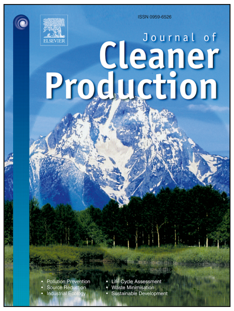

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Graphical abstract

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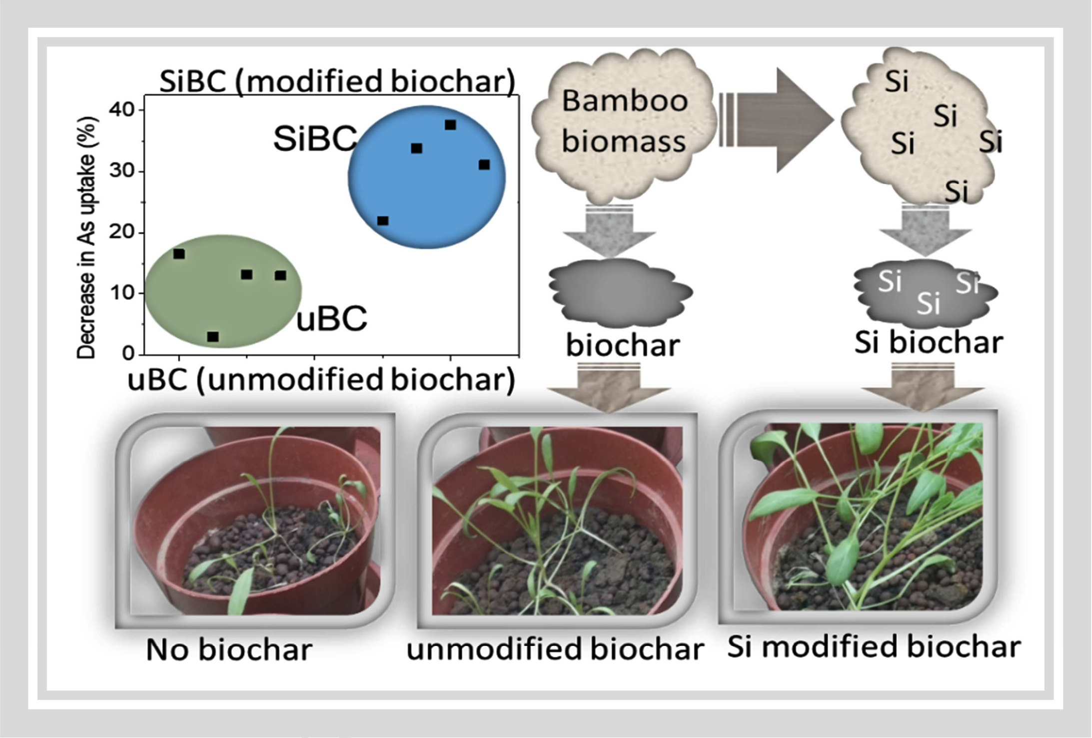

Silicon (Si) biochar for the mitigation of arsenic (As) bioaccumulation in spinach (*Spinacia oleracean*) and improvement in the plant growth

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Abstract

In many parts of the world, growing crops on polluted soils often leads to elevated levels of pollutants in plant tissues. Minimizing the transfer of these pollutants into edible plant tissues while improving plant growth and productivity is a major area of research. In this study, we investigated the efficiency of silicon-modified biochar in reducing the uptake of As(III) in spinach (*Spinacia oleracean*) while simultaneously increasing the plant biomass. Unmodified biochars (uBC) and silicon-modified biochars (SiBC) were prepared from bamboo at 300 and 600 °C and characterized by Scanning Electron Microscopy with Energy Dispersive X-ray (SEM EDX), Fourier Transform Infrared Spectrometry (FTIR), X-ray Photoelectron Spectrometry (XPS), and X-ray Diffraction analysis (XRD). The bioaccumulation of As(III) in the edible part of spinach significantly decreased by 33.8 and 37.7 % following the amendment of, respectively, 2 % and 5 % SiBC in soil. Biochar amendment increased the concentration of As(III) in pore water by 64.4 % as a result of increased soil pH from 6.83 ± 0.4 to 8.01 ± 0.1 and dissolved organic carbon (DOC) from 7.02 ± 3.7 to 22.58 ± 3.7 g kg^{-1}. However, the uptake of As(III) into spinach was prevented by silicon, which was preferentially transported to the plant through the same transport pathway as As(III). Dry biomass yield in spinach also significantly increased by 67.7 % and strongly correlated ($R^2 = 0.97$) with $CaCl_2$ extractable Si in the plant. The results highlighted the effectiveness of SiBC in reducing the toxic effects of As in the environment and overall dietary exposure to the pollutant. The slow release of Si from biochars (< 48.42 %) compared to soil (87.39 %) also suggested that SiBC can be efficient sources of Si fertilization for annual crops which can significantly reduce the increasing demand for Si fertilizers and their sustainable use in the environment.

Key words

Silicon, biochar, modified, arsenic contamination, spinach bioaccumulation.

1. Introduction

Pollution from potentially toxic elements (PTEs) such as arsenic (As), cadmium (Cd), lead (Pb), chromium (Cr), and zinc (Zn) is one of the major environmental challenges of the modern world (Sun and Chen, 2018). Due to its toxic nature, As contamination has received much attention from environmental researchers who are keen to developing sustainable As removal technologies from environmental media (notably, soil and water). In the soil, arsenic is generally oxo-anionic, existing mainly as arsenite (As(III)) and arsenate (As(V)). As(III) is more toxic and resistant to removal in the environment due to its lower mobility compared to As(V) (Wang et al., 2015). Soil and most Fe-rich carbonaceous materials have been reported to easily adsorb the less toxic As(V) compared to As(III) although they lack the ability to retain it (Agrafioti et al., 2014). Under anaerobic conditions, As(V) is easily converted to the less mobile As(III) which often increases its concentration in pore water (Peng et al., 2016). Apart from human toxicity, As concentrations greater than 3 mg L^{-1} (Hartley et al., 2009) may cause widespread phyto-toxicity. Meharg and Hartley (2002) noted that As phyto-toxicity (particularly As(V)), in non-As resistant plants causes considerable stress with symptoms ranging from inhibition of root growth to death. Si application in soil has been reported to have a significant effect in decreasing total As concentrations in plant tissue (Guo et al., 2007) although it may also cause significant increases in As concentrations in pore water (Gang et al., 2017).

Silicon (Si) is a highly beneficial element known to play a key role in soil-plant interactions. Si confers strong benefits to plant growth through its ability to increase plant tolerance to various biotic and abiotic stressors such as drought, salinity, disease and toxicity (Kaur et al., 2016). The influence of Si on plant growth and development under stressed conditions has been documented widely in literatures with increased yield (2-3 folds) (Gottardi et al., 2012; Wang et al., 2016a) and increased biomass production (Manivannan et al., 2017). Various mechanisms have been suggested to explain silicon's influence on plant adaptation such as the establsihement of a barrier in plant cell walls (formed through $Si(OH)_4$ polymerisation) as a mechanism for disease tolerance or chemical resistance (Fawe et al., 1998) and the regulation of antioxidant and nutrient uptake mechanisms especially under salt stress conditions (Soundararajan et al., 2014). According to the results of Debona et al. (2017), Si regulates stress from metal toxicity by modulating the pH range of soil or changing metal speciation while Xiao et al. (2014) suggested metal co-precipitation and the formation of inorganic crystals (facilitated by Si) in carbonaceous materials like biochar as a mechanism to abate metal toxicity. Recently, Manivannan and Ahn (2017) suggested the involvement of Si in regulating genes that affect photosynthesis during metal toxicity and the modulation of the expression of housekeeping genes during disease infection. Genes involved in water uptake and transportation and those involved in the expression of defense response in plants are also modulated by Si (Manivannan and Ahn, 2017).

Associating biochar with materials and compounds of interest to enhance its sorption capacity for target contaminants has been done frequently although biochar itself is a good sorbent. Such associations often alter the physical or chemical properties of biochar to produce novel and more adaptable materials with well-defined characteristics (Zama et al., 2017). Chemical modification of biochar by acid-base and alkali treatments (Ahmed et al., 2016) or impregnation with minerals (Rajapaksha et al., 2016) produces these model biochars. Modifying biochar is therefore seen as a novel approach to inducing beneficial surface functionalities (Lehmann and Joseph, 2015) to sorb or immobilize contaminants in both soil and water (Rajapaksha et al., 2016). In the past, Fe has been incorporated into biochar to produce magnetic biochars with better sorption capacities for As (Lin et al., 2017). Treating biochar with MnO_2 has also been reported to be beneficial in converting (through oxidation) As(III) to As(V) which is more easily sorbed (Manning et al., 2002). Similarly, nitrogen has been incorporated on biochar to produce biochar-based slow-release nitrogen fertilizers with exceptional water retention capacities (Wen et al., 2017). These compounds and other nutrients are often retained by biochar and released slowly which benefits plants growth or form complexes for the sequestration of contaminants. The control of contaminants in soil (through sorption or immobilization) by modified biochar and subsequent reductions in plant uptake makes biochar a potentially excellent soil amendment. This adds to biochar’s key role to improve soil quality and plant health physically, chemically and biologically. A role often attributed to biochar’s redox property, liming effects, and high nutrient/water holding capacity (Cornelissen et al., 2013).

Across the world, crops are often cultivated on soils contaminated by arsenic (As), which puts millions of people (especially in Asia) at risk of As exposure through consumption of tainted produce (Zhou et al., 2018). Increasing populations and the increasing need for safe and healthy food supply means that urgent measures are needed to limit the transfer of As into crops. Adsorption, using carbonaceous materials like biochar is considered a reliable method to minimize the toxic effects of As in the soil (Paz-Ferreiro et al., 2014). However, adsorption processes on As using biochar have largely been ineffective especially when the biochar is not modified. The fact that Si has been widely used to counter As toxicity in some plants, including rice (Seyfferth and Fendorf, 2012) and maize (Latef and Tran, 2016) means that biochar can be modified with Si to yield a product with dual benefits. That is, reducing As uptake by crops and improving crop growth. Biochars from Si bio-accumulators, such as rice, maize, sugar cane and bamboo have been produced, and widely used in heavy metals remediation (Tubana et al., 2016).

However, given the relatively low bioavailability of Si in these biochars from Si bio-accumulators, its influence on heavy metal remediation is minimal (Tripathi et al., 2016). The synthesis of Si-modified biochars (containing intentionally elevated concentrations of Si) aimed at remediating heavy metals in soil, is a novel modification approach that has received very little attention.

The main objective of this study was to investigate the effectiveness of Si-modified biochar in reducing the uptake of As by spinach (*Spinacia oleracean*) and simultaneously increase biomass yield in the plant. Specifically, the study (1) investigated the influence of silicon biochars on the mobility of As in soil, (2) assessed the inhibitory effects of Si on As uptake by spinach in As contaminated soil, and (3) examined the influence of Si-modified biochars on the plant growth (measured by biomass yield).

2. Materials and Methods

2.1. Quality control and data analysis

All reagents used were analytical grade. Stock and working solutions of As(III) and Si were prepared in ultra-pure water (Milli-Q, 18.2 MΩ cm, TOC 3 ppb) using $NaAsO_2$ and $K_2SiO_3 \bullet 2.5H_2O$, respectively. All experimental samples were prepared in triplicate and experiments were run at room temperature (25 ± 1.0 °C). In all experiments, controls without biochar were included. The graphical data from FTIR, XRD and XPS was analysed using OriginPro 8.5 (OriginLab, USA) and Microsoft excel 2016.

2.2. Biochars and soil preparation

Biochar was made from bamboo (*Bambusoideae*) through dry pyrolysis at 300 or 600 °C. Bamboo was chosen for two main reasons. Firstly, bamboo has a higher lignocellulosic content compared to grasses and other agricultural wastes, which produces desired biochars with higher micro and macropores (Novak et al., 2014). Secondly, bamboo is increasingly being used for paper making and construction works especially in many parts of Asia (Schneider et al., 2011). Wastes generated from these activities can be converted to biochar as added value. Prior to pyrolysis, the biomass was milled and oven-dried at 70 °C for 24 h. The milled biomass was then pyrolysed in steel crucibles mounted in a Neytech Muffle Furnace (Vulcan 3-1750A) (Agrafioti et al., 2014) under limited oxygen conditions. Temperature was increased at the rate of 10 °C min^{-1} and maintained at 300 or 600 °C for 4 h to allow for slow pyrolysis.

Modified biochars were made by pre-treating milled bamboo biomass with $K_2SiO_3 \cdot 2.5H_2O$ solution containing 5 g L^{-1} of Si in large beakers sonicated at room temperature (25 ± 1.0 °C) for 48 h. This was a slightly modified procedure from Hamels et al. (2014). The supernatant was decanted and the solid material rinsed with distilled water and then oven-dried at 100 °C for 48 h. The Si-loaded dry biomass was then pyrolysed at 300 or 600 °C as described above. Following pyrolysis, all biochars were allowed to cool down to room temperature before being ground and sieved to obtain a particle size of 0.2 mm. The Si-modified biochars at 300 °C and 600 °C were coded “SiBC3 and SiBC6” respectively. The unmodified biochars prepared at the same temperatures were coded “uBC3 and uBC6”. When biochars were amended in soil at 2 % or 5 %, they were coded as 2uBC3, 2uBC6, 5uBC3, 5uBC6, 2SiBC3, 2SiBC6, 5SiBC3 and 5SiBC6. For example, 2uBC3 codes for 2 % amendment of unmodified biochar, pyrolysed at 300 °C.

Contaminated soil from the outskirts of Beijing, China was collected according to the guidelines of ISO 10381-1 and 10381-2. About 50 kg of soil was collected from the top 20 cm in a 1 ha block of crop land historically contaminated by As and other heavy metals including, Cd and Pb.

Soil was air-dried for one week and was thoroughly homogenized by hand and shovel. The homogenized soil was then sieved to obtain a particle size of 2 mm for subsequent experiments.

2.3. Analysis of physicochemical properties of soil and biochars

The pH of soil and biochar was measured using a pH meter (Mettler Toledo 320-S) after mixing and shaking soil or biochar with distilled water, for 2 h in an end-to-end shaker, and at a ratio of 1:5 and 1:20, respectively. The cation exchange capacity (CEC) of biochar and soil was determined by summation of cations extracted by 1 mol L^{-1} ammonium acetate at pH 7 (Gregory et al., 2015) and analysed by the Inductively Coupled Plasma Mass Spectrometry (ICP-MS, 7500a, Agilent Technologies, USA). This equipment detects metals and several non-metals at concentrations as low as one part in 10^{15} (part per quadrillion, ppq) on non-interfered low-background isotopes. Soil DOC was determined by shaking 5 g of soil in 25 mL of 0.5 M K_2SO_4 for 2 h (Liu, 2008). The slurry was centrifuged at 5000 rpm for 5 min and the supernatant removed using a syringe. DOC content in the supernatant was analysed using Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES, Optima 2000, PerkinElmer Co., USA). This instrument detects metals using the flame technique with a flame temperature ranging from 6000 to 10000 K.

An elemental analyzer (Vario EL III) was used to measure the elemental composition (total C, H, and N) of the biochars while O content was calculated by subtracting total C, H and N (%) from 100 % (Yousaf et al., 2017). The surface area of biochars was measured from isotherms at 77K using a Surface Area and Porosity Analyzer (ASAP, 2020 HD88). Biochar structure and relative atomic percent of elements on the surface of biochars was analysed using the Field Emission

Scanning Electron Microscope with Energy Dispersive X-Ray Spectroscopy (FE SEM-EDX, SU8000). SEM micrographs and X-ray spectra were obtained at a magnification of x15.0k over a working distance of 16.4 mm and an acceleration voltage of 15 kV (Hagemann et al., 2017). Bond stretches in organic functional groups on the surface of biochars were analysed using biochar samples prepared in pellets of fused KBr in a Thermo Scientific Nicolet FT-IR spectrometer (Nicolet 8700) and scans were made within the 4000 – 400 cm^{-1} regions (Zama et al., 2017). The ESCALAB 250Xi X-ray Photoelectron Spectrometer (XPS) equipped with monochromated Al K α (1486.68 eV, 150W) at a spot size of 500 µm under high-vacuum conditions ($<2\times10^{-9}$ M bar) was used to assess the elemental composition and chemical bonds of unmodified and modified biochars in the outermost 10 nm (Goldstein et al., 1986). X-ray diffractometer (XRD) (X'pert Pro, Netherlands) fitted with a Ni filter and CuKα radiation for crystalline phase identification was used to record the X-Ray diffraction pattern.

2.4. Analysis of biomass yield and bioaccumulation of As in spinach

Pots were each filled with 1 kg of contaminated soil amended with 2 or 5 % uBC or SiBC and incubated for 14 days before seeding (Gregory et al., 2015). Pots without biochar amendment were included as control treatments. Spinach (*Spinacia oleracean*) seeds were disinfected by treating them in 30 % H_2O_2 solution for 10 min before seeding directly into pots (Szopińska, 2014). Five seeds were planted in each pot and shortly after germination, three were discarded and two seedlings were allowed to continue growing. The moisture content was maintained at 50 % throughout the experiment. Plants were grown for 40 days in a greenhouse (25 ± 2 °C; 70 % relative humidity and 14 h light) and the above ground biomass (edible portion of the vegetable) harvested, rinsed in DI water and oven-dried at 70 °C for 72 h. The weight of dry biomass from each pot was taken to compare changes in biomass yield. The dry biomass from each pot was crushed and acid-digested (0.2 g) in 10 mL of 14 M HNO_3 according to Hartley et al. (2009) and Silva et al. (2015). The concentration of As in the digest was analysed using ICP-MS.

2.5. Analysis of As mobility in soil

Experiments were conducted to determine the effects of uBC and SiBC on As mobility in soil. Arsenic mobility in soil was determined by the amount of As in pore water following the addition of biochar. Prior to incubating soil and biochar, the As levels in soil were elevated by treating the soil in As solution (40 mg L^{-1}) for 72 h mounted on an end-to-end shaker at 25 °C until equilibrium (Romero-Freire et al., 2014). The pH was maintained at 4.5 ± 0.1 using 0.1 M NaOH or HNO_3 (Uchimiya, 2014) to enhance As sorption by the soil. At equilibrium, the soil was allowed to settle overnight. It was then decanted and rinsed with DI water three times and oven dried at 100 °C for 72 h. The dry soil was re-crushed and passed through sieve to obtain a particle size of 2 mm. Biochar amendments (uBC, and SiBC) were applied to the resulting As-spiked soil at the rate of 2 % and 5 % (w/w). Control treatments were also set up without biochar amendment. The amended soils were carefully homogenized by shovel and all treatments were soaked to 80 % soil water holding capacity and incubated for 40 days without further modification of pH. Soil pore water samplers were inserted in each pot at angle of 45° to collect pore water every 10 days. The concentration of As in the extracted pore water was measured using ICP-MS.

2.6. Analysis of the rate of Si release from biochar

Batch desorption experiments were carried out to determine the rate at which silicon is released by the biochars (modified and unmodified) into the environment. A control treatment comprising soil without biochar was also included to compare Si release rate from soil. The batch experiment was made with 0.05 g of uBC and SiBC, measured into 50 mL of 0.01 M $CaCl_2$ (extractant) and mounted on an end to end shaker (150 rpm, 25.0 ± 1.0 ºC) for 36 days. Samples were withdrawn every 4 days, and centrifuged at 5000 rpm for 5 min and the Si concentration in the supernatant was measured using the silicon-molybdenum blue colorimetry method (Chinese national industry standards, SL 91.2-1994) as explained in Xiao et al. (2014). The quantity of dissolved silicon was also calculated using equation 1. The corresponding pH of the sample solutions was measured to determine the influence of pH on the quantity of silicon released by the biochars.

$$Q = \frac{\mathrm{c} \times \mathrm{V}}{\mathrm{m}} \tag{1}$$

Where Q is quantity of silicon released from biochar (mg g^{-1}), c is concentration of silicon in solution (mg L^{-1}), V is volume of solution used (mL) and m is the quantity of biochar added (mg).

3. Results and Discussion

3.1. Silicon-induced structural and chemical changes on the surface of biochars

As expected, the percentage of total C increased with increasing pyrolysis temperature (**Table 1**) because of increased carbonization and dehydration (Rafiq et al., 2016) although the carbon content in silicon biochar (SiBC3 and SiBC6) significantly decreased compared to unmodified biochar (uBC3 and uBC6) **(Table 1)**. This decrease was probably due to the increase of Si through impregnation or encapsulation of biochar (Ahmad et al., 2017) by amorphous Si during modification which decreased carbonization and the formation of Si-C bonds (Guo and Chen, 2014). Si encapsulation in silicon biochar (SiBC) may have also affected aromaticity which resulted in no change on the O:C atomic ratios (**Table 1**) while, as expected, unmodified biochars (uBC) became less hydrophilic with increasing pyrolysis temperature indicated by the significant decrease in O:C atomic ratio (**Table 1**). Biochar modification also resulted in an increase of polar groups on SiBC biochars compared to uBC biochars as indicated by a decrease in (O+N):C atomic ratio in uBC biochars and a corresponding slight increase in the (O+N):C atomic ratio in SiBC biochars with increasing pyrolysis temperature (**Table 1**).

Table 1 Physicochemical properties of silicon modified (SiBC) and unmodified (uBC) biochars at 300 and 600 °C

BC	C (%)	N (%)	H (%)	O (%)	N:C	H:C	O:C	(O+N):C	*Si ($mg\ g^{-1}$)	SSA ($m^2\ g^{-1}$)	CEC ($cmol_c\ kg^{-1}$)	Ash (%)	pH
uBC3	65.3	0.53	4.56	29.7	144	0.84	0.34	1.86	2.12	14.2	9.13 ± 2.0	2.75 ± 0.0	6.70 ± 0.3
uBC6	84.3	0.60	1.93	13.2	164	0.27	0.12	0.83	3.54	16.9	11.52 ± 1.1	4.00 ± 0.0	10.2 ± 0.1
SiBC3	54.7	0.36	3.84	41.1	177	0.84	0.56	2.57	16.4	10.3	16.8 ± 1.5	18.5 ± 0.0	8.84 ± 0.5
SiBC6	56.1	0.32	1.87	41.7	205	0.40	0.56	2.61	18.5	8.63	21.3 ± 0.4	26.3 ± 0.0	9.83 ± 0.0

*Si, 0.01 M $CaCl_2$ extractable Si, SSA, specific surface area, CEC, cation exchange capacity, mean ± standard deviation (n=3)

Scanning Electron Microscopy **(SEM)** was used to observe changes in the morphology of biochars due to pyrolysis temperature and Si modification. As seen on **Fig. 1a**, EDX analysis detected small amounts of Si (3.26 %) on unmodified biochar (uBC6) compared to larger amounts (9.48 %) on silicon modified biochars (SiBC6) (**Fig. 1b**) indicating that additional Si was successfully loaded on the biochars during modification. Detail EDX analysis of the SiBC biochars in two locations showed that the concentration of Si was higher inside pores than other points on the biochar surface (**Fig. 1c**). This implies that pore filling (where the biochar pores served as active sorptive sites for Si) contributed substantially to the sorption of the element on biochar during modification. EDX analysis also revealed increased carbonization in biochars with increase in pyrolysis temperature. Total C was 70.8 and 67.3 % for uBC6 and SiBC6 respectively compared to 62.0 and 49.8 % for uBC3 and SiBC3 respectively (**Fig. S1a and b**). Inorganic mineral elements such as Na, Mg and P which often participate in exchange and precipitation reactions with contaminant ions were also present in small quantities on the surface of the biochars. The formation of a porous network within biochars was clearly visible for SiBC biochar at 300 °C (**Fig. S1c**) but these pores collapsed at higher pyrolysis temperatures (600 °C) (**Fig. S1d**) possibly due to biochars becoming more aromatic and brittle-like. Silicon modification did not influence the pore structure of biochars but may have significantly influenced the BET surface area of biochars which decreased from 14.2 and 16.9 m^2 g^{-1} in uBC3 and uBC6 biochars respectively to 10.3 and 8.63 m^2 g^{-1} in SiBC3 and SIBC6 biochars, respectively (**Table 1**). Clogging of pores by silicon and K occlusion may be responsible for this decrease in surface area when biochar was modified with silicon (Li et al., 2014).

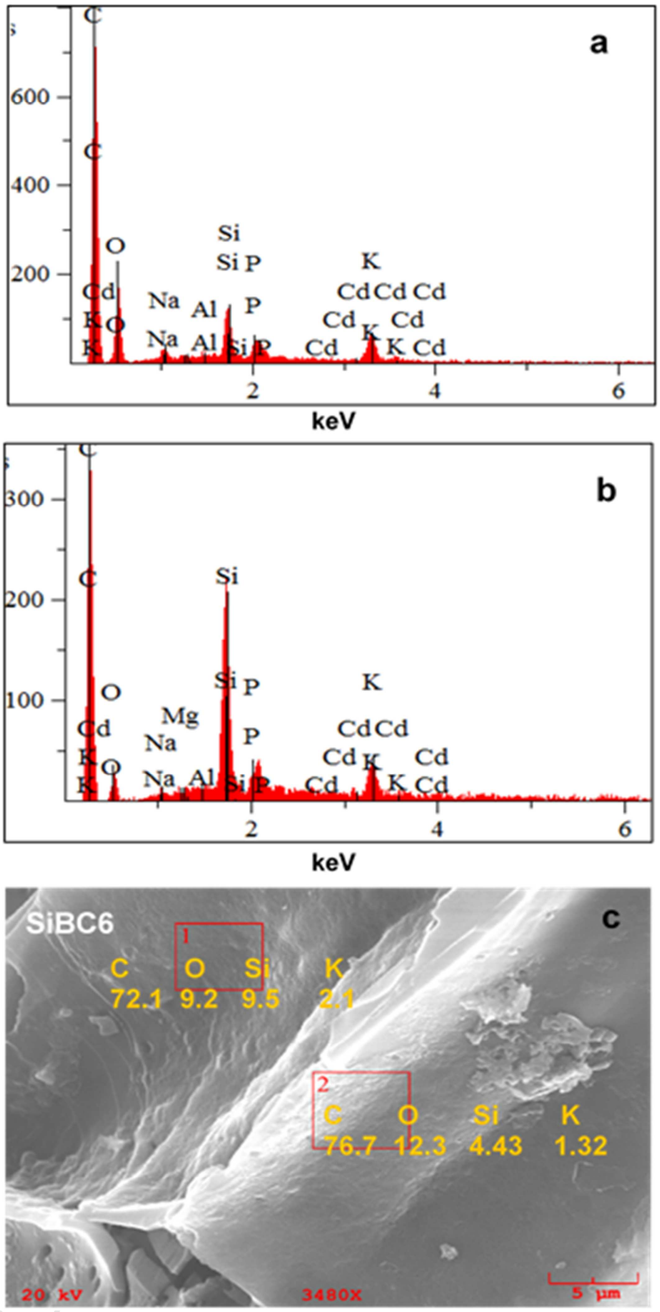

Fig. 1 SEM-EDX analysis of biochars indicating changes in morphology and elemental content. (**a**) the composition of elements in unmodified biochar (uBC6), (**b**) the composition of elements in silicon modified biochar (SiBC6) indicating increased Si concentration after modification, (**c**) detail EDX analysis of two locations on biochar (inner pores and exposed surface) showing differences in Si composition.

3.2. Silicon-induced changes in bond stretches on biochar

XPS analysis revealed significant differences in carbon speciation between unmodified (uBC) and modified (SiBC) biochars with the occurrence of more oxidized carbon species (e.g. C-O and C-OH) and C-F bonds in the modified biochars (**Fig. 2**). The occurrence of a Si2p peak in modified biochar (SiBC3) (**Fig. 2b**) which was absent in unmodified biochars (uBC3) (**Fig. 2a**) was also an indication that Si was successfully incorporated in the biochar. Deconvulated Si2p scans in unmodified biochars (uBC3) showed no peaks (**Fig. 2c**). However, up to three peaks at 101.9 eV, 102.9 eV and 103.4 eV corresponding to C–Si–O, Al–Si and Si-O bond stretches (Meng et al., 2015) were revealed in modified biochar (SiBC3) after Si2p scan (**Fig 2d**). A detailed assessment of deconvulated C1s scan also revealed a major peak at 284.8 eV on uBC6 corresponding to C-H, C-C, or C=C bond stretches (**Fig. 2e**). This peak shifted to 284.5 eV in SiBC6 following silicon modification but still corresponded to C-H, C-C, and C=C bond stretches (**Fig. 2f**) (Swain, 2006). The peak at 286.1 eV on uBC6 corresponding to C-O and C-NR_2 (Dementjev et al., 2000) also shifted to 286.6 eV in SiBC6 corresponding to C-N, C-O and C-OH (Meng et al., 2015). Biochar modification induced unexpected fluoride bond stretches on SiBC6 such as C-F and C-F_2 at 288.7 and 293.1 eV respectively (Şahin et al., 2011).

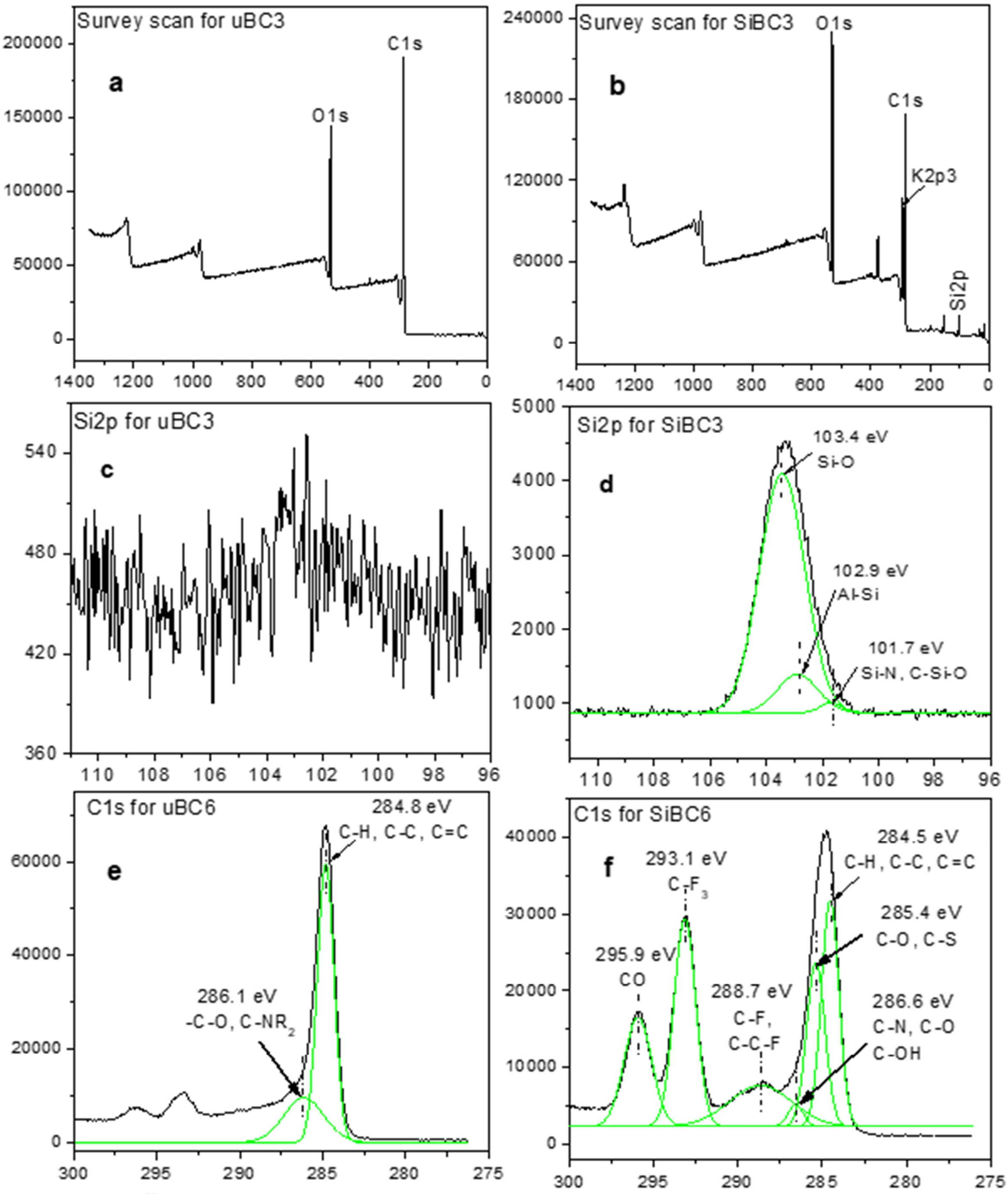

Fig. 2 XPS analysis indicating differences in carbon speciation of silicon modified biochars (SiBC3 and SiBC6) and unmodified biochars (uBC3 and uBC6). (a and b) survey scans for uBC3 and SiBC3, (c and d) Si2p scans for uBC3 and SiBC3, (e and f) C1s scans uBC6 and SiBC6.

3.3. Silicon-induced changes in organic functional groups on biochar

The bonding behavior of organic functional groups on the surface of uBC and SiBC biochars was determined by FTIR analysis (**Fig. 3a**). The spectra revealed three major peaks representing alkanes, carboxylates, nitrates, silicates and phosphates occurring especially on uBC3 and SiBC3 (**Fig. 3a**). The majority of aliphatic C-H bonds occurring mainly between 2700 and 2900 cm^{-1} in lower temperature biochars (300 °C) disappeared in higher temperatures biochars (600 °C). This may be the result of increased dehydration at higher pyrolysis temperatures which also affected biochar carbonization with the occurrence of peaks at 1400 to 1600 cm^{-1} corresponding to C=C and C-C groups (Ramola et al., 2014). Biochar modification had little effects on changes in dehydration but affected carbonization where fewer or no C=C and C-C groups occurred on modified biochars (**Fig. 3a**). Instead, the occurrence of many peaks at 1000 - 1090 cm^{-1} corresponding to C-O, SiO_4^{2-} and PO_4^{3-} on modified biochars was consistent with increased accumulation of silicates and phosphates. The formation of C-Si bonds evidenced by peaks at 978-980 cm^{-1} which were attributed to $SiC\text{-}H_3$ bond stretching (Swain, 2006) in modified biochars may have also contributed to the disappearance of C-H and C=C/C-C groups. Hydroxyl (O-H) groups, which are common on biochars, have been reported to occur mainly between 3000 and 3500 cm^{-1} (Trigo et al., 2016). However in this study, an O-H group occurred only in unmodified biochar at 600 °C and was completely absent in the modified biochars. This may be due to the feedstock material used and the possibility that modification affected its occurrence.

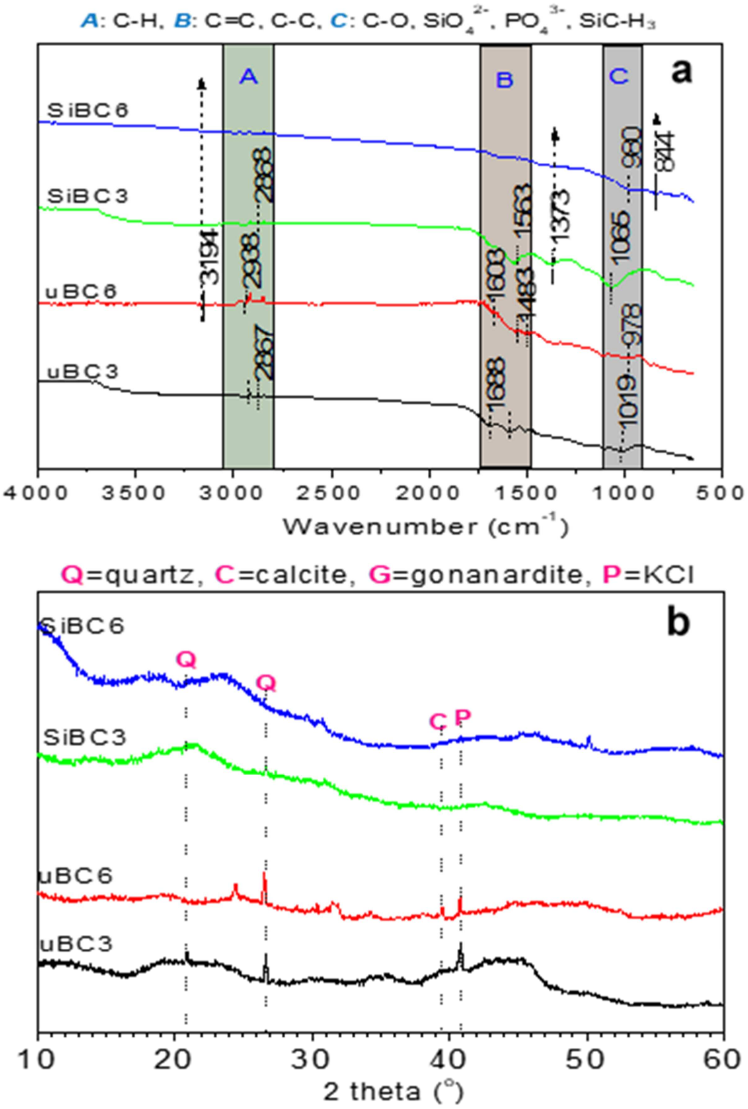

Fig. 3 (**a**) FTIR analysis of bond stretching in unmodified biochar (uBC) and silicon modified biochars (SiBC) at 300 and 600 °C, (**b**) XRD analysis of the various crystalline faces on unmodified biochars (uBC) and silicon modified biochars (SiBC) produced at 300 and 600 °C.

3.4. Silicon-induced changes in mineral phases on biochar

The occurrence of various mineral phases were evident in the XRD spectra of unmodified (uBC) and modified (SiBC) biochars made at 300 and 600 °C (**Fig. 3b**). Biochar modification by Si affected crystalization considerably. Compared to unmodified biochar which may have contained more amorphous Si phases, crytalline Si phases were more abundant on modified biochars with predominantly distinct and greater intensity peaks occuring at 2θ = 26.6° and 39.4°, which were attributed to quartz (SiO_2) and calcite ($CaCO_3$), respectively (Nartey and Zhao, 2014). These peaks emphasized the presence of Si in the modified biochars compared to the unmodified biochars. Furthermore, Si in the bamboo feedstock may have acumulated particularly at higher pyrolysis temperatures. Xiao et al. (2014) reported that increase in pyrolysis temperature led to Si accumulation and a morphology change from amorphous to crystalline. Traces of K (possibly from the K_2O_3Si treatment) were observed with a peak at 2θ = 40.8° consistent with KCl (Treacy and Higgins, 2007) (**Fig. 3b**). Following As sorption, Quartz and Calcite persisted on the biochars but one new peak was observed at 2θ = 31° representing Gonardite [$(Na, Ca, K)_2$ $(Si, Al)_5O_{10}\cdot 3H_2O$] (**Fig. 3b**) (Treacy and Higgins, 2007). Pyrolysis temperature may have had only a slight effect on crystallinity implying that biochar Si-modification effected most of the changes in crystal forms.

3.5. Silicon retention and release from biochar

Both unmodified (uBC) and silicon-modified (SiBC) biochars demonstrated extraordinary capacities to retain and slowly release Si compared to soil (used as control) (**Fig. 4**). For 36 days, only 41.10, 34.27, 48.42 and 45.27 % of Si was released from biochars (uBC3, uBC6, SiBC3 and SiBC6 respectively), compared to 87.39 % from soil (**Fig. S2**). The slow release of Si from biochars over a long period of time was an indication that silicon biochar could be an efficient source of Si fertilization especially for annual crops. The release of Si from biochars was aparently dependent on the amount of silicon available on the biochars. More Si was released from SiBC biochars (SiBC3 and SiBC6) with a daily rate higher than uBC biochars (uBC3 and uBC6) and soil (**Fig. 5**). This was possibly due to the original amounts of dissolved Si on the biochars (**Table 1**). Silicon release by uBC3 and uBC6 followed a linear curve which largely leveled out after day 4 and day 12, respectively (**Fig. 4**). This implies that after day 4 and day 12, insignificant amounts of Si were released by the unmodified biochars compared to silicon modified biochars (SiBC3 and SiBC6) with Si release rates following a nonlinear curve (**Fig. 4**). Large amounts of Si were released by SiBC3 and SiBC6 within the first 8 days followed by small increments from day 12 to day 36 although a different behavior was observed for SiBC3 from day 24 which corresponded to a drop in solution pH. The control treatment (soil without biochar) contained a relatively small amount of Si (~ 0.11 mg g^{-1}) which was rapidly released and the concentration of dissolved Si remained largely unchanged throughout the 36 days. Xiao et al. (2014) studied the release of Si on biochar using rice straw and observed that the process of silicon release on biochar may be controlled by silicon speciation in biochar (amorhous or crystalline), silicon content on biochar and the interaction of silicon with carbon. The study also observed that biochar pyrolysis temperature (which influences biochar pH), affects the realease of Si on biochar. This is in line with our observations where higher temperature biochars (uBC6 and SiBC6) released slightly more Si compared to lower temperature biochars (uBC3 and SiBC3) (**Fig. 4**). Overall, Si was slowly released from biochar, compared to soil, over the 36 days period which served as a steady source of Si fertilization for the spinach plant.

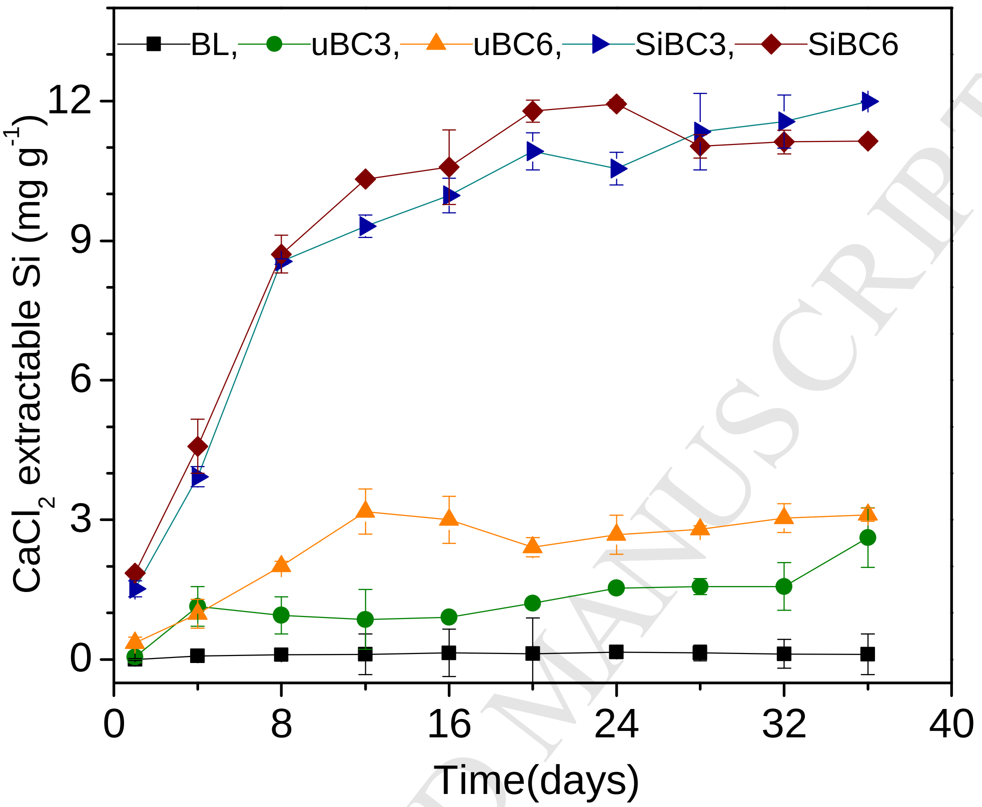

Fig. 4 The rate of Si release ($CaCl_2$ extractable) from unmodified and silicon modified biochars (uBC3, uBC6, SiBC3 and SiBC6) compared to soil (control) over a period of 36

3.6. Effects of silicon biochar on biomass yield in spinach plant

The application of silicon biochar significantly enhanced plant growth (**Fig. 5**). Unmodified biochars applied at the rate of 2 % and 5 % (i.e. 2uBC3, 2uBC6, 5uBC3 and 5uBC6), increased dry mass yield in spinach by 1.2, 2.3, 1.9 and 1.4 g respectively, compared to 1.05 g in the control treatment which was made without biochar (**Fig. 5**). However, this was only a slight increase compared to modified biochars (i.e. 2SiBC3, 2SiBC6, 5SiBC3, and 5SiBC6) which significantly increased dry mass yield by 2.9, 4.1, 2.7, and 3.3 g respectively compared to 1.05 g in the control treatment (**Fig. 5**). This significant increase in dry mass production in SiBC corresponded to a percentage increase of 63.6, 60.4, 74.1 and 67.7 %, respectively compared to 10.5, 43.3, 53.9, and 25.3 %, respectively, for uBC biochars (**Fig. S3**). The results clearly indicated that the modification of biochar with silicon resulted in a significant increase in the growth of spinach. Other factors may have contributed to this inreased growth such as the preexisting N, P and K in the soil. However, the influence of Si biochar was clearly observed when modified and unmodified biochars were used on soil under the same experimental conditions. There was a strong positive correlation ($R^2 = 0.97$) between the amount of $CaCl_2$ extractable Si in the spinach and the amount of dry biomass produced (**Fig. S4**) which indicated that higher doses of Si benefited plant growth. These results were consistent with many studies relating to the influnce of Si on plant growth. For example, Wang and Galletta (1998) reported the influence of Si on the growth of strawberries and observed that plants treated with Si developed shorter petioles but significantly more dry matter even at very low Si concentration (4.25 mM) in dosing solution. Recently, Costa et al. (2016) also observed that Si concentrations of 0.28 and 0.55 g pot^{-1} (pots contained 1100 g of tropstrato(r) substrate) yielded the highest stem dry weight of 1.32 and 1.38 g respectively, in passion fruit, compared to 0.81 g of dry weight in the control treatment. Liang et al., (2015) also observed that the effects of Si on plant growth are often complemented by other factors such as pH adjustment and the acquisition of macro/micro nutrients contained in silicate fertilizers. In our study, the addition of SiBC raised the soil pH from 6.83 ± 0.4 in unmodified soil to 8.01 ± 0.1 in SiBC + soil (**Table 2**) which may have also influence biomass production. Biochar dosage also influenced biomass yield considerably. At 2 % SiBC application, spinach biomass ranged from 2.26 to 2.88 g and at 5 % SiBC application the spinach biomass ranged from 3.25 – 4.05 g (**Fig. 5**) indicating that biochar dose had a considerable influence on plant growth possibly because of the availability of a larger amount of Si which correlated positively with biomass yield (Fig. S4). The entrapment of this Si on biochar and its subsequent slow release as a source of Si fertilizer was highly beneficial to the efficient growth of the plant. Similar observations were made by Hagemann et al. (2017) who noted the formation of an organic coating on the surface of biochars, which functions in nutrient retention and subsequent slow release into the soil. Biochar pyrolysis temperature appeared not to have any significant influence on spinach biomass production. There was no significant correlation between pyrolysis temperature and spinach dry biomass.

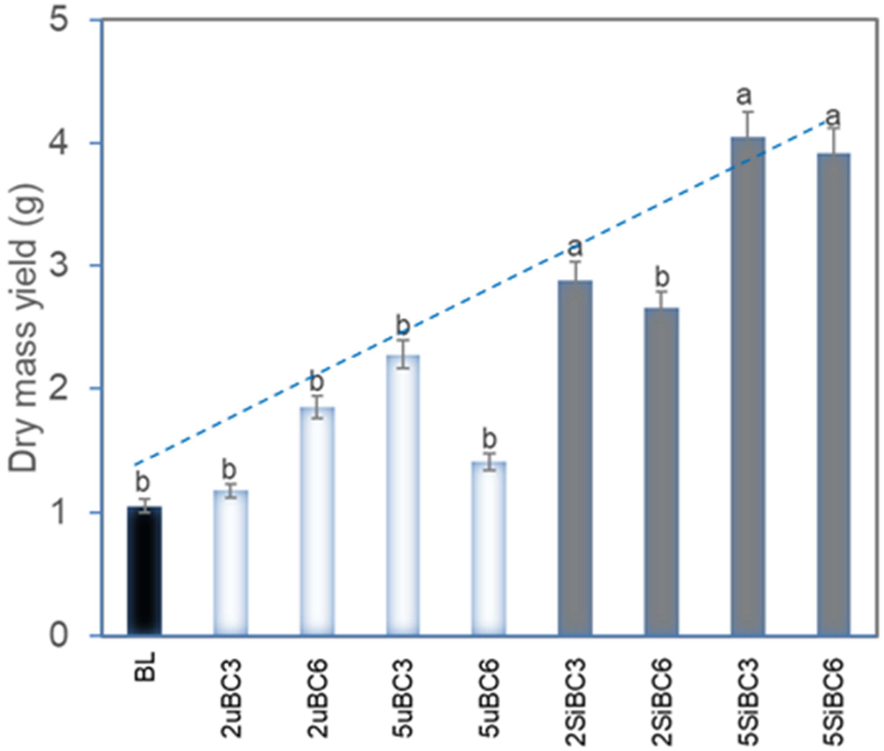

Fig. 5 The influence of unmodified biochar (uBC) and silicon modified biochars (SiBC) on biomass production in spinach (*Spinacia oleracean*).

3.7. Effects of silicon biochar on the mobility of As in soil

The effects of biochar addition on As mobility in soil was studied over a period of 40 days (**Fig. 6**). Within the first 10 days of biochar incubation, there was a rapid increase in As concentration in pore water but this trend slowed down after day 10 with no significant changes until day 40 for all the biochars (**Fig. 6**) suggesting that a new equilibrium had been attained within the first 10 days of incubation. At 2 % and 5 % SiBC amendment, As concentration in pore water ranged from 16.5 to 21.04 µg L^{-1} and from 11.83 to 22.94 µg L^{-1} respectively, indicating that biochar dose had no significant influence on As mobility in soil. Unmodified biochar mobilized more As in pore water ranging from 15.2 to 28.35 µg L^{-1} in 2 % uBC and 17.99 to 25.15 µg L^{-1} in 5 % uBC compared to modified biochar where minimal Si-As bonds may have formed. However, both biochars (modified and unmodified) mobilized more As in pore water compared to the control (no biochar amendment) which ranged from 10.04 to 16.3 mg L^{-1}. For example, 2SiBC3, 5SiBC3, 2uBC3, and 5uBC3 increased pore water As concentration by 64.4, 128, 193 and 257 % respectively compared to the control. Increase in As concentration in pore water following the addition of biochar, as observed in this study, is consistent with previous reports. For example, Beesley et al. (2013) reported a 365 % increase of total As in pore water when biochar derived from orchard prune residues (produced at 500 °C) was added to As contaminated soil. Zheng et al. (2012) also reported a 290 % increase in pore water As concentration in the presence of fine bran-char (produced at 500 °C). Both studies cited the presence of phosphorus in biochar as being partly responsible for the significant increase in As concentration. The reports suggested that phosphorus displaced sorbed As and enhances its concentration is pore water. Zheng et al. (2012) also proposed that increase in pH (from 7.1 to 8.2) following the addition of biochar was another reason for the significant increase in As concentration in pore water. Increasing pH on the surface of biochar disfavors the sorption of As which is predominantly oxo anionic. This therefore promotes its mobility into pore water (Baig et al., 2014). The level of phosphorus in the biochars used in the current study (uBC and SiBC) were low and it is therefore unlikely that phosphate was a major influence upon As concentrations in pore water. However, the addition of biochars was observed to increase pore water pH (from 6.83 in control soil to 7.73 in uBC and 8.01 in SiBC amended soils) (**Table 2**). This increase in pH is suggested to be the underpinning reason responsible for the significant increase in As concentration in pore water as supported by the positive correlation ($R^2 = 0.83$) between As concentration in soil and soil pH (**Fig. S5**). The concentration of DOC in soil may have also influenced As release to pore water. Biochar, and in particular silicon modified biochars, amendment to soil increased the concentration of DOC (**Table 2**) which corresponded to the increase in As mobility in pore water. The influence of DOC on As mobility in soil has been reported previously. For example, Hartley et al. (2009) reported the competition between DOC and As for sorption sites on iron-oxide surfaces which results in DOC being preferentially sorbed and large amounts of As released in pore water. However Liu et al. (2016) reported that increase in soil water holding capacity due to the addition of biochar may result to an increase in DOC leaching.

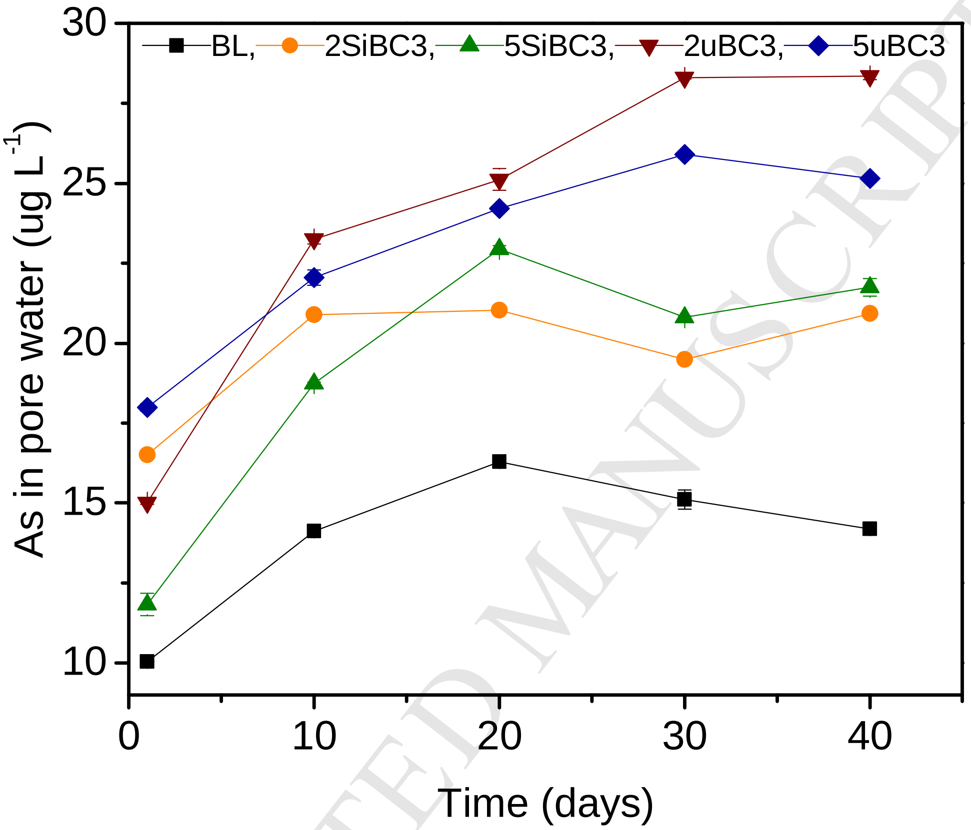

Fig. 6 Changes in As concentration (mobility) in soil solution after 40 days following the addition of unmodified biochars (uBC) and silicon modified biochars (SiBC) at the rate of 2 % and 5 %.

Table 2 Physicochemical properties of unamended soil and soils amended with silicon modified (SiBC) and unmodified (uBC) biochars.

Soil	**pH**	**DOC** (g kg^{-1})	**CEC** (cmol kg^{-1})	***Si** (mg kg^{-1})	**Mn** (mg kg^{-1})	**As** (mg kg^{-1})	**Cd** (mg kg^{-1})	**Pb** (mg kg^{-1})
Unamended soil	6.83 ± 0.4	7.02 ± 3.7	10.23 ± 2.7	113 ± 2.7	90.0 ± 2.4	16.50 ± 2.8	5.58 ± 1.4	14.4 ± 0.4
Soil + 2uBC	7.73 ± 0.1	18.50 ± 1.7	14.05 ± 1.9	137 ± 0.6	67.8 ± 1.4	15.5 ± 3.4	7.00 ± 1.2	12.1 ± 3.0
Soil + 2SiBC	8.01 ± 0.1	22.58 ± 3.7	25.84 ± 4.6	283 ± 2.4	99.4 ± 3.1	13.8 ± 2.1	3.05 ± 0.4	11.9 ± 1.8

DOC, dissolve organic carbon, CEC, cation exchange capacity, *Si, 0.01 M $CaCl_2$ extractable Si, mean ± standard deviation (n=3)

3.8. The inhibition of As accumulation in spinach plant by Silicon biochar

Both silicon modified (SiBC) and unmodified (uBC) biochars were effective in minimizing the bioaccumulation of As in spinach. The addition of uBC decreased As concentration in the edible tissues of spinach from 12.6 µg kg^{-1} in the control treatment to 10.6, 12.3, 10.9 and 11.0 µg kg^{-1} in 2uBC3, 2uBC6, 5uBC3, and 5uBC6 respectively. This corresponded to a percentage decrease in As concentration of 16.5, 3.0, 13.1 and 12.9 % respectively with respect to the control treatment (**Fig. 7a**). Compared to uBC, the SiBC was more effective in reducing As uptake by spinach. For example, the addition of 2SiBC3, 2SiBC6, 5SiBC3, and 5SiBC6 resulted in a significant decrease in As concentration in the biomass of spinach by, respectively, 9.86, 8.37, 7.88 and 8.31 µg kg^{-1} compared to 12.6 µg kg^{-1} in the control treatment. This also corresponded to a percentage decrease of As uptake by 22.0, 33.8, 37.7 and 31.1 %, respectively (**Fig. 7a**). Biochar pyrolysis temperature correlated weakly with As uptake indicating that pyrolysis temperature did not influence the uptake of As in the plant. Unmodified biochar dosage did not also have a significant influence in As uptake. However, silicon modified biochar dosage had a significant influence on As uptake with 5 % SiBC addition decreasing uptake by 57.0 % compared to 25.3 % for 2 % SiBC addition (**Fig. 7a**). In all cases of biochar amendment, As concentration in pore water was well below the range that could potentially cause phyto-toxicity (3 to 10 mg L^{-1}) (Hartley et al., 2009). Increased Si concentrations on the biochars after modification contributed substantially to the inhibition of As uptake by the plant and its mobility in pore water. Similar results have been reported in previous studies dealing with Si and As interaction especially on rice plant in paddy soils. They attribute Si inhibition of As uptake in plants to the competition between H_4SiO_4 and H_3AsO_3 which share the same transport pathway in plants (Lee et al., 2014). The Lis1 and Lis2 silicic acid transporters in plants (uncharged at pH

< 8) are primarily the same transport systems used by arsenite (As(III)) (pKa of 9.2) and Silicon (Ma et al., 2008).

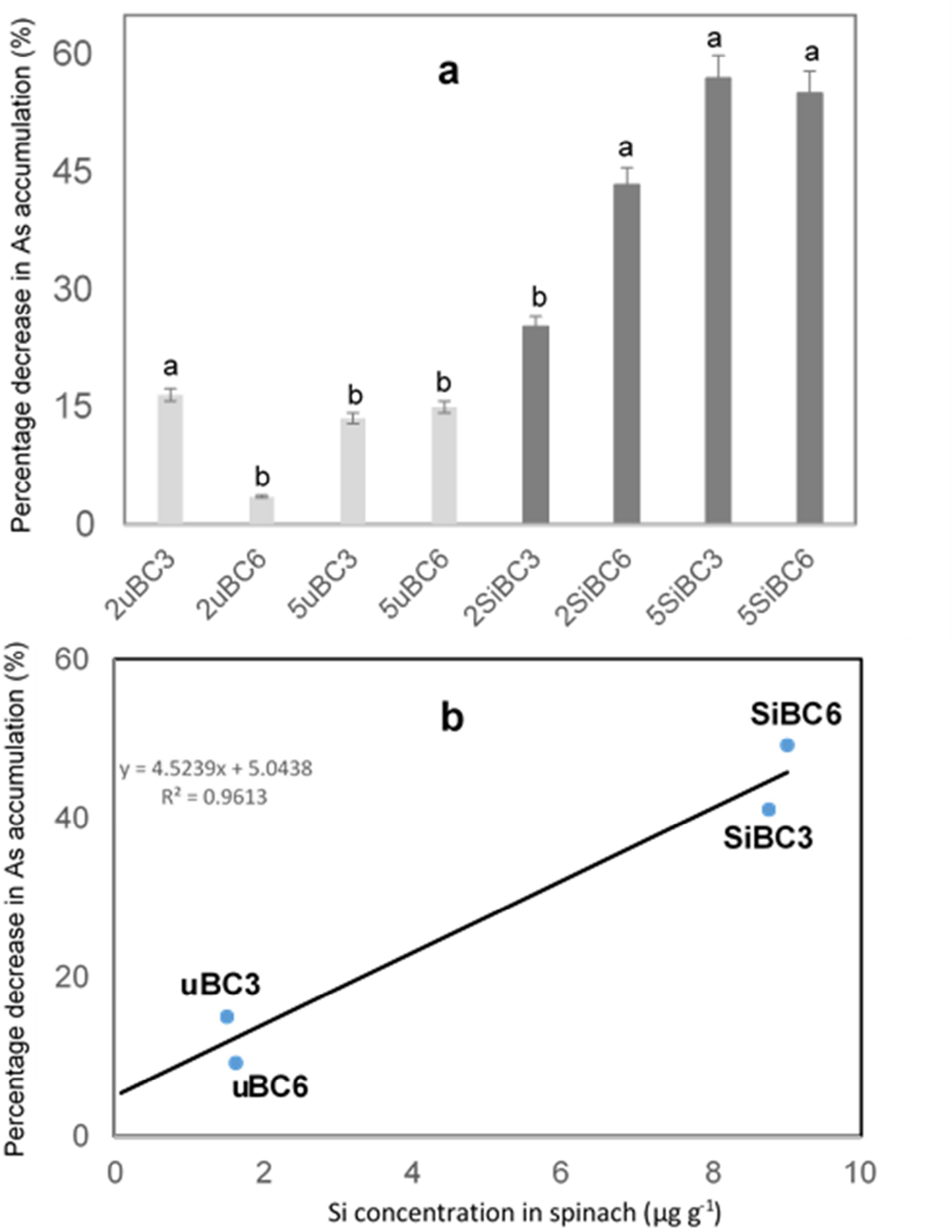

Fig. 7 (**a**) Percentage decrease in As uptake by spinach (*Spinacia oleracean*) following the addition of unmodified biochars (uBC) and silicon modified biochars (SiBC) at 2 % and 5 %. **(b)** Relationship between the concentration of silicon in spinach plant and the percentage decrease in As uptake by the plant following the addition of uBC and SiBC

In the presence of Si, the transport of As(III) in spinach is therefore suppressed as Si is preferentially taken up through the root cells of plants and transferred towards the xylem. This may explain why Si concentration significantly increased from 0.09 µg g^{-1} in spinach grown on non-amended soils to 1.63 and 8.74 µg g^{-1} in spinach grown on the soils amended with uBC and SiBC respectively (data not shown). There was a strong positive correlation ($R^2 = 0.96$) between the concentration of Si in spinach and the degree of As(III) uptake by the plant (**Fig. 7b**). Arsenite uptake inhibition was higher when more Si was deposited in the plants by SiBC biochars and lower when less Si was deposited by uBC biochars. Results also suggested that Si biochar had very little influence on the sorption of As in soil as opposed to its influence on the sorption of phosphorus in aqueous solution which was reportedly very high (Wang et al., 2016b). However, Si biochar controls As in soil by preventing its uptake by plants. This process helps to limit As phytotoxicity and eventual transfer into the food chain.

4. Conclusions

Vegetables and other crops like rice and maize are grown all over the world especially by subsistence farmers. These crops are often grown on soils contaminated by toxic elements like arsenic (As), cadmium (Cd), lead (Pb), chromium (Cr), and zinc (Zn) with the risk of contaminant transfer into the food chain. Due to the toxic nature of As, the need to produce safe and healthy crops on soils contaminated by As is as important as the need to increase crop yield for the growing human population. A novel silicon-biochar composite was synthesized with the aim of decreasing As uptake in spinach (*Spinacia oleracean*) while at the same time increasing the crop yield. Up to 37.7 % reduction in As uptake was achieved by the Si modified biochar compared to 13.1 % reduction rate in unmodified biochar. In addition, Si biochar increased dry biomass yield in spinach by 67.7 % compared to 25.3 % in unmodified biochar. These results suggested that silicon-modified biochar can be an effective means of reducing the toxic effects of As in crops grown on contaminated soils and also significantly increase crop production. The slow release of Si from biochars (< 48.42 %) compared to soil (87.39 %) means that the use of silicon modified biochar can significantly reduce the global demand for Si chemical fertilizers and their sustainable use in the environment. Silicon modified biochars are therefore very essential in sustainable soil-plant management and beneficial in the long term in climate change mitigation through carbon sequestration.

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Highlights

- Biochars (unmodified and silicon modified) were made from bamboo at 300 and 600 ^{o}C
- Silicon biochar was effective in decreasing As bioaccumulation in spinach by 37.7 %
- Silicon prevented As uptake by spinach although pore water As increased by 64.4 %
- Dry biomass in spinach increased by 67.7% correlating positively with the plant Si
- Si biochars mitigate As accumulation in crops and release Si slowly for crop growth