorption (b), Freundlich relative adsorption capacity (K_F), Freundlich parameter related to the energy of adsorption ($1/n$), and goodness of fit value (R^2) for Langmuir and Freundlich models. Models with statistically smaller variance with respect to the experimental data according to the F test ($p < 0.05$) are in bold font.

Adsorbent	Oxidation state	Temp.	Langmuir model			Freundlich model		
			Q_m	b	R^2	K_F	$1/n$	R^2
		°C	$\mu g\ g^{-1}$	$L\ \mu g^{-1}$		$(\mu g\ g^{-1})\cdot(L\ \mu g^{-1})^{1/n}$		
SC07	As(V)	25	**481**	**4.82×10^{-3}**	**0.86**	4.20	0.77	0.95
SC07	As(V)	35	**653**	**3.20×10^{-3}**	**0.91**	3.61	0.80	0.98
CAC	As(V)	25	146	9.78×10^{-4}	0.61	0.64	0.69	0.83
CAC	As(V)	35	168	1.02×10^{-3}	0.89	**0.97**	**0.64**	**1.00**
SC07	As(III)	25	557	2.15×10^{-3}	0.83	1.96	0.83	0.99
SC07	As(III)	35	**619**	**1.40×10^{-3}**	**0.85**	1.49	0.84	1.00
CAC	As(III)	25	58	1.93×10^{-3}	0.38	**3.61×10^{-3}**	**1.24**	**0.95**
CAC	As(III)	35	360	1.34×10^{-4}	0.19	9.07×10^{-2}	0.89	0.98

7.4 Competing effect of other water constituents (Cl^-, PO_4^{3-}, SO_4^{2-}, Mn^{2+}, Si) on arsenic(V) and arsenic(III) adsorption

7.4.1 Experimental methodology

The effect of other water constituents on arsenic removal onto SC07 and CAC was investigated in batch experiments. The chemical species investigated were chloride (Cl^-) at 25 and 250 mg L^{-1}, phosphate (PO_4^{3-}) at 0.1 and 10 mg L^{-1}, sulphate (SO_4^{2-}) at 10 and 100 mg L^{-1}, manganese (Mn^{2+}) at 0.1 and 0.4 mg L^{-1}, and silicon (Si) at 5 and 50 mg L^{-1}. The upper limits for Cl^- and Mn^{2+} were set in agreement with the World Health Organisation drinking water guidelines values; 250 mg L^{-1} for Cl^-, and 0.4 mg L^{-1} for Mn^{2+}. The upper limits for PO_4^{3-} and Si were based on the 2009 Bangladesh national drinking water quality survey, in which 93 per cent of samples had a PO_4^{3-} concentration below 6 mg L^{-1} and the highest Si concentration found was 50 mg L^{-1}.

The experiment was run for arsenic(V) and arsenic(III) separately. The experiment was conducted at room temperature, at an initial pH ≈ 8, and with an adsorbent dose of 5 g L^{-1}. Stock solutions of Cl^- at 2,500 mg L^{-1}, PO_4^{3-} at 100 mg L^{-1}, SO_4^{2-} at 1,000 mg L^{-1}, Mn^{2+} at 100 mg L^{-1} and Si at 500 mg L^{-1} were prepared with reagent grade water. These stock solutions were added in appropriate quantities to arsenic solutions with a concentration of ≈ 250 µg L^{-1}. A sample of the arsenic solution and a sample of the arsenic with the spiked chemical species were kept for analysis of arsenic concentration and for calculating recovery rates for arsenic for each solution. The pH at equilibrium was measured for each sample.

The percentage of arsenic recovery for samples spiked with Cl^-, PO_4^{3-}, SO_4^{2-} and Mn^{2+} was between 85 and 115 per cent. Arsenic recovery was 116 per cent for arsenic(III) for SC07 samples spiked with Si at 5 mg L^{-1}, 121 per cent for arsenic(III) for SC07 samples spiked with Si at 50 mg L^{-1}, 112 per cent per cent for arsenic(III) CAC samples spiked with Si at 5 mg L^{-1} and 117 per cent per cent for arsenic(III) CAC samples spiked with Si at 50 mg L^{-1}.

7.4.2 Results of the effect of competing water constituents on percentage of arsenic adsorption

The effect of water constituents on arsenic adsorption onto SC07 is presented in Figure 7.11. Arsenic removal diminishes with all chemical species investigated. Arsenic(V) and arsenic(III) adsorption are affected in a similar fashion by the water constituents investigated. The size of this negative effect seems to be related to the concentration of the chemical species; with the exception of Mn^{2+}. Arsenic(V) adsorption is especially affected by Cl^- at 250 mg L^{-1} and by Si at 50 mg L^{-1}, causing negligible adsorption of arsenic(V). The negative effect of PO_4^{3-} at 0.1 mg L^{-1} and Mn^{2+} at 0.1 and 0.4 mg L^{-1} on arsenic adsorption is small.

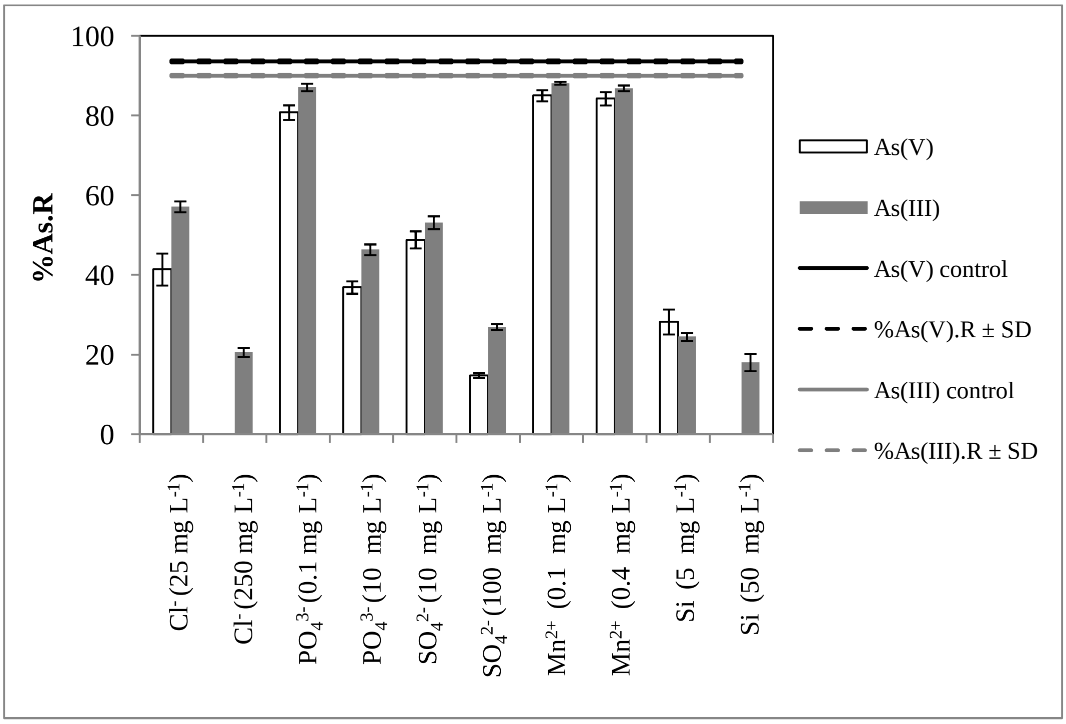


Figure 7.11 Effect of Cl^- (25 and 250 mg L^{-1}), PO_4^{3-} (0.1 and 10 mg L^{-1}), SO_4^{2-} (10 and 100 mg L^{-1}), Mn^{2+} (0.1 and 0.4 mg L^{-1}) and Si (5 and 50 mg L^{-1}) on arsenic(III) and arsenic(V) adsorption onto SC07 at an initial arsenic concentration of ≈ 250 µg L^{-1}.

The effect of the Cl^-, PO_4^{3-}, SO_4^{2-}, Mn^{2+} and Si on arsenic removal with CAC is presented in Figure 7.12. Arsenic(V) removal in reagent grade water is 41 per cent. For most ions, arsenic removal falls to values between 21 to 33 per cent; with the exception of PO_4^{3-} at 10 mg L^{-1} and Si at 50 mg L^{-1} for which arsenic adsorption falls below 10 per cent. Once again, the size of the negative effect on arsenic(V) adsorption is related to the concentration of the spiked chemical species. On the other hand, arsenic(III) adsorption is less affected by SO_4^{2-} at 100 mg L^{-1} than at 10 mg L^{-1}; the same behaviour is observed with $PO4^{-3}$. The effect of SO_4^{2-} at 100 mg L^{-1} on arsenic(III) removal is negligible, and the effect of Si at 5 mg L^{-1} is relatively small.

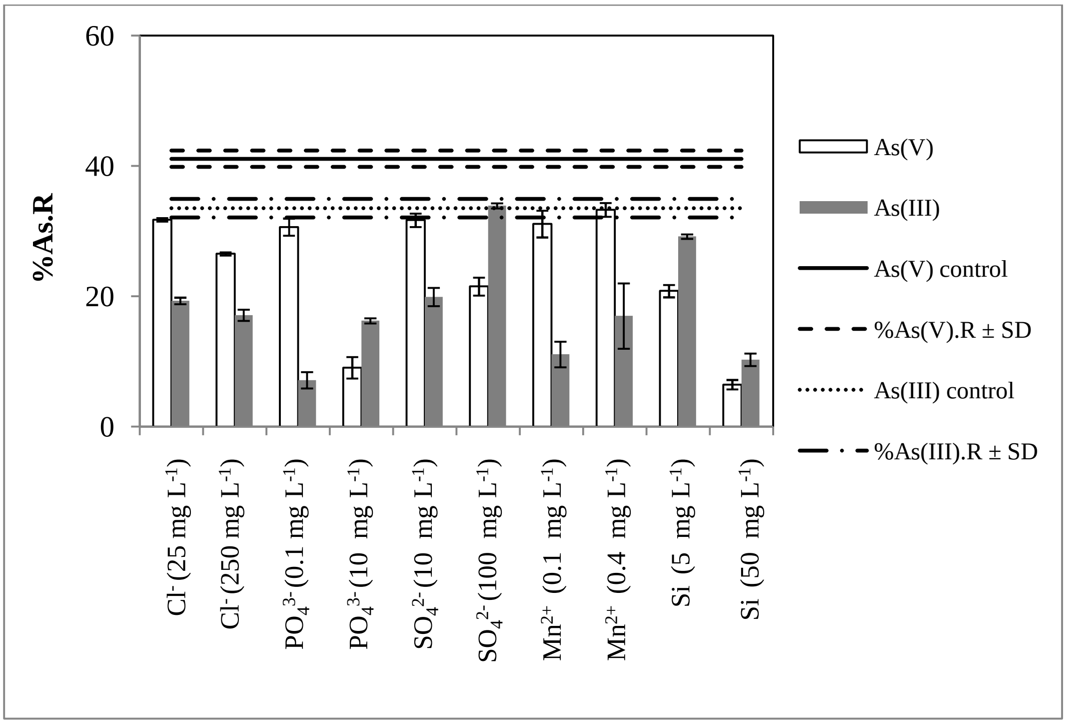


Figure 7.12 Effect of Cl^- (25 and 250 mg L^{-1}), PO_4^{3-} (0.1 and 10 mg L^{-1}), SO_4^{2-} (10 and 100 mg L^{-1}), Mn^{2+} (0.1 and 0.4 mg L^{-1}) and Si (5 and 50 mg L^{-1}) on arsenic(III) and arsenic(V) adsorption onto CAC at an initial arsenic concentration of ≈ 250 µg L^{-1}.

Effect of competing water constituents on the pH at equilibrium (pH_e)

In arsenic adsorption with SC07, pH_e values for samples spiked with most ions were between 6.8-7.5; the exception was Si at 50 mg L^{-1} with a pH_e of 8.3. For CAC the range of pH_e values found was 5.6-6.3; Si at 50 mg L^{-1} is again outside this range at pH_e 6.7. In similar experimental conditions (with no spiked chemical species) pH_e values for SC07 vary between 7.3 and 7.6, and for CAC vary between 5.1 and 6.4.

7.5 Simulation of column experiments for arsenic(V) and arsenic(III) adsorption with SC07 and CAC

7.5.1 Column simulation methodology

Simulation of adsorption column experiments with SC07 and CAC was carried out with the software Fixed-bed Adsorption Simulation Tool (FAST) version 2.0. The

FAST software uses the homogeneous surface diffusion model (HSDM) to compute adsorption. The HSDM uses partial differential equations to describe mass transport through the column and into the adsorbent particles (Sperlich et al., 2008). The HSDM assumes that: the velocity of the fluid is constant across any cross-section of the column perpendicular to the axis of the column, mass transfer in the liquid-phase is linear, mass transfer occurs exclusively through surface diffusion in the solid-phase, hydraulic loading rate is constant, diffusion coefficients are constant, and adsorbent particles are of spherical shape (Sperlich et al., 2008). Also, the Freundlich isotherm is used to describe adsorption equilibrium (Sperlich et al., 2008).

The simulation column experiment was run using an adsorbent weight of a real size filter, 10 Kg. Simulations were carried out for SC07 and CAC at initial arsenic(V) and arsenic(III) concentrations of 250, 500 and 1,000 µg L^{-1} and flow rates of 2.5 and 5 L h^{-1}. The parameters empty bed contact time and bed volume were adjusted to achieve the desired flow rate and adsorbent weight. The liquid-phase mass transfer coefficient and the solid-phase mass transfer coefficient were estimated with the methods used by Mohan *et al.* (2002) and Biswas *et al.* (2007), respectively.

7.5.2 Column simulation results

Breakthrough curves simulated with FAST are shown for SC07 in Figure 7.13 and for CAC in Figure 7.14. Concentration in the breakthrough curves is represented as a ratio of the arsenic concentration in the effluent and the arsenic concentration in the influent (As_E/As_I). Table 7.3 shows the number of days that SC07 can remove arsenic at flow rates of 2.5 and 5 L h^{-1} before the concentration in the effluent exceeds 10 and 50 µg L^{-1} of arsenic(V) and arsenic(III). According to the breakthrough curves for CAC, the fraction of arsenic concentration in the effluent exceeds 10 and 50 µg L^{-1} in less than 14 days.

The volume of water treated by mass of adsorbent (adsorbent weight = 10 Kg, flow rate=2.5-5.0 L h^{-1}) before the concentration in the effluent reaches 10 µg L^{-1} (50 µg L^{-1}) is from 1.1 L g^{-1} (1.1 L g^{-1}) at an influent concentration of arsenic(V) of 250 µg L^{-1} to 0.8 L g^{-1} (0.6 L g^{-1}) at an influent concentration of arsenic(V) of 1,000 µg L^{-1}; and from 0.7 L g^{-1} (0.7 L g^{-1}) at an influent concentration of arsenic(III) of 250 µg L^{-1} to 0.5 L g^{-1} (0.5 L g^{-1}) at an influent concentration of arsenic(III) of 1,000 µg L^{-1}.

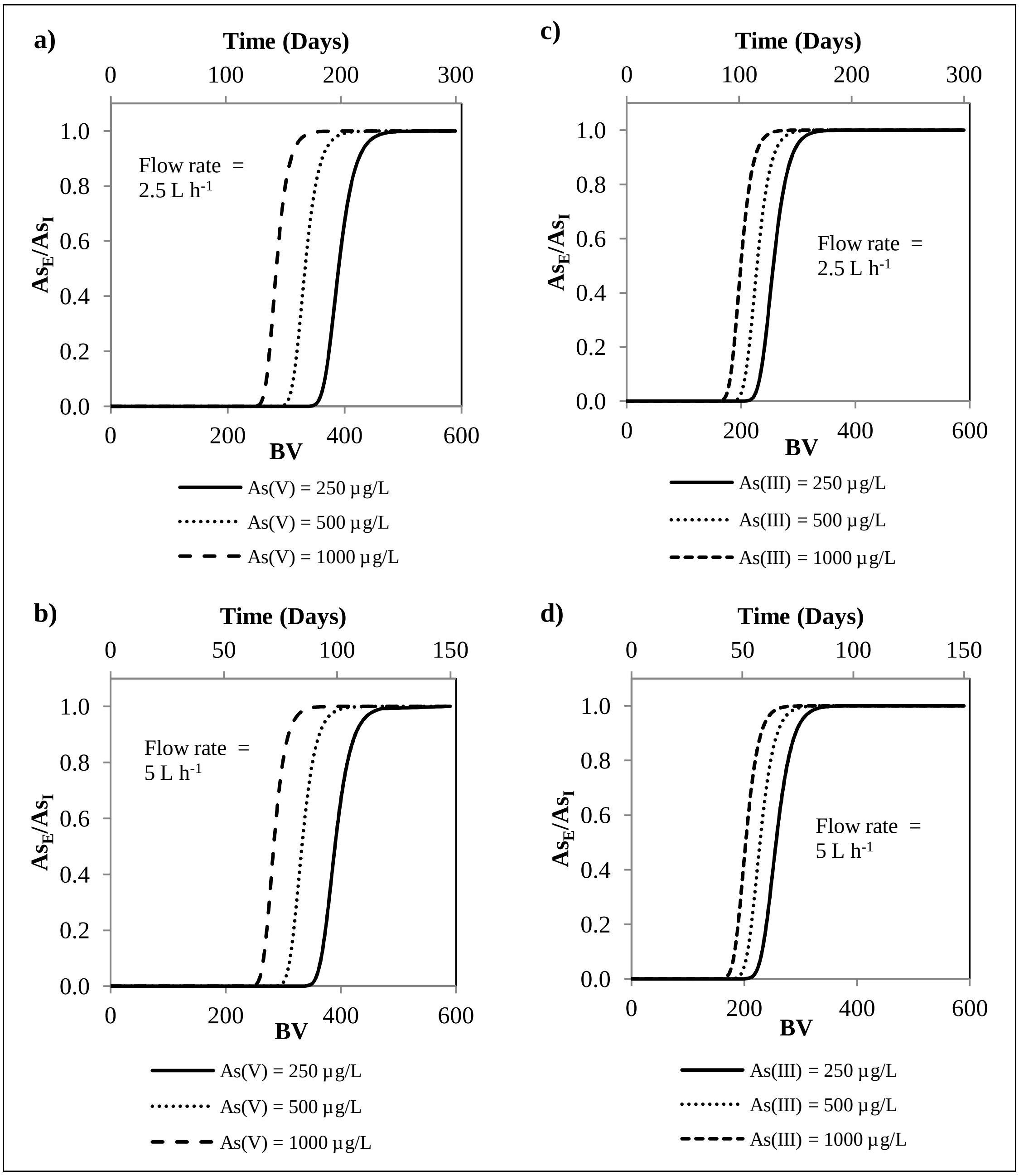


Figure 7.13 Simulation of column experiments for arsenic adsorption onto SC07, adsorbent mass of 10 Kg. a) arsenic(V) initial concentrations from 250 to 1,000 µg L^{-1} at a flow rate of 2.5 L h^{-1}, b) arsenic(III) initial concentrations from 250 to 1,000 µg L^{-1} at a flow rate of 2.5 L h^{-1}, c) arsenic(V) initial concentrations from 250 to 1,000 µg L^{-1} at a flow rate of 5 L h^{-1}, and d) arsenic(III) initial concentrations from 250 to 1,000 µg L^{-1} at a flow rate of 5 L h^{-1}.

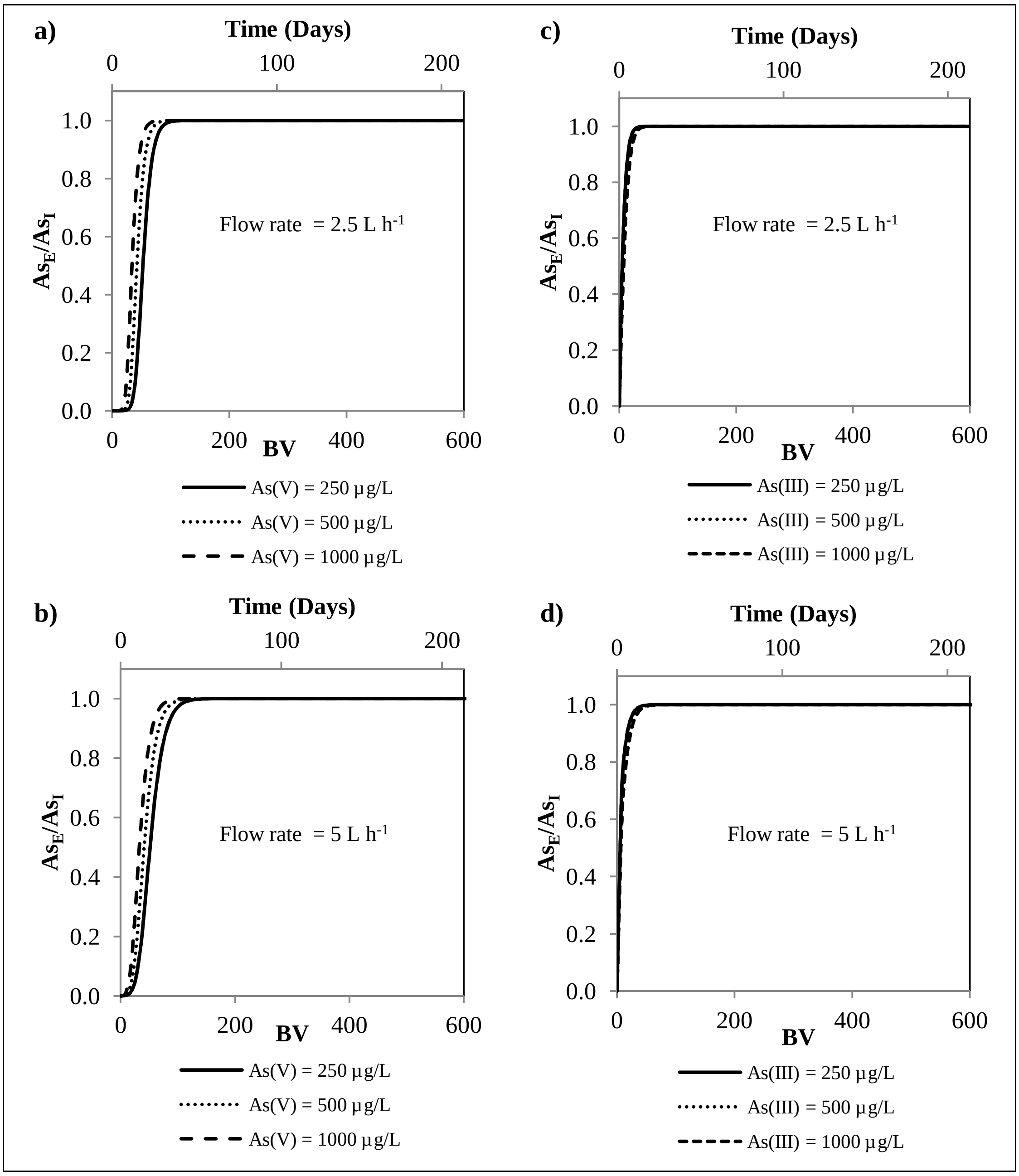


Figure 7.14 Simulation of column experiments for arsenic adsorption onto CAC adsorbent mass of 10 Kg. a) arsenic(V) initial concentrations from 250 to 1,000 µg L^{-1} at a flow rate of 2.5 L h^{-1}, b) arsenic(III) initial concentrations from 250 to 1,000 µg L^{-1} at a flow rate of 2.5 L h^{-1}, c) arsenic(V) initial concentrations from 250 to 1,000 µg L^{-1} at a flow rate of 5 L h^{-1}, and d) arsenic(III) initial concentrations from 250 to 1,000 µg L^{-1} at a flow rate of 5 L h^{-1}.

Table 7.3 Number of days that SC07 can remove arsenic before the effluent concentration exceeds 10 and 50 µg L^{-1} of arsenic(V) and arsenic(III). The weight of the adsorbent was set at 10 Kg, and the flow rate was set at 2.5 and 5 L h^{-1}.

Flow rate	Influent concentration	Days			
		Breakthrough $As(V)_0$		Breakthrough $As(III)_0$	
L h^{-1}	µg L^{-1}	10 µg L^{-1}	50 µg L^{-1}	10 µg L^{-1}	50 µg L^{-1}
2.5	250	183	190	115	123
	500	155	159	100	106
	1,000	130	133	87	91
5	250	91	95	57	61
	500	77	79	50	52
	1,000	65	67	43	45

7.6 Discussion

Possible mechanisms for metal adsorption with activated carbon (AC) are ion exchange and complexation, which can occur in isolation or in combination (Di Natale et al., 2008; Budinova et al., 2009). These processes are regulated by the interaction between the adsorbate and the adsorbent, which depend on the AC surface chemistry and the distribution of ionic arsenic(V) and arsenic(III) species in solution. In the following paragraphs a summary of the surface chemistry of AC and arsenic speciation is shortly introduced in order to assist an explanation of the possible mechanisms of arsenic adsorption.

Surface chemistry of activated carbon

AC presents both surface acidity and basicity. Surface acidity is related to the functional groups carboxyl, lactone, phenol and lactol (Montes-Morán et al., 2004). The origin of surface basicity is still under discussion in the literature. While surface functional groups like chromene, quinine and pyrone are believed to contribute to surface basicity, there is some consensus that pi-electrons on the basal layers of activated carbon are mainly responsible for the basicity on AC (Marsh et al., 2006). Figure 7.15 presents the oxygen functional surface groups found on the surface of ACs.

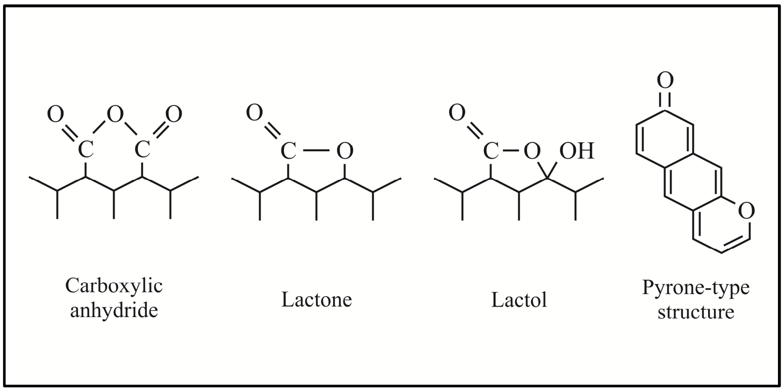


Figure 7.15 Oxygen functional surface groups found on the surface of AC (Boehm 2002).

Arsenic(V) and arsenic(III) speciation

The distribution of arsenic(V) and arsenic(III) species, at the conditions at which the experiments were run, was determined with the programme Visual MINTEQ 3.0. Visual MINTEQ is a freeware chemical equilibrium model used for the calculation of metal speciation and solubility equilibrium. The speciation diagrams were derived for arsenic(V) and arsenic(III) concentrations of 250 and 2,500 µg L^{-1}, ionic strength (I) of 0 and 0.1 M, and temperatures of 20, 25 and 35 °C. Visual MINTEQ 3.0 uses the following equilibrium constants (at 25 °C) for arsenic aqueous species:

$H_3AsO_3^0 = H_2AsO_3^- + H^+$ log K = -9.17,

$H_3AsO_3^0 = HAsO_3^{2-} + 2H^+$ log K =-23.27,

$H_3AsO_3^0 = AsO_3^{3-} + 3H^+$ log K =-38.27,

$H_3AsO_4^0 = H_2AsO_4^- + H^+$ log K =-2.3,

$H_3AsO_4^0 = HAsO_4^{2-} + 2H^+$ log K =-9.29,

$H_3AsO_4^0 = AsO_4^{3-} + 3H^+$ log K =-21.08,

$H_3AsO_4^0 + 2H^+ + 2e^- = H_3AsO_3^0 + H_2O$ log K =19.35

Selected equilibrium concentration diagrams of arsenic(V) and arsenic(III) species as a function of arsenic concentration, ionic strength (I) and temperature (T) are presented in Figure 7.16. In these diagrams, the equilibrium concentration of arsenic species is shown as a percentage of the total arsenic concentration. The percentage distribution of arsenic species within the experimental conditions changes very little; including the concentration of the neutrally charged species $H_3AsO_4^0$ and $H_3AsO_3^0$.

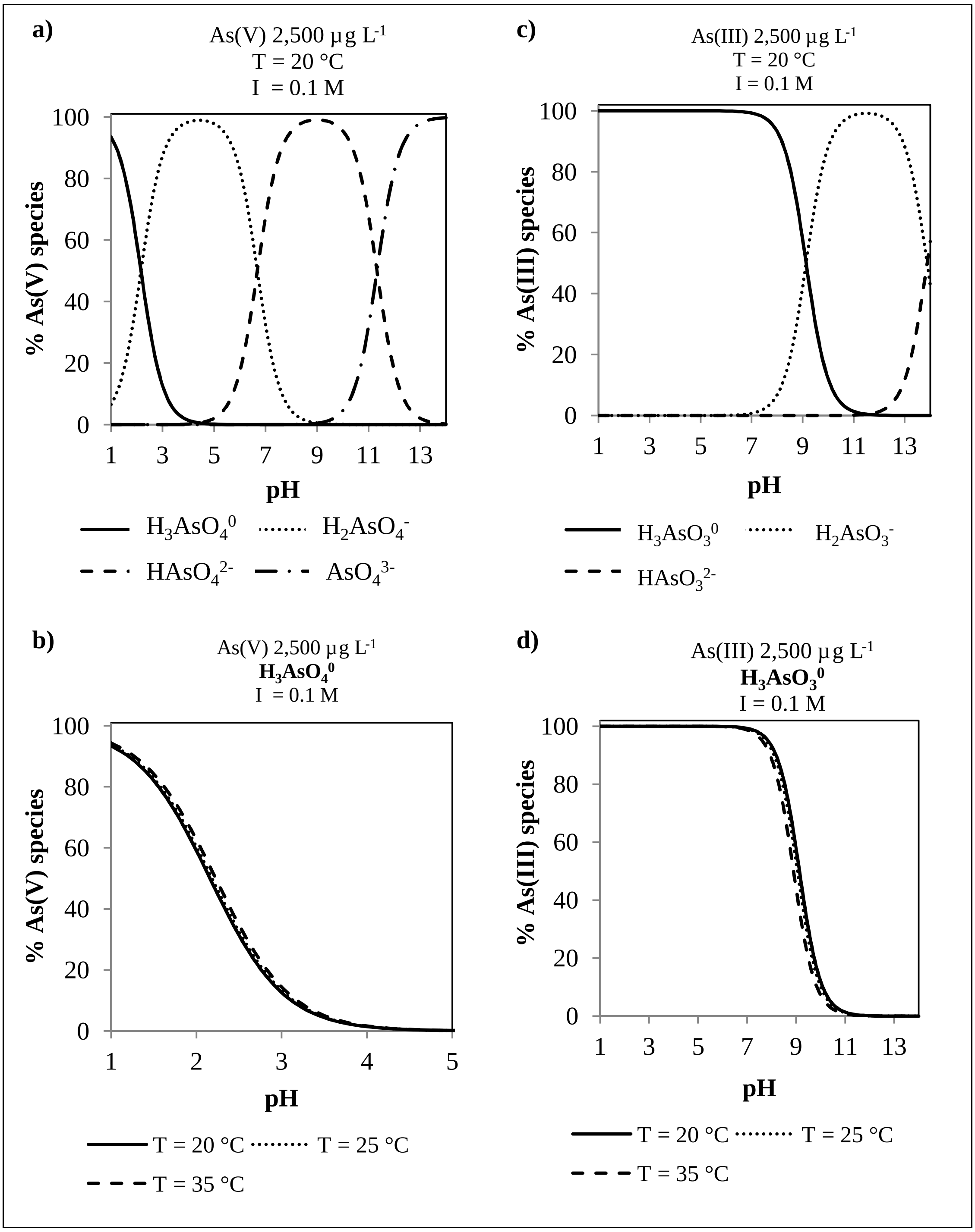


Figure 7.16 Equilibrium concentration of arsenic(V) and arsenic(III) species as a function of arsenic concentration, ionic strength (I) and temperature (T). a) arsenic(V) concentration = 2,500 µg L^{-1}, T = 20 °C and I = 0.1 M, b) percent distribution of the arsenic(V) species $H_3AsO_4^0$ at 2,500 µg L^{-1}, I = 0.1 M and T = 20, 25 and 35 °C, c) arsenic(III) concentration = 2,500 µg L^{-1}, T = 20 °C and I = 0.1 M, and d) percent distribution of the arsenic(III) species $H_3AsO_3^0$ at 2,500 µg L^{-1}, I = 0.1 M and T = 20, 25 and 35 °C.

7.6.1 Kinetics of arsenic(V) and arsenic(III) adsorption

An insight into arsenic concentration and pH changes throughout the arsenic adsorption process was obtained from kinetic experiments in *Section 7.1*. Electrostatically favourable conditions were maintained for arsenic(V) adsorption onto SC07 throughout adsorption; pH of the solution was always smaller than the pH_{ZC} = 9.2 of SC07. For the CAC, the initial pH was higher than the pH_{ZC} = 6.8 of CAC, but after 15 minutes the pH of solution was smaller than the pH_{ZC} of CAC. For both adsorbents a drop in pH in the aqueous phase was registered during the first 15-30 minutes of adsorption.

The percentage of arsenic(III) adsorption at low initial concentration from the kinetic experiment is substantially smaller that the values obtained in the factorial experiment (*Section 5.2.1*), the variation of initial pH experiment (*Section 7.2*), and the isotherm experiment (*Section 7.3*). There are two possible explanation for this: arsenic(III) adsorption in the kinetic experiment was affected by an uncontrolled experimental variable (such as contamination from glassware), or variability within the adsorbent's preparation conditions or in the raw material.

Regarding kinetic absorption data, the pseudo-second order model better fits the experimental data for adsorption of arsenic(V) and arsenic(III) onto SC07 and CAC; the experimental adsorption capacity (q_{exp}) is underestimated with the pseudo-first order model in half of the experimental conditions. The arsenic adsorption capacity (q) of the adsorbent increases rapidly at the beginning of the reaction, but as the reaction progresses the rate of reaction decreases rapidly as q approaches the equilibrium adsorption capacity of the adsorbent (q_{exp}).

Theoretically, the rate constant (k_2) should be independent of the initial arsenic concentration. However, k_2 is inversely proportional to the initial concentration. The most drastic change occurred in arsenic(III) adsorption onto SC07; in which k_2 decreased two orders of magnitude. According to the rate constants estimated with the pseudo-second order model, adsorption of arsenic(V) is faster with SC07 (k_2 from 2.7×10^{-3} to 4.9×10^{-3} g μg^{-1} min^{-1}) than with CAC (k_2 from 2.3×10^{-5} to 1.6×10^{-4} g μg^{-1} min^{-1}). Arsenic(III) adsorption with SC07 is faster at low arsenic concentration (8.5×10^{-3} g μg^{-1} min^{-1}) than with CAC (1.6×10^{-4} g μg^{-1} min^{-1}).

Arsenic(III) adsorption at high initial concentration has the same order of magnitude with SC07 (2.1×10^{-5} g µg^{-1} min^{-1}) than with CAC (8.5×10^{-5} g µg^{-1} min^{-1}).

7.6.2 Effect of pH on arsenic(V) and arsenic(III) adsorption

According to the equilibrium concentration diagrams and experimental pH_{ZC} values presented earlier, adsorption of arsenic(V) onto SC07 is favourable for typical drinking water pH values (6.5-8.5). Although the neutral arsenic(III) ion $H_3AsO_3^0$ is predominant for pH < 9.0, the percentage of arsenic(III) removal was only slightly below percentage of arsenic(V) adsorption from pH 5 to 9. Arsenic(III) adsorption is driven by the small concentration of the negatively charged ions $H_2AsO_3^-$. Le Châtelier principle indicates that if a system in equilibrium is subjected to a change, the system will respond with a net reaction that will reduce the effect of the change. So, when $H_2AsO_3^-$ ions are adsorbed onto the surface of the AC, the equilibrium in the reaction

$$H_3AsO_3^0 \quad = \quad H_2AsO_3^- \quad + \quad H^+$$

will move towards the right side to compensate the change in concentration of ions $H_2AsO_3^-$ in solution.

Results in *Section 7.2* show that arsenic(V) and arsenic(III) adsorption with SC07 and CAC is highly dependent on pH; which is the case for most arsenic removal methods. Variation of arsenic removal with respect to initial pH values is smaller with CAC than with SC07, however the percent of arsenic removal is significantly lower. Arsenic(V) and arsenic(III) adsorption with SC07 drops below 15 per cent at $pH \leq 2$ and $pH \geq 11$. Low adsorption levels of arsenic(V) at $pH \leq 2$ could be explained in terms of the high concentration of the species $H_3AsO_4^0$, and at $pH \geq 11$ in terms of the repulsion of negatively charged arsenic(V) species from the negatively charged surface of the AC.

The trend observed in adsorption of arsenic(III) onto SC07 is very similar to arsenic(V) adsorption; which may suggest that some arsenic(III) undergoes oxidation to arsenic(V) prior to adsorption and/or that adsorption of arsenic(III) is not fully controlled by electrostatic attraction. On the other hand, the highest adsorption of arsenic(III) with CAC occurred from pH 8 to 11; at these pH values the concentration of the arsenic(III) ion $H_2AsO_3^-$ steadily increases (Figure 7.16) and the surface of the activated carbon is negatively charged. Thus, this observation confirms that arsenic(III) adsorption is not totally due to electrostatic attraction.

7.6.3 Arsenic(V) and arsenic(III) isotherms at 25 and 35 °C

Adsorption is very often an exothermic process; increasing temperature is expected to decrease adsorption (Housecroft et al., 2006). However, this trend is not always observed in experimental data. Results in *Section 6.3.3* show that the effect of increasing temperature from 25 to 35 °C on the arsenic(V) and arsenic(III) adsorption capacity (q_{exp}) of SC07 and CAC was very small or negligible. However, an increment in temperature from 25 to 35 °C enhanced slightly arsenic(III) adsorption with CAC.

Arsenic(V) and arsenic(III) adsorption is adequately described by the Langmuir and the Freundlich equations for SC07. The Langmuir equation is believed to better fit the data since the variance in the Langmuir model with respect to the experimental data was statistically smaller ($p < 0.050$) than the variance from the Freundlich model for 3 out of 4 different experimental conditions, and the Freundlich model overestimated q_{exp} at high C_e values.

The Langmiur parameter b is a measure of the affinity of the adsorbate molecule with the surface of the adsorbent, the larger the value of b then the adsorbents surface is covered more with adsorbate. The b Langmuir parameter was estimated from 1.40 to 4.82 L mg^{-1} for the SC07 adsorbent. The b parameter is below 0.4 L mg^{-1} for most adsorbents presented in Table 2.2; with exception of an oat hull AC in which b was estimated in 43 L mg^{-1}. The monolayer adsorption capacity, Q_m, obtained for SC07 was considerably lower than those reported in Table 2.2. However, concentration of arsenic solutions used in this research was up to 2.7 mg L^{-1} whereas most of the studies reported in Table 2.2 used considerably higher concentrations (22 to 150 mg L^{-1}). On the other hand, activated carbon is classed as a high adsorption capacity adsorbent when it can remove more than 500 mg g^{-1} of substance/element/compound (ICA 2008).

Arsenic(V) and arsenic(III) adsorption onto CAC is adequately described by the Freundlich isotherm. The bigger the $1/n$ parameter the more favourable the adsorption. Values for the parameter $1/n$ for arsenic(V) are significantly lower (0.69

at 25 °C and 0.64 at 35 °C) than for arsenic(III) (1.24 at 25 °C and 0.89 at 35 °C). These values are slightly higher than those reported in Table 2.3.

Performance of adsorbents is usually compared in terms of the experimental adsorption capacity (q_{exp}), the Langmuir monolayer adsorption capacity (Q_m), or the Freundlich relative sorption capacity (K_F). However, these parameters are system dependent; they are valid for the experimental conditions from which they were derived. Rigorously speaking, comparisons of these parameters are not appropriate when experiments have been conducted at different experimental conditions. Langmuir and Freundlich models are simple representations of adsorption; they do not reflect the processes occurring at molecular or ionic level. However, they are the first steps to explore adsorption of new adsorbents which are not fully characterised.

To illustrate the dependence of the adsorption capacity on the experimental conditions, consider the case of arsenic adsorption with an iron-AC. For this adsorbent, Q_m was calculated at 6.6 mg g^{-1} at pH of 4.7 with arsenic initial concentrations up to 30 mg L^{-1} (Gu et al., 2005). Q_m of this adsorbent is much higher that that obtained for SC07. However, at arsenic(V) initial concentrations from 105 to 1,031 µg L^{-1}, a temperature of 25 °C, pH of 4.7 and adsorbent dose of 3 g L^{-1} percentage arsenic removal for the iron impregnated AC was from 15.8 to 99.5. These values are comparable with SC07 values of 94 per cent (for arsenic(V) at 227.9 µg L^{-1}) and 82 per cent (for arsenic(V) at 2,481.2 µg L^{-1}) at 20 °C, initial pH of 8, and adsorbent dose of 5 g L^{-1}.

7.6.4 Effect of competing water constituents (Cl^-, PO_4^{3-}, SO_4^{2-}, Mn^{2+}, Si) on arsenic(V) and arsenic(III) adsorption

Occurrence of competing anions with arsenic species is expected to have a negative effect on the arsenic(V) adsorption capacity of AC. According to the results presented in *Section 7.4*, arsenic(V) adsorption onto SC07 follows the order Mn^{2+} (0.1 mg L^{-1}) ≈ Mn^{2+} (0.4 mg L^{-1}) ≈ PO_4^{3-} (0.1 mg L^{-1}) > SO_4^{2-} (10 mg L^{-1}) ≈ Cl^- (25 mg L^{-1}) > PO_4^{3-} (10 mg L^{-1}) > Si (5 mg L^{-1}) > SO_4^{2-} (100 mg L^{-1}) > Cl^- (250 mg L^{-1}) ≈ Si (50 mg L^{-1}). Arsenic(III) adsorption onto SC07 follows the order Mn^{2+} (0.1 mg L^{-1}) ≈ Mn^{2+} (0.4 mg L^{-1}) ≈ PO_4^{3-} (0.1 mg L^{-1}) > Cl^- (25 mg L^{-1}) > SO_4^{2-} (10 mg L^{-1}) > PO_4^{3-} (10 mg L^{-1}) > SO_4^{2-} (100 mg L^{-1}) ≈ Si (5 mg L^{-1}) ≈ Cl^- (250 mg L^{-1}) ≈ Si (50 mg L^{-1}).

Arsenic adsorption onto CAC is affected by most of the ions tested; the only exception is SO_4^{2-} at 100 mg L^{-1}. Interestingly, the higher the concentration of PO_4^{3-} and SO_4^{2-} ions the smaller the negative effect on arsenic(III) adsorption. Silicate solutions were prepared from a reagent with a < 10 % v/v NaOH concentration; it is believed that the high concentration of OH^- had a significant detrimental effect on arsenic removal.

The equilibrium concentration diagrams of PO_4^{3-}, SO_4^{2-}, Mn^{2+} and Si, the ions used in the interfering ions experiment in *Section 7.4*, are presented below in Figure 7.17. Also, the effect of Cl^-, PO_4^{3-}, SO_4^{2-}, Mn^{2+} and Si on arsenic speciation can be seen on the equilibrium diagrams from Figure 7.18 to 7.22. Equilibrium diagrams were built in MINTEQ 3.0. The initial and final pH at which the adsorption experiments were carried on are marked in the diagrams with double pointed arrows. The PO_4^{3-} diagram (Figure 7.17a) is extremely similar to the arsenic(V) diagram presented in Figure 7.16. According to Figures 7.18 and 7.19 arsenic(V) and arsenic(III) speciation does not change with Cl^- concentrations up to 250 mg L^{-1} and PO_4^{3-} concentrations up to 10 mg L^{-1}.

For SC07 and the ions Cl^- and PO_4^{3-} the predominant species at pH_f are $HAsO_4^{2-}$ and $H_2AsO_4^-$ for arsenic(V) and $H_3AsO_3^0$ (≈ 100 per cent) for arsenic(III). Competition between arsenic(V) negatively charged ions and Cl^-, $H_2PO_4^-$, HPO_4^{2-} and PO_4^{3-} could explain the drop observed in arsenic adsorption. As shown from Figure 7.20 to 7.22, the predominant arsenic species at pH_f for SC07 and the ions SO_4^{2-}, Mn^{2+} and Si are $HAsO_4^{2-}$ and $H_2AsO_4^-$ for both arsenic(V) and arsenic(III) reactors. The relatively small effect of Mn^{2+} on arsenic(V) and arsenic(III) adsorption onto SC07 could be explained by the absence of negatively charged competing ions. For CAC and the ions Cl^- and PO_4^{3-}, $H_2AsO_4^-$ is the predominant species for arsenic(V) reactors and $H_3AsO_3^0$ is the predominant species for arsenic(III) reactors at pH_f. For the chemical species SO_4^{2-}, Mn^{2+} and Si, $H_2AsO_4^-$ is the predominant ion for arsenic(V) and arsenic(III) in CAC reactors at pH_f.

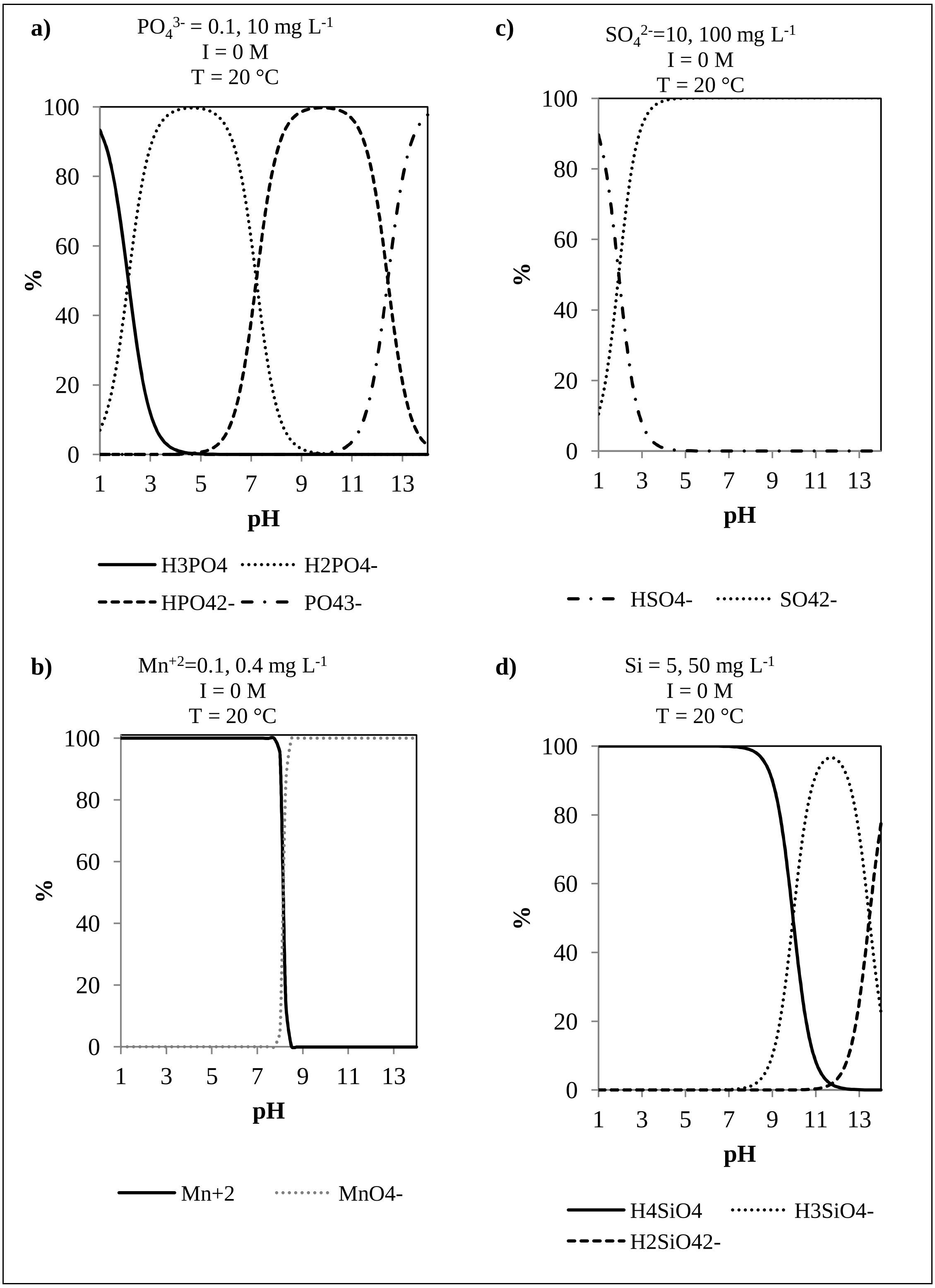


Figure 7.17 Equilibrium concentrations of the ions used in the interfering ions experiment (*Section 7.4*) at a ionic strength of 0 M and temperature of 20 °C. a) PO_4^{3-} concentration from 0.1 to 10 mg L^{-1}, b) Mn^{2+} concentration from 0.1 to 0.4 mg L^{-1}, c) SO_4^{2-} concentration from 10 to 100 mg L^{-1} and d) Si concentration from 5 to 50 mg L^{-1}.

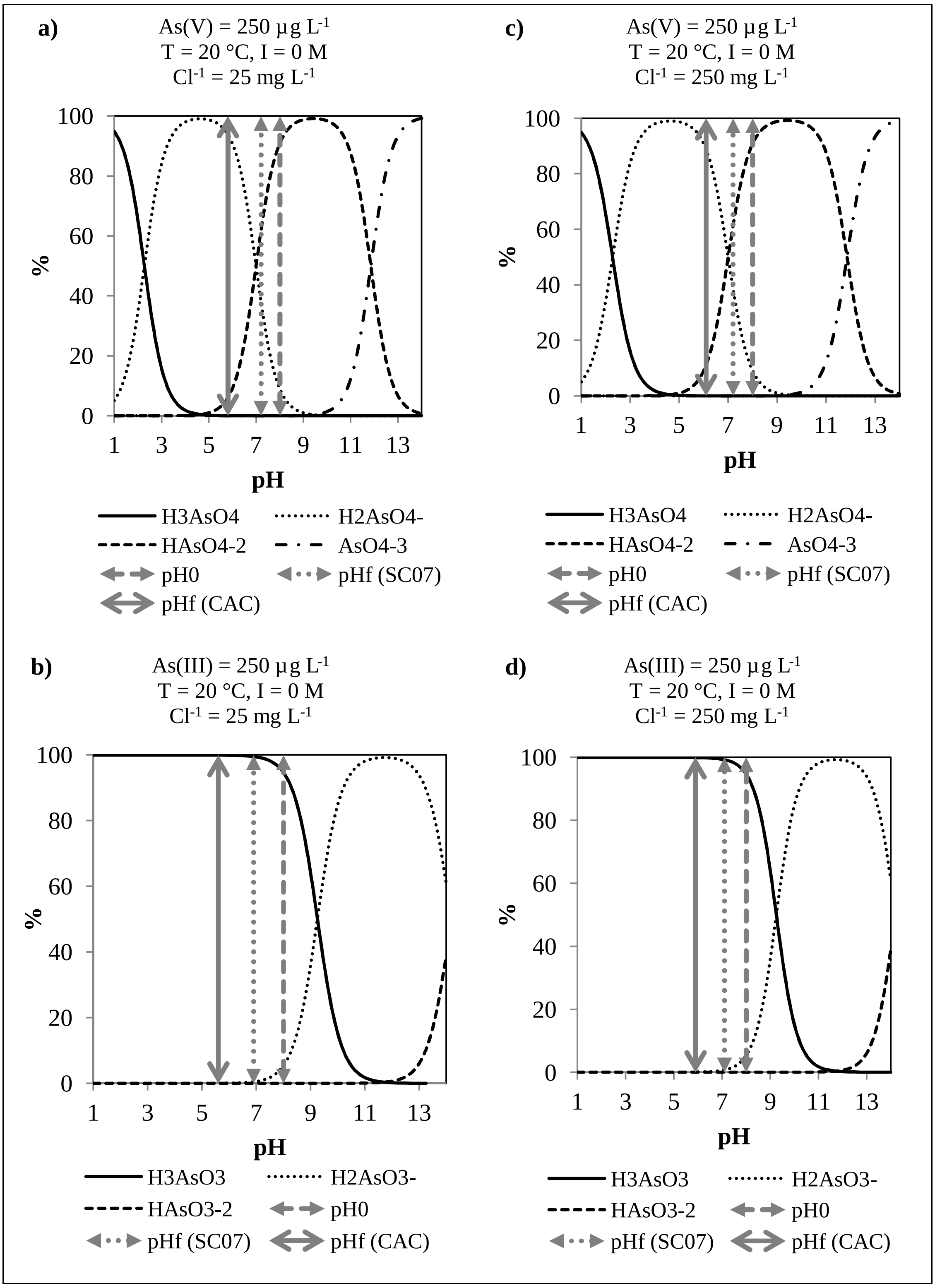


Figure 7.18 Equilibrium concentration of arsenic(V) and arsenic(III) species at a Cl^- concentration of 25 and 250 mg L^{-1} and at a ionic strength of 0 M and a temperature of 20 °C. The double pointed arrows indicate the initial and final pH adsorption experiments. a) arsenic(V) = 250 µg L^{-1} and Cl^- = 25 mg L^{-1}, b) arsenic(III) = 250 µg L^{-1} and Cl^- = 25 mg L^{-1}, c) arsenic(V) = 250 µg L^{-1} and Cl^- = 250 mg L^{-1} and d) arsenic(III) = 250 µg L^{-1} and Cl^- = 250 mg L^{-1}.

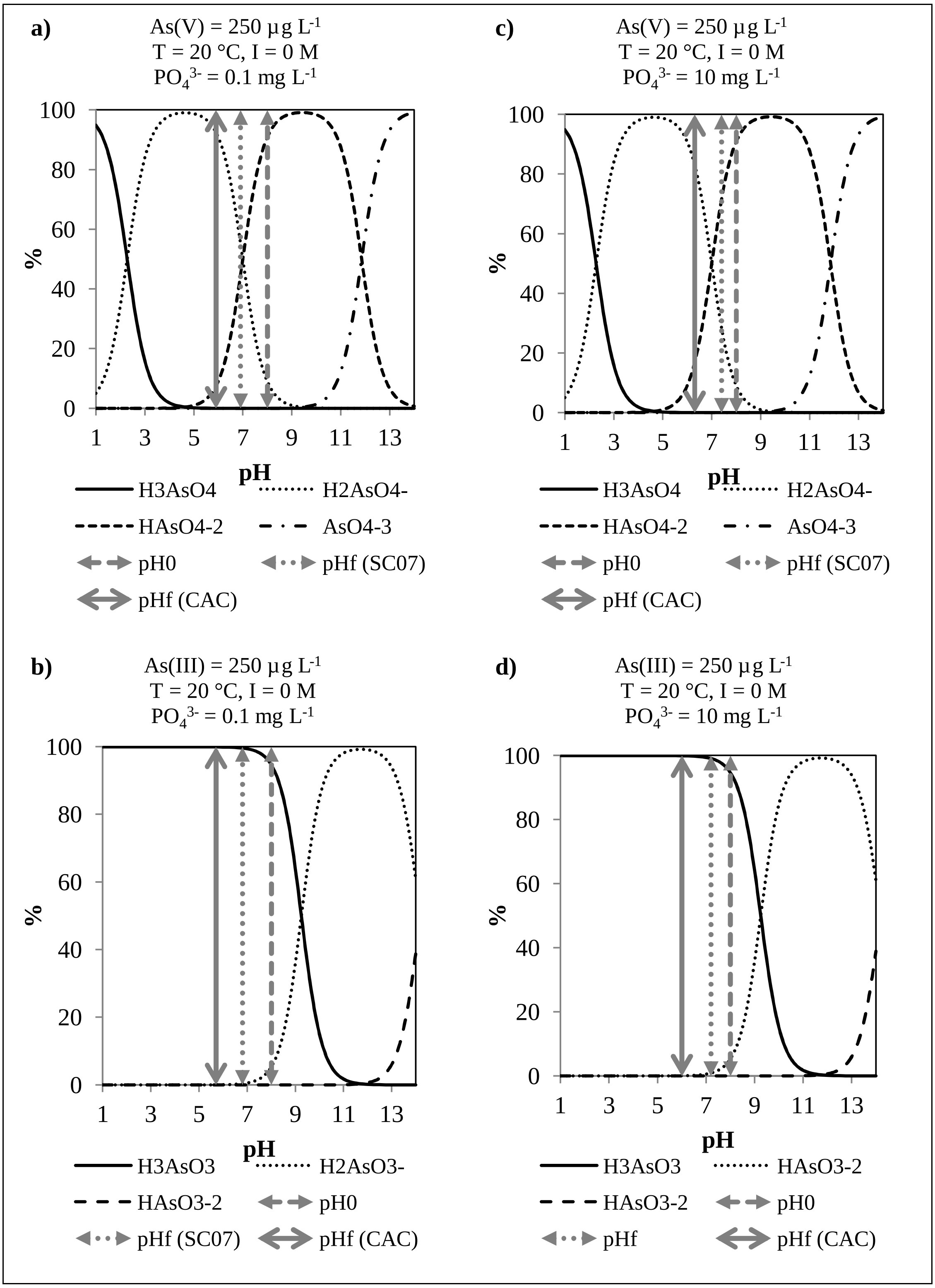


Figure 7.19 Equilibrium concentration of arsenic(V) and arsenic(III) species at a PO_4^{3-} concentration of 0.1 and 10 mg L^{-1} and at a ionic strength of 0 M and a temperature of 20 °C. The double pointed arrows indicate the initial and final pH of adsorption experiments. a) arsenic(V) = 250 µg L^{-1} and PO_4^{3-} = 0.1 mg L^{-1}, b) arsenic(III) = 250 µg L^{-1} and PO_4^{3-} = 0.1 mg L^{-1}, c) arsenic(V) = 250 µg L^{-1} and PO_4^{3-} = 10 mg L^{-1} and d) arsenic(III) = 250 µg L^{-1} and PO_4^{3-} = 10 mg L^{-1}.

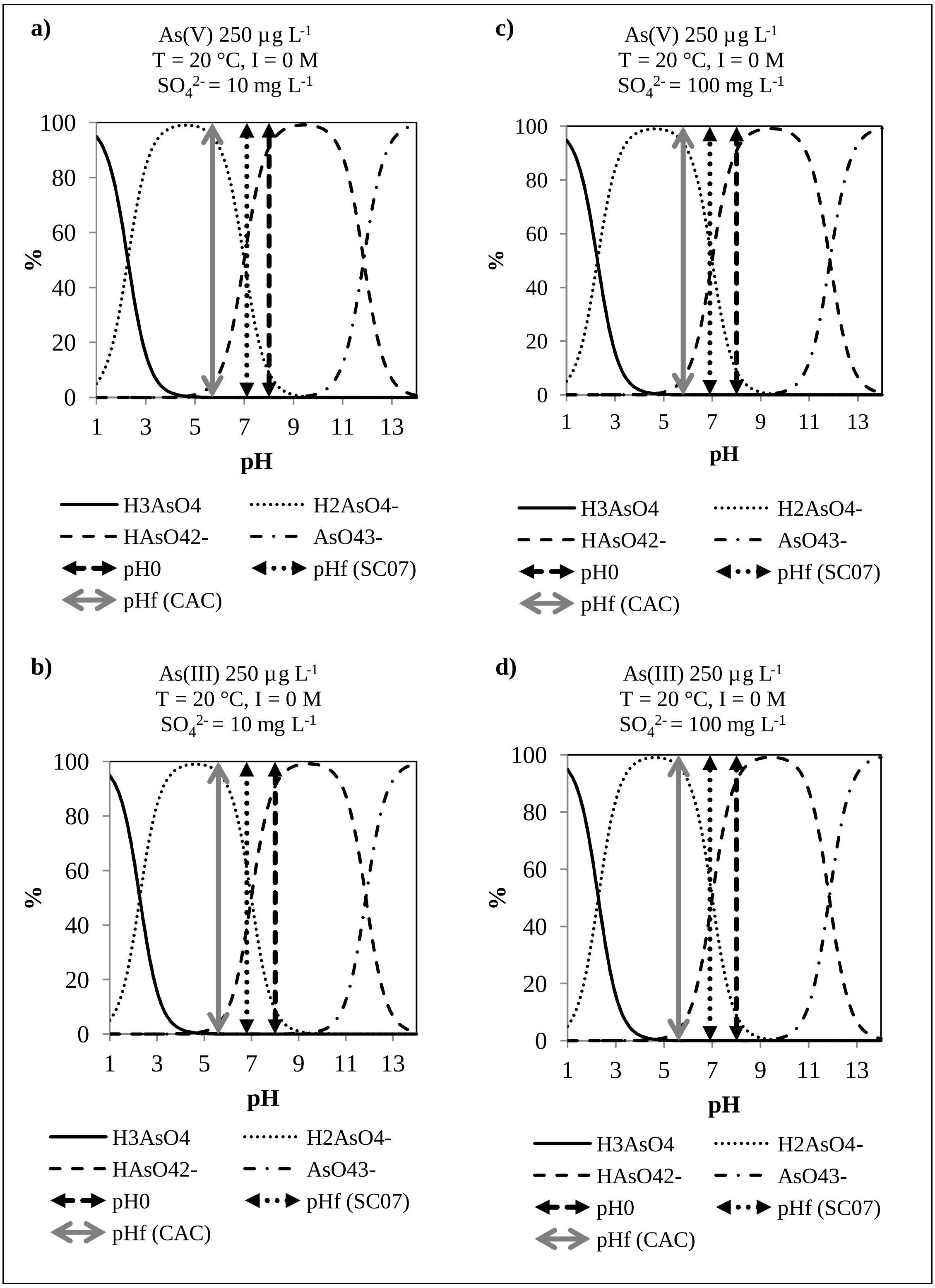


Figure 7.20 Equilibrium concentration of arsenic(V) and arsenic(III) species at a SO_4^{2-} concentration of 10 and 100 mg L^{-1} and at a ionic strength of 0 M and a temperature of 20 °C. The double pointed arrows indicate the initial and final pH of adsorption experiments. a) arsenic(V) = 250 µg L^{-1} and SO_4^{2-} = 10 mg L^{-1}, b) arsenic(III) = 250 µg L^{-1} and SO_4^{2-} = 10 mg L^{-1}, c) arsenic(V) = 250 µg L^{-1} and SO_4^{2-} = 100 mg L^{-1} and d) arsenic(III) = 250 µg L^{-1} and SO_4^{2-} = 100 mg L^{-1}.

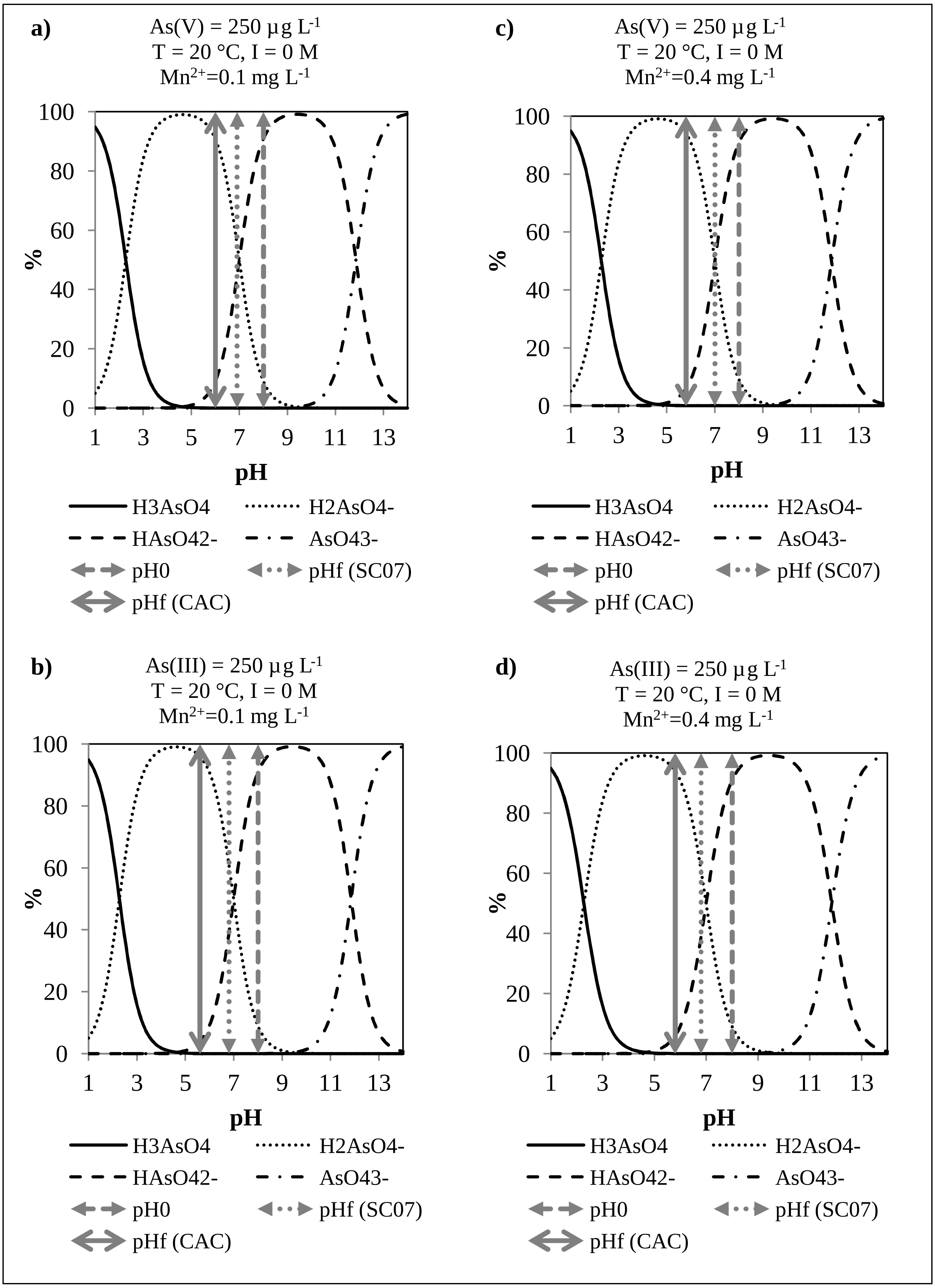


Figure 7.21 Equilibrium concentration of arsenic(V) and arsenic(III) species at a Mn^{2+} concentration of 0.1 and 0.4 mg L^{-1} and at a ionic strength of 0 M and a temperature of 20 °C. The double pointed arrows indicate the initial and final pH of adsorption experiments. a) arsenic(V) = 250 µg L^{-1} and Mn^{2+} = 0.1 mg L^{-1}, b) arsenic(III) = 250 µg L^{-1} and Mn^{2+} = 0.1 mg L^{-1}, c) arsenic(V) = 250 µg L^{-1} and Mn^{2+} = 0.4 mg L^{-1} and d) arsenic(III) = 250 µg L^{-1} and Mn^{2+} = 0.4 mg L^{-1}.

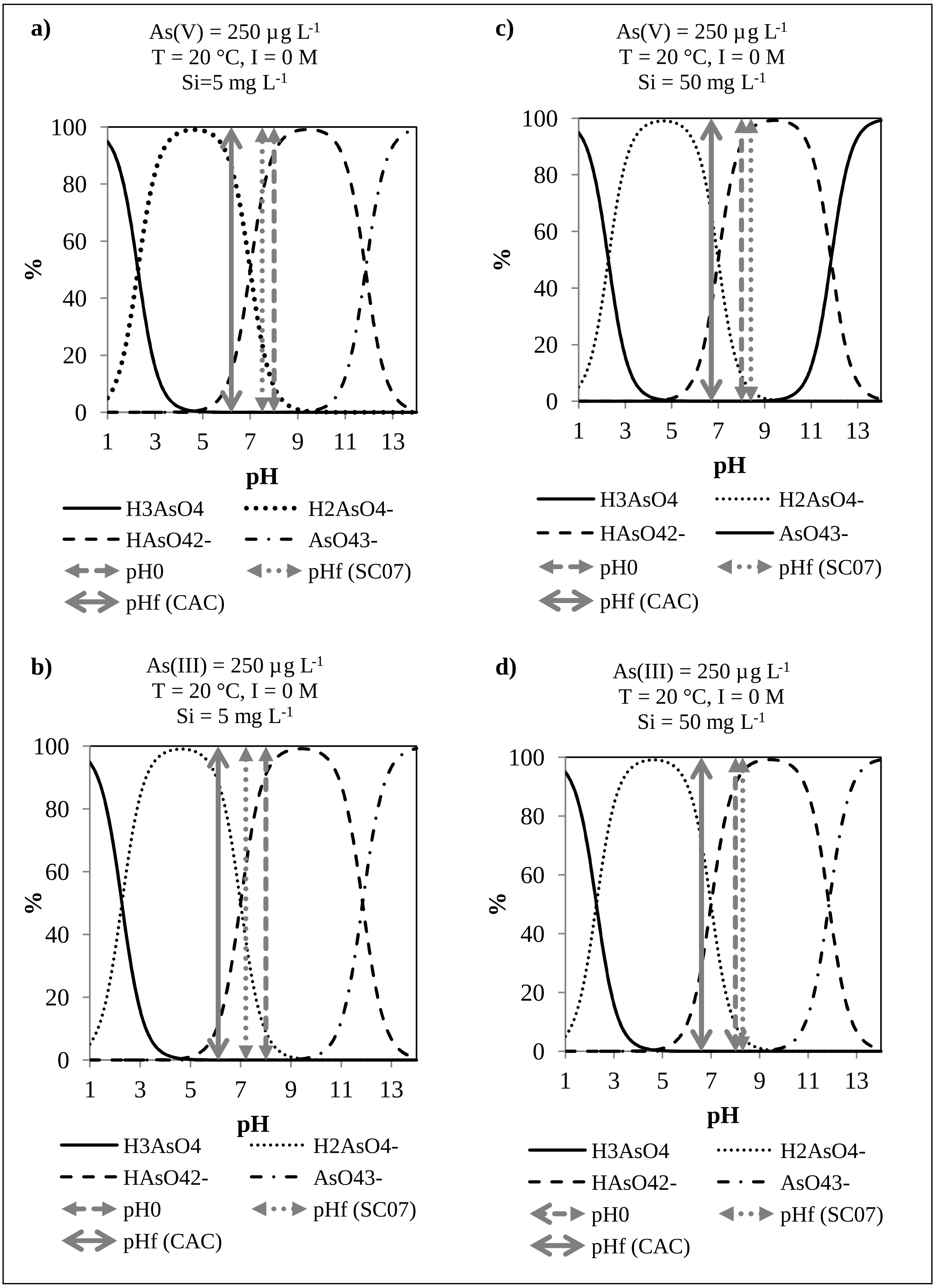


Figure 7.22 Equilibrium concentration of arsenic(V) and arsenic(III) species at a Si concentration of 5 and 50 mg L^{-1} and at a ionic strength of 0 M and a temperature of 20 °C. The double pointed arrows indicate the initial and final pH of adsorption experiments. a) arsenic(V) = 250 µg L^{-1} and Si = 5 mg L^{-1}, b) arsenic(III) = 250 µg L^{-1} and Si = 5 mg L^{-1}, c) arsenic(V) = 250 µg L^{-1} and Si = 50 mg L^{-1} and d) arsenic(III) = 250 µg L^{-1} and Si = 50 mg L^{-1}.

7.6.5 Simulation of column experiments for arsenic(V) and arsenic(III) adsorption with SC07 and CAC

The results of the simulation of column experiments suggest that in the best scenario CAC could remove arsenic below 10 or 50 µg L^{-1} for a maximum of 14 days. Also, these results indicate that the frequency of regeneration or change of adsorbent for SC07 would depend on the initial influent concentration and on the initial oxidation state of arsenic. The flow rate has no effect on the volume of water per gram of SC07 that can be treated before the arsenic concentration in the effluent is above 10 or 50 µg L^{-1}. However, the higher the flow rate the lower the number of days the column could remove arsenic below 10 or 50 µg L^{-1}.

Another factor that may have an effect on adsorption is the atomic radius of arsenic(V) and arsenic(III) ions. The atomic radius was estimated in 0.397 nm for $HAsO_4^{2-}$, 0.416 nm for $H_2AsO_4^-$ and $H_3AsO_4^0$, and 0.480 nm for $H_2AsO_3^-$ and $H_3AsO_3^0$ (Kim et al., 2004). The greater size of arsenic(III) ions and smaller percentage of arsenic(III) adsorption may indicate that there may also be a steric impediment for arsenic(III) adsorption. SC07 is a microporous adsorbent; the mode for pore width for SC07 is 1.5 nm (Table 6.6).

Overall, arsenic adsorption is faster with SC07 than with CAC. Arsenic adsorption is less sensitive to changes in the initial pH with CAC than with SC07. However, higher percentages of arsenic removal are achieved with SC07 than for CAC from pH > 4 to pH < 9. Adsorption with SC07 is less sensitive to the initial oxidation state of arsenic than CAC. The percentage of arsenic(V) and arsenic(III) removal, within the range of the initial arsenic concentration investigated during the isotherm experiment, was always higher with SC07 than with CAC at both 25 and 35 °C. Arsenic adsorption in the presence of the interfering water elements Cl^- at 25 mg L^{-1}, PO_4^{3-} at 0.1 and 10 mg L^{-1}, SO_4^{2-} at 10 mg L^{-1}, and Mn^{2+} at 0.1 and 0.4 mg L^{-1} is higher with SC07 than for CAC. For the ions Cl^- at 250 mg L^{-1}, SO_4^{2-} at 100 mg L^{-1}, and Si at 5 and 50 mg L^{-1} arsenic adsorption with SC07 is comparable to adsorption with CAC. In summary, adsorption is faster and adsorption capacity is higher and less affected by interfering ions with SC07 than with CAC.

7.7 Summary

Experiments were carried out to investigate the arsenic(V) and arsenic(III) adsorption capacity of SC07 and CAC. Separate experiments were run for arsenic(V) adsorption onto SC07, arsenic(III) adsorption onto SC07, arsenic(V) adsorption onto CAC and arsenic(III) adsorption onto CAC. An AC dose of 5 g L^{-1} was maintained in all tests. Experiments were run in triplicate and with a blank; with the average of the triplicates presented as the results. Adsorption performance is reported as the percentage of arsenic removal or the adsorption capacity in µg g^{-1}.

Firstly, the kinetics of arsenic(V) and arsenic(III) adsorption was investigated at two initial concentrations; ≈ 240 and 2,500 µg L^{-1}. Then, the effect of the initial pH of solutions was tested at arsenic(V) and arsenic(III) initial concentrations of 206-235 µg L^{-1} and pH values from 2 to 11. Next, sorption isotherms at 25 and 35 °C were investigated at initial arsenic(V) and arsenic(III) concentrations from 66 to 2,337 µg L^{-1} and initial pH of 8. Finally, the competing effect of the water constituents Cl^- (25 and 250 mg L^{-1}), PO_4^{3-} (0.1 and 10 mg L^{-1}), SO_4^{2-} (10 and 100 mg L^{-1}), Mn^{+2} (0.1 and 0.4 mg L^{-1}) and Si (5 and 50 mg L^{-1}) was investigated at an initial arsenic(V) and arsenic(III) concentration of ≈ 250 µg L^{-1}.

Arsenic(V) and arsenic(III) adsorption onto SC07 and CAC followed a pseudo-second order kinetic equation. Rate constants (k_2) from 2.14×10^{-5} to 4.19×10^{-3} and from 2.30×10^{-5} to 1.64×10^{-4} g µg^{-1} min^{-1} were found for SC07 and CAC, respectively. Arsenic adsorption was found to vary with initial pH values. Arsenic(V) and arsenic(III) adsorption onto SC07 followed a similar trend. Negligible arsenic adsorption onto SC07 occurs at pH ≤ 2 and pH ≥ 11. Adsorption with CAC is lower than for SC07 at most pH values, but CAC is more robust to changes in initial pH.

Arsenic(V) and arsenic(III) experimental adsorption isotherms are adequately described by the Langmuir isotherm, whereas arsenic adsorption onto CAC is adequately described by the Freundlich isotherm. For SC07, the adsorption monolayer capacity in µg g^{-1} (Q_m) and affinity parameter in L µg^{-1} (b) were 481 and 4.82×10^{-3} for arsenic(V) at 25 °C, 653 and 3.20×10^{-3} for arsenic(V) at 35 °C, 557 and 2.15×10^{-3} for arsenic(III) at 25 °C, and 619 and 1.40×10^{-3} for arsenic(III) at 35 °C. For CAC, the Freundlich relative adsorption capacity (K_F) and the Freundlich parameter related to the energy of adsorption (1/*n*) were 0.64 and 0.69 for arsenic(V) at 25 °C, 0.97 and 0.64 for arsenic(V) at 35 °C, 3.61×10^{-3} and 1.24 for arsenic(III) at 25 °C, and 9.07×10^{-2} and 0.89 for arsenic(III) at 35 °C.

Arsenic(V) and arsenic(III) are affected in a similar way by the water constituents investigated. Arsenic(V) adsorption onto SC07 was negligible with solutions spiked with Cl^- at 250 mg L^{-1} and with Si at 50 mg L^{-1}. The negative effect of PO_4^{3-} at 0.1 mg L^{-1}, and Mn^{2+} at 0.1 and 0.4 mg L^{-1} on arsenic(V) adsorption was small. Arsenic(V) and arsenic(III) adsorption onto CAC was affected by all chemical species but especially by PO_4^{-3} at 10 mg L^{-1} and Si at 50 mg L^{-1} for which it falls to below 10 per cent. The size of the negative effect is directly related to the concentration of the chemical species; with the exception of arsenic(III) adsorption onto CAC for which arsenic adsorption is less affected by SO_4^{2-} and PO_4^{3-} at high rather than at low concentrations.

Column simulation experiments show that arsenic(V) and arsenic(III) could be removed below 10 or 50 µg L^{-1} with CAC (adsorbent mass=10 Kg, arsenic influent concentration 250-1,000 µg L^{-1}, flow rate = 2.5-5.0 L h^{-1}) for a maximum of 14 days. Column simulation experiments for SC07 indicate that the volume of water treated by mass of adsorbent before the concentration in the effluent is above 10 or 50 µg L^{-1} depends on the concentration on the influent and the oxidation state of arsenic. A higher volume of water by mass of adsorbent can be treated for lower arsenic concentrations and arsenic(V). The flow rate does not have an effect on the volume of water treated per gram of adsorbent, but does have an effect on the number of days that the column could remove arsenic below 10 or 50 µg L^{-1} (Table 7.3).

Possible adsorption mechanisms for arsenic are ion exchange and formation of inner and outer complexes. Although the specific mechanism is unknown, since the surface chemistry of AC is still an area of active research, some observations can be made. The driver for arsenic(III) adsorption is the small concentration of the $H_2AsO_3^-$ ion present in solution, for the equilibrium to be maintained the reaction ($H_3AsO_3^0 = H_2AsO_3^- + H^+$) moves towards the right side. Also, results obtained in the variation of initial pH experiment, in which high arsenic(III) adsorption was observed at unfavourable electrostatic conditions, suggests that arsenic(III) is oxidised to arsenic(V) prior to adsorption and that adsorption of arsenic(III) is not fully regulated by electrostatic attraction. In the case of arsenic(V) adsorption onto

SC07 and CAC electrostaticaly favourable conditions were maintained throughout the adsorption, with the pH of the solution < pH_{ZC}. Finally, the size of arsenic ions and pores of SC07 may have an effect on adsorption, the pore size mode for SC07 is 1.5 nm and the atomic radius for arsenic(V) ions is 0.397-0.416 nm and for arsenic(III) ions is 0.480 nm.

8. Discussion

Access to clean water is of critical importance for human development; halving the proportion of people without sustainable access to safe drinking water is part of the 2015 United Nations Millennium Development Goals to eradicate extreme poverty (UN 2011). However, drinking water and sanitation programmes have failed to engage international attention and economic funds comparable to AIDS/HIV or malaria programmes (Bartram et al., 2010; McCann 2007).

Microbiological contamination and the occurrence of fluoride, arsenic and nitrate are the main hazards to human health in drinking water. Many middle and low income countries (MLICs) were already struggling to increase coverage of microbiologically-safe water when the natural occurrence of arsenic in aquifers worldwide was discovered. This was the case for Bangladesh; during the early 1990s this country almost achieved universal coverage of drinking water, but in 1984 widespread occurrence of arsenic was suspected and in 1998-1999 was confirmed with a hydro-chemical survey (Atkins et al., 2007; BGS 2001).

From the early stages in this research, it was obvious that the development of an adsorbent for arsenic removal in middle and low income countries (MLICs) required a multidisciplinary approach. This was reflected in the aims of the thesis: to investigate some of the issues affecting implementation of arsenic mitigation programmes in MLICs and to evaluate the feasibility of using sugarcane activated carbon (SCAC) as a low-cost arsenic adsorbent for water treatment.

The importance of social sciences in implementing effective solutions to complex environmental problems was acknowledged in the literature review (*Section 2.4*). On one hand, natural sciences significantly influence the identification of potential environmental problems. Yet on the other hand, social sciences are key in understanding the cultural, social and political processes that shape environmental problems (Hannigan 2006).

In the case of arsenic mitigation, social sciences can be applied during the implementation phase of programmes. Cultural factors need to be incorporated in health education campaigns and arsenic awareness programmes. Also, social sciences have been applied to the study of the problems caused by arsenic contamination in Bangladeshi society (Sultana 2007a, 2007b, 2006a, 2006b; Hanchett 2004, 2002).

Through the years the approach to increase drinking water coverage has evolved; it has gone from a position in which technological and engineering aspects were central to a position in which social, political and cultural aspects are also important (Coates et al., 2005; Regmi et al., 1999; Bell et al., 1995). It is widely recognised that access to drinking water is affected not only by distance to water sources and the mere existence of water infrastructure but also by customary water rights, affordability of water options, and household preferences (Sultana 2007b; White 1972).

The extensive experience in sanitation and water programmes has demonstrated to some extent that subsidies for hardware do not benefit the poor and, more importantly, may retard the long-term adoption of hardware. For instance, sanitation in Bangladesh took off when the *Community led total sanitation programme* adopted the policy to not subsidise latrines (WAB 2011). Subsidised hardware creates problems with long-term sustainability of programmes making them vulnerable to withdrawal of funding, and failing to create ownership and demand for hardware. On the other hand, the current approach to favour programmes in which users are able to contribute towards the capital cost of water infrastructure and to the full cost of operation and maintenance strongly limits the capacity of the poorest to access water programmes (Hanchett 2004). Hence, a careful balance has to be achieved between cost-recovery, long-term sustainability and access to clean water.

The pace and effectiveness of delivery of arsenic mitigation programmes in some MLICs has been extensively criticised. In the survey conducted as part of this research, the median efficiency for arsenic mitigation programmes in Bangladesh was 4.5/10.0 (*Section 3.4.2*). According to the survey results and in the literature, advances in arsenic mitigation in Bangladesh have been modest. In part, this is due to the scale of contamination found in Bangladesh and the huge number of water wells (> 11 millions). However, political, social, and cultural issues have also played an important role.

In Bangladesh, tube well water and piped water are the options with highest user acceptability. However, these are unavailable to water users under some circumstances. Then, the use of removal technologies is necessary to make surface water microbiologically-safe or groundwater arsenic-safe. Water treatment in some regions, especially in rural areas, depends on water users.

Non-governmental organisations (NGOs) have implemented programmes, with various degrees of success, for removal of microbiological contamination with low-cost technologies in many MLICs for more than 20 years (McCann 2007). Most of these programmes share the same weakness; the limited follow up of the programme and technologies, the lack of an independent evaluation of the performance of technologies and of the programme, the tendency to measure effectiveness of programmes with the hardware that was delivered, and the constant requirement of health education and technology training programmes to increase the likelihood that technologies are consistently and correctly used. The survey results in this study suggest that some arsenic mitigation programmes have the same limitations.

Measuring effectiveness of programmes in terms of delivery of technologies can be misleading since it does not account for the actual use and access to hardware (in community-based options). In the case of arsenic mitigation in Bangladesh, a survey respondent mentioned that the lack of follow up of programmes was causing a mismatch between the number of people accessing arsenic-safe water options on paper and for real. According to the literature, arsenic removal technologies are generally abandoned after a few days of usage (Hoque et al., 2004; Johnston 2001).

Eighty six per cent of respondents surveyed in this study considered that there are problems affecting arsenic mitigation programmes in MLICs (*Section 3.4.6*). Political issues and technological issues accounted for 50 per cent of responses in the survey: the role of government and NGOs in implementing, administering and monitoring programmes; sustainability of programmes; coordination of mitigation actions between the government, NGOs and water users; and availability of arsenic-safe water options were all cited as issues. The role of NGOs in implementing development programmes in MLIC has been extensively and critically reviewed in the literature (Easterly et al., 2006).

The response of the public to arsenic mitigation programmes has been low. The general opinion is that arsenic mitigation is not a priority for much of the affected population (Caldwell et al., 2005; Paul, 2004). This may in part be due to the low awareness of the public to their personal risk to arsenic and lack of knowledge about the available options to them for reduction of exposure to arsenic. However, some individuals are aware of the health risk associated with arsenic and continue to drink arsenic contaminated water (see the knowledge-behaviour gap in *Section 3.5.6*). This could be compared to cigarette smoking; people keep on smoking regardless of the well known health impacts of tobacco.

Some characteristics of arsenic may contribute also to the low uptake of mitigation programmes. First, arsenic is tasteless, odourless, and colourless. Second, the latency period for chronic arsenic poisoning is from 5 to 20 years. Thirdly, water treatment is an additional work load for women or girls, who are mainly responsible for collecting household water in some MLIC.

Regarding arsenic removal technologies, good performance is just one of the many requirements for their successful implementation. In the opinion of some of the respondents of the survey there is no technology capable of producing chemically- and microbiologically-safe water. Results from the survey suggest that the following operation and maintenance issues need addressing (*Sections 3.4.4* and *3.4.5*): amount and quality of water treated, availability of spare parts, ease of operation and maintenance, frequency of maintenance routines, adequate training to users, support for monitoring microbiological and chemical quality of water and for regeneration or replacement of the arsenic removal media.

From the few field trials of arsenic removal technologies that have been independently carried out, it is apparent that performance of different units of the same technology is not uniform, and that performance of a technology unit may vary with time (Chiew et al., 2009; Noubactep 2009; BCSIR 2003; Sutherland et al., 2001). The importance of monitoring arsenic concentrations in water produced by arsenic removal technologies was raised in the survey. In this regard, logistics for testing of arsenic concentrations not only for removal technologies but also other arsenic-safe options should be accounted for during the planning stage.

For all the limitations of low-cost technologies, there have been some successful experiences. For instance, the Kanchan and Sono filters have been successfully field tested in some regions in Asia. Also, an independent assessment of 11 different types (18 units) of arsenic removal technologies in India found that 3 units were in use after two years, but only two technologies achieved consistent removal below 50 µg L^{-1} (*Section 2.3.1*) (Hossain et al., 2005). According to the literature available, the most efficient arsenic removal technologies are based on iron-containing removal media; however performance of these technologies strongly depends on the iron-arsenic ratio found in raw water (EPA 2005). Hence, the need to develop treatments for arsenic contaminated waters with non-optimum iron content.

The use of chemicals in low-cost technologies is undesirable since there are some inherent risks. Firstly, inadequate disposal of different technologies (or the arsenic removal media contained in them) is a cause of concern because arsenic and other chemicals may leach into the environment. If use of arsenic removal technologies becomes widespread, then this issue is more relevant. Of the survey respondents, 67 per cent considered that arsenic removal technologies were a potential contamination source. Secondly, chemicals present in arsenic removal media could leach into the treated water. Finally, use of chemicals in the manufacturing of adsorbents could be problematic in a rural environment.

Activated carbon (AC) made from agricultural wastes was considered to be an attractive option for use in low-cost technologies due to its widespread use in water treatment for removal of organic compounds, taste, odour and dissolved organic matter. Also, research suggested that AC may oxidise arsenic(III) to arsenic(V) (Budinova et al., 2009). In addition, AC does not contain chemicals that may change the chemical composition of water.

The main issues to overcome with AC for arsenic adsorption were identified in this research as its relatively high cost and its low arsenic adsorption capacity. Sugarcane bagasse is a by-product of the sugar refinery industry. Currently, sugarcane bagasse is burnt to produce energy for the sugar refinery process and excess bagasse is disposed of. Burning of sugarcane bagasse is an energetically inefficient process. Gasification processes, still under development, could simultaneously produce fuels and AC (Manahan et al., 2007). Sugar refinery plants could use the fuel produced in gasification for the refinery process and also sell the AC. Alternatively, sugarcane activated carbon (SCAC) could be produced with a similar process to commercially available carbon. Hence, use of agricultural by-products for production of AC has the potential to add income to deprived agricultural rural areas.

In this research, the use of SCAC for arsenic adsorption in MLIC settings was investigated. The development of the adsorbent consisted of three stages. First, the optimisation of the preparation conditions of SCAC for maximising arsenic(V) and arsenic(III) adsorption. Then, SCAC samples were characterised to determine the strength of the relationship of the properties of SCAC and arsenic adsorption. Finally, adsorption batch experiments were conducted at different conditions to estimate the adsorption capacity of SCAC. Adsorption experiments with the lignite granular activated carbon type Darco® 12x20 (CAC) were conducted in parallel.

The preparation of SCAC was optimised using a 2^3 factorial experimental design. This approach was chosen due to the limited available information of arsenic adsorption with SCAC and the relative large number of variables involved in preparation of SCAC. This design permitted the study of three preparation variables (factors) at two different levels. The effect of the preparation conditions on arsenic adsorption can be clearly observed in the results presented in Table 5.2. Thus, making a case for optimisation of the synthesis of materials not only for adsorption of arsenic, but also for removal of other target contaminants.

The factorial design successfully identified the factors and combination of factors with an effect on arsenic adsorption and on yield, and the experimental conditions at which arsenic adsorption was maximised with SCAC. Carbonisation temperature, activation temperature, and the interaction between activation temperature and activation time have a statistically significant effect ($p < 0.050$) on arsenic(V) and arsenic(III) removal percentage and yield. Activation time has a statistically significant effect ($p < 0.050$) on yield and arsenic(III) percentage removal. The interaction between carbonisation temperature and activation temperature has a statistically significant effect ($p < 0.050$) on arsenic(V) percentage removal.

The combination of factors that maximise arsenic(V) and arsenic(III) adsorption were a carbonisation temperature from 700 to 850 °C and an activation temperature of 900 °C. However, these combinations produce AC samples with low yield (10-13.5 per cent). High temperatures and low yield are undesirable since they can increase the production cost of adsorbents. A limitation of this experimental design is the assumption of a linear relationship between the two levels of each factor studied. In the case of activation temperature and arsenic adsorption, this assumption was proved wrong with an additional experiment.

Modelling of the effect of the preparation conditions of SCAC on arsenic adsorption was an additional advantage of the factorial experimental design. This allowed prediction of the effect of small variations in the preparation conditions on arsenic adsorption. In this case, arsenic adsorption is highly sensitive to activation temperature. Hence, the temperature of the process has to be carefully monitored to ensure the adsorption capacity of the AC would not be affected. Some suspicion exists regarding the feasibility of this in a MLIC setting. Since adsorbents prepared at different temperatures are indistinguishable to the naked eye, substantial savings may be achieved by reducing the values of preparation temperatures.

Five different types of SCAC were characterised with the aim of identifying the properties that may have an effect on arsenic adsorption (*Chapter 6*). The properties analysed were the pH of zero charge (pH_{ZC}) with the immersion technique, topographic analysis with scanning electron microscopy, surface area and pore size distribution with gas adsorption, and particle size distribution with laser diffraction. The characterised SCAC samples had arsenic removal percentages from 2.8 to 93.

The role of the pH_{ZC} on arsenic adsorption is unclear; in electrostatic terms arsenic(V) is favourable with all SCAC samples but not with CAC at the pH at which the factorial experiment was conducted. However, CAC has higher arsenic(V) and arsenic(III) adsorption capacity than SCAC samples SC05 and SC06. Also, SCAC samples SC07 and SC05 have similar pH_{ZC} but very different arsenic adsorption capacity. This suggests that electrostatic attraction is not the only process controlling arsenic adsorption onto SCAC.

The percentage of arsenic(V) and arsenic(III) removal and the properties of AC samples are summarised in Figures 6.15 and 6.16. The Pearson test, run exclusively for SCAC samples, found a strong and positive correlation ($R = 0.939$, $p = 0.018$) for surface area, and a strong and negative correlation for micropore/pore volume ratio ($R = -0.975$, $p = 0.005$) and percentage of sand-size fraction ($R = -0.960$, $p = 0.010$) for arsenic(V) percentage removal (Table 6.10). For percentage of arsenic(III) removal a strong and positive correlation ($R = 0.956$, $p = 0.011$) for surface area, and a strong and negative correlation for micropore/pore volume ratio ($R = -0.968$, $p = 0.007$) and percentage of sand-size-fraction ($R = -0.960$, $p = 0.007$) were found (Table 6.10).

Since the Pearson test can be used only to analyse sets of data with linear relationships, surface area was the only variable where the strength of the relationship with arsenic per cent removal could be tested for the CAC sample and the SCAC samples. Surface area was correlated with arsenic(V) ($R = 0.938$, $p = 0.006$) and arsenic(III) ($R = 0.942$, $p = 0.005$) percentage removal (Table 6.11).

The Pearson test proves that there is a relationship between the variables, but it does not prove that this relationship is causal. The relationships between surface area, micropore/pore volume ratio and adsorption have been observed with organic compounds (Mohan el at., 2007; Mondal el at., 2007). However, adsorbents with higher surface areas do not always have higher adsorption capacities for metals (Mohan el at., 2007). In a study by Juang *et al.* (2002), calcium content and surface area of calcium chloride activated rice husk carbon were directly proportional to arsenic(III) adsorption capacity. However, it is not clear if high adsorption capacities where causally related to calcium content, surface area or both. The relationship between percentage of sand-size-fraction and arsenic adsorption can be explained in terms of the well known inverse relationship between surface area and particle size.

According to the results of the optimisation of the preparation parameters of SCAC, the sample SC07 was used to estimate the arsenic adsorption capacity of SCAC under different experimental conditions (*Chapter 7*). The sample SC07 was prepared at a carbonisation temperature of 700 °C, an activation temperature of 900 °C and an activation time 180 min. Adsorption experiments were run for the CAC sample in parallel.

Kinetics of arsenic(V) and arsenic(III) adsorption onto SC07 and CAC fit the pseudo-second order model at initial concentrations of ≈ 250 and 2,500 $\mu g\ L^{-1}$, and initial pH of 8 (*Section 7.1*). Most arsenic(V) adsorption onto SC07 occurred during the first 15-30 minutes; arsenic(III) adsorption onto SC07 was slower than arsenic(V) adsorption. Arsenic(V) and arsenic(III) adsorption onto CAC increased gradually with time.

Arsenic removal is more sensitive to initial pH values with SC07 than with CAC and more sensitive to changes in the initial arsenic oxidation state with CAC than with SC07 (*Section 7.2*). The similar trend in arsenic(V) and arsenic(III) adsorption with SC07 observed in this experiment and the relatively high arsenic(III) adsorption at pH > 8 with CAC (when the concentration of the ion $H_2AsO_3^-$ steadily increases and the surface of the adsorbent is negatively charged) suggest that some arsenic(III) is oxidised to arsenic(V) prior to adsorption and that arsenic adsorption is not fully controlled by electrostatic forces.

Adsorption is nearly always an exothermic phenomenon; hence increments in temperature should lead to a decrease in adsorption. However, the effect of temperature from 25 to 35 °C observed in this research on arsenic adsorption is from very small to negligible (*Section 7.3*). Experimental adsorption data for SC07 fit the Langmuir isotherm and for CAC fits the Freundlich isotherm. The monolayer adsorption capacity (Q_m) of SC07 for arsenic(V) at 25 °C was 481 µg g^{-1}, for arsenic(V) at 35 °C was 653 µg g^{-1}, for arsenic(III) at 25 °C was 557 µg g^{-1}, and for arsenic(III) at 35 °C was 619 µg g^{-1}. The Freundlich relative adsorption capacity (K_F) of CAC for arsenic(V) at 25 °C was 0.64 (µg g^{-1}) (L µg^{-1})$^{1/0.69}$, for arsenic(V) at 35 °C was 0.97 (µg g^{-1}) (L µg^{-1})$^{1/0.64}$, for arsenic(III) at 25 °C was 3.61×10^{-3} (µg g^{-1}) (L µg^{-1})$^{1/1.24}$, and for arsenic(III) at 35 °C was 9.07×10^{-2} (µg g^{-1}) (L µg^{-1})$^{1/0.89}$.

Arsenic adsorption is negatively affected by the interfering water elements Cl^-, PO_4^{3-}, SO_4^{2-}, Mn^{2+} and Si with both SC07 and CAC. Overall, arsenic(III) adsorption is affected less by the presence of other water constituents than arsenic(V) adsorption with SC07 (*Section 7.4*). Cl^- at 250 mg L^{-1} and Si at 50 mg L^{-1} reduced to negligible levels arsenic(V) adsorption onto SC07. Arsenic adsorption in the presence of Si is believed to have been affected by the high concentration of NaOH of the Si solution. The negative effect of PO_4^{3-} at 0.1 mg L^{-1} and Mn^{2+} at 0.1 and 0.4 mg L^{-1} is very small with SC07. In the presence of Cl^- at 25 mg L^{-1}, PO_4^{3-} at 0.1 and 10 mg L^{-1}, SO_4^{2-} at 10 mg L^{-1}, and Mn^{2+} at 0.1 and 0.4 mg L^{-1}, arsenic adsorption is higher with SC07 than with CAC. For the ions Cl^- at 250 mg L^{-1}, SO_4^{2-} at 100 mg L^{-1} and Si at 5 and 50 mg L^{-1}, arsenic adsorption with SC07 is comparable to adsorption with CAC.

The column simulation experiments suggest that a filter containing 10 Kg of SC07 adsorbent continuously working at a flow rate of 2.5 L h^{-1} (5 L h^{-1}) could remove arsenic(V) below 10 µg L^{-1} from 183 days (91 days) at arsenic(V) influent concentration of 250 µg L^{-1} to 130 days (65 days) at arsenic(V) influent concentration of 1,000 µg L^{-1}; and from 115 days (57 days) at arsenic(III) influent concentration of 250 µg L^{-1} to 57 days (45 days) at arsenic(III) influent concentration of 1,000 µg L^{-1} of otherwise clean water. Also, a filter containing 10 Kg of SC07 adsorbent would occupy a volume of 26 L and could treat a maximum of 60 L per day at a flow rate of 2.5 L h^{-1}. Then, the filter could be used for a family and would require a significant space for placing the technology and storing the treated water. Although in terms of the weight and volume of water treated could be possible to have a smaller filter (adsorbent weight = 500 g) for use in the inside of the house the volume that occupies the adsorbent (1.3 L) may make this impractical. The feasibility of using SC07 filters would be attached to the frequency of replacement of the adsorbent and the willingness of the users to replace the adsorbent.

Overall, the performance of the SCAC sample SC07 for arsenic adsorption was better than performance of the CAC sample. SC07 has higher adsorption capacity, and adsorption is faster and less affected by interfering ions. In addition, the pH of water treated with SC07 was within the pH of most natural waters, 6.5-8.5. The pH of water treated with CAC was below 6 in some experiments.

The concentration of the ion $H_2AsO_3^-$ (< 1%) is considered one of the main drivers for arsenic(III) adsorption. At the pH at which the adsorption experiments were carried out (≈8), arsenic(III) is mostly neutrally charged ($H_3AsO_3^0$) and the SC07 surface has a positive net charge. Then, when $H_2AsO_3^-$ ions are adsorbed the reaction ($H_3AsO_3^0 = H_2AsO_3^- + H^+$) moves towards the right side to maintain the equilibrium. Adsorption data suggest also that arsenic(III) may undergo oxidation to arsenic(V), and the size of arsenic(III) ions and arsenic(V) ions may also influence adsorption in the pores of SC07, which is a microporous adsorbent.

Comparison of the performance of SCAC with other arsenic adsorbents is more complex. In general, adsorption capacity and percentage of adsorption are used as indicators of the adsorbent ability to remove pollutants from solution. However, these values are very much dependent on the experimental conditions for which they were obtained. In this regard, the adsorption capacity of the SCAC is considerably lower to that of other adsorbents. However, the initial concentration of arsenic used in this research is lower (up to 2.7 mg L^{-1}) than those used by other researchers (150 mg L^{-1} and higher).

The concentration range in this research was chosen in agreement with the arsenic concentrations found in most groundwater. A relatively low arsenic adsorption capacity does not always mean that the adsorbents will perform poorly. For instance, Muñiz *et al.* (2009) successfully removed arsenic from natural well water from Mexico with an iron impregnated carbon with a maximum adsorption capacity of 36.0 µg g^{-1}.

Finally, Table 8.1 presents the cost of removing one gram of arsenic for the Sono filter (a system field tested in Bangladesh), the commercially available activated alumina AAFS50 from Alcan Activated Speciality Aluminas (used in the USA for arsenic removal in central water treatment systems) and the SCAC produced in this research. The comparison is limited due to the data available for each adsorbent; the cost for the Sono filter was obtained in 2007 US$, the cost of the activated alumina was obtained in 2011 US$, and the cost of the SCAC in this research is an estimation by Ng *et al.* in 2003 US$. The cost estimation of SCAC assumes that the adsorbent was prepared using technology and processes similar to those used in production of conventional AC. This cost includes the equipment cost and capital cost of installing the production plant.

Table 8.1 Comparison of the cost (in US$) of adsorbing one gram of arsenic with Sono filter, Alcan activated alumina and SCAC.

Adsorbent	Adsorption capacity	Cost of adsorbing 1 g of arsenic	References
	mg g^{-1}	US$	
Sono	0.2-17.6	2.5×10^{-6}-2.4×10^{-4}	Hussam et al., 2007
Alcan activated alumina	1.1 (pH 6.5)	6.2	Binkowski 2011
	0.2 (pH 8.5)	34.2	ASA 2005
SCAC	0.653 (pH 8, As(V), 35°C)	4.8	
	0.619 (pH 8, As(III), 35 °C)	5.0	This research
	0.481 (pH 8, As(V), 25°C)	6.5	Ng et al., 2003
	0.557 (pH 8, As(III), 25 °C)	5.6	

A direct comparison between the Alcan activated alumina, the SONO filter and the SCAC is not strictly possible since the arsenic adsorption capacity for the Sono filter was calculated from the total arsenic adsorbed from actual filters that have been continuously running for 2.3-4.5 years; and for the adsorption capacity of activated alumina and the SCAC the values were derived from batch adsorption experiments only. Nevertheless, the cost of adsorbing a gram of arsenic with the Sono filter is extremely low. The estimated cost of removing one gram of arsenic with the SCAC is comparable if not lower that with the Alcan activated alumina. Also, the production of SCAC has the additional advantage of using an agricultural by-product of the sugar refinery industry; reducing disposal in landfills. In addition, gasification processes could generate fuels to power the sugar refinery process and AC for water treatment (Manahan et al., 2007).

9. Conclusions and recommendations for further research

This chapter presents the conclusions in relation to the original aims and objectives of the thesis, and recommendations for further research. The main aims of the research were to investigate some of the issues affecting the implementation of arsenic mitigation programmes in middle and low income countries (MLICs) and to evaluate the feasibility of using sugarcane activated carbon (SCAC) as a low-cost arsenic adsorbent for water treatment.

9.1 Conclusions

The *Expert survey: arsenic mitigation in MLICs* investigated some of the issues affecting arsenic mitigation and the implementation of arsenic removal technologies in MLICs. The response rate for the survey was low and responses relating to arsenic mitigation in Bangladesh predominated. Nevertheless, some general conclusions applicable to arsenic mitigation and implementation of arsenic removal technologies in MLICs were reached:

- Nationwide development policies should incorporate arsenic mitigation programmes. Arsenic contamination clearly fits in the wider context of the supply of clean water.

- Both technological and non-technological aspects are important for implementing successful mitigation programmes. This is demonstrated by the number of water technologies that have fallen into and remained in disrepair in MLICs. The preferences of water users, affordability of water options, and customary norms need to be considered when planning arsenic mitigation programmes.

- The increase in knowledge on arsenic contamination problems and health effects among the affected population achieved through arsenic awareness programmes is rarely reflected in the proportion of households using arsenic-safe options. This is an example of the knowledge-behaviour gap in health social sciences.

- Given the complexities of widespread arsenic contamination in some MLICs, programmes in which a unique arsenic-safe water option is offered are inadequate. Since all water options have advantages and disadvantages in different cultural and hydro-chemical settings a choice of options should be offered to water users.

- Acceptability of arsenic removal technologies among water users is low. However, the use of technologies is unavoidable when piped water is not available or surface water and groundwater are chemically or microbiologically contaminated. Technologies are an alternative to the high capital investment necessary to provide piped water to rural populations.

- Independent evaluation of programmes and performance of arsenic removal technologies is essential. This eliminates the possible conflict of interest created when implementers of programmes or technology developers carry out the evaluation process. In addition, the outcome from evaluations will support identification of the type of programmes with higher impact on arsenic mitigation and improve the implementation process. Feedback from evaluation and monitoring of technologies should also be used to improve the design of the next generation of technologies.

- Monitoring of the chemical and microbiological quality of arsenic removal technologies is necessary. Since dissolved arsenic is odourless, colourless and with no particular taste, it is necessary to perform a chemical analysis to know if the arsenic removal media has been exhausted. Microbiological contamination of water is still the main hazard in drinking water, not only in MLICs but also in high income countries.

- Implementation plans for arsenic removal technologies should include the logistics for monitoring water quality, disposal of arsenic-laden media and technologies, and account for the cost of operation and maintenance of water options.

- Availability of spare parts and ease and frequency of maintenance of technologies are among the main issues affecting routine use of arsenic removal technologies.

The evaluation of the feasibility of using SCAC as a low-cost arsenic adsorbent for water treatment consisted of the optimisation of the preparation parameters of SCAC for maximum arsenic(V) and arsenic(III) adsorption, the characterisation of the physical and chemical properties of SCAC relevant to arsenic adsorption and the conduction of batch arsenic(V) and arsenic(III) adsorption experiments to determine the adsorption capacity of SCAC under different experimental settings. The following conclusions were reached:

- The 2^3 factorial experiment was very valuable in identifying the factors and combination of factors with an effect on arsenic adsorption and the preparation conditions that maximised arsenic(V) and arsenic(III) adsorption with SCAC. Arsenic(V) and arsenic(III) adsorption was the highest at a carbonisation temperature of 700 °C and an activation temperature of 900 °C.

- Carbonisation and activation temperature affect the percentage of arsenic removal, especially activation temperature. Hence, special care should be placed in ensuring the established temperatures are reached in the preparation process of SCAC.

- According to the Pearson correlation test, the surface area of SCAC has a strong positive correlation with arsenic(V) ($R = 0.939$, $p = 0.018$) and arsenic (III) ($R = 0.956$, $p = 0.011$) percentage of adsorption. The micropore/pore volume ratio of SCAC has a strong and negative correlation with percentage of arsenic(V) ($R = -0.975$, $p = 0.005$) and arsenic(III) ($R = -0.968$, $p = 0.007$) adsorption. The percentage of sand-size fraction of SCAC has a strong and negative correlation with percentage of arsenic(V) ($R = -0.960$, $p = 0.010$) and arsenic(III) ($R = -0.966$, $p = 0.007$) adsorption.

- The main driver for arsenic(III) adsorption is the small concentration (< 1%) of the ion $H_2AsO_3^-$ that is present below pH = 9. when $H_2AsO_3^-$ ions are adsorbed onto the surface of the AC, the equilibrium in the reaction ($H_3AsO_3^0 = H_2AsO_3^- + H^+$) will move towards the right side to compensate the change in concentration of ions $H_2AsO_3^-$ in solution.

- Batch experiments suggest that arsenic(III) undergoes oxidation to arsenic(V) prior to adsorption onto SCAC.

- Arsenic adsorption onto SCAC is not entirely due to electrostatic attraction. The Pearson test found no correlation between the pH_{ZC} of SCAC samples and arsenic(V) and arsenic(III) percentage removal. SCAC samples with equal pH_{ZC} had contrasting arsenic adsorption capacity.

- The estimated monolayer adsorption capacity of SCAC is low compared to the values reported in the literature of 500 mg g^{-1}. However, the experiments in this research were carried out at considerably lower arsenic concentrations to those found in the literature. Hence, a potential limitation of SCAC is the amount of adsorbent required to remove arsenic below drinking water standards.

A number of conclusions are drawn as to the utility and cost-effectiveness of using SCAC as an arsenic removal treatment technology for drinking water supplies, as follows:

- The performance of SCAC is approximately constant from $pH > 4$ to $pH < 10$, and is therefore within the range of values for most natural waters. Also, arsenic removal with SCAC is robust to the initial oxidation state of arsenic.

- In comparing the cost of removing one gram of arsenic using SCAC with removing one gram using Alcan activated alumina, it is shown that SCAC has the potential to be economically cheaper than conventional treatments. However, the production cost of SCAC may vary from one geographical region to another depending on factors such as: the availability of the raw material, transportation costs, and marketing costs.

- The production cost of arsenic removal technologies cannot be abated by mass production since technologies should be ideally produced in the proximity of the arsenic affected area.

- Recommending the use of SCAC in a water treatment system has the advantage of using an agricultural by-product of the sugar refinery industry, and so reducing the amount of waste requiring disposal. Also, a gasification process can create a more efficient use of sugarcane waste by producing energy to power sugar refineries while at the same time producing SCAC for application in water treatment.

9.2 Recommendations for further research

The conclusions reached through the *Expert survey* and the laboratory work indicate that arsenic removal with SCAC could be commercially feasible. However, in order to increase the understanding of the chemical processes involved in arsenic adsorption with SCAC and to evaluate in more detail the adsorption capacity of SCAC the following suggestions are made:

- Exploration of the effect of carbonisation temperature at lower values than those investigated in this research (< 700 °C). Lower carbonisation temperatures could further reduce the cost of the adsorbents produced.

- Column experiments to estimate the arsenic adsorption capacity of SCAC under continuous flow conditions. Such experiments should include simultaneous removal of arsenic(V) and arsenic(III).

- Desorption and regeneration studies to investigate the feasibility of these options and the potential of contamination from inadequately disposed of arsenic-loaded SCAC.

- Investigation of the concentrations of microbiological entities of interest in water treated with SCAC.

- Construction and testing of a prototype of water treatment system with SCAC as the removal media. The performance of the system in producing chemically and microbiologically safe water, the acceptability of the technology to potential users, and arsenic awareness levels of water users should also be investigated. In addition, this investigation should elaborate on the sources of raw material available, and on the logistics for testing water samples and for disposal of arsenic-laden adsorption media.

- Investigation of the adsorption capacity of SCAC for other contaminants of interest and the feasibility of incorporating SCAC in centralised water treatment systems in high and middle income countries.

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Appendix A. Expert survey: arsenic mitigation in middle and low income countries

A1. Survey instrument

Expert survey: Arsenic mitigation in middle and low income countries

If you need any technical support (such as provision of the file in another format) please do not hesitate to contact me. Once you have completed the survey please e-mail me the file to both e-mail addresses provided below:

e-mail addresses: maryvela29@gmail.com
m.velasco-perez@uea.ac.uk

United Kingdom mobile: +44 79 48 27 33 26

Office telephone (United Kingdom): +44 01 603 59 39 89

Thank you very much for your time and for your worthy collaboration!

Maribel Velasco-Perez

Information about you

Q1. What is your gender?

☐ Female

☐ Male

Q2. What is your nationality?

Q3. From the drop-down list below please choose your highest academic qualification.

None

Primary (5-11 years old)

Secondary (11-18 years old)

Vocational (manual skills)

Diploma (pre-university qualification)

Teacher

First degree (undergraduate courses)

Medical practitioner

Masters

PhD

Other

Q4. Do you belong to any professional association?

☐ No

☐ Yes. Please specify:

Q5. Who is your main employer?

Q6. Which category best describes your job sector?
☐ Academic ☐ Development practitioner ☐ Policy maker ☐ Other. Please specify:

Q7. Do you have any experience in arsenic-related issues?
☐ Yes (*Go to Q8*) ☐ No (*This is the end of the questionnaire. The following only apply to people with experience in arsenic. I would like to thank you very much for your time. Now please e-mail your completed questionnaire.*)

Q8. How would you describe your professional experience in arsenic related issues?
Little Some Intermediate Expert

Box 1

Fieldwork definition

Fieldwork is considered as any kind of practical activity that is carried out (at least in part) away from laboratories and offices.

Q9. Have you conducted any fieldwork on arsenic-related issues? (See definition of fieldwork in Box 1 above)

☐ Yes (*Go to Q10*)

☐ No (*Go to Q11*)

Q10. Please write the name in English of the countries where you have conducted fieldwork(s) on arsenic-related issues? (See definition of fieldwork in Box 1 above)

Box 2

Arsenic mitigation definition
Set of actions that are performed with the objective to lessen a population's exposure to arsenic and to improve the quality of life of persons that have been affected by arsenic in any way.

Q11. Please tick the boxes that best describe the areas in which you have experience in arsenic-related issues. You can tick as many options as necessary.

☐ Elaboration of national policies for arsenic mitigation (see definition of arsenic mitigation in Box 2 above)

☐ Testing drinking water for arsenic

☐ Hydrochemical surveys

☐ Identification of alternative arsenic-free water sources

☐ Design or implementation of arsenic removal technologies for drinking water

☐ Arsenic awareness programmes

☐ Identification of arsenic patients

☐ Health care for arsenic patients

☐ Mental health care for arsenic patients and their families

☐ Social care for arsenic patients and their families

☐ Epidemiological surveys

☐ Arsenic toxicity studies

☐ Arsenic studies in food, soil or air

☐ Other arsenic-related issues. Please specify:

Information about arsenic mitigation

Q12. Are you aware of any policies or programmes that have been (or are being) undertaken in middle or low income countries to mitigate arsenic? (See definition of arsenic mitigation in Box 2 above). In the document called **Notes** you will find a list of middle and low income countries.

☐ Yes (*Go to Q13*)

☐ No (*Go to Q14*)

Q13. In the right column, list a maximum of six policies or programmes undertaken in middle or low income countries to mitigate arsenic. In the middle column, write the name of the country where these programmes were undertaken. In the right column, rate **each** of these programmes or policies from **10** (very efficient) to **0** (very inefficient).

Policies or programmes	***Country***	***Rate***
2)		0
3)		0
4)		0
5)		0
6)		0
7)		0

Q14. Presented below is a list of types of technologies that have been used to remove arsenic from drinking water. In the first column please tick the technologies that you are familiar with. For the technologies that you know please indicate whether you consider them chemically safe, bacteriologically safe, cost-effective and if you consider they have any problems with operation and maintenance. In the last column, please add any comments, if you wish. At the bottom of the table there are some blank spaces if you wish to add technologies to the list. (In the document called **Notes** you will find a short description and references for these technologies).

1	*2. Technology name*	*3. Do you consider it chemically safe?*			*4. Do you consider it bacteriologically safe?*			*5. Do you consider it cost- effective?*			*6. Do you consider it to have operation and maintenance problems?*			*7. Comments*
		Yes	*No*	*Don't know*	*Yes*	*No*	*Don't know*	*Yes*	*No*	*Don't know*	*Yes*	*No*	*Don't know*	
☐	**Household technologies using imported activated alumina** (e.g. Alcan)	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	
☐	**Household technologies using locally produced activated alumina** (e.g. BUET in Bangladesh)	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	
☐	**Coagulation-flocculation processes with aluminium salts** (e.g. Danida bucket)	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	

☐	**Coagulation-flocculation processes with iron salts** (e.g. Steven's Institute of Technology)	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	
☐	**Co-polymer adsorbent technologies** (e.g. Read-F)	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	
☐	**Granular ferric hydroxide technologies** (e.g. Sidko ADSORPAS)	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	
☐	**Composite iron matrix technologies** (e.g. SONO filter)	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	
☐	**Ion exchange technologies** (e.g. Tetrahedron)	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	
☐	Other 1:	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	
☐	Other 2:	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	
☐	Other 3:	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	
☐	Other 4:	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	
☐	Other 5:	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	
☐	Other 6:	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	

Q15. Considering the technologies that produce chemically and bacteriologically safe water. How can be operation and maintenance problems resolved (if they have any)?

Q16. In your opinion are wastes produced by arsenic removal technologies a potential contamination source?

☐ Yes
☐ No
☐ Don’t know

Q17. In your opinion, which factors may affect the ***routine*** use of arsenic removal technologies in a household in a rural community?

Q18. In your opinion are there any issues that may be hindering arsenic mitigation in middle and low income countries?

☐ Yes (*Go to Q19*)
☐ No (*Go to Q20*)
☐ Don’t know (Go to Q20)

Q19. Please list from **most** important to **less** important the problems that in your opinion may be hindering arsenic mitigation in middle and low income countries.

Q20. Please use the following space to add any further comments about arsenic mitigation in middle and low income countries.

I would like to thank you very much for your time in answering this survey. Your responses will be extremely useful in my work!

Maribel Velasco-Perez

A2. Notes for the expert survey

Q12. List of low middle and low income countries[1]

Middle income countries

Albania
Algeria
American Samoa
Angola
Argentina
Armenia
Azerbaijan
Belarus
Belize
Bhutan
Bolivia
Bosnia and Herzegovina
Botswana
Brazil
Bulgaria
Cameroon
Cape Verde
Chile
China
Colombia
Congo, Rep.
Costa Rica
Croatia
Cuba
Djibouti
Dominica
Dominican Republic
Ecuador
Egypt, Arab Rep.
El Salvador
Fiji
Gabon
Georgia
Grenada
Guatemala
Guyana
Honduras
India
Indonesia
Iran, Islamic Rep.
Iraq
Jamaica
Jordan
Kazakhstan
Kiribati
Latvia
Lebanon
Lesotho
Libya
Lithuania
Macedonia, FYR
Malaysia
Maldives
Marshall Islands
Mauritius
Mayotte
Mexico
Micronesia, Fed. Sts.
Moldova
Mongolia
Montenegro
Morocco
Namibia
Nicaragua
Palau
Panama
Paraguay
Peru
Philippines
Poland
Romania
Russian Federation
Samoa
Serbia
Seychelles
South Africa
Sri Lanka
St. Kitts and Nevis
St. Lucia
St. Vincent and the Grenadines
Sudan
Suriname
Swaziland
Syrian Arab Republic
Thailand
Timor-Leste
Tonga
Tunisia
Turkey
Turkmenistan
Ukraine
Uruguay
Vanuatu
Venezuela, RB
West Bank and Gaza

Low income countries

Afghanistan
Bangladesh
Benin
Burkina Faso
Burundi
Cambodia
Central African Republic
Chad
Comoros
Congo, Dem. Rep
Côte d'Ivoire
Eritrea
Ethiopia
Gambia, The
Ghana
Guinea
Guinea-Bissau
Haiti
Kenya
Korea, Dem Rep.
Kyrgyz Republic
Lao PDR
Liberia
Madagascar
Malawi
Mali
Mauritania
Mozambique
Myanmar
Nepal
Niger
Nigeria
Pakistan
Papua New Guinea
Rwanda
São Tomé and Principe
Senegal
Sierra Leone
Solomon Islands
Somalia
Tajikistan
Tanzania
Togo
Uganda
Uzbekistan
Vietnam
Yemen, Rep.
Zambia
Zimbabwe

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[1] WB (World Bank), 2008. The World Bank list of economies.

Q14. Short description of technologies

Alcan media based technology

Alcan household technology uses the patented adsorbent ActiGuard AAFS50. This adsorbent is an activated alumina. According to the Bangladesh Council of Scientific and Industrial Research (BCSIR), Alcan household technology can treat 45 litres of water per day. This technology consists of two plastic buckets filled with the ActiGuard alumina. Buckets are placed in a metal frame. Treated water is collected in other bucket (BCSIR, 2003).

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Alcan international web site: http://www.alcan.com/

BCSIR Bangladesh Council of Scientific and Industrial Research (2003). Performance evaluation and verification of five arsenic removal technologies. ETV-AM field testing and technology verification program. Dhaka, Bangladesh, Bangladesh Council of Scientific and Industrial Research: 79.

BUET activated alumina filter

The BUET filter consists of three units; the oxidation-sedimentation unit, the sand filtration unit, and the activated alumina unit. Units consist of plastic buckets. In the oxidation-sedimentation unit arsenic(III) is oxidised to arsenic(V) and insoluble iron is precipitated. In the sand filtration unit precipitates are removed in a sand layer of 20 cm thick. Finally, arsenic is removed in the activated alumina unit (Jalil et al., 2001).

References

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Danida bucket treatment unit

Danida bucket technology uses coagulation/flocculation processes to remove arsenic from drinking water (Sutherland et al., 2001). Danida’s technology consists of two buckets placed in series. In the upper bucket chemicals are added to the drinking water and mixed. The formed precipitate is allowed to settle. Finally, water is filtered in a sand bed in the lower bucket (Ahmed, 2001).

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Sutherland, D., S. Wood, Monhemius, J., Woolgar, M. (2001). "Rapid assessment of household level arsenic removal. Phase 1, final draft report." Water Aid.

Read-F household unit

Read-F is a technology that uses an adsorbent produced by Shin Nihon Salt Co., Ltd. Japan. Read-F adsorbent is an ethylene vinyl alcohol copolymer-borne hydrous cerium oxide in which hydrous cerium oxide ($CeO_2 \cdot n\ H2O$).

References

Web site of distributors of Read-F: http://www.generalpharma.com/arsenic_0.php

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Sidko ADSORPAS-granular ferric hydroxide technology

Sidko technology uses an adsorption proprietary media called AdsorpAs. The adsorbent is granular ferric hydroxide. This adsorbent was developed at the Technical University of Berlin in Germany. Sidko technology involves two filtration processes. Firs the water is filtered through a gravel filter and then through the AdsorpAs media (Pal, 2001). This technology can be used to provide drinking water to 50 families (BCSIR, 2003).

References

BCSIR Bangladesh Council of Scientific and Industrial Research (2003). Performance evaluation and verification of five arsenic removal technologies. ETV-AM field testing and technology verification program. Dhaka, Bangladesh, Bangladesh Council of Scientific and Industrial Research: 79.

Pal, B. N. (2001). Granular ferric hydroxide for elimination of arsenic from drinking water. BUET-UNU International workshop on Technologies for arsenic removal from drinking water, Dhaka, Bangladesh.

SONO filter

The SONO filter consists of two plastic buckets with taps. The buckets are placed one above the other, and clean water is collected in a third bucket. The filter in the top bucket has layers of coarse sand, composite iron matrix, and brick chips. The bottom bucket contains coarse sand, wood charcoal, fine sand and brick chips (Hussam, 2007). This technology was awarded with the 2007 Grainger Challenge Prize for Sustainability Gold Award from the National Academy of Engineering.

References

Delowar H. K. M., Uddin I., Abou El Hassan W. H., Perveen F., Irshad M., Saiful Islam A. F. M., Yoshida I. (2006). “A comparative study of household groundwater arsenic removal technologies and their water quality parameters”. Journal of Applied Sciences 6(10):2193-2200.

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Munir A. K. M., Rasul S.B., Habibuddowla M., Alauddin M., Hussam A., Khan A. H. (2001). Evaluation of performance of Sono 3-Kolshi filter for arsenic removal from groundwater using zero valent iron through laboratory and field studies. Workshop on technologies for arsenic removal from drinking water, Dhaka, Bangladesh, Bangladesh University of Engineering and Technology, The United Nations University.

Steven’s Institute of Technology

The Stevens Institute technology removes arsenic by coagulation and filtration. First, a packet of chemicals is added to the water and mixed from 5 to 10 minutes in a plastic bucket. Finally, water has to be filtered to remove iron oxyhydroxide flocs formed. The filter is a plastic bucket with a sand layer and a spout near the bottom. A piece of fabric is placed over the outlet inside the bucket to prevent lost of sand particles (Cheng et al., 2004; Meng et al., 2001).

References

Cheng, Z., A. vanGeen, Jing, C., Meng, X., Seddique, A., Ahmed, K. M. (2004). "Performance of a household-level arsenic removal system during 4-month deployments in Bangladesh." Environmental Science and Technology 38(12): 3442-3448.

Meng, X., G. P. Korfiatis, Christodoulatos, C., Bang, S. (2001). "Treatment of arsenic in Bangladesh well water using a household co-precipitation and filtration system." Water Research 35(12): 2805-2810.

Tetrahedron

Tetrahedron, an ion exchange resin, is used in combination with chlorine to remove arsenic from water. Chlorine is used as an oxidising agent for arsenic(III) and as disinfectant (WAB, 2003). Regeneration of the resin is carried out with sodium chloride (NaCl) (WAB, 2003).

References

WAB Water Aid Bangladesh (2003). Arsenic 2002: An overview of arsenic issues and mitigation initiatives in Bangladesh, NGOs Arsenic Information & Support Unit (NAISU) and NGO Forum for Drinking Water Supply & Sanitation.

A3. Informed consent

I agree to participate in the “Expert survey: Arsenic mitigation in middle and low income countries” conducted by Maribel Velasco-Perez as part of her PhD thesis at the University of East Anglia. I am aware that confidentiality of the data gathered during this survey will be maintained and information will be used only by those involved in the research. Any link between answers and names of interviewees will be destroyed. The report derived from this survey will be part of Maribel’s PhD thesis and will include statistical information and unattributable quotations. Results derived from the survey may be published as part of the research conducted during Maribel’s PhD.

Name of the interviewee:

Appendix B. Instrument and method detection limits for total arsenic in ICP-MS

The instrument detection limits (IDL) and method detection limits (MDL) were determined for the working calibration curve method with internal standard (rhodium at 10 µg L^{-1}). The IDL is the analyte signal equivalent to three times the standard deviation of ten replicate analysis of the calibration blank signal[2]. The MDL is the minimum concentration at which the analyte can be identified with a 99 per cent statistical confidence that the concentration is greater than zero[3]. The MDL was determined with the following procedure. First, a solution with 2 to 5 times the IDL analyte concentration was prepared with an arsenic standard and reagent grade water. Then, seven aliquots of that solution were analysed using the sample preparation method. Finally, the MDL was calculated by multiplying the standard deviation of the concentration of the seven aliquots by the student's t value for a 99 per cent confidence level at 6 degrees of freedom. The IDL was measured at 0.083 µg L^{-1} (Table B1), the MDL for a concentration range of 0-350 µg L^{-1} at 0.150 µg L^{-1} (Table B2), and the MDL for a concentration range of 0-3,000 µg L^{-1} at 0.795 µg L^{-1} (Table B3).

Table B1 Determination of the instrument detection limit for arsenic in the inductively coupled plasma mass spectrometer.

	As µg L^{-1}	SD µg L^{-1}	RSD %
replicate 1	0.087	0.010	11.2
replicate 2	0.069	0.002	3.3
replicate 3	0.049	0.025	51.0
replicate 4	0.050	0.018	36.3
replicate 5	0.049	0.011	22.2
replicate 6	0.058	0.016	27.2
replicate 7	0.012	0.017	144.3
replicate 8	0.006	0.007	108.2
replicate 9	0.025	0.010	40.3
replicate 10	0.008	0.004	46.8
Average	0.041		
SD	0.028		
IDL	0.083		

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[2] US EPA Environmental Protection Agency (1994). "Determination of trace elements in waters by inductively coupled plasma-mass spectrometry." EPA Methods and Guidance for Analysis of Water, version 2.0.

Table B2 Determination of the method detection limit for arsenic and the working calibration curve method (0 – 350 µg L^{-1}) with internal standard (rhodium at 10 µg L^{-1}) in the inductively coupled plasma mass spectrometer.

	As µg L^{-1}	SD µg L^{-1}	RSD %
sample 1	0.172	0.027	15.9
sample 2	0.057	0.016	28.5
sample 3	0.030	0.029	97.4
sample 4	0.068	0.009	13.2
sample 5	0.064	0.056	88.1
sample 6	0.073	0.038	51.2
sample 7	0.031	0.029	69.5
Average	0.071		
SD	0.048		
MDL	0.150		

Table B3 Determination of the method detection limit for arsenic and the working calibration curve method (0 – 3,000 µg L^{-1}) with internal standard (rhodium at 10 µg L^{-1}) in the inductively coupled plasma mass spectrometer.

	As µg L^{-1}	SD µg L^{-1}	SD %
sample 1	1.504	0.074	4.9
sample 2	1.120	0.024	2.1
sample 3	0.938	0.044	4.7
sample 4	0.907	0.020	2.3
sample 5	0.809	0.009	1.1
sample 6	0.827	0.023	2.8
sample 7	0.804	0.005	0.7
average	0.987		
SD	0.253		
MDL	0.795		

Appendix C. Total arsenic concentrations per experiment as analysed with ICP-MS

This appendix contains the raw data, obtained from adsorption experiments, presented in the result *Chapters 4*, *5* and *7*. The data is organised in tables, each table represents one experiment. Data from preliminary experiments (*Chapter 4*) it is presented in Table C1 to Table C3. Data from absorption experiments with SC07 and CAC (*chapters 5* and *7*) is presented from Table C4 to Table C31; these tables have similar structure. The first column contains the sample name; i.e. control, replicate 1, and so on. The second, third and fourth column are the average (As), standard deviation (SD) and relative standard deviation (RSD) of the arsenic concentration of the triplicate analysis of individual samples as analysed in the ICP-MS, respectively. The fifth, sixth and seventh columns are the average arsenic concentration (average), SD and RSD of the replicates of each experimental condition, respectively.

Table C1 Arsenic recovery in samples with iron content from 0 to 1800 µg L^{-1} (*Section 4.1*).

	Actual concentrations		Concentration measured in the ICP-MS		
	Fe µg L^{-1}	As µg L^{-1}	As µg L^{-1}	SD µg L^{-1}	RSD %
sample 1	1800	10.0	4.0	0.3	8.3
sample 2	1000	9.9	1.7	0.1	8.5
sample 3	100	10.0	0.5	0.1	23.1
sample 4	50	10.0	2.8	0.1	2.7
sample 5	0	10.0	9.7	0.2	2.4
sample 6	1500	50.0	36.9	0.6	1.6
sample 7	1000	50.0	14.5	0.1	0.6
sample 8	500	50.0	7.8	0.1	1.6
sample 9	100	50.0	21.5	0.2	0.8
sample 10	50	50.0	37.9	0.2	0.5
sample 11	10	50.0	51.8	0.4	0.8
sample 12	1800	249.6	60.9	2.9	4.8
sample 13	1000	249.8	54.1	3.0	5.6
sample 14	100	249.5	194.1	5.8	3.0
sample 15	50	248.4	226.0	6.9	3.1
sample 16	0	250.0	250.0	6.2	2.5

Table C2 Arsenic recovery for samples without pre-treatment and with Dowex 26G pre-treatment; samples with iron content up to 1800 µg L^{-1} (*Section 4.1*).

	Actual concentration		Concentration measured in the ICP-MS					
			No treatment			Treatment with Dowex 26G		
	As µg L^{-1}	Fe µg L^{-1}	As µg L^{-1}	SD µg L^{-1}	RSD %	As µg L^{-1}	SD µg L^{-1}	RSD %
Sample 1	10.0	1800	4.0	0.3	8.3	13.2	1.8	13.5
Sample 2	9.9	1000	1.7	0.1	8.5	7.3	0.8	11.6
Sample 3	10.0	100	0.5	0.1	23.1	1.9	0.9	47.1
Sample 4	10.0	50	2.8	0.1	2.7	3.5	0.6	16.5
Sample 5	10.0	0	9.7	0.2	2.4			
Sample 6	249.6	1800	60.9	2.9	4.8	214.6	14.3	6.6
Sample 7	249.8	1000	54.1	3.0	5.6	132.1	11.4	8.6
Sample 8	249.5	100	194.1	5.8	3.0	226.6	11.3	5.0
Sample 9	248.4	50	226.0	6.9	3.1	249.5	11.1	4.4
Sample 10	248.9	0	250.0	6.2	2.5	221.3	5.8	2.6

Table C3 Preliminary adsorption experiments that served to identify interferences on sample analysis (*Section 4.2*).

Arsenic oxidation state	Adsorbent type	Time min	As µg L^{-1}	SD µg L^{-1}	RSD %
As(III)	CAC	0	183.9	1.1	0.6
		120	221.7	4.3	2.0
		360	182.5	1.9	1.0
		720	161.1	14.8	9.2
	Fe	0	183.9	1.1	0.6
		120	171.1	4.4	2.6
		360	0.2	0.1	57.3
		720	0.2	0.1	65.9
	FeOOH	0	183.9	1.1	0.6
		120	2.6	0.9	35.3
		360	0.2	0.2	99.6
		720	3.2	0.5	16.7
As(V)	CAC	0	247.1	2.4	1.0
		24	285.6	7.1	2.5
		415	205.9	4.9	2.4
		1497	140.0	2.4	1.7
	Fe	0	247.1	2.4	1.0
		24	247.6	7.7	3.1
		415	25.9	0.9	3.3
		1497	7.2	0.1	1.7
	FeOOH	0	247.1	2.4	1.0
		24	4.6	0.3	5.6
		415	4.9	0.3	6.2
		1497	34.2	0.2	0.5
As(V)	A-0.1M Fe	0	99.9	7.7	7.7
		60	14.1	0.8	5.4
		360	9.1	0.4	4.6
		1440	8.1	0.6	7.6
	A-0.1M Fe	0	472.3	5.5	1.2
		60	39.7	1.7	4.3
		360	22.3	1.1	4.8
		1440	19.3	0.0	0.2
	A-0.01M Fe	0	350.4	1.9	0.5
		60	12.4	4.6	36.9
		360	6.0	1.4	22.9
		1440	4.2	0.1	2.6
As(V)	B-0.1M Fe	0	99.9	7.7	7.7
		60	27.8	2.5	9.1
		360	11.7	1.0	8.4
		1440	10.4	0.7	6.5
	B-0.1M Fe	0	472.3	5.5	1.2
		60	33.5	0.6	1.8
		360	15.3	0.8	5.0
		1440	17.0	0.8	4.4
	B-0.01M Fe	0	350.4	1.9	0.5
		60	301.5	0.8	0.3
		360	222.2	4.7	2.1
		1440	190.3	23.4	12.3

Table C4 Arsenic(V) factorial experiment (*Section 5.1*).

	As µg L^{-1}	SD µg L^{-1}	%RSD	Average µg L^{-1}	SD µg L^{-1}	RSD %
Control SC01-SC08	246.3	0.0	0.0			
Control CAC	246.2	0.1	0.0			
SC01						
Replicate 1	231.8	0.1	0.0	228.5	21.4	9.3
Replicate 2	248.0	0.7	0.3			
Replicate 3	205.6	0.6	0.3			
SC02						
Replicate 1	206.7	0.4	0.2	203.3	4.8	2.3
Replicate 2	197.8	0.4	0.2			
Replicate 3	205.3	0.1	0.0			
SC03						
Replicate 1	48.6	0.1	0.2	52.1	3.1	5.9
Replicate 2	54.5	0.2	0.3			
Replicate 3	53.3	0.2	0.4			
SC04						
Replicate 1	49.1	0.1	0.2	48.2	5.2	10.7
Replicate 2	42.6	0.1	0.3			
Replicate 3	52.8	0.2	0.3			
SC05						
Replicate 1	242.7	0.2	0.1	239.4	3.3	1.4
Replicate 2	236.1	0.5	0.2			
Replicate 3	239.3	0.3	0.1			
SC06						
Replicate 1	222.3	0.5	0.2	217.5	4.4	2.0
Replicate 2	216.6	0.4	0.2			
Replicate 3	213.7	0.4	0.2			
SC07						
Replicate 1	31.6	0.1	0.4	30.4	2.0	6.4
Replicate 2	28.2	0.1	0.3			
Replicate 3	31.5	0.0	0.1			
SC08						
Replicate 1	14.1	0.1	0.4	16.2	1.9	11.8
Replicate 2	16.6	0.1	0.6			
Replicate 3	17.9	0.1	0.3			
CAC						
Replicate 1	155.7	0.2	0.1	155.0	3.2	2.0
Replicate 2	157.7	0.5	0.3			
Replicate 3	151.6	0.3	0.2			

Table C5 As(III) factorial experiment (*Section 5.1*).

	As µg L^{-1}	SD µg L^{-1}	RSD %	Average µg L^{-1}	SD µg L^{-1}	RSD %
Control	246.3	0.0	0.0			
SC01						
Replicate 1	229.8	0.7	0.3	227.6	1.9	0.9
Replicate 2	226.4	0.3	0.1			
Replicate 3	226.6	0.7	0.3			
SC02						
Replicate 1	217.2	0.2	0.1	219.8	2.2	1.0
Replicate 2	221.0	0.6	0.3			
Replicate 3	221.2	0.6	0.3			
SC03						
Replicate 1	57.2	0.1	0.3	52.8	3.9	7.4
Replicate 2	49.9	0.0	0.1			
Replicate 3	51.1	0.2	0.3			
SC04						
Replicate 1	46.1	0.1	0.1	45.3	1.0	2.1
Replicate 2	44.3	0.1	0.3			
Replicate 3	45.6	0.2	0.3			
SC05						
Replicate 1	232.8	0.4	0.2	234.5	1.6	0.7
Replicate 2	235.9	0.1	0.0			
Replicate 3	234.7	0.2	0.1			
SC06						
Replicate 1	230.4	0.3	0.1	230.4	0.7	0.3
Replicate 2	229.7	0.2	0.1			
Replicate 3	231.1	0.3	0.1			
SC07						
Replicate 1	25.0	0.1	0.4	24.8	0.3	1.1
Replicate 2	24.8	0.1	0.3			
Replicate 3	24.5	0.1	0.4			
SC08						
Replicate 1	19.7	0.1	0.3	19.8	0.1	0.3
Replicate 2	19.8	0.1	0.3			
CAC						
Replicate 1	186.6	0.3	0.2	184.4	5.0	2.7
Replicate 2	187.8	0.5	0.3			
Replicate 3	178.7	0.1	0.1			

Table C6 Arsenic(V) variation of activation temperature experiment (*Section 5.2*).

	As µg L^{-1}	SD µg L^{-1}	RSD %	Average µg L^{-1}	SD µg L^{-1}	RSD %
Control	246.2	0.1	0.0			
SC09						
Replicate 1	208.2	0.4	0.2	208.1	0.4	0.2
Replicate 2	207.7	0.8	0.4			
Replicate 3	208.4	0.2	0.1			
SC10						
Replicate 1	167.4	0.1	0.0	160.9	6.0	3.8
Replicate 2	159.8	0.2	0.1			
Replicate 3	155.5	0.1	0.1			
SC11						
Replicate 1	91.4	0.1	0.1	85.2	8.3	9.7
Replicate 2	88.5	0.2	0.2			
Replicate 3	75.8	0.2	0.3			
SC12						
Replicate 1	15.9	0.0	0.3	16.3	1.3	8.3
Replicate 2	15.2	0.1	0.4			
Replicate 3	17.8	0.0	0.3			

Table C7 Arsenic(III) variation of activation temperature experiment (*Section 5.2*).

	As µg L^{-1}	SD µg L^{-1}	RSD %	Average µg L^{-1}	SD µg L^{-1}	RSD %
Control	246.3	0.0	0.0			
SC09						
Replicate 1	222.4	0.6	0.2	223.2	0.8	0.4
Replicate 2	223.1	0.4	0.2			
Replicate 3	224.1	0.3	0.2			
SC10						
Replicate 1	182.7	0.1	0.1	182.6	3.7	2.0
Replicate 2	178.8	0.2	0.1			
Replicate 3	186.1	0.1	0.1			
SC11						
Replicate 1	70.3	0.1	0.1	72.9	2.6	3.6
Replicate 2	72.9	0.1	0.1			
Replicate 3	75.5	0.1	0.1			
SC12						
Replicate 1	17.2	0.1	0.5	17.3	0.2	1.3
Replicate 2	17.6	0.1	0.5			
Replicate 3	17.2	0.0	0.2			

Table C8 Kinetics of arsenic(V) adsorption onto SC07 at an initial concentration of 227.9 µg L^{-1} (*Section 7.1*).

	As µg L^{-1}	SD µg L^{-1}	RSD %	Average µg L^{-1}	SD µg L^{-1}	RSD %
Control	227.9	0.1	0.0			
15 min						
Replicate 1	34.0	0.2	0.5	31.8	2.4	7.6
Replicate 2	29.3	0.0	0.1			
Replicate 3	32.2	0.1	0.2			
30 min						
Replicate 1	22.8	0.1	0.4	25.4	2.3	9.1
Replicate 2	26.9	0.0	0.0			
Replicate 3	26.6	0.1	0.5			
45 min						
Replicate 1	26.1	0.0	0.1	26.2	2.0	7.8
Replicate 2	28.3	0.1	0.3			
Replicate 3	24.2	0.0	0.2			
60 min						
Replicate 1	27.5	0.1	0.3	26.3	1.3	5.0
Replicate 2	24.9	0.1	0.2			
Replicate 3	26.4	0.0	0.1			
180 min						
Replicate 1	23.1	0.1	0.3	22.9	0.4	1.6
Replicate 2	22.5	0.1	0.3			
Replicate 3	23.2	0.1	0.3			
360 min						
Replicate 1	19.9	0.0	0.2	19.4	0.5	2.5
Replicate 2	19.4	0.1	0.3			
Replicate 3	18.9	0.0	0.2			
720 min						
Replicate 1	19.0	0.1	0.6	16.8	2.2	13.3
Replicate 2	17.0	0.0	0.3			
Replicate 3	14.5	0.0	0.3			
1440 min						
Replicate 1	15.1	0.1	0.4	15.5	0.4	2.8
Replicate 2	15.9	0.0	0.2			
Replicate 3	15.6	0.0	0.2			
2880 min						
Replicate 1	15.0	0.0	0.0	14.6	0.5	3.7
Replicate 2	14.0	0.0	0.3			
Replicate 3	14.8	0.1	0.4			

Table C9 Kinetics of arsenic(V) adsorption onto CAC at an initial concentration of 229.3 μg L^{-1} (*Section 7.1*).

	As μg L^{-1}	SD μg L^{-1}	RSD %	Average μg L^{-1}	SD μg L^{-1}	RSD %
Control	229.3	0.64	0.28			
15 min						
Replicate 1	222.2	1.33	0.60	226.1	3.5	1.6
Replicate 2	228.9	0.93	0.41			
Replicate 3	227.2	0.88	0.39			
30 min						
Replicate 1	217.8	1.04	0.48	213.4	6.6	3.1
Replicate 2	216.6	0.96	0.44			
Replicate 3	205.7	0.70	0.34			
45 min						
Replicate 1	203.7	1.38	0.68	208.6	4.7	2.3
Replicate 2	209.1	1.02	0.49			
Replicate 3	213.1	1.05	0.49			
60 min						
Replicate 1	202.6	0.70	0.34	205.0	2.2	1.1
Replicate 2	207.0	0.46	0.22			
Replicate 3	205.5	0.56	0.27			
180 min						
Replicate 1	187.1	0.88	0.47	195.2	7.3	3.7
Replicate 2	197.5	0.71	0.36			
Replicate 3	201.1	0.56	0.28			
360 min						
Replicate 1	166.3	0.93	0.56	179.1	12.2	6.8
Replicate 2	180.3	0.26	0.15			
Replicate 3	190.6	0.28	0.15			
720 min						
Replicate 1	167.5	0.67	0.40	172.2	4.6	2.7
Replicate 2	176.7	0.43	0.24			
Replicate 3	172.4	0.49	0.28			
1440 min						
Replicate 1	158.4	0.32	0.20	160.7	2.3	1.4
Replicate 2	163.0	0.48	0.30			
Replicate 3	160.8	0.45	0.28			
2880 min						
Replicate 1	131.8	0.26	0.20	135.0	2.8	2.1
Replicate 2	136.2	0.52	0.38			
Replicate 3	137.0	0.68	0.50			

Table C10 Kinetics of arsenic(V) adsorption onto SC07 at an initial concentration of 2481.2 µg L^{-1} (*Section 7.1*).

	As µg L^{-1}	SD µg L^{-1}	RSD %	Average µg L^{-1}	SD µg L^{-1}	RSD %
Control	2481.2	6.8	0.3			
15 min						
Replicate 1	899.2	1.9	0.2	881.0	27.9	3.2
Replicate 2	848.9	1.2	0.1			
Replicate 3	894.9	1.3	0.1			
30 min						
Replicate 1	749.2	2.2	0.3	729.6	38.9	5.3
Replicate 2	754.8	0.7	0.1			
Replicate 3	684.8	2.2	0.3			
45 min						
Replicate 1	728.7	1.9	0.3	683.4	54.3	7.9
Replicate 2	698.2	0.6	0.1			
Replicate 3	623.3	1.6	0.3			
60 min						
Replicate 1	681.9	4.6	0.7	659.7	19.4	2.9
Replicate 2	651.0	0.8	0.1			
Replicate 3	646.3	1.6	0.2			
180 min						
Replicate 1	501.6	0.6	0.1	490.3	10.3	2.1
Replicate 2	487.8	0.8	0.2			
Replicate 3	481.6	2.1	0.4			
360 min						
Replicate 1	404.2	1.1	0.3	449.1	40.1	8.9
Replicate 2	481.4	0.2	0.0			
Replicate 3	461.7	1.5	0.3			
720 min						
Replicate 1	347.2	0.5	0.2	395.9	43.1	10.9
Replicate 2	411.4	0.8	0.2			
Replicate 3	429.0	0.7	0.2			
1440 min						
Replicate 1	413.5	1.1	0.3	403.9	18.1	4.5
Replicate 2	415.1	0.9	0.2			
Replicate 3	383.0	0.4	0.1			
2880 min						
Replicate 1	434.6	0.6	0.1	448.5	12.8	2.9
Replicate 2	459.9	0.3	0.1			
Replicate 3	451.1	0.1	0.0			

Table C11 Kinetics of arsenic(V) adsorption onto CAC at an initial concentration of 2499.7 µg L^{-1} (*Section 7.1*).

	As µg L^{-1}	SD µg L^{-1}	RSD %	Average µg L^{-1}	SD µg L^{-1}	RSD %
Control	2499.7	3.88	0.16			
15 min						
Replicate 1	2510.4	5.0	0.2	2509.8	22.1	0.9
Replicate 2	2487.4	8.7	0.4			
Replicate 3	2531.5	4.8	0.2			
30 min						
Replicate 1	2451.1	12.3	0.5	2448.2	4.4	0.2
Replicate 2	2450.3	8.1	0.3			
Replicate 3	2443.1	8.4	0.3			
45 min						
Replicate 1	2415.8	8.6	0.4	2400.5	13.2	0.6
Replicate 2	2392.3	8.2	0.3			
Replicate 3	2393.5	8.6	0.4			
60 min						
Replicate 1	2355.2	7.3	0.3	2347.0	19.9	0.8
Replicate 2	2361.5	6.1	0.3			
Replicate 3	2324.3	8.7	0.4			
180 min						
Replicate 1	2199.1	5.8	0.3	2201.0	2.2	0.1
Replicate 2	2200.6	6.7	0.3			
Replicate 3	2203.4	5.5	0.2			
360 min						
Replicate 1	2110.7	6.3	0.3	2126.8	16.3	0.8
Replicate 2	2143.4	7.6	0.4			
Replicate 3	2126.3	5.3	0.2			
720 min						
Replicate 1	2069.1	9.0	0.4	2058.2	13.4	0.7
Replicate 2	2062.2	6.7	0.3			
Replicate 3	2043.2	5.5	0.3			
1440 min						
Replicate 1	1940.0	6.3	0.3	1958.3	27.5	1.4
Replicate 2	1990.0	7.0	0.4			
Replicate 3	1945.1	5.3	0.3			
2880 min						
Replicate 1	1894.2	9.5	0.5	1854.5	41.3	2.2
Replicate 2	1857.6	3.9	0.2			
Replicate 3	1811.8	8.6	0.5			

Table C12 Kinetics of arsenic(III) adsorption onto SC07 at an initial concentration of ≈ 242.4 µg L^{-1} (*Section 7.1*).

	As µg L^{-1}	SD µg L^{-1}	RSD %	Average µg L^{-1}	SD µg L^{-1}	RSD %
Control C1	246.8	1.2	0.5			
Control C2	237.9	1.8	0.8			
15 min (C1)						
Replicate 1	129.7	0.4	0.3	129.3	1.0	0.8
Replicate 2	128.2	0.4	0.3			
Replicate 3	130.0	0.7	0.5			
30 min (C1)						
Replicate 1	129.3	0.3	0.2	126.4	2.8	2.2
Replicate 2	123.8	0.4	0.3			
Replicate 3	126.0	0.5	0.4			
45 min (C1)						
Replicate 1	123.7	0.1	0.1	122.8	0.9	0.7
Replicate 2	122.6	0.1	0.1			
Replicate 3	122.0	0.5	0.4			
60 min (C1)						
Replicate 1	123.6	0.3	0.3	121.7	2.0	1.6
Replicate 2	121.7	0.4	0.3			
Replicate 3	119.7	0.6	0.5			
180 min (C2)						
Replicate 1	119.6	0.2	0.2	116.8	4.9	4.2
Replicate 2	119.6	0.1	0.1			
Replicate 3	111.1	0.1	0.1			
360 min (C2)						
Replicate 1	129.6	0.2	0.2	130.4	2.3	1.8
Replicate 2	128.5	0.3	0.2			
Replicate 3	132.9	0.5	0.4			
720 min (C2)						
Replicate 1	139.3	0.1	0.1	142.3	2.6	1.8
Replicate 2	144.2	0.4	0.3			
Replicate 3	143.3	0.8	0.5			
1440 min (C1)						
Replicate 1	134.4	0.2	0.2	138.4	4.4	3.2
Replicate 2	143.2	0.6	0.4			
Replicate 3	137.6	0.4	0.3			
2880 (C1)						
Replicate 1	134.8	0.2	0.1	132.1	2.6	2.0
Replicate 2	132.0	0.3	0.2			
Replicate 3	129.6	0.1	0.1			

Table C13 Kinetics of arsenic(III) adsorption onto CAC at an initial concentration of ≈ 242.8 μg L^{-1} (*Section 7.1*).

	As μg L^{-1}	SD μg L^{-1}	RSD %	Average μg L^{-1}	SD μg L^{-1}	RSD %
Control C1	240.7	1.7	0.7			
Control C2	244.9	1.3	0.5			
15 min (C1)						
Replicate 1	235.1	0.6	0.2	227.6	13.2	5.8
Replicate 2	235.3	0.4	0.2			
Replicate 3	212.3	0.6	0.3			
26 min (C1)						
Replicate 1	229.2	0.1	0.0	231.9	2.4	1.0
Replicate 2	232.7	0.7	0.3			
Replicate 3	233.9	0.8	0.3			
45 min (C1)						
Replicate 1	227.6	0.2	0.1	227.7	1.0	0.4
Replicate 2	228.8	0.4	0.2			
Replicate 3	226.8	0.8	0.4			
60 min (C1)						
Replicate 1	226.5	0.7	0.3	226.4	1.1	0.5
Replicate 2	225.3	0.7	0.3			
Replicate 3	227.5	0.9	0.4			
180 min (C2)						
Replicate 1	220.7	0.5	0.2	220.5	1.1	0.5
Replicate 2	221.5	0.5	0.2			
Replicate 3	219.3	0.9	0.4			
360 min (C2)						
Replicate 1	211.1	0.9	0.4	211.2	0.4	0.2
Replicate 2	211.7	0.8	0.4			
Replicate 3	210.8	0.1	0.0			
720 min (C1)						
Replicate 1	195.0	0.8	0.4	196.2	1.8	0.9
Replicate 2	195.3	0.9	0.5			
Replicate 3	198.3	0.2	0.1			
1440 min (C1)						
Replicate 1	181.2	0.6	0.3	179.9	1.1	0.6
Replicate 2	179.8	0.5	0.3			
Replicate 3	178.9	0.4	0.2			
2880 (C1)						
Replicate 1	161.8	0.4	0.2	161.4	2.8	1.7
Replicate 2	158.5	0.3	0.2			
Replicate 3	164.0	1.0	0.6			

Table C14 Kinetics of arsenic(III) adsorption onto SC07 at an initial concentration of 2575.3 µg L^{-1} (*Section 7.1*).

	As µg L^{-1}	SD µg L^{-1}	RSD %	Average µg L^{-1}	SD µg L^{-1}	RSD %
Control C1	2728.7	56.2	2.1	2575.3	48.5	1.9
Control C2	2422.0	40.7	1.7			
15 min (C1)						
Replicate 1	1545.8	26.6	1.7	1572.6	96.5	6.1
Replicate 2	1679.7	21.2	1.3			
Replicate 3	1492.4	20.2	1.4			
30 min (C1)						
Replicate 1	1435.9	15.3	1.1	1397.4	51.6	3.7
Replicate 2	1338.7	15.3	1.1			
Replicate 3	1417.6	12.4	0.9			
45 min (C1)						
Replicate 1(*)	**2523.0**	**16.9**	**0.7**	1400.8	24.6	1.8
Replicate 2	1418.2	19.4	1.4			
Replicate 3	1383.4	19.4	1.4			
60 min (C1)						
Replicate 1	1332.6	12.3	0.9	1456.7	210.2	14.4
Replicate 2	1699.4	13.0	0.8			
Replicate 3	1338.0	12.7	1.0			
180 min (C2)						
Replicate 1	1216.9	21.5	1.8	1178.2	54.7	4.6
Replicate 2(*)	**2244.0**	**16.6**	**0.7**			
Replicate 3	1139.5	14.2	1.2			
360 min (C2)						
Replicate 1	960.5	9.3	1.0	1060.7	239.0	22.5
Replicate 2	888.0	5.7	0.6			
Replicate 3	1333.5	9.1	0.7			
720 min (C2)						
Replicate 1	600.4	5.8	1.0	571.7	26.7	4.7
Replicate 2	547.6	5.7	1.0			
Replicate 3	567.1	2.6	0.5			
1440 min (C1)						
Replicate 1	471.5	0.7	0.1	469.9	2.3	0.5
Replicate 2(*)	**753.0**	**1.1**	**0.1**			
Replicate 3	468.3	2.3	0.5			
2880 min (C1)						
Replicate 1	359.2	2.4	0.7	418.0	83.1	19.9
Replicate 2	476.8	1.8	0.4			
Replicate 3(*)	**624.5**	**2.7**	**0.4**			

(*) samples in **bold font** were not included in the data analysis because irregularities in the sample analysis; the concentration of these samples is extremely high because the low values for the internal standard (< 60 per cent) pushed the arsenic concentration up.

Table C15 Kinetics of arsenic(III) adsorption onto CAC at an initial concentration of 2739.0 µg L^{-1} (*Section 7.1*).

	As µg L^{-1}	SD µg L^{-1}	RSD %	Average µg L^{-1}	SD µg L^{-1}	RSD %
Control	2739.0	15.5	0.6			
15 min						
Replicate 1	1934.2	17.0	0.9	2123.4	164.1	7.7
Replicate 2	2209.6	24.7	1.1			
Replicate 3	2226.5	24.5	1.1			
26 min						
Replicate 1	2245.7	20.0	0.9	2273.9	35.1	1.5
Replicate 2	2262.8	18.2	0.8			
Replicate 3	2313.3	15.1	0.7			
45 min						
Replicate 1	2316.3	15.0	0.6	2309.3	8.6	0.4
Replicate 2	2299.7	20.2	0.9			
Replicate 3	2312.0	23.8	1.0			
60 min						
Replicate 1	2307.8	14.6	0.6	2310.1	13.3	0.6
Replicate 2	2298.1	12.9	0.6			
Replicate 3	2324.4	18.8	0.8			
180 min						
Replicate 1	2289.6	4.8	0.2	2290.4	6.7	0.3
Replicate 2	2297.5	2.9	0.1			
Replicate 3	2284.1	7.1	0.3			
360 min						
Replicate 1	2196.8	4.4	0.2	2199.5	4.3	0.2
Replicate 2	2204.4	2.0	0.1			
Replicate 3	2197.2	0.5	0.0			
720 min						
Replicate 1	2135.4	4.7	0.2	2152.2	14.9	0.7
Replicate 2	2163.8	3.4	0.2			
Replicate 3	2157.3	4.1	0.2			
1440 min						
Replicate 1	2101.4	6.3	0.3	2099.7	6.4	0.3
Replicate 2	2092.6	2.0	0.1			
Replicate 3	2105.2	6.6	0.3			
2880 min						
Replicate 1	2018.1	6.3	0.3	2026.5	13.0	0.6
Replicate 2	2020.0	4.6	0.2			
Replicate 3	2041.5	6.3	0.3			

Table C16 Effect of pH on arsenic(V) adsorption onto SC07 experiment (*Section 7.2*).

	As µg L^{-1}	SD µg L^{-1}	RSD %	Average µg L^{-1}	SD µg L^{-1}	RSD %
Control	221.9	1.4	0.6			
pH = 2.14						
Replicate 1	208.5	0.4	0.2	208.2	1.2	0.6
Replicate 2	207.0	0.4	0.2			
Replicate 3	209.2	0.2	0.1			
pH = 5.02						
Replicate 1	17.4	0.1	0.5	14.8	2.4	16.2
Replicate 2	14.3	0.1	0.8			
Replicate 3	12.7	0.1	0.8			
pH = 6.90						
Replicate 1	25.7	0.1	0.5	25.2	1.3	5.3
Replicate 2	26.3	0.0	0.1			
Replicate 3	23.7	0.2	0.8			
pH = 8.95						
Replicate 1	18.3	0.1	0.3	21.5	4.6	21.5
Replicate 2	19.3	0.0	0.2			
Replicate 3	26.8	0.2	0.7			
pH = 10.93						
Replicate 1	195.5	1.3	0.6	195.0	1.6	0.8
Replicate 2	196.3	0.6	0.3			
Replicate 3	193.2	0.8	0.4			

Table C17 Effect of pH on arsenic(V) adsorption onto CAC experiment (*Section 72*).

	As μg L^{-1}	SD μg L^{-1}	RSD %	Average μg L^{-1}	SD μg L^{-1}	RSD %
Control	224.8	1.1	0.5			
pH = 2.09						
Replicate 1	155.4	0.8	0.5	159.3	3.4	2.1
Replicate 2	161.0	0.4	0.3			
Replicate 3	161.4	0.5	0.3			
pH = 4.93						
Replicate 1	132.6	0.3	0.3	133.5	0.8	0.6
Replicate 2	133.6	0.3	0.2			
Replicate 3	134.3	0.2	0.2			
pH = 7.00						
Replicate 1	149.1	0.5	0.3	143.2	5.1	3.6
Replicate 2	140.7	0.3	0.2			
Replicate 3	139.9	0.3	0.2			
pH = 8.92						
Replicate 1	138.4	0.5	0.3	141.6	3.5	2.5
Replicate 2	145.4	1.0	0.7			
Replicate 3	141.0	0.4	0.3			
pH = 10.91						
Replicate 1	190.6	0.3	0.1	185.3	5.5	3.0
Replicate 2	185.9	0.7	0.4			
Replicate 3	179.6	0.2	0.1			

Table C18 Effect of pH on arsenic(III) adsorption onto SC07 experiment (*Section 7*.2).

	As µg L^{-1}	SD µg L^{-1}	RSD %	Average µg L^{-1}	SD µg L^{-1}	RSD %
Control pH (2.07-5.1, 7.06-10.95)	235.1	0.4	0.2			
Control pH 6.02	224.5	2.4	1.1			
pH = 2.07						
Replicate 1	210.3	0.1	0.1	222.1	15.1	6.8
Replicate 2	239.2	0.2	0.1			
Replicate 3	216.9	0.2	0.1			
pH = 4.02						
Replicate 1	86.7	0.6	0.7	83.3	12.8	15.4
Replicate 2	94.1	0.2	0.2			
Replicate 3	69.1	0.1	0.1			
pH = 5.1						
Replicate 1	34.5	0.1	0.2	34.9	4.0	11.5
Replicate 2	31.0	0.1	0.3			
Replicate 3	39.0	0.0	0.1			
pH = 6.02						
Replicate 1	14.8	0.1	0.8	15.7	1.0	6.1
Replicate 2	15.6	0.1	0.6			
Replicate 3	16.7	0.2	1.5			
pH = 7.06						
Replicate 1	35.2	0.2	0.7	32.0	3.4	10.6
Replicate 2	28.4	0.1	0.3			
Replicate 3	32.5	0.1	0.2			
pH = 9.03						
Replicate 1	38.0	0.1	0.2	36.0	1.8	5.0
Replicate 2	35.5	0.1	0.4			
Replicate 3	34.6	0.0	0.1			
pH = 10						
Replicate 1	98.8	0.1	0.1	92.1	14.1	15.3
Replicate 2	101.5	0.1	0.1			
Replicate 3	75.9	0.1	0.2			
pH = 10.95						
Replicate 1	231.1	0.5	0.2	228.6	2.7	1.2
Replicate 2	228.8	0.7	0.3			
Replicate 3	225.8	0.7	0.3			

Table C19 Effect of pH on arsenic(III) adsorption onto CAC experiment (*Section 7.2*).

	As µg L^{-1}	SD µg L^{-1}	RSD %	Average µg L^{-1}	SD µg L^{-1}	RSD %
Control	206.1	0.3	0.1			
pH = 2.03						
Replicate 1	163.2	1.3	0.8	174.4	9.8	5.6
Replicate 2	178.9	1.2	0.6			
Replicate 3	181.1	1.0	0.6			
pH = 3.99						
Replicate 1	176.2	0.3	0.2	163.9	10.6	6.5
Replicate 2	157.7	0.4	0.3			
Replicate 3	157.9	0.5	0.3			
pH = 5.04						
Replicate 1	154.5	0.2	0.2	167.8	11.5	6.9
Replicate 2	175.3	0.8	0.4			
Replicate 3	173.5	0.8	0.4			
pH = 6.09						
Replicate 1	167.3	0.7	0.4	170.5	3.1	1.8
Replicate 2	170.8	0.5	0.3			
Replicate 3	173.5	0.4	0.2			
pH = 7.01						
Replicate 1	174.1	0.3	0.2	175.5	1.3	0.7
Replicate 2	176.7	0.5	0.3			
Replicate 3	175.7	0.6	0.3			
pH = 9.00						
Replicate 1	150.7	0.2	0.1	150.9	0.2	0.1
Replicate 2	150.9	0.4	0.2			
Replicate 3	151.1	0.5	0.4			
pH = 9.97						
Replicate 1	148.6	0.4	0.2	148.5	0.5	0.4
Replicate 2	147.9	0.1	0.1			
Replicate 3	149.0	0.3	0.2			
pH = 10.98						
Replicate 1	153.4	0.7	0.4	149.2	3.7	2.4
Replicate 2	147.4	0.3	0.2			
Replicate 3	146.8	0.1	0.1			

Table C20 Arsenic(V) adsorption isotherm experiment at 25 °C for SC07 (*Section 7.3*).

	As µg L^{-1}	SD µg L^{-1}	RSD %	Average µg L^{-1}	SD µg L^{-1}	RSD %
As(V)$_0$	95.4	0.5	0.5			
Replicate 1	12.2	0.0	0.4	9.6	2.4	24.5
Replicate 2	9.0	0.1	1.1			
Replicate 3	7.6	0.1	1.0			
As(V)$_0$	254.0	0.7	0.3			
Replicate 1	16.8	0.1	0.4	16.7	0.7	4.3
Replicate 2	17.4	0.1	0.5			
Replicate 3	16.0	0.1	0.5			
As(V)$_0$	488.3	0.9	0.2			
Replicate 1	56.1	0.3	0.5	59.3	2.8	4.8
Replicate 2	60.2	0.3	0.4			
Replicate 3	61.5	0.5	0.8			
As(V)$_0$	735.6	2.2	0.3			
Replicate 1	70.8	0.2	0.3	64.4	5.6	8.6
Replicate 2	61.3	0.3	0.4			
Replicate 3	61.1	0.1	0.2			
As(V)$_0$	988.6	1.1	0.1			
Replicate 1	106.9	0.6	0.5	107.3	3.8	3.6
Replicate 2	111.3	0.1	0.1			
Replicate 3	103.6	0.0	0.0			
As(V)$_0$	1241.2	1.2	0.1			
Replicate 1	183.9	0.5	0.3	171.0	11.3	6.6
Replicate 2	162.8	0.4	0.2			
Replicate 3	166.2	0.8	0.5			
As(V)$_0$	1465.4	1.3	0.1			
Replicate 1	185.2	0.5	0.2	204.9	20.8	10.1
Replicate 2	226.6	0.1	0.0			
Replicate 3	202.8	0.5	0.2			
As(V)$_0$	1744.1	1.6	0.1			
Replicate 1	336.4	1.3	0.4	322.1	12.8	4.0
Replicate 2	311.6	0.7	0.2			
Replicate 3	318.4	0.9	0.3			

Table C21 Arsenic(V) adsorption isotherm experiment at 25 °C for CAC (*Section 7.3*)

	As µg L^{-1}	SD µg L^{-1}	RSD %	Average µg L^{-1}	SD µg L^{-1}	RSD %
As(V)$_0$	99.4	0.5	0.5			
Replicate 1	72.0	0.7	1.0	62.1	8.8	14.1
Replicate 2	59.1	0.2	0.4			
Replicate 3	55.3	0.0	0.1			
As(V)$_0$	366.2	1.1	0.3			
Replicate 1	164.7	0.6	0.4	157.8	6.3	4.0
Replicate 2	152.2	1.3	0.8			
Replicate 3	156.5	0.6	0.4			
As(V)$_0$	565.5	0.5	0.1			
Replicate 1	465.3	2.6	0.6	422.4	39.5	9.3
Replicate 2	414.4	2.0	0.5			
Replicate 3	387.6	1.5	0.4			
As(V)$_0$	800.9	0.9	0.1			
Replicate 1	557.4	4.5	0.8	546.1	9.9	1.8
Replicate 2	541.9	2.9	0.5			
Replicate 3	538.9	1.8	0.3			
As(V)$_0$	1040.9	3.1	0.3			
Replicate 1	719.2	2.1	0.3	717.6	5.9	0.8
Replicate 2	722.5	3.7	0.5			
Replicate 3	711.1	1.0	0.1			
As(V)$_0$	1266.7	2.8	0.2			
Replicate 1	908.6	2.6	0.3	925.5	24.0	2.6
Replicate 2	914.9	2.7	0.3			
Replicate 3	953.0	4.5	0.5			
As(V)$_0$	1533.0	1.7	0.1			
Replicate 1	1136.5	3.2	0.3	1146.6	9.0	0.8
Replicate 2	1153.4	1.7	0.1			
Replicate 3	1150.0	4.6	0.4			
As(V)$_0$	1787.3	4.6	0.3			
Replicate 1	1305.6	2.7	0.2	1354.5	44.1	3.3
Replicate 2	1366.4	5.1	0.4			
Replicate 3	1391.4	2.3	0.2			

Table C22 Arsenic(V) adsorption isotherm experiment at 35 °C for SC07 (*Section 7.3*).

	As µg L^{-1}	SD µg L^{-1}	RSD %	Average µg L^{-1}	SD µg L^{-1}	RSD %
$As(V)_0$	99.4	0.2	0.2			
Replicate 1	10.1	0.1	0.6	9.7	0.4	3.8
Replicate 2	9.5	0.1	0.6			
Replicate 3	9.5	0.1	1.2			
$As(V)_0$	302.6	0.4	0.1			
Replicate 1	22.7	0.2	0.8	24.1	2.2	9.2
Replicate 2	23.1	0.1	0.6			
Replicate 3	26.7	0.0	0.2			
$As(V)_0$	607.9	0.6	0.1			
Replicate 1	77.0	0.2	0.3	75.8	2.4	3.1
Replicate 2	77.3	0.3	0.4			
Replicate 3	73.1	0.2	0.3			
$As(V)_0$	914.2	3.2	0.3			
Replicate 1	84.8	0.4	0.5	90.1	4.8	5.4
Replicate 2	94.3	0.4	0.5			
Replicate 3	91.1	0.3	0.3			
$As(V)_0$	1225.7	4.4	0.4			
Replicate 1	155.7	0.6	0.4	148.9	8.8	5.9
Replicate 2	151.9	0.6	0.4			
Replicate 3	139.0	0.3	0.2			
$As(V)_0$	1511.6	4.4	0.3			
Replicate 1	210.0	1.0	0.5	211.6	1.6	0.7
Replicate 2	213.0	0.3	0.1			
Replicate 3	211.8	0.4	0.2			
$As(V)_0$	1859.6	6.6	0.4			
Replicate 1	288.8	1.4	0.5	278.3	9.7	3.5
Replicate 2	269.7	1.1	0.4			
Replicate 3	276.5	1.1	0.4			
$As(V)_0$	2171.7	8.7	0.4			
Replicate 1	377.1	1.6	0.4	387.5	10.0	2.6
Replicate 2	397.0	0.5	0.1			
Replicate 3	388.3	1.0	0.3			

Table C23 Arsenic(V) adsorption isotherm experiment at 35 °C for CAC (*Section 7.3*).

	As µg L^{-1}	SD µg L^{-1}	RSD %	Average µg L^{-1}	SD µg L^{-1}	RSD %
$As(V)_0$	101.8	0.6	0.6			
Replicate 1	44.1	0.2	0.5	46.5	2.4	5.2
Replicate 2	49.0	0.2	0.5			
Replicate 3	46.3	0.1	0.2			
$As(V)_0$	312.0	0.5	0.2			
Replicate 1	174.9	1.1	0.6	172.3	2.3	1.4
Replicate 2	171.5	0.5	0.3			
Replicate 3	170.4	0.7	0.4			
$As(V)_0$	585.3	4.4	0.7			
Replicate 1	381.5	3.2	0.8	383.0	2.4	0.6
Replicate 2	385.8	2.6	0.7			
Replicate 3	381.7	3.4	0.9			
$As(V)_0$	937.7	3.5	0.4			
Replicate 1	623.8	2.5	0.4	637.5	19.1	3.0
Replicate 2	659.3	1.6	0.2			
Replicate 3	629.2	3.4	0.5			
$As(V)_0$	1269.6	2.8	0.2			
Replicate 1	895.6	4.3	0.5	907.4	35.1	3.9
Replicate 2	879.6	2.1	0.2			
Replicate 3	946.8	8.1	0.9			
$As(V)_0$	1629.1	3.1	0.2			
Replicate 1	1199.0	2.8	0.2	1193.2	8.2	0.7
Replicate 2	1183.8	6.4	0.5			
Replicate 3	1196.9	5.4	0.4			
$As(V)_0$	1979.9	4.3	0.2			
Replicate 1	1450.2	7.5	0.5	1469.6	21.5	1.5
Replicate 2	1466.0	5.3	0.4			
Replicate 3	1492.7	6.4	0.4			
$As(V)_0$	2337.8	5.3	0.2			
Replicate 1	1720.1	7.8	0.5	1743.0	21.3	1.2
Replicate 2	1746.4	5.9	0.3			
Replicate 3	1762.3	8.0	0.5			

Table C24 Arsenic(III) adsorption isotherm experiment at 25 °C for SC07 (*Section 7.3*).

	As µg L^{-1}	SD µg L^{-1}	RSD %	Average µg L^{-1}	SD µg L^{-1}	RSD %
As(III)$_0$	68.5	0.2	0.2			
Replicate 1	10.6	0.1	0.6	9.6	1.0	10.2
Replicate 2	9.6	0.1	0.5			
Replicate 3	8.6	0.1	1.1			
As(III)$_0$	198.2	0.7	0.3			
Replicate 1	29.2	0.1	0.3	29.2	2.2	7.5
Replicate 2	31.4	0.1	0.4			
Replicate 3	27.0	0.2	0.6			
As(III)$_0$	430.8	0.3	0.1			
Replicate 1	75.5	0.1	0.1	71.7	10.2	14.3
Replicate 2	60.1	0.3	0.4			
Replicate 3	79.5	0.2	0.2			
As(III)$_0$	679.5	0.9	0.1			
Replicate 1	131.5	0.2	0.1	135.4	10.9	8.0
Replicate 2	127.1	0.7	0.6			
Replicate 3	147.7	0.2	0.1			
As(III)$_0$	972.4	0.6	0.1			
Replicate 1	156.9	0.4	0.2	149.9	6.6	4.4
Replicate 2	143.7	0.4	0.2			
Replicate 3	149.0	0.2	0.2			
As(III)$_0$	1186.0	3.0	0.2			
Replicate 1	266.1	1.5	0.6	265.1	0.9	0.3
Replicate 2	264.8	0.6	0.2			
Replicate 3	264.4	1.3	0.5			
As(III)$_0$	1466.5	3.5	0.2			
Replicate 1	311.8	0.5	0.2	325.7	12.4	3.8
Replicate 2	335.7	0.4	0.1			
Replicate 3	329.6	1.7	0.5			
As(III)$_0$	1741.0	10.6	0.6			
Replicate 1	421.5	0.1	0.0	395.1	33.6	8.5
Replicate 2	406.5	1.7	0.4			
Replicate 3	357.3	1.4	0.4			

Table C25 Arsenic(III) adsorption isotherm experiment at 25 °C for CAC (*Section 7.3*).

	As µg L^{-1}	SD µg L^{-1}	RSD %	Average µg L^{-1}	SD µg L^{-1}	RSD %
As(III)$_0$	76.7	0.7	0.8			
Replicate 1	72.0	0.6	0.8	73.8	2.2	3.0
Replicate 2	76.3	0.2	0.2			
Replicate 3	73.1	0.6	0.8			
As(III)$_0$	255.3	2.8	1.1			
Replicate 1	213.5	0.8	0.4	228.5	13.3	5.8
Replicate 2	233.3	0.7	0.3			
Replicate 3	238.8	0.9	0.4			
As(III)$_0$	535.7	0.7	0.1			
Replicate 1	489.5	0.9	0.2	492.0	4.0	0.8
Replicate 2	496.6	0.3	0.1			
Replicate 3	489.9	0.8	0.2			
As(III)$_0$	803.8	13.2	1.6			
Replicate 1	745.8	6.8	0.9	755.7	8.8	1.2
Replicate 2	758.7	1.6	0.2			
Replicate 3	762.5	0.4	0.1			
As(III)$_0$	1108.9	11.4	1.0			
Replicate 1	1024.2	0.7	0.1	1029.6	11.9	1.2
Replicate 2	1043.2	3.2	0.3			
Replicate 3	1021.3	0.2	0.0			
As(III)$_0$	1409.7	13.4	1.0			
Replicate 1	1286.6	1.0	0.1	1292.1	4.8	0.4
Replicate 2	1294.4	2.3	0.2			
Replicate 3	1295.3	2.3	0.2			
As(III)$_0$	1681.8	26.5	1.6			
Replicate 1	1522.8	3.9	0.3	1515.6	9.0	0.6
Replicate 2	1505.6	5.4	0.4			
Replicate 3	1518.4	2.1	0.1			
As(III)$_0$	2056.1	10.1	0.5			
Replicate 1	1806.5	6.7	0.4	1800.0	6.5	0.4
Replicate 2	1799.9	4.0	0.2			
Replicate 3	1793.6	3.0	0.2			

Table C26 Arsenic(III) adsorption isotherm experiment at 35 °C for SC07 (*Section 7.3*).

	As µg L^{-1}	SD µg L^{-1}	RSD %	Average µg L^{-1}	SD µg L^{-1}	RSD %
$As(III)_0$	72.1	0.5	0.7			
Replicate 1	11.4	0.1	0.7	11.5	0.3	2.3
Replicate 2	11.8	0	0.4			
Replicate 3	11.3	0	0.3			
$As(III)_0$	205.5	0.8	0.4			
Replicate 1	36.9	0.2	0.5	43.6	5.9	13.6
Replicate 2	45.6	0.2	0.4			
Replicate 3	48.2	0.2	0.3			
$As(III)_0$	394.1	0.7	0.2			
Replicate 1	85.8	0.2	0.2	86.6	1.7	2.0
Replicate 2	88.6	0	0			
Replicate 3	85.4	0.2	0.3			
$As(III)_0$	640.3	1.4	0.2			
Replicate 1	126.3	0.1	0.1	140.5	15.5	11.0
Replicate 2	157	0.4	0.3			
Replicate 3	138.1	0.5	0.4			
$As(III)_0$	907.6	1.3	0.1			
Replicate 1	213.2	0.1	0	207.9	10.8	5.2
Replicate 2	215.1	0.1	0			
Replicate 3	195.5	0.6	0.3			
$As(III)_0$	1147.5	1.1	0.1			
Replicate 1	264.4	0.2	0.1	278.4	18.3	6.6
Replicate 2	271.7	0.8	0.3			
Replicate 3	299.1	0.4	0.1			
$As(III)_0$	1402.2	2.5	0.2			
Replicate 1	370.4	0.7	0.2	355.2	13.6	3.8
Replicate 2	344.4	0.6	0.2			
Replicate 3	350.7	0.3	0.1			
$As(III)_0$	1667.8	3.6	0.2			
Replicate 1	461.3	0.9	0.2	454.9	7.5	1.6
Replicate 2	456.8	0.6	0.1			
Replicate 3	446.7	1.2	0.3			

Table C27 Arsenic(III) adsorption isotherm experiment at 35 °C for CAC (*Section 7.3*).

	As µg L^{-1}	SD µg L^{-1}	RSD %	Average µg L^{-1}	SD µg L^{-1}	RSD %
As(III)$_0$	93.0	0.1	0.2			
Replicate 1	68.8	0.3	0.4	71.8	2.7	3.7
Replicate 2	72.6	0.3	0.4			
Replicate 3	73.9	0.3	0.3			
As(III)$_0$	287.3	0.6	0.2			
Replicate 1	226.4	0.9	0.4	226.8	1.5	0.6
Replicate 2	228.5	0.8	0.4			
Replicate 3	225.6	0.3	0.2			
As(III)$_0$	559.1	6.8	1.2			
Replicate 1	472.4	0.7	0.1	475.5	3.3	0.7
Replicate 2	479.0	2.6	0.5			
Replicate 3	475.1	1.0	0.2			
As(III)$_0$	883.2	3.5	0.4			
Replicate 1	729.8	1.6	0.2	735.9	5.9	0.8
Replicate 2	741.7	1.3	0.2			
Replicate 3	736.2	2.3	0.3			
As(III)$_0$	1176.8	2.5	0.2			
Replicate 1	979.5	2.7	0.3	987.8	7.2	0.7
Replicate 2	992.3	1.6	0.2			
Replicate 3	991.4	1.4	0.1			
As(III)$_0$	1528.1	5.6	0.4			
Replicate 1	1246.4	2.0	0.2	1237.7	7.6	0.6
Replicate 2	1233.9	1.8	0.1			
Replicate 3	1232.6	0.4	0.0			
As(III)$_0$	1809.4	4.9	0.3			
Replicate 1	1506.7	4.3	0.3	1495.4	13.4	0.9
Replicate 2	1480.7	2.2	0.1			
Replicate 3	1498.7	6.5	0.4			
As(III)$_0$	2131.1	27.1	1.3			
Replicate 1	1778.5	5.1	0.3	1775.0	10.7	0.6
Replicate 2	1783.6	1.4	0.1			
Replicate 3	1763.0	2.8	0.2			

Table C28 Effect of competing ions on arsenic(V) adsorption onto SC07 (*Section 7.4*).

	As	SD	RSD	Average	SD	RSD
	µg L^{-1}	µg L^{-1}	%	µg L^{-1}	µg L^{-1}	%
Control	246.9	0.7	0.3			
Control (Cl^- = 25 mg L^{-1})	250.3	0.5	0.2			
Replicate 1	158.1	1.1	0.7	146.7	10.0	6.8
Replicate 2	139.4	0.9	0.6			
Replicate 3	142.5	0.9	0.6			
Control (Cl^- = 250 mg L^{-1})	266.4	1.9	0.7			
Replicate 1	256.2	0.6	0.2	272.4	33.6	12.3
Replicate 2	250.0	0.7	0.3			
Replicate 3	311.0	0.7	0.2			
Control (PO_4^2 = 0.1 mg L^{-1})	275.2	0.8	0.3			
Replicate 1	58.1	0.5	0.8	52.8	5.0	9.5
Replicate 2	48.1	0.1	0.2			
Replicate 3	52.3	0.2	0.4			
Control (PO_4^2 = 10 mg L^{-1})	258.0	0.8	0.3			
Replicate 1	166.2	0.8	0.5	162.8	3.9	2.4
Replicate 2	158.5	0.2	0.1			
Replicate 3	163.8	0.8	0.5			
Control (SO_4^2 = 10 mg L^{-1})	258.7	1.9	0.7			
Replicate 1	128.9	0.7	0.5	132.4	5.5	4.2
Replicate 2	129.6	0.1	0.1			
Replicate 3	138.7	0.3	0.2			
Control (SO_4^2 = 100 mg L^{-1})	249.9	1.2	0.5			
Replicate 1	214.0	3.1	1.5	213.0	0.9	0.4
Replicate 2	212.9	1.1	0.5			
Replicate 3	212.1	1.4	0.7			
Control (Mn = 0.1 mg L^{-1})	244.8	0.8	0.3			
Replicate 1	40.6	0.4	1.0	36.6	3.5	9.4
Replicate 2	34.5	0.2	0.5			
Replicate 3	34.7	0.1	0.2			
Control (Mn = 0.4 mg L^{-1})	253.0	0.4	0.1			
Replicate 1	36.4	0.4	1.2	39.8	4.2	10.6
Replicate 2	38.4	0.3	0.8			
Replicate 3	44.5	0.1	0.3			
Control (Si = 5 mg L^{-1})	253.0	0.9	0.4			
Replicate 1	185.6	0.5	0.3	181.6	7.9	4.4
Replicate 2	186.7	0.6	0.3			
Replicate 3	172.5	1.8	1.0			
Control (Si = 50 mg L^{-1})	264.5	2.2	0.8			
Replicate 1	273.6	0.8	0.3	276.6	6.5	2.3
Replicate 2	272.1	2.0	0.7			
Replicate 3	284.1	1.0	0.4			

Table C29 Effect of competing ions on arsenic(V) adsorption onto CAC (*Section 7.4*).

	As µg L^{-1}	SD µg L^{-1}	RSD %	Average µg L^{-1}	SD µg L^{-1}	RSD %
Control	255.9	0.3	0.1			
Control (Cl^{-} = 25 mg L^{-1})	265.4	0.7	0.2			
Replicate 1	180.7	1.7	0.9	181.1	0.5	0.3
Replicate 2	180.9	0.6	0.3			
Replicate 3	181.7	0.7	0.4			
Control (Cl^{-} = 250 mg L^{-1})	271.4	0.6	0.2			
Replicate 1	199.0	0.2	0.1	199.5	0.4	0.2
Replicate 2	199.5	0.9	0.5			
Replicate 3	199.9	1.0	0.5			
Control (PO_4^{2} = 0.1 mg L^{-1})	268.4	1.2	0.5			
Replicate 1	182.9	1.1	0.6	186.1	3.4	1.8
Replicate 2	189.7	1.6	0.8			
Replicate 3	185.8	1.0	0.5			
Control (PO_4^{2} = 10 mg L^{-1})	250.1	2.3	0.9			
Replicate 1	225.3	1.9	0.9	227.6	3.6	1.6
Replicate 2	225.7	2.4	1.1			
Replicate 3	231.7	1.9	0.8			
Control (SO_4^{2} = 10 mg L^{-1})	278.1	0.9	0.3			
Replicate 1	187.0	0.9	0.5	190.0	2.8	1.5
Replicate 2	190.6	0.7	0.4			
Replicate 3	192.4	1.5	0.8			
Control (SO_4^{2} = 100 mg L^{-1})	253.5	0.3	0.1			
Replicate 1	202.0	1.3	0.6	199.0	3.4	1.7
Replicate 2	199.7	1.2	0.6			
Replicate 3	195.2	2.1	1.1			
Control (Mn = 0.1 mg L^{-1})	269.0	1.0	0.4			
Replicate 1	179.5	1.1	0.6	185.3	5.5	3.0
Replicate 2	186.1	0.3	0.2			
Replicate 3	190.4	0.6	0.3			
Control (Mn = 0.4 mg L^{-1})	285.1	1.4	0.5			
Replicate 1	187.5	0.1	0.1	190.3	2.9	1.5
Replicate 2	190.1	1.3	0.7			
Replicate 3	193.2	0.3	0.1			
Control (Si = 5 mg L^{-1})	246.6	0.8	0.3			
Replicate 1	194.3	2.0	1.0	195.3	2.3	1.2
Replicate 2	193.7	0.6	0.3			
Replicate 3	197.9	0.8	0.4			
Control (Si = 50 mg L^{-1})	260.2	1.3	0.5			
Replicate 1	243.3	0.4	0.2	243.4	1.4	0.6
Replicate 2	242.0	1.3	0.5			
Replicate 3	244.9	0.6	0.3			

Table C30 Effect of competing ions on arsenic(III) adsorption onto SC07 (*Section 7.4*).

	As µg L^{-1}	SD µg L^{-1}	RSD %	Average µg L^{-1}	SD µg L^{-1}	RSD %
Control	216.8	2.5	1.1			
Control (Cl^{-} = 25 mg L^{-1})	234.3	2.4	1.0			
Replicate 1	98.4	0.5	0.5	100.4	3.0	3.0
Replicate 2	99.0	0.2	0.2			
Replicate 3	103.9	0.2	0.2			
Control (Cl^{-} = 250 mg L^{-1})	242.7	0.9	0.4			
Replicate 1	194.3	0.6	0.3	192.7	2.6	1.3
Replicate 2	194.1	0.3	0.2			
Replicate 3	189.7	0.2	0.1			
Control (PO_4^{2} = 0.1 mg L^{-1})	207.0	2.0	1.0			
Replicate 1	28.5	0.2	0.6	26.6	1.9	7.2
Replicate 2	26.7	0.2	0.8			
Replicate 3	24.7	0.0	0.1			
Control (PO_4^{2} = 10 mg L^{-1})	192.6	2.4	1.3			
Replicate 1	102.6	0.2	0.2	103.3	2.2	2.2
Replicate 2	105.8	0.4	0.4			
Replicate 3	101.5	1.2	1.1			
Control (SO_4^{2} = 10 mg L^{-1})	207.1	4.6	2.2			
Replicate 1	94.1	0.3	0.3	97.0	2.5	2.6
Replicate 2	98.1	0.2	0.2			
Replicate 3	98.7	0.1	0.1			
Control (SO_4^{2} = 100 mg L^{-1})	233.3	0.9	0.4			
Replicate 1	169.9	2.0	1.1	170.4	1.6	0.9
Replicate 2	169.2	0.8	0.5			
Replicate 3	172.2	1.0	0.6			
Control (Mn = 0.1 mg L^{-1})	219.6	0.8	0.4			
Replicate 1	26.0	0.2	0.6	26.0	0.8	3.1
Replicate 2	25.3	0.1	0.4			
Replicate 3	26.9	0.1	0.4			
Control (Mn = 0.4 mg L^{-1})	219.9	1.8	0.8			
Replicate 1	27.1	0.1	0.3	28.8	1.6	5.4
Replicate 2	29.2	0.1	0.3			
Replicate 3	30.2	0.2	0.7			
Control (Si = 5 mg L^{-1})	250.6	2.6	1.1			
Replicate 1	188.8	2.7	1.4	189.2	1.5	0.8
Replicate 2	188.0	0.8	0.5			
Replicate 3	190.9	2.0	1.1			
Control (Si = 50 mg L^{-1})	261.5	1.5	0.6			
Replicate 1	217.6	2.2	1.0	214.4	5.5	2.6
Replicate 2	217.6	1.0	0.5			
Replicate 3	208.1	1.5	0.7			

Table C31 Effect of competing ions on arsenic (III) adsorption onto CAC (*Section 7.4*).

	As	SD	RSD	Average	SD	RSD
	$\mu g\ L^{-1}$	$\mu g\ L^{-1}$	%	$\mu g\ L^{-1}$	$\mu g\ L^{-1}$	%
Control	224.5	2.4	1.1			
Control (Cl^- = 25 mg L^{-1})	243.9	1.4	0.6			
Replicate 1	196.9	0.6	0.3	196.8	0.4	0.2
Replicate 2	197.2	0.9	0.4			
Replicate 3	196.4	1.1	0.6			
Control (Cl^- = 250 mg L^{-1})	248.8	0.3	0.1			
Replicate 1	203.9	0.8	0.4	206.3	2.1	1.0
Replicate 2	208.0	0.2	0.1			
Replicate 3	206.9	0.6	0.3			
Control (PO_4^2 = 0.1 mg L^{-1})	211.0	2.5	1.2			
Replicate 1	194.6	0.3	0.2	196.0	1.2	0.6
Replicate 2	196.7	0.5	0.2			
Replicate 3	196.6	0.6	0.3			
Control (PO_4^2 = 10 mg L^{-1})	194.8	1.7	0.9			
Replicate 1	211.7	0.3	0.1	211.9	1.0	0.5
Replicate 2	211.1	3.1	1.5			
Replicate 3	213.0	2.1	1.0			
Control (SO_4^2 = 10 mg L^{-1})	250.3	3.5	1.4			
Replicate 1	198.1	0.6	0.3	200.5	2.1	1.0
Replicate 2	202.0	0.7	0.4			
Replicate 3	201.5	0.6	0.3			
Control (SO_4^2 = 100 mg L^{-1})	234.8	0.9	0.4			
Replicate 1	196.6	1.5	0.8	195.4	1.1	0.5
Replicate 2	195.0	2.0	1.0			
Replicate 3	194.5	1.8	0.9			
Control (Mn = 0.1 mg L^{-1})	227.4	2.9	1.3			
Replicate 1	199.1	0.9	0.5	202.2	3.7	1.8
Replicate 2	201.3	0.6	0.3			
Replicate 3	206.3	0.1	0.1			
Control (Mn = 0.4 mg L^{-1})	241.2	1.8	0.8			
Replicate 1	208.6	0.6	0.3	200.3	12.0	6.0
Replicate 2	186.5	0.3	0.1			
Replicate 3	205.7	0.1	0.0			
Control (Si = 5 mg L^{-1})	250.5	1.9	0.8			
Replicate 1	201.0	1.3	0.7	201.9	0.8	0.4
Replicate 2	202.3	0.7	0.4			
Replicate 3	202.4	2.5	1.2			
Control (Si = 50 mg L^{-1})	262.4	2.2	0.8			
Replicate 1	237.0	1.1	0.5	235.5	1.6	0.7
Replicate 2	235.7	2.7	1.2			
Replicate 3	233.9	1.9	0.8			

Appendix D. Propagation of error for calculations with arsenic average concentrations

This appendix is included to clarify the handling of the experimental data from adsorption experiments. During adsorption experiments two parameters were measured, the pH and the arsenic concentration in the liquid phase of samples (C_t). These values are reported in the result section as the average of the triplicates ± the standard deviation of the triplicates. However in some occasions it was necessary to perform mathematical calculations with the raw data; for instance, the calculation of the fraction of arsenic in solution, the percentage of arsenic removed or the uptake capacity of adsorbents.

The theory of propagation of random errors was used to calculate the error of these calculations. If Y = f(X, Z, . . .), then the standard deviation (SD) of Y can be estimated with Equation D1[4]. This formula is limited to small random errors and uncorrelated independent variables. Table D1 shows the functions used to handle data from adsorption experiments and the formulae used for calculation of the standard deviation.

$$SD_Y = \sqrt{\left(\frac{\partial Y}{\partial X}\right)^2 SD_X^2 + \left(\frac{\partial Y}{\partial Z}\right)^2 SD_Z^2 + \ \ldots} \qquad \text{Equation D1}$$

Table D1 Functions used on arsenic adsorption experiments and the formula for calculation of the standard deviation.

	Function	Standard deviation (SD)
Fraction of arsenic in solution	$f(\mathrm{C_0}, \mathrm{C_e}) = \frac{C_e}{C_0}$	$\frac{C_e}{C_0}\sqrt{\frac{(SD_{Ce})^2}{{C_e}^2} + \frac{(SD_{C0})^2}{{C_0}^2}}$
Uptake capacity, q_t	$f(C_t, C_0) = \frac{C_0 - C_t}{m} \times V$	$\frac{V}{m}\sqrt{{SD_{Ct}}^2 + {SD_{C0}}^2}$
% Arsenic removal	$f(\mathrm{C_0}, \mathrm{C_e}) = \frac{C_0 - C_e}{C_0} \times 100$	$100\frac{C_e}{C_0}\sqrt{\frac{(SD_{Ce})^2}{{C_e}^2} + \frac{(SD_{C0})^2}{{C_0}^2}}$

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[4] Emery, W. J. and R. E. Thomson (2004). Data Analysis Methods in Physical Oceanography, Elsevier Science & Technology.

Appendix E. Supporting information for Chapter 5

Table E1 ANOVA test for yield. Tests of within-subjects effects (sphericity assumed).

Source	Type III sum of squares	df	Mean square	F	Sig.
CT	13.547	1	13.547	7.477	.041
Error(CT)	9.059	5	1.812		
AT	715.335	1	715.335	157.625	.000
Error(AT)	22.691	5	4.538		
At	70.325	1	70.325	43.647	.001
Error(At)	8.056	5	1.611		
CT -AT	2.125	1	2.125	2.837	.153
Error(CT-AT)	3.746	5	.749		
CT-At	4.142	1	4.142	1.562	.267
Error(CT-At)	13.254	5	2.651		
AT-At	37.277	1	37.277	40.436	.001
Error(AT-At)	4.609	5	.922		
CT-AT-At	11.505	1	11.505	4.678	.083
Error(CT-AT-At)	12.296	5	2.459		

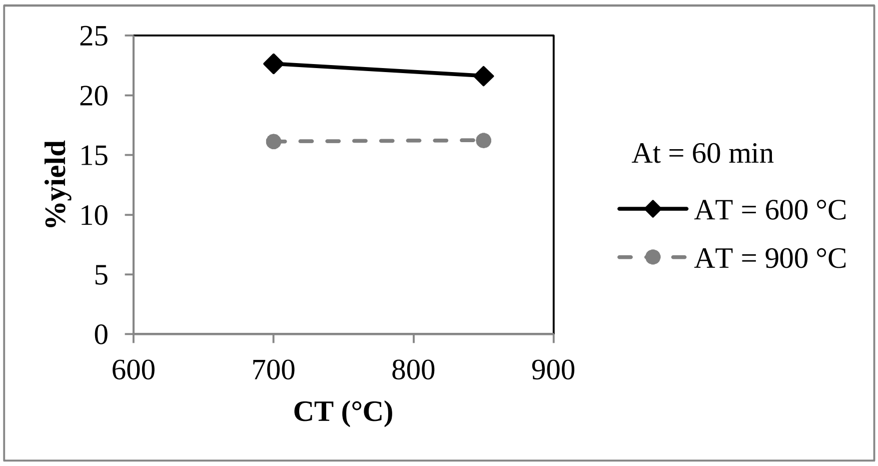


Figure E1 Effect of CT at an AT of 600 and 900 °C and an At of 60 min on %yield of SCAC.

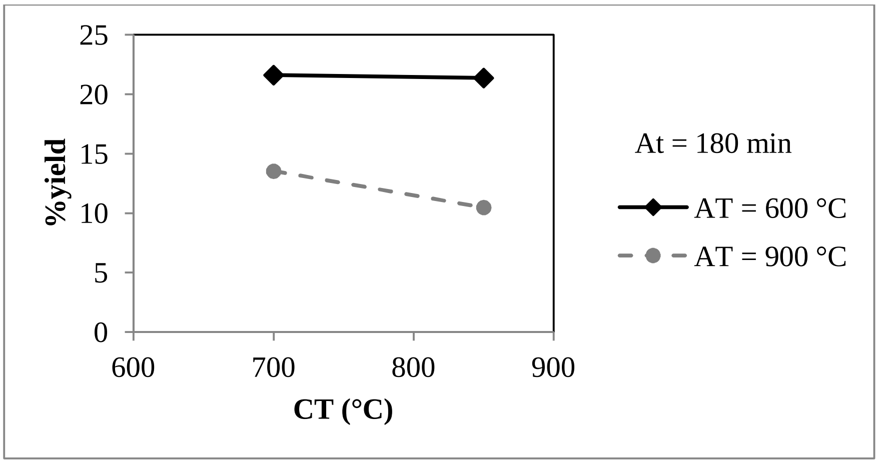


Figure E2 Effect of CT at an AT of 600 and 900 °C, and an At of 180 min on %yield of SCAC.

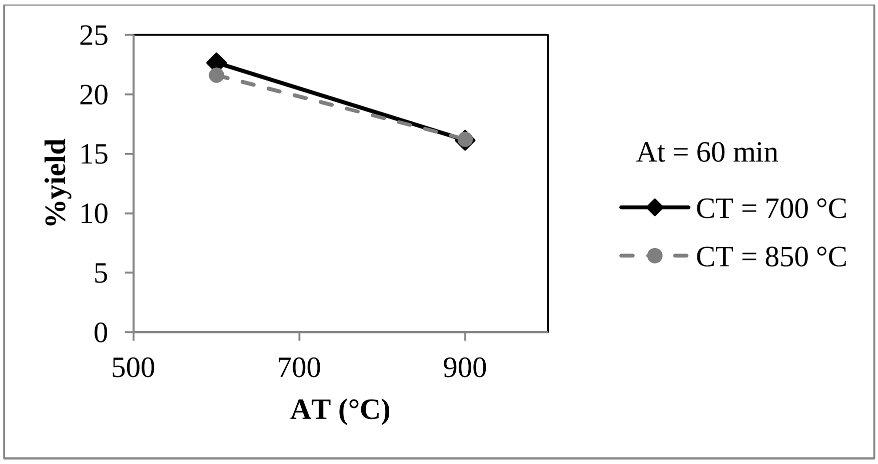


Figure E3 Effect of AT at an CT of 700 and 850 °C, and an At of 60 min on %yield of SCAC.

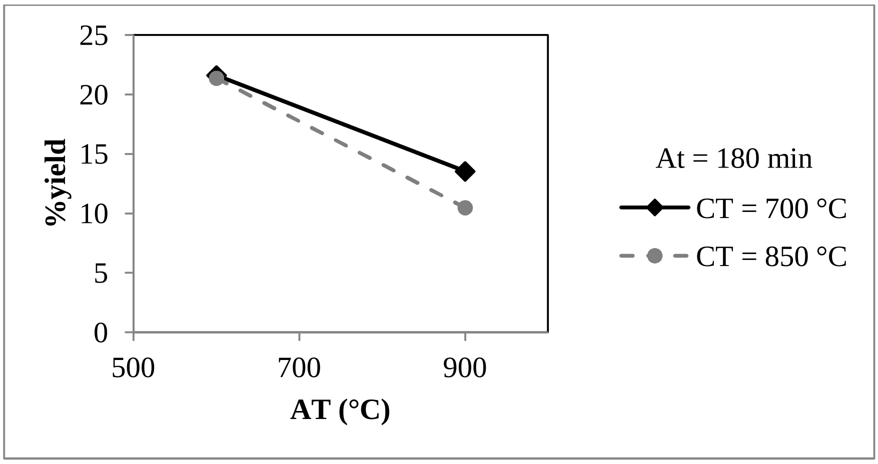


Figure E4 Effect of AT at an CT of 700 and 850 °C, and an At of 180 min on %yield of SCAC.

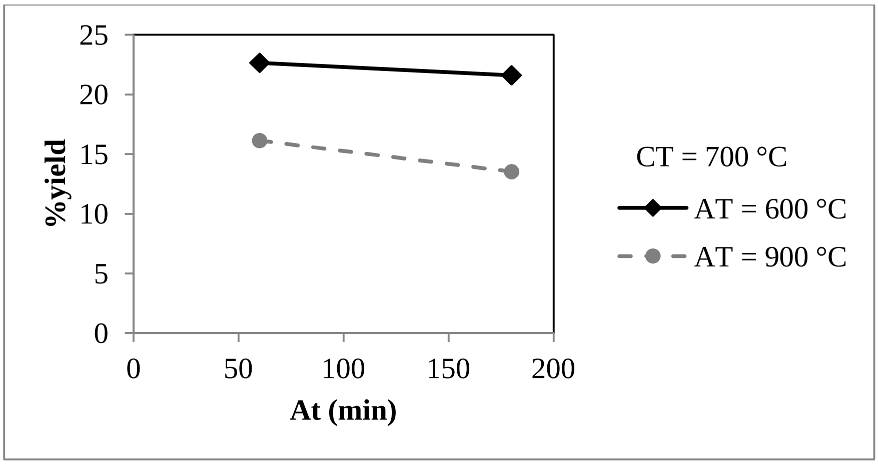


Figure E5 Effect of At at an AT of 600 and 900 °C, and an CT of 700 °C on %yield of SCAC.

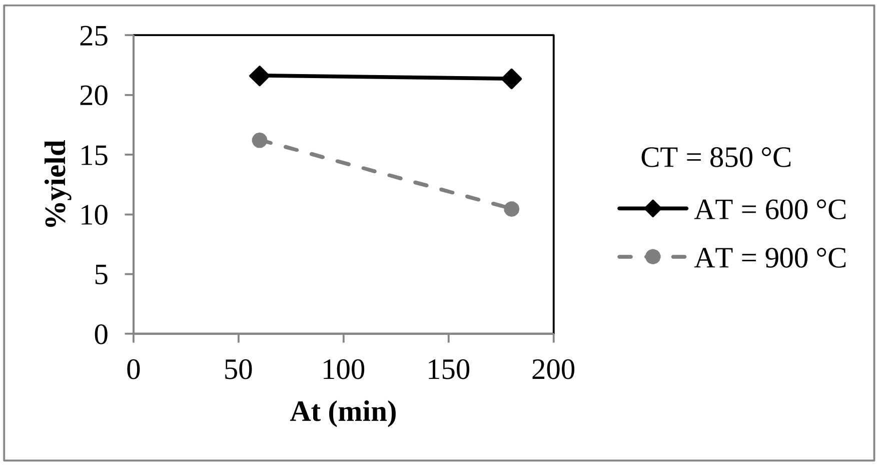


Figure E6 Effect of At at an AT of 600 and 900 °C, and an CT of 850 °C on %yield of SCAC.

Table E2 Results from the ANOVA test of the 2^3 factorial experiment for per cent arsenic(V) removal.

Source	Type III sum of squares	Degrees of freedom	Mean square	F	Significance
CT	262.48	1	262.48	23.04	< 0.001
AT	33995.70	1	33995.70	2983.65	< 0.001
At	50.32	1	50.32	4.42	0.052
CT -AT	51.30	1	51.31	4.50	0.050
CT-At	3.02	1	3.02	0.27	0.614
AT-At	384.08	1	384.08	33.71	< 0.001
CT-AT-At	11.72	1	11.72	1.03	0.326
Error	182.30	16	11.39		
Total	88985.52	24			

R^2 = 0.995 (adjusted R^2= 0.992)

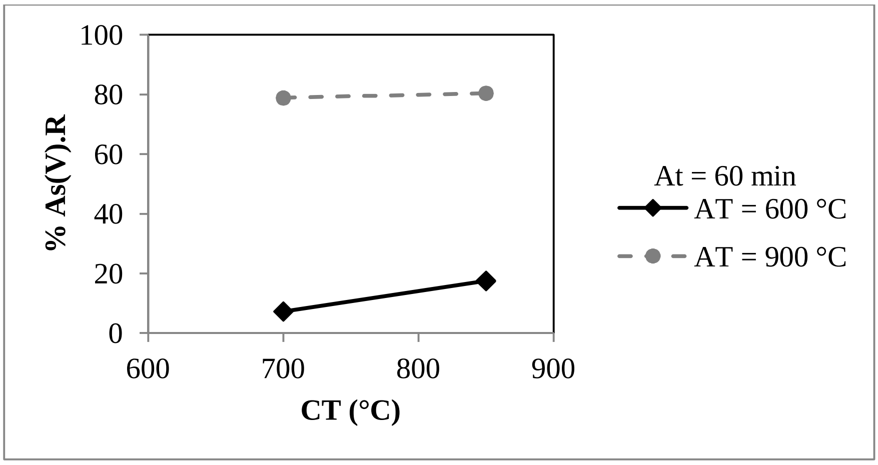


Figure E7 Effect of CT at an AT of 600 and 900 °C and an At of 60 min on per cent arsenic(V) removal.

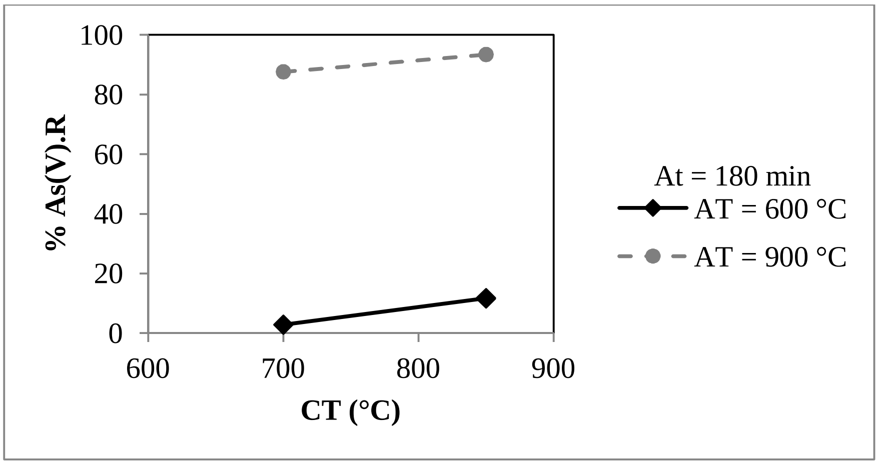


Figure E8 Effect of CT at an AT of 600 and 900 °C, and an At of 180 min on per cent arsenic(V) removal.

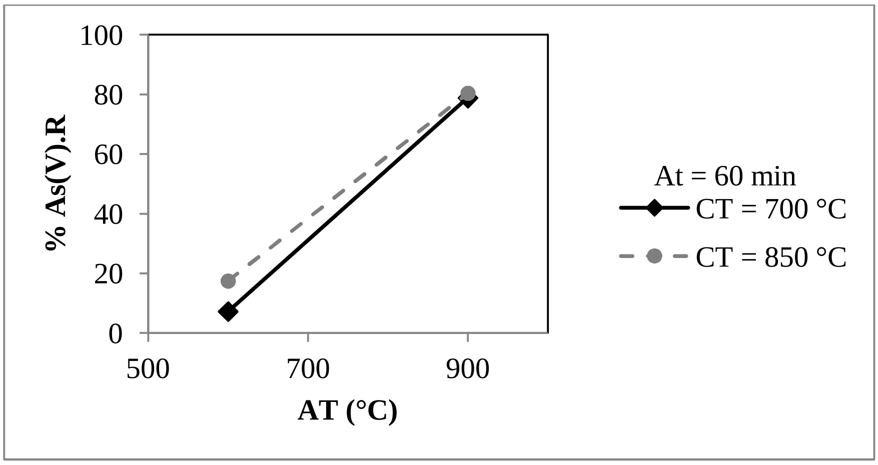


Figure E9 Effect of AT at an CT of 700 and 850 °C, and an At of 60 min on per cent arsenic(V) removal.

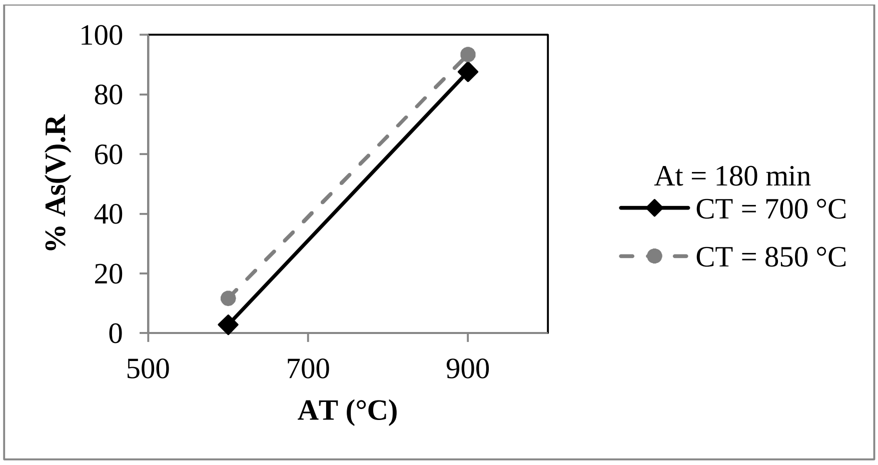


Figure E10 Effect of AT at an CT of 700 and 850 °C, and an At of 180 min on per cent arsenic(V) removal.

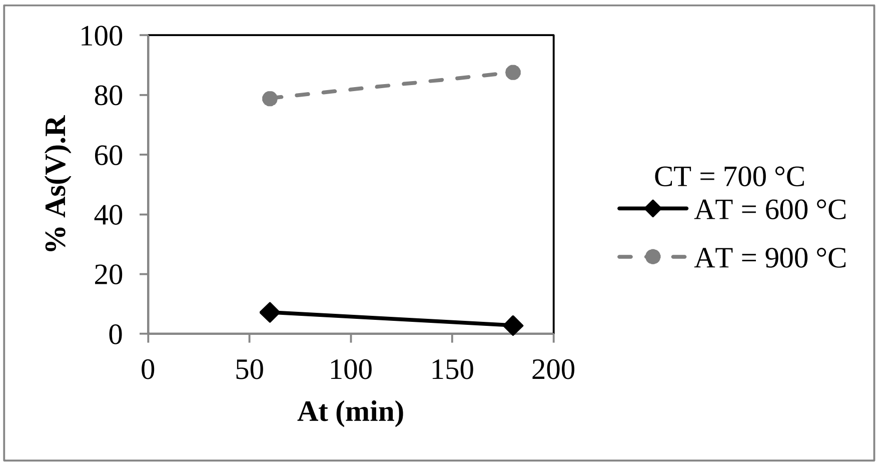


Figure E11 Effect of At at an AT of 600 and 900 °C, and an CT of 700 °C on per cent arsenic(V) removal.

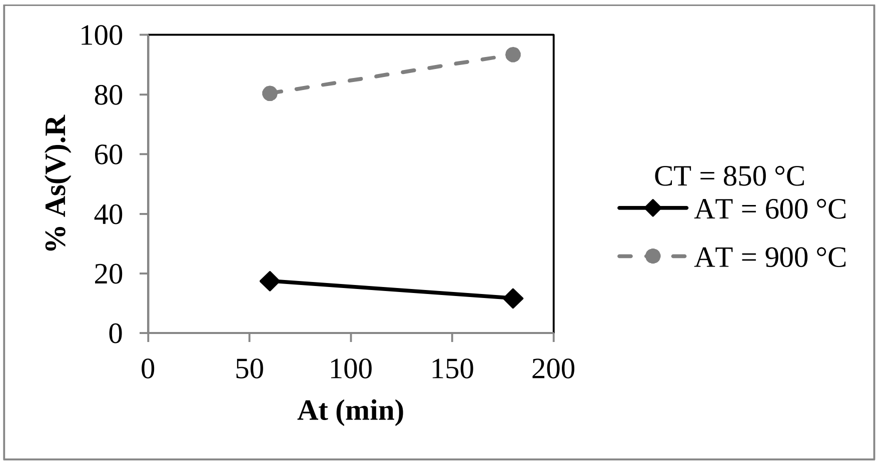


Figure E12 Effect of At at an AT of 600 and 900 °C, and an CT of 850 °C on per cent arsenic(V) removal.

Table E3 Results from the ANOVA test of the 2^3 factorial experiment for per cent arsenic(III) removal.

Source	Type III sum of squares	Degrees of freedom	Mean square	F	Significance
CT	36.43	1	36.43	62.89	< 0.001
AT	36615.63	1	36615.63	63208.04	< 0.001
At	80.63	1	80.63	139.19	< 0.001
CT-AT	0.03	1	0.03	0.04	0.839
CT-At	2.30	1	2.30	3.97	0.064
AT-At	312.12	1	312.12	538.80	< 0.001
CT-AT-At	0.10	1	0.10	0.18	0.679
Error	9.27	16	0.58		
Total	88886.36	24			

(a) R^2= 1.000 (adjusted R^2 = 1.000)

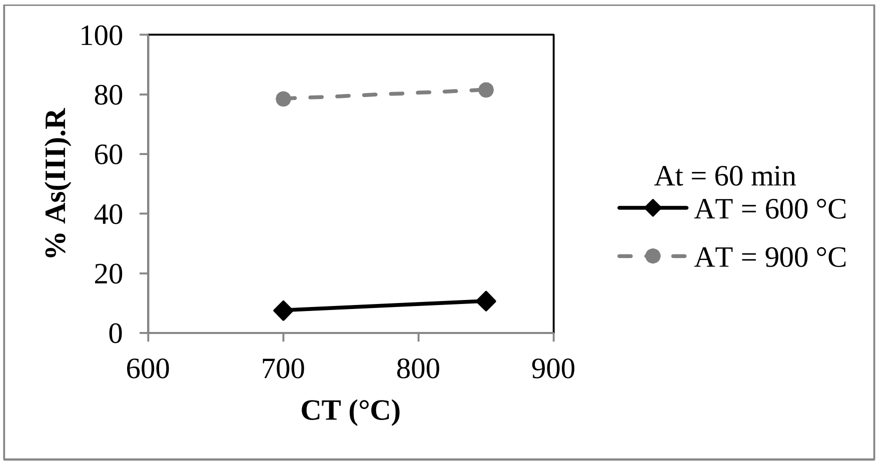


Figure E13 Effect of CT at an AT of 600 and 900 °C and an At of 60 min on per cent arsenic(III) removal.

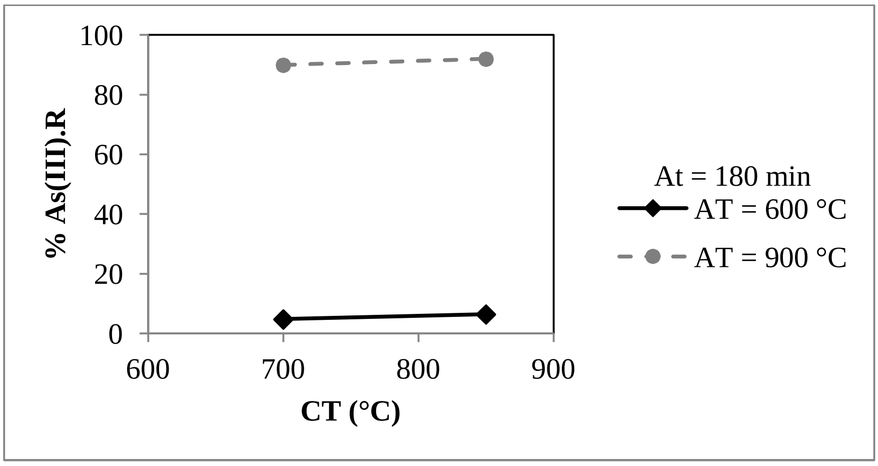


Figure E14 Effect of CT at an AT of 600 and 900 °C, and an At of 180 min on per cent arsenic(III) removal.

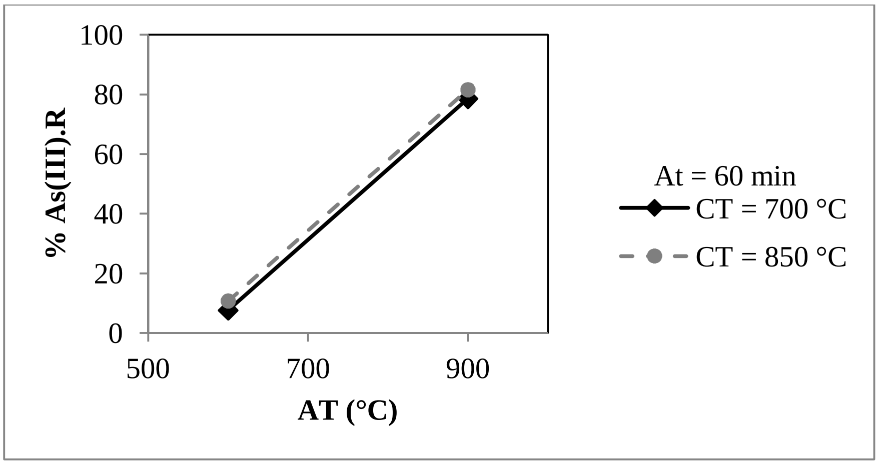


Figure E15 Effect of AT at an CT of 700 and 850 °C, and an At of 60 min on per cent arsenic(III) removal.

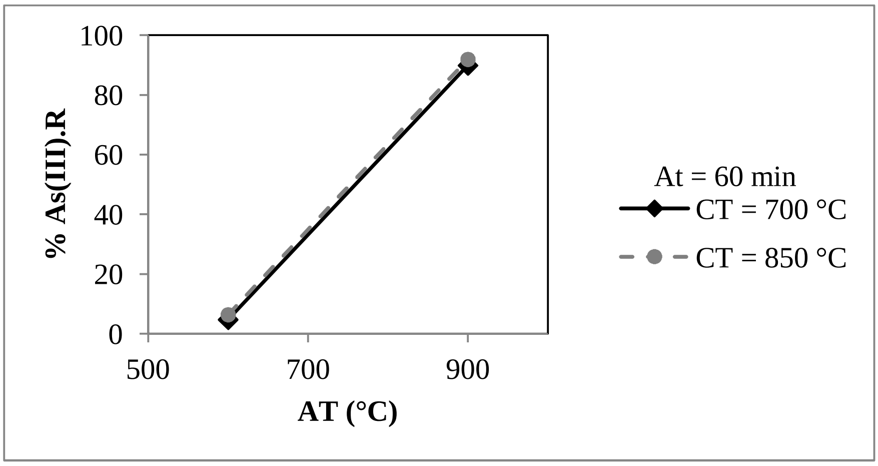


Figure E16 Effect of AT at an CT of 700 and 850 °C, and an At of 180 min on per cent arsenic(III) removal.

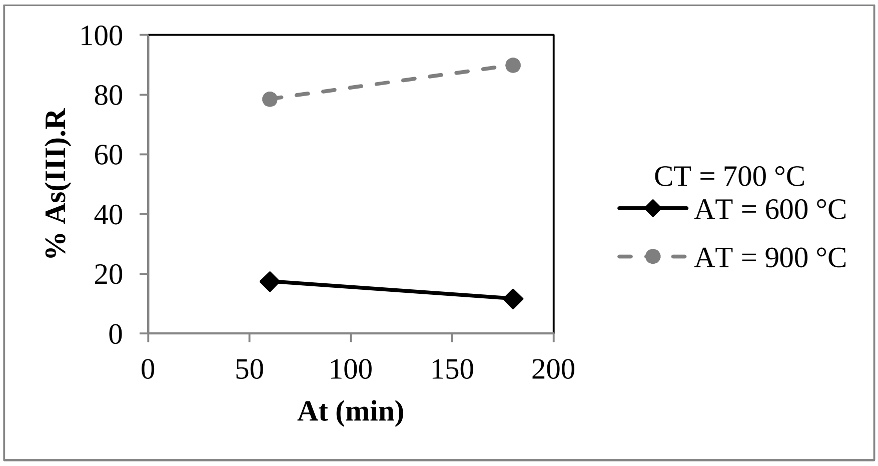


Figure E17 Effect of At at an AT of 600 and 900 °C, and an CT of 700 °C on per cent arsenic(III) removal.

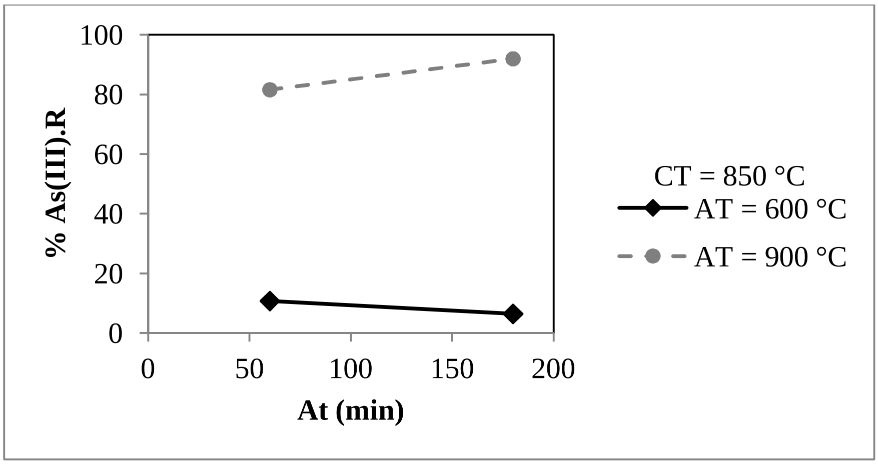
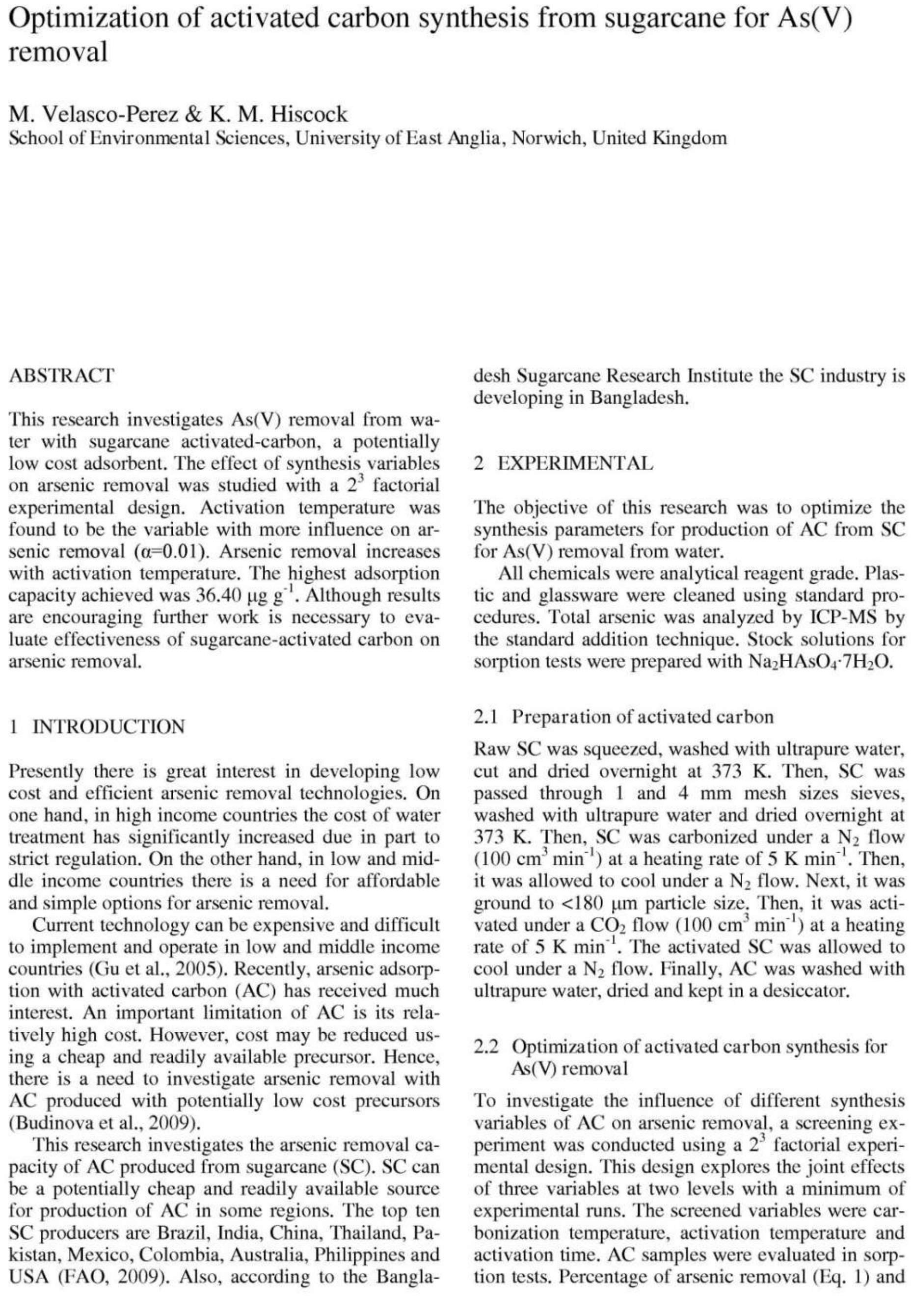


Figure E18 Effect of At at an AT of 600 and 900 °C, and an CT of 850 °C on per cent arsenic(III) removal.

Appendix F. Conference papers

Velasco-Perez, M., Hiscock, K.M., 2010. Optimisation of activated carbon synthesis from sugarcanr for As(V) removal. In: J. Jiin-Shuh, J. Bundschuh, P. Bhattacharya (Eds.), Third international Congress: arsenic in geosphere and human diseases. CRC Press Taylor and Francis Group, Tainan, Taiwan, pp. 448-449.



Optimization of activated carbon synthesis from sugarcane for As(V) removal

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ABSTRACT

This research investigates As(V) removal from water with sugarcane activated-carbon, a potentially low cost adsorbent. The effect of synthesis variables on arsenic removal was studied with a 2^3 factorial experimental design. Activation temperature was found to be the variable with more influence on arsenic removal (α=0.01). Arsenic removal increases with activation temperature. The highest adsorption capacity achieved was 36.40 $\mu g\ g^{-1}$. Although results are encouraging further work is necessary to evaluate effectiveness of sugarcane-activated carbon on arsenic removal.

1 INTRODUCTION

Presently there is great interest in developing low cost and efficient arsenic removal technologies. On one hand, in high income countries the cost of water treatment has significantly increased due in part to strict regulation. On the other hand, in low and middle income countries there is a need for affordable and simple options for arsenic removal.

Current technology can be expensive and difficult to implement and operate in low and middle income countries (Gu et al., 2005). Recently, arsenic adsorption with activated carbon (AC) has received much interest. An important limitation of AC is its relatively high cost. However, cost may be reduced using a cheap and readily available precursor. Hence, there is a need to investigate arsenic removal with AC produced with potentially low cost precursors (Budinova et al., 2009).

This research investigates the arsenic removal capacity of AC produced from sugarcane (SC). SC can be a potentially cheap and readily available source for production of AC in some regions. The top ten SC producers are Brazil, India, China, Thailand, Pakistan, Mexico, Colombia, Australia, Philippines and USA (FAO, 2009). Also, according to the Bangladesh Sugarcane Research Institute the SC industry is developing in Bangladesh.

2 EXPERIMENTAL

The objective of this research was to optimize the synthesis parameters for production of AC from SC for As(V) removal from water.

All chemicals were analytical reagent grade. Plastic and glassware were cleaned using standard procedures. Total arsenic was analyzed by ICP-MS by the standard addition technique. Stock solutions for sorption tests were prepared with $Na_2HAsO_4 \cdot 7H_2O$.

2.1 Preparation of activated carbon

Raw SC was squeezed, washed with ultrapure water, cut and dried overnight at 373 K. Then, SC was passed through 1 and 4 mm mesh sizes sieves, washed with ultrapure water and dried overnight at 373 K. Then, SC was carbonized under a N_2 flow (100 $cm^3\ min^{-1}$) at a heating rate of 5 K min^{-1}. Then, it was allowed to cool under a N_2 flow. Next, it was ground to <180 μm particle size. Then, it was activated under a CO_2 flow (100 $cm^3\ min^{-1}$) at a heating rate of 5 K min^{-1}. The activated SC was allowed to cool under a N_2 flow. Finally, AC was washed with ultrapure water, dried and kept in a desiccator.

2.2 Optimization of activated carbon synthesis for As(V) removal

To investigate the influence of different synthesis variables of AC on arsenic removal, a screening experiment was conducted using a 2^3 factorial experimental design. This design explores the joint effects of three variables at two levels with a minimum of experimental runs. The screened variables were carbonization temperature, activation temperature and activation time. AC samples were evaluated in sorption tests. Percentage of arsenic removal (Eq. 1) and percentage of activation burn off (Eq. 2) were calculated to compare AC's performance.

$$\% \text{ As removal} = \frac{As_0 - As_f}{As_0} \times 100 \qquad (1)$$

where As_0 and As_f are the initial and final concentrations of arsenic, respectively.

$$\% \text{ burn off} = 100 - \left[\frac{W_{Act}}{W_{SC}} \times 100\right] \qquad (2)$$

where W_{Act} is the dry weight of SC after activation and W_{SC} is the dry weight of the precursor. Also, the adsorption capacity (q) was calculated for some AC samples. q is usually reported as the amount of arsenic adsorbed per gram of adsorbent at equilibrium.

The effect of the synthesis variables in terms of their influence on arsenic removal and burn off were further investigated with an optimization experiment. Carbonization temperature was set at 973 K, carbonization time at 90 min and activation time at 120 min. Activation temperatures studied were 1023, 1073, 1123 and 1173 K.

3 RESULTS

An ANOVA test was run on the screening experiment results to evaluate the individual and joint effects of synthesis variables on arsenic removal. It was found that activation temperature had the greatest influence on arsenic removal (α=0.01). The influence of activation temperature is clearly seen in Table 1-A. Samples with the highest arsenic removal were prepared at the highest activation temperature (1173 K). Burn off increases considerably with activation temperature. AC activated at 873 K had a burn off lower than 78.01 %. Whereas AC activated at 1173 K had a burn off as high as 88.34 %.

Table 1. Synthesis parameters, % As removal and % burn off for A-Screening experiment and B-Optimization experiment. As_0=250 μg l^{-1}, pH_0 ≈8 and sorbent dose = 5 g l^{-1}.

Activated carbon sample	Carbonization temp. K	Activation temp. K	Activation time min	As removal %	Burn off %
A-Screening experiment					
AC01	973	873	60	7.51	76.62
AC02	1123	873	60	3.62	78.01
AC03	973	1173	60	46.94	84.02
AC04	1123	1173	60	45.98	83.39
AC05	973	873	180	2.19	77.30
AC06	1123	873	180	2.72	77.78
AC07	973	1173	180	57.00	88.34
AC08	1123	1173	180	53.89	88.15
B-Optimization experiment					
AC09	973	1023	120	11.29	78.15
AC10	973	1073	120	15.11	79.76
AC11	973	1123	120	45.28	83.13
AC12	973	1173	120	64.74	88.96

The effect of activation temperature on arsenic removal was also observed in the optimization experiment (Table 1-B). Arsenic removal increases with activation temperature. Considering adsorption capacity and losses by burn off, AC samples with better performance are AC07 (q = 28.83 μg g^{-1}, burn off = 88.34 %), AC11 (25.41 μg g^{-1}, 83.13 %) and AC12 (36.40 μg g^{-1}, 88.96 %).

pH values of samples treated with AC was little affected. Initial pH was set at ≈8 and final pH ranged from 7.02 to 7.71.

4 CONCLUSIONS

Sorption experiments revealed that high activation temperature yields more efficient AC for arsenic removal. However, % burn off increases significantly with activation temperature. Consequently more SC is needed to prepare equal amounts of AC with high burn off than for AC with low burn off. AC12 achieved the highest arsenic removal of 64.74 %. This AC was prepared at a carbonization temperature of 973 K, activation temperature of 1173 K and activation time of 120 min.

Arsenic adsorption capacity was found to be relatively low at 36.40 μg g^{-1}. However, the AC dose used on sorption experiments was very conservative (5 g l^{-1}). Further work is necessary to assess the dose effect of AC on arsenic removal. Also, arsenic removal can be improved by loading AC with metals such as Zn and Fe. This possibility needs to be explored too.

5 ACKNOWLEDGEMENTS

Authors would like to thank CONACyT-Mexico and SEP-Mexico for their financial support. Also, the authors are grateful to the University of East Anglia for technical support and laboratory facilities provided.

6 REFERENCES

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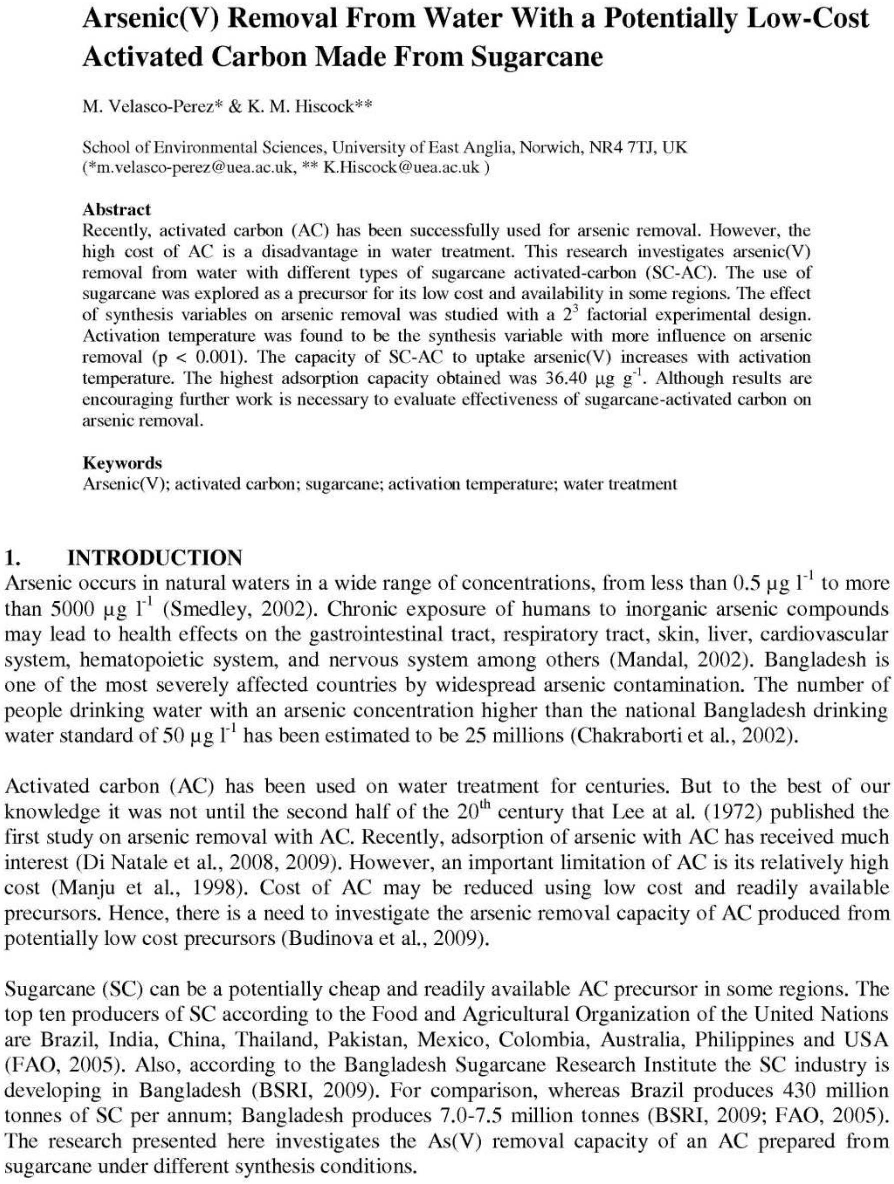
Gu, Z., Fang, J. & Deng, B. 2005. Preparation and evaluation of GAC-based iron-containing adsorbents for arsenic removal. Environmental Science and Technology 39(10):3833-3843.

Velasco-Perez, M., Hiscock, K.M., 2010. Arsenic(V) removal from water with a potentially low-cost activated carbon made from sugarcane International Water Association (IWA) Conference. UK Young Water Professionals. International Water Association, Cranfield, UK, pp. 57-63.



Arsenic(V) Removal From Water With a Potentially Low-Cost Activated Carbon Made From Sugarcane

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Abstract
Recently, activated carbon (AC) has been successfully used for arsenic removal. However, the high cost of AC is a disadvantage in water treatment. This research investigates arsenic(V) removal from water with different types of sugarcane activated-carbon (SC-AC). The use of sugarcane was explored as a precursor for its low cost and availability in some regions. The effect of synthesis variables on arsenic removal was studied with a 2^3 factorial experimental design. Activation temperature was found to be the synthesis variable with more influence on arsenic removal ($p < 0.001$). The capacity of SC-AC to uptake arsenic(V) increases with activation temperature. The highest adsorption capacity obtained was 36.40 $\mu g\ g^{-1}$. Although results are encouraging further work is necessary to evaluate effectiveness of sugarcane-activated carbon on arsenic removal.

Keywords
Arsenic(V); activated carbon; sugarcane; activation temperature; water treatment

1. INTRODUCTION

Arsenic occurs in natural waters in a wide range of concentrations, from less than 0.5 $\mu g\ l^{-1}$ to more than 5000 $\mu g\ l^{-1}$ (Smedley, 2002). Chronic exposure of humans to inorganic arsenic compounds may lead to health effects on the gastrointestinal tract, respiratory tract, skin, liver, cardiovascular system, hematopoietic system, and nervous system among others (Mandal, 2002). Bangladesh is one of the most severely affected countries by widespread arsenic contamination. The number of people drinking water with an arsenic concentration higher than the national Bangladesh drinking water standard of 50 $\mu g\ l^{-1}$ has been estimated to be 25 millions (Chakraborti et al., 2002).

Activated carbon (AC) has been used on water treatment for centuries. But to the best of our knowledge it was not until the second half of the 20th century that Lee at al. (1972) published the first study on arsenic removal with AC. Recently, adsorption of arsenic with AC has received much interest (Di Natale et al., 2008, 2009). However, an important limitation of AC is its relatively high cost (Manju et al., 1998). Cost of AC may be reduced using low cost and readily available precursors. Hence, there is a need to investigate the arsenic removal capacity of AC produced from potentially low cost precursors (Budinova et al., 2009).

Sugarcane (SC) can be a potentially cheap and readily available AC precursor in some regions. The top ten producers of SC according to the Food and Agricultural Organization of the United Nations are Brazil, India, China, Thailand, Pakistan, Mexico, Colombia, Australia, Philippines and USA (FAO, 2005). Also, according to the Bangladesh Sugarcane Research Institute the SC industry is developing in Bangladesh (BSRI, 2009). For comparison, whereas Brazil produces 430 million tonnes of SC per annum; Bangladesh produces 7.0-7.5 million tonnes (BSRI, 2009; FAO, 2005). The research presented here investigates the As(V) removal capacity of an AC prepared from sugarcane under different synthesis conditions.

2. MATERIALS AND METHODS

2.1 Preparation of activated carbon

Sugarcane-activated carbon (SC-AC) was prepared with the following procedure. Raw SC was squeezed, washed with ultrapure water, cut and dried overnight at 100 °C. Next, SC was passed through 1 and 4 mm mesh size sieves, washed with ultrapure water and dried overnight at 100 °C. Then, SC was carbonized under a N_2 flow of 100 cm^3 min^{-1} at a heating rate of 5 °C min^{-1}. Then, it was allowed to cool under a N_2 flow. The carbonized SC was ground to <180 µm particle size and activated under a CO_2 flow of 100 cm^3 min^{-1} at a heating rate of 5 °C min^{-1}. The SC-AC was allowed to cool under a N_2 flow. Finally, each gramme of SC-AC was washed 5 times with 200 mL of ultrapure water, dried overnight at 100 °C and kept in a desiccator. Carbonisation and activation were carried out in a horizontal tube furnace Carbolite CTF12-65-301.

2.2 Sorption experiments

All chemicals were of at least analytical reagent grade. Reusable plastic and glassware were cleaned using standard procedures. Total arsenic was analyzed with ICP-MS (Thermo Electron Corporation, model: X Series I) by the standard addition technique. Standards for analysis were prepared with ultrapure water and commercially available arsenic standards.

Sorption experiments were conducted with ultrapure water spiked with As(V). Stock As(V) solutions were prepared with dibasic sodium arsenate heptahydrate ($Na_2HAsO_4.7H_2O$). Experiments were conducted in duplicate; the average of duplicates is reported here. For all sorption experiments the SC-AC dose was set at 5 g l^{-1}, As(V) concentration at 250 µg l^{-1} and pH at 8. The pH of solutions was adjusted with 0.1 M sodium hydroxide (NaOH) or 2.25 M nitric acid (HNO_3). Reactors were shook for 24 hours. At collection samples were filtered through a 0.2 µm membrane acetate filter and acidified with double distilled nitric acid (HNO_3). Samples were stored at 4°C until analysis. Analysis was conducted within a month of collection.

2.2.1 Screening experiment

The objective of the screening experiment was to investigate the influence of different synthesis variables of SC-AC on As(V) removal. This experiment was planned using a 2^3 factorial experimental design. Factorial designs can be used to study the effects of several factors on a response (Montgomery, 2005). Also, factorial designs allow studying a process under a wide range of conditions with a minimum of experimental runs. The 2^3 factorial design studies the individual and joint effects of 3 factors at 2 levels on a response. In this research, the factors studied were carbonisation temperature (700 & 850 °C), activation temperature (600 & 900 °C) and activation time (60 & 180 min). The response studied was percentage of As(V) removal (Eq. 1)

$$\% \text{ As(V) removal} = \frac{\text{As(V)}_0 - \text{As(V)}_f}{\text{As(V)}_0} \times 100 \qquad (1)$$

where As(V)_0 is the initial concentration of As(V), As(V)_f is the final concentration of As(V). Other parameters used to evaluate the performance of SC-AC samples were percentage of burn off and adsorption capacity. Percentage burn off (Eq. 2) is defined as the loss of mass of the adsorbent due to carbonisation and activation (Ioannidou et al., 2007),

$$\% \text{ burn off} = 100 - \left[\frac{W_{Act}}{W_{SC}} \times 100\right] \qquad (2)$$

were W_{Act} is the dry weight of SC after activation and W_{SC} is the dry weight of the precursor. The adsorption capacity, q, is usually reported as the amount of arsenic adsorbed per gramme of adsorbent at equilibrium. The adsorption capacity is expressed in units of μg g^{-1} or mg g^{-1} as convenient.

2.2.2 Optimization experiment

The effect of the synthesis variables in terms of their influence on arsenic removal and burn off were closely investigated through an optimization experiment. The values of variables used in this experiment were selected on the basis of the results of the factorial experimental design (Section 2.2.1). Carbonisation temperature was set at 700 °C, carbonisation time at 90 min and activation time at 120 min. The activation temperatures studied were 750, 800, 850 and 900 °C. All other parameters remained unchanged.

2.3 pH of zero charge and scanning electron microscopy of selected sugarcane-activated carbons

The pH of zero charge (pH_{ZC}) is an important sorbent property. The pH_{ZC} is the pH at which the surface of the adsorbent has a net neutral charge (Hiscock, 2005). At higher pH values the surface has a net negative charge and at lower pH values the surface has a net positive charge. Depending on the pH_{ZC} of the adsorbent and the pH of solutions, the adsorbent will either attract cations or anions.

The pH_{ZC} of selected samples of SC-AC was investigated. Four SC-AC samples were selected for this study; samples AC05 and AC06 (Table 1) with low % As(V) removal; and samples AC11 and AC12 with high % As(V) removal. The pH_{ZC} was measured with the immersion technique (Bourikas et al., 2003). First, a 0.01 M sodium nitrate ($NaNO_3$) solution was prepared with free carbon dioxide (CO_2) water. Then, solutions of different pH values were prepared with this nitrate solution. Next, 0.15 g of SC-AC were placed in glass vials. Then, 20 ml of the pH-adjusted sodium nitrate solution was added and the reactors were sealed and placed on a bottle shaker. After 48 hours the pH was measured and recorded. The pH_{ZC} was identified by plotting the initial pH value versus the difference between initial and final pH values.

The scanning electron microscope (SEM/EDX) was used to analyse the topography and surface composition of selected SC-AC samples. Samples were qualitatively analysed. A JEOL JSM-5900 LV microscope was used for the analysis. The samples analysed under the SEM include SA-AC with low % As(V) removal (AC05 & AC06; Table 1-A) and SA-AC with high % As(V) removal (AC07, AC11& AC12).

3. RESULTS

3.1 Sorption experiments

Table 1 presents the synthesis parameters, % As(V) removal, % burn off and As(V) adsorption capacity for SC-AC samples from the screening experiment (Section 2.2.1) and optimization experiment (Section 2.2.2). A rapid examination of the data reveals that samples activated at 900°C remove a greater percentage of As(V) than those activated at 600°C. Also, As(V) removal is almost unaffected by variations on carbonisation temperatures and slightly affected by variations in activation time. A rigorous examination of the data was conducted through an analysis of variance (ANOVA) test. The ANOVA test was performed with the software SPSS version 14.0. The ANOVA test (Table 2) confirms the previous observations. The factor with the greatest influence on arsenic removal was activation temperature ($p < 0.001$). This factor contributed nearly 94% of the total variability in arsenic removal. On the other hand, % burn off increases drastically with activation temperature. AC prepared at an activation temperature of 600 °C had a burn off lower than 78.01 %. Whereas AC prepared at 900 °C had a burn off as high as 88.34%.

Table 1. Synthesis parameters, % As(V) removal, % burn off and adsorption capacity, q, for (A) Screening experiment (Section 2.2.1) and (B) Optimization experiment (Section 2.2.2). Initial As=250 μg l^{-1}; pH = 8; and sorbent dose = 5 g l^{-1}.

Sample	Carbonisation temperature (°C)	Activation temperature (°C)	Activation time (min)	As(V) removal (%)	Burn off (%)	Adsorption capacity, q (μg g^{-1})
A- Screening experiment						
AC01	700	600	60	7.51	76.62	3.81
AC02	850	600	60	3.62	78.01	1.82
AC03	700	900	60	46.94	84.02	24.24
AC04	850	900	60	45.98	83.39	23.52
AC05	700	600	180	2.19	77.30	1.12
AC06	850	600	180	2.72	77.78	1.38
AC07	700	900	180	57.00	88.34	28.83
AC08	850	900	180	53.89	88.15	27.57
B- Optimization experiment						
AC09	700	750	120	11.29	78.15	6.34
AC10	700	800	120	15.11	79.76	8.42
AC11	700	850	120	45.28	83.13	25.41
AC12	700	900	120	64.74	88.96	36.40

The effect of activation temperature on As(V) removal was observed again in the optimisation experiment (Table 1-B). This experiment intended to reach a trade off between arsenic removal capacity and burn off of AC. The sample with highest As(V) removal was AC12 (As removal = 64.74 %, q = 36.40 μg g^{-1}, burn off = 88.96 %) followed by AC07 (57.00%, 28.83 μg g^{-1}, 88.34%) and AC08 (53.89%, 27.57 μg g^{-1}, 88.15 %). Also, it was found that the pH of samples treated with SC-AC was little affected. The initial pH was set at 8.01 ± 0.22 for the screening experiment and 8.00 ± 0.25 for the optimization experiment. Final pH ranged from 7.02 to 7.71 for both experiments.

Table 2. ANOVA test for the screening experiment

Source of variation	Sum of squares	Degrees of freedom	Mean square	F_0	Prob>F
Carbonisation temperature	13.820	1	13.820	0.279	0.612
Activation temperature	8813.924	1	8813.924	177.739	<0.001
Activation time	34.545	1	34.545	0.697	0.428
Carbonisation temperature & activation temperature	0.124	1	0.124	0.003	0.961
Carbonisation temperature & activation time	1.283	1	1.283	0.026	0.876
Activation temperature & activation time	146.229	1	146.229	2.949	0.124
Carbonisation temperature, activation temperature & activation time	10.775	1	10.775	0.217	0.654
Error	396.714	8	49.589		
Total	21501.468	16			
Corrected total	9417.413	15			

3.2 pH of zero charge and scanning electron microscopy of selected sugarcane-activated carbons

The pH_{ZC} was found to be 9.13 for AC05, 10.13 for AC06, 9.77 for AC11 and 9.57 for AC12. These values reveal that SC-AC has a very basic character. SEM analysis of the surface of SC-AC samples reveals that samples are mainly composed of carbon and oxygen. Most samples presented silica ions at trace levels. Some samples presented concentrations below the detection limits of sodium, calcium, magnesium, sulphur and iron. These results are confirmed by an ICP-MS mass scan of a SC-AC blank sample (not shown here). Figure 1 shows photographs of SC-AC samples taken with the SEM. These photographs illustrate the assortment of topographies found on SC-AC samples. In general, samples are formed of particles of laminar structure of various shapes and sizes. Particles with laminar structures with both defined and undefined pore patterns were present in all samples. Particles with non-laminar structures were observed in sample AC02 and AC12. These particles seem to have a rough surface and a structure similar to a honeycomb. However, there is not apparent relation between the synthesis parameters of SC-AC and development of certain type of structures.

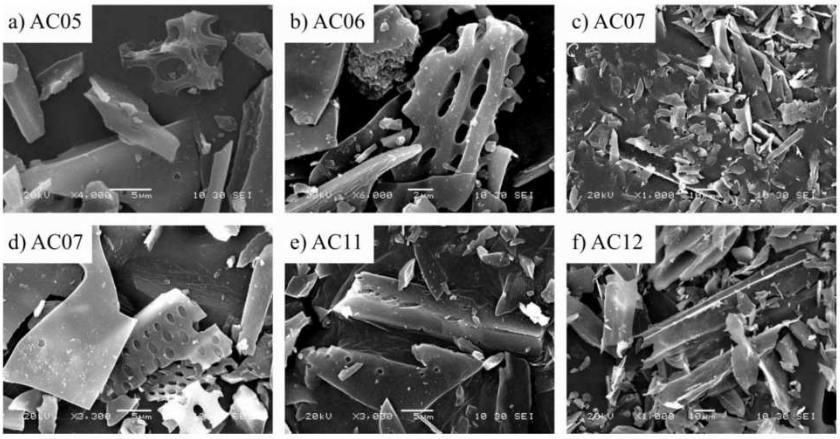

Figure 1. Scanning electron microscopy photographs of different types of sugarcane-activated carbons. Micrographs have different magnifications.

DISCUSSION

Sorption experiments showed that high activation temperatures yield AC with higher As(V) removal capacity. Juang et al. (2002) also noticed that higher activation temperatures increased the adsorption capacity of AC made from bagasses for dye removal (Juang et al., 2002). However, samples activated at high temperatures have high burn off. A high burn off implies that a great proportion of the raw material will be lost during carbonisation and activation. A greater amount of precursor is needed to prepare AC with high burn off than AC with low burn off. Also, activation at high temperature requires more energy than activation at low temperatures.

The pH_{ZC} for both SC-AC samples with high and low arsenic sorption varies from 9.13 to 10.13. Sorption experiments were set at a pH of ≈8. At this pH arsenate ions are expected to be negatively charged (Vaughan et al., 2005; Smedley et al., 2005). Hence, under the experimental conditions arsenic sorption on SC-AC may be favoured. However, the relationship between pH and As(V) adsorption on SC-AC needs to be studied in more detail to find the optimum pH conditions.

Comparisons of performance of adsorbents, in terms of their ability to remove pollutants from solutions, are difficult to make. The adsorption capacity, q, is generally used as an indication of adsorbent performance. However, experimental q values are obtained under a wide range of experimental conditions. Hence, direct comparison of q values obtained under different experimental conditions is not possible. In this study the highest value of q was 36.40 μg g^{-1} (obtained with AC12). This value is modest compared with other values published in the literature. For instance, in a study by Pattanayak et al. (2000), the adsorption capacity of fly ash AC obtained for As(V) was 34.46 mg g^{-1}. The adsorption capacity of fly ash reported by Pattanayak et al. (2000) is three orders of magnitude greater that the maximum adsorption capacity obtained for SC-AC in this study. However, the experimental setting is very different too. The AC dose is the same in both studies, 5g l^{-1}. But, initial As(V) concentration and pH values differ greatly. In the present study sorption experiments were carried out at an As(V) concentration of 250 μg l^{-1} and a pH of 8. Pattanayak et al. (2000) used an As(V) initial concentration of 490 mg l^{-1} and a pH of 2.2.

4. CONCLUSIONS

This research investigated the influence of synthesis parameters of SC-AC samples on As(V) removal. A 2^3 factorial experimental design was used for this purpose. The synthesis parameters studied were carbonisation temperature, activation temperature and activation time. An analysis of variance revealed that the variable with most influence on As(V) removal is activation temperature. The SC-AC samples with highest As(V) uptake were AC12 (36.40 μg g^{-1}), AC07 (28.83 μg g^{-1}) and AC08 (27.57 μg g^{-1}). All of these samples were prepared at an activation temperature of 900 °C, the highest activation temperature evaluated here. The As(V) uptake obtained in this research by SC-AC sorbents is modest. Nevertheless, SC-AC sorbent showed a fair sorption capacity for As(V). More studies are necessary to evaluate the sorption capacity of SC-AC. As(V) uptake can be improved with pre-treatment with acids and impregnation with metals. However, all this modifications will make more complicated and costly the production process.

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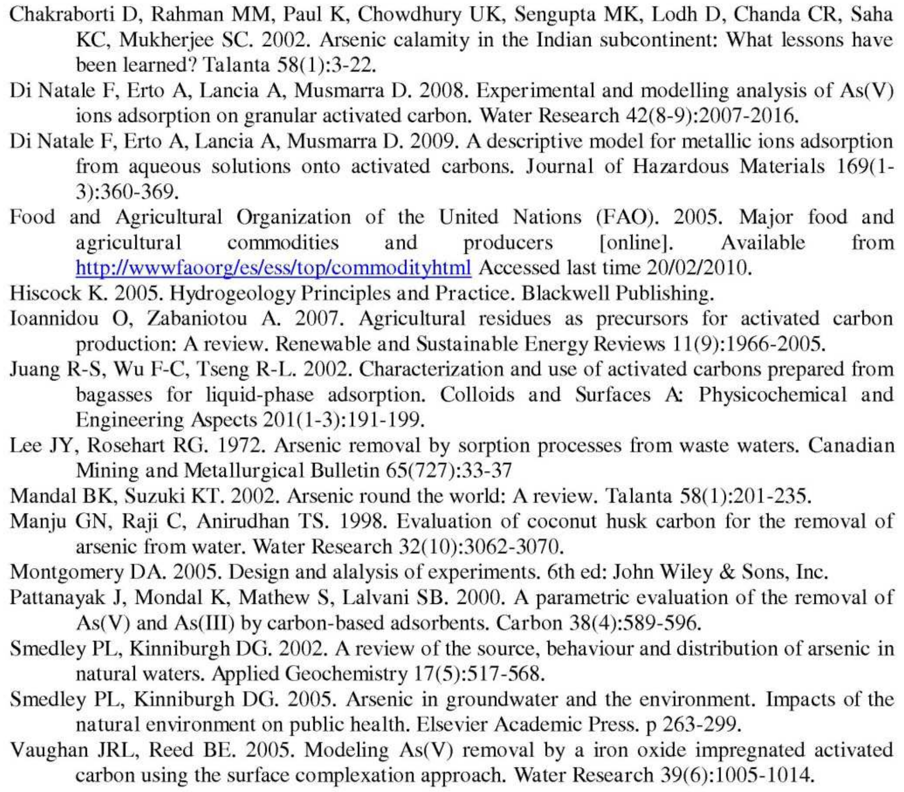

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