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Graphical abstract
Simultaneous Removal of Ammonia and Phosphate by Electro-oxidation and Electrocoagulation Using RuO$_2$-IrO$_2$/Ti and Microscale Zero-valent Iron Composite Electrode

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Abstract: Electro-oxidation using RuO$_2$-IrO$_2$/Ti plate anode and electrocoagulation using iron plate anode were widely applied to remove ammonia and phosphate in an aquatic environment, respectively. In this work, we designed magnetically bound ZVI microparticles on RuO$_2$-IrO$_2$/Ti plate as a composite electrode for the simultaneous removal of ammonia and phosphate from aqueous solution via combined EO and EC (EO/EC) processes. We present a series of experiments to study such simultaneous removal under an electric field via the EO/EC process. In the electrochemical unit, mZVI-RuO$_2$-IrO$_2$/Ti, mZVI-graphite, and RuO$_2$-IrO$_2$/Ti electrodes were used as anodes. The influence of applied voltage, initial pH, zero-valent iron dosage, reaction temperature, and organic compounds on the EO/EC process was also examined. Ammonia and phosphate could be completely removed at an applied voltage of 10 V, pH of 7, zero-valent iron dosage of 0.1 g, and reaction temperature of 35 °C using mZVI-RuO$_2$-IrO$_2$/Ti anode when influent ammonia and phosphate concentrations is 200 and 100 mg·L$^{-1}$. Ammonia degradation was consistent with pseudo-zero-order kinetic model. The characterization was analyzed by scanning electron microscope-energy dispersive spectrometer (SEM-EDS), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). Hence, the mZVI-RuO$_2$-IrO$_2$/Ti electrode can be used for efficient simultaneous removal of ammonia and phosphate.

Key words: ammonia; phosphate; electro-oxidation; electrocoagulation; zero-valent iron
1. Introduction

In recent years, eutrophication of freshwater and coastal marine ecosystems has become an increasingly serious problem (Smith and Schindler 2009). In particular, the large amounts of ammonia and phosphate emitted in municipal and industrial plants were considered the main cause of eutrophication (Irdemez et al. 2006, Zhang et al. 2018a). Excessive amounts of nitrogen and phosphate in the water will stimulate the blue-green algae to multiply under appropriate temperature conditions and consume a large amount of dissolved oxygen, leading to the death of aquatic organisms (Su et al. 2013).

Many technologies are used for ammonia and phosphate wastewater treatment such as nitrification and denitrification (Jih et al. 2001, Ruiz et al. 2006), anaerobic ammonium oxidation (Laureni et al. 2016), breakpoint chlorination (Pressley et al. 1972), ammonia-stripping (Bonmati and Flotats 2003), adsorption (Boujelben et al. 2008, Huang et al. 2010), ion exchange (Bashir et al. 2010, Choi et al. 2011), microwave radiation (Lin et al. 2009), chemical precipitation (Jaffer et al. 2002), and capacitive deionization methods (Ma et al. 2018). The methods for simultaneously removing nitrogen and phosphate are mainly biodegradation and adsorption. Bassin et al. investigated laboratory-scale sequencing batch reactors that were operated at different temperatures (20 and 30 °C) for aerobic granular sludges, and simultaneous nitrogen and phosphate removal was achieved (Bassin et al. 2012). Huang et al. found that natural zeolite can be modified by magnesium salts and used as an adsorbent
material to simultaneously remove ammonia and phosphate from simulated swine wastewater (Huang et al. 2014). Yin et al. investigated the use of natural calcium-rich attapulgite to develop a versatile adsorbent that can simultaneously remove ammonia and phosphate from contaminated waters (Yin and Kong 2014).

In recent years, electrochemical technology has been increasingly used to treat wastewater containing ammonia and phosphate due to its short reaction process, small footprint, easy operation, and high removal efficiency. Among these electrochemical technologies, the most studied are electro-oxidation (EO) and electrocoagulation (EC) for ammonia and phosphate wastewater, respectively.

EO is an advanced oxidation process that efficiently converts ammonia into harmless nitrogen gas by either direct or indirect oxidation (Li and Liu 2009). Direct EO involves ammonia adsorption onto the anode surface, its direct electron transfer, and ultimately, its conversion into nitrogen gas (Kapałka et al. 2010a). Conversely, indirect EO of ammonia is performed via anodic reaction to form an intermediate oxidant (e.g., Cl₂, HClO, and ClO⁻), which is then reacted with ammonia for ammonia removal (Kapałka et al. 2010b). Considerable investigations have been conducted on different anode materials for EO. Ammonia was removed thoroughly when boron-doped diamond anode was used for the treatment of cooking wastewater (Zhu et al. 2009). Furthermore, ammonia was almost completely removed when metal oxide electrodes (Ti/PbO₂ and Ti/SnO₂ anodes) were used for the treatment of landfill leachate (Cossu et al. 1998). Dimensional stability anode containing Ru, Ir, or Ti has
been widely used in wastewater treatment due to its good electrocatalytic performance, greater stability, long service life, low price and higher availability (Costa et al. 2008, Li et al. 2013, Profeti et al. 2006). Ihara et al. found that RuO$_2$-IrO$_2$/Ti was a more suitable anode for decreasing ammonia and controlling nitrate accumulation than Ti/PbO$_2$ (Ihara et al. 2006).

Meanwhile, EC has been widely used in wastewater treatment because of its high efficiency and simple operation (Fernandes et al. 2015, Heidmann and Calmano 2008). Chemical coagulation requires a large amount of coagulant, but EC overcomes this problem by directly generating coagulants via anodic dissolution (Zhang et al. 2018b). In EC, coagulants are generated in situ via electrically dissolving metal ions, such as Fe$^{2+}$/Fe$^{3+}$ and Al$^{3+}$, from metal electrodes. The generated Fe$^{2+}$/Fe$^{3+}$ or Al$^{3+}$ ions are effective coagulants for particle flocculation (Chen 2004). Iron and aluminum plates are the most commonly used electrodes for phosphate removal; specifically, aluminum plate exhibits high and stable removal efficiency (Bektas et al. 2004). Zheng et al. evaluated the effects of various experimental parameters, including current density, gap between electrodes, urine dosage, dilution, and hydrolysis, on phosphate removal from urine via EC using iron as anode (Zheng et al. 2009).

Previous studies have suggested the potential of RuO$_2$-IrO$_2$/Ti plate as an anode for ammonia removal through EO and iron plate as an anode for phosphate removal through EC. However, the use of pure RuO$_2$-IrO$_2$/Ti anode can only remove ammonia and cannot remove phosphate because the latter cannot be oxidized. On the contrary,
the use of pure iron anode can only remove phosphate and is less effective in removing ammonia because it is prone to oxygen evolution side reaction. To achieve the purpose of simultaneous ammonia and phosphate removal, we designed a zero-valent iron powder and RuO$_2$-IrO$_2$/Ti plat composite electrode (mZVI-RuO$_2$-IrO$_2$/Ti). Iron powder was bound to the RuO$_2$-IrO$_2$/Ti plat by a magnetic field. This system has both oxidation and coagulation compared to a single EO and a single EC system. In addition, this system is simple in operation, high in efficiency, and short in reaction time compared to the biological method.

The reaction in the electrode and in the aqueous solution is as follows (Gendel and Lahav 2012, Omwene et al. 2018, Tian et al. 2018):

**Anode:**

\[2\text{Fe} \rightarrow \text{Cl}_2 + 2\text{e}^- \] (1)

\[\text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^- \] (2)

**Aqueous phase:**

\[\text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{HClO} + \text{H}^+ + \text{Cl}^- \] (3)

\[\text{HClO} \rightarrow \text{H}^+ + \text{ClO}^- \] (4)

\[3\text{HClO} + 2\text{NH}_4^+ \rightarrow \text{N}_2 + 3\text{H}_2\text{O} + 5\text{H}^+ + 3\text{Cl}^- \] (5)

\[3\text{Fe}^{2+} + 2\text{PO}_4^{3-} \rightarrow \text{Fe}_3(\text{PO}_4)_2 \] (6)

\[4\text{Fe}^{2+} + \text{O}_2 + 2\text{H}_2\text{O} \rightarrow 4\text{Fe}^{3+} + 4\text{OH}^- \] (7)

\[\text{Fe}^{3+} + \text{PO}_4^{3-} \rightarrow \text{FePO}_4 \] (8)

\[\text{Fe}^{3+} + \text{PO}_4^{3-} + (3n-3)\text{OH}^- \rightarrow \text{Fe}_3\text{PO}_4(\text{OH})_{3n-3} \] (9)
Cathode:

The present study examines the combined EO and EC (EO/EC) processes for ammonia and phosphate removal in aqueous solution. The evaluated parameters were anode materials, applied voltage, and initial pH. The effects of zero-valent iron dosage, reaction temperature and organic compounds were also evaluated. The characteristics of the precipitation were investigated via scanning electron microscopy–energy dispersive spectrometry, X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS). This study is the first to investigate and propose the possible mechanism of the simultaneous removal of ammonia and phosphate under an electric field in a magnetically bound zero-valent iron powder and RuO$_2$-IrO$_2$/Ti composite anode by combining EO and EC processes.

2. Materials and methods

2.1 Chemical reagents and synthetic solution

The synthetic solution was obtained by dissolving (NH$_4$)$_2$SO$_4$, KH$_2$PO$_4$, and NaCl in ultrapure water with resistivity of 18.2 MΩ-cm from the Milli-Q (Millipore) water purification system. The synthetic solution contains 200, 100, and 500 mg·L$^{-1}$ of N, P, and Cl$^-$. The influent ammonia and phosphate concentrations were close to some aquaculture wastewater that we had encountered. The pH of aqueous solution was adjusted by adding 3 M of NaOH or 1 M of H$_2$SO$_4$ according to the requirements of...
the experimental design. The conductivity of aqueous solution was adjusted to 750 µS cm\(^{-1}\) by adding 1 M of Na\(_2\)SO\(_4\). All reagents were obtained from Aladdin Chemistry Co., Ltd. (Shanghai, China). They were of analytical grade and used without further refinement. Furthermore, microscale zero-valent iron powder (>98%) was purchased from Tianjin Shentai Chemical Reagent Co., Ltd. RuO\(_2\)-IrO\(_2\)/Ti plate and graphite flakes were supplied by Hebei Mingxuan Metal Materials Co., Ltd. and Qingdao Baofeng Graphite Co., Ltd., respectively. The surface of the titanium plate is an oxide coating of Ru and Ir, the mass ratio of Ru to Ir is about 7:3.

2.2 Experimental setup

All batch mode experiments were conducted in a 200 mL electrolyte glass tank and maintained at a constant temperature (25, 35, 45, and 55 °C) by heating in a water bath. The area of the RuO\(_2\)-IrO\(_2\)/Ti plate immersed in the solution was 15 cm\(^2\). A certain amount of mZVI powder was evenly distributed on a RuO\(_2\)-IrO\(_2\)/Ti plate with a size of 2.5×10 cm\(^2\) and a thickness of 0.1 cm, and the mZVI powder occupied an area of 8 cm\(^2\) (2 cm×4 cm). The mZVI powder was fixed on the surface of the RuO\(_2\)-IrO\(_2\)/Ti plate through a 4 cm × 2 cm × 0.5 cm magnet (surface magnetic field strength ~ 2004 gauss) outside the glass reactor as mZVI-RuO\(_2\)-IrO\(_2\)/Ti composite anode. An mZVI-graphite composite anode was also prepared by replacing the RuO\(_2\)-IrO\(_2\)/Ti plate with a graphite sheet. The mZVI-RuO\(_2\)-IrO\(_2\)/Ti anode and graphite cathode were placed in parallel, and the gap between them was maintained at 1 cm.
The electrodes were connected to a DC power source to assemble the EO/EC reactor. The experimental setup is shown in Fig. 1.

2.3 Experimental methods

Numerous factors influencing ammonia and phosphate removal in the EO/EC process were investigated. These factors include anode materials, applied voltage, initial pH, zero-valent iron dosage, reaction temperature, and organic compounds. The mZVI-RuO$_2$-IrO$_2$/Ti, mZVI-graphite, and RuO$_2$-IrO$_2$/Ti electrodes were used as the anodes in our experiments. Given that the iron powder was bound to the electrode, the effective area of the electrode cannot be accurately calculated, and obtaining the current density was difficult; hence, we used constant voltage (ranging from 4 V to 10 V) from DC power supply. The initial pH (3 to 11) of the solution was adjusted by adding 1 M of H$_2$SO$_4$ or 3 M of NaOH. The amount of iron powder was also investigated as a factor influencing the efficiency of phosphate removal. The experiment was performed at different temperatures (25, 35, 45, and 55 °C).

Each set of experiments was performed for 4 h to 6 h, and samples of the solution were collected at designated times during the experiment. Before analysis, each sample was filtered through membrane filters with 0.45 µm pore diameter. Ammonia, nitrate, nitrite and phosphate were determined with a continuous flowing analyzer (Seal AA3, Germany). After the reaction, the total soluble iron ion concentration in the solution was measured by inductively coupled plasma emission spectroscopy. The
Cl\textsuperscript− concentration was determined using standard methods, such as silver nitrate titration method. The conductivity and pH of the solution were determined using conductivity (Rex Chemical Corp., Shanghai) and pH meters (SevenMulti, Mettler-Toledo International Inc.).

The removal rate based on initial and final concentrations was calculated. It can be expressed as follows (Bashir et al. 2010):

$$\eta = \frac{C_0 - C_t}{C_0} \times 100\%$$  \hspace{1cm} (11)

where \( \eta \) is the ammonia and phosphate removal rate, \( C_0 \) is the initial concentration (mg·L\textsuperscript{−1}) of ammonia or phosphate, and \( C_t \) is the final concentration (mg·L\textsuperscript{−1}) of ammonia or phosphate.

Energy consumption is generally used to evaluate the performance of an electrochemical technology. It can be expressed as follows (Xue et al. 2020):

$$\text{Energy consumption} = \frac{U \times I \times t}{V}$$  \hspace{1cm} (12)

where \( U \) is the voltage applied (V), \( I \) is the current intensity (A), \( t \) is the EO/EC process time (h), and \( V \) represents the volume of the electrolyte (0.2 L).

2.4 Characterization techniques

The precipitate was collected after the reaction and then vacuum-dried. The partially dried precipitate was calcined at 600 °C for 2 h under nitrogen atmosphere. XRD patterns before and after calcination were recorded using the PANalytical X'Pert PRO (Netherlands) diffractometer with monochromatic Cu Kα irradiation in the 2θ range.
angular regions between 5° and 80°. The surface morphologies and atomic composition, as well as distribution, of the precipitate were determined by scanning electron microscope (SEM, Phenom ProX, Phenom-World, Netherlands). XPS measurements were performed on the Thermo Fisher Scientific ESCALAB 250Xi XPS spectrometer (USA) using Al Kα radiation with photon energy of 1486.6 eV as the radiation source.

3. Results and discussion

3.1 Influencing factors of the EO/EC process

3.1.1 Anode materials

Anode materials play an important role in the EO/EC process. To investigate the role of anode materials in ammonia and phosphate removal, we compared the EO/EC performance of mZVI-RuO$_2$-IrO$_2$/Ti, mZVI-graphite, and RuO$_2$-IrO$_2$/Ti anodes. SEM image of zero-valent iron powder is shown in Fig. S1. As can be seen, zero-valent iron powder agglomeration is evident. The agglomerated iron powder was found to have a particle size of less than 100 µm, which confirmed that the iron powder we used was micron-sized. The mZVI-RuO$_2$-IrO$_2$/Ti and RuO$_2$-IrO$_2$/Ti anodes were considerably better than the mZVI-graphite anode for ammonia removal (Fig. 2a). The mZVI-graphite anode only removed 19.87% of the ammonia after 4 h of electrolysis. This finding can be attributed to the fact that the RuO$_2$-IrO$_2$/Ti anode has a higher oxygen evolution potential than the graphite electrode (Fan et al. 2013), resulting in a
large amount of oxygen on the mZVI-graphite anode surface but with slight intermediate oxidation (Cl\textsubscript{2}). Although RuO\textsubscript{2}-IrO\textsubscript{2}/Ti and mZVI-RuO\textsubscript{2}-IrO\textsubscript{2}/Ti anodes both could completely remove the ammonia, the former anode removed ammonia at a slightly faster rate than the latter (120 and 180 min for RuO\textsubscript{2}-IrO\textsubscript{2}/Ti anode and mZVI-RuO\textsubscript{2}-IrO\textsubscript{2}/Ti anode, respectively). Hence, on the surface of RuO\textsubscript{2}-IrO\textsubscript{2}/Ti anode, only Cl\textsuperscript{−} lost electrons, whereas on the surface of mZVI-RuO\textsubscript{2}-IrO\textsubscript{2}/Ti anode, in addition to the loss of electrons from Cl\textsuperscript{−}, electron transfer in iron powder occurred. However, the pure RuO\textsubscript{2}-IrO\textsubscript{2}/Ti anode has no effect on phosphate removal (Fig. 2d). This is mainly due to that the dissolved Fe\textsuperscript{2+} forms a precipitate with the phosphate in the solution. With dissolved oxygen, Fe\textsuperscript{2+} was oxidized to Fe\textsuperscript{3+}, and Fe\textsuperscript{3+} also reacted with phosphate to form a precipitate. Compared with that of the mZVI-RuO\textsubscript{2}-IrO\textsubscript{2}/Ti anode during the EO/EC process, the surface of the RuO\textsubscript{2}-IrO\textsubscript{2}/Ti anode had no iron powder; hence, only EO process occurred when RuO\textsubscript{2}-IrO\textsubscript{2}/Ti plate was used as the anode. This phenomenon confirmed the feasibility of using mZVI-RuO\textsubscript{2}-IrO\textsubscript{2}/Ti anode for the simultaneous removal of ammonia and phosphate.

In the EO/EC process using mZVI-RuO\textsubscript{2}-IrO\textsubscript{2}/Ti anode, the Cl\textsuperscript{−} and NH\textsubscript{4}\textsuperscript{+} concentrations in the solution consistently demonstrated the same decreasing trend during the first 180 min of reaction time (Fig. 3a). A cycle of chloride–chlorine–hypochlorite–chloride occurred in the EO process (Chen et al. 2007). When NH\textsubscript{4}\textsuperscript{+} was almost completely removed, Cl\textsuperscript{−} concentration decreased
rapidly. This result may be due to the fact that the HClO produced did not react with
more NH$_4^+$, resulting in the interruption of the chloride–chlorine–hypochlorite–chloride cycle. In addition, no nitrite was formed in
the solution, but nitrate and total soluble iron ions, which were lower than 3 and 2
mg·L$^{-1}$, respectively, in the solution slightly accumulated. When the reaction
proceeded to 5 min, the total iron content in the solution increased (1.89 mg·L$^{-1}$), but
after the 30 min reaction, no iron ions were detected in the solution. At the same time,
the phosphate was completely removed within 30 min, and after 30 min, the iron ion
concentration in the solution gradually increased to finally reach 2.00 mg·L$^{-1}$. This
occurrence may be due to the fact that the solution gradually becomes acidic as the
reaction proceeds, and the iron ions in the resulting precipitate gradually dissolve. It
can be seen from Fig. S2 that the soluble iron ions in the solution mainly exist in the
form of Fe$^{3+}$, and the concentration of Fe$^{2+}$ in the solution was below 0.2 mg·L$^{-1}$
throughout the reaction.

3.1.2 Applied voltage

To fix the iron powder on the RuO$_2$-IrO$_2$/Ti plate, we applied a magnetic field. At
first, the iron powder was uniformly coated in an area of 8 cm$^2$ and then stacked and
erected on the RuO$_2$-IrO$_2$/Ti plate with a needle shape after the magnetic field was
applied. Therefore, the area occupied by the iron powder was less than 8 cm$^2$, but the
surface area of the entire mZVI-RuO$_2$-IrO$_2$/Ti anode increased. Accurate calculation
of the surface area and current density of the mZVI-RuO$_2$-IrO$_2$/Ti anode was difficult;
thus, this experiment was performed in a constant voltage mode. Different constant
voltages of 4, 6, 8, and 10 V were applied in the experiments to investigate their
influence on ammonia and phosphate removal. With the application of increasing
voltage from 4 V to 10 V, the ammonia removal efficiency increased from 33.61% to
98.95% (Fig. 2b). As the voltage increased, the ammonia removal rate simultaneously
increased. The increase in voltage caused the current and the electron transfer rate on
the electrode to increase, thereby promoting the formation of active intermediates (Cl₂,
HClO, and ClO⁻) that have strong oxidizing properties and increase the rate of
ammonia oxidation. At a voltage of 10 V, the phosphate can be completely removed
within 15 min only, whereas that at 4 V was within 90 min (Fig. 2e). As the voltage
was increased from 4 V to 10 V, the dissolution rate of iron powder on the anode
increased. The rate at which Fe²⁺/Fe³⁺ and phosphate reacted to form precipitates also
increased. Ammonia removal rate was considerably lower than the phosphate removal
rate (Figs. 2b and 2e). The voltage should not be excessively low during simultaneous
ammonia and phosphate removal; otherwise, it would result in lower ammonia
removal efficiency.

3.1.3 Initial pH

In our electrical system, initial pH exerted considerably less significant influence
on ammonia removal compared with either anode materials or voltage. Fig. 2c shows
that pH increased as the ammonia removal rate increased. Under acidic conditions
(pH from 3 to 7), the removal rate of ammonia increased gradually, but such rate was relatively fast under alkaline conditions (pH from 7 to 11). Furthermore, under acidic conditions, the Cl₂ produced by the anode was more likely to escape and cause Cl₂ loss. However, an increased pH condition was more conducive to chloride–chlorine–hypochlorite–chloride cycle, thereby increasing the amount of free Cl₂ produced in the solution and accelerating ammonia degradation (Chen et al. 2007).

Fig. 2f illustrates the effect of initial pH from 3 to 11 on the phosphate concentration remaining in the solution. Phosphate can be completely removed at pH values of 3, 5, and 7. At pH 9, the phosphate removal rate slightly decreased but could achieve 97.42% of the removal rate within 4 h. However, such rate was only 37.53% at pH 11. Thus, Fe(OH)₃ was easily formed when the OH⁻ concentration in the solution was high, and the solubility of FePO₄ increased under strong alkaline conditions (Irdemez et al. 2006). When the initial pH of the solution was 3 to 7, the final pH dropped to approximately 2–3 after 4 h of electrolysis (Fig. 3b). The initial pH was 9, and the final pH was reduced to 6.22 after the reaction. The pH of the strong alkaline solution did not change substantially before and after the reaction (initial pH=11 and final pH=11.15). Chen et al. found that the final pH decreased when ammonia was removed by RuO₂-IrO₂-TiO₂/Ti electrodes (Chen et al. 2007). This finding could be due to the fact that pH is influenced by both cathodic and anodic processes, as well as by the reactions of chlorine in water. The pH gradually
decreased as the electrolysis progressed because the Cl\textsubscript{2} generated by Cl\textsuperscript{-} electrolysis was dissolved in water, and reactions (3) and (4) occurred to gradually lower the pH. In the electrolyte where Cl\textsuperscript{-} and NH\textsubscript{4}\textsuperscript{+} coexist, the ammonia was oxidized by free chlorine, and the reaction is shown in Eq. (5). The ammonia oxidation reaction produced hydrochloric acid, and the pH of the solution gradually decreased as the electrolytic oxidation reaction proceeded. Lacasa et al. found that the final pH increased when phosphate was removed by iron anodes (Lacasa et al. 2011). As shown in Eq. (10), the cathode consumed hydrogen ions under acidic and neutral conditions to produce hydrogen, or generated hydroxide ions under alkaline conditions, causing the pH in the solution to rise. Thus, the pH change caused by the oxidation of ammonia plays a major role in the EO/EC process.

3.1.4 Zero-valent iron dosage

Zero-valent iron dosage is an important part of the composite electrode. The amount of iron powder may dramatically affect the removal of ammonia and phosphate. As depicted in Fig. 4a, when the zero-valent iron dosage was increased from 0.1 g to 0.4 g, the degradation rate of ammonia gradually decreased. Hence, the more the amount of iron powder on the anode surface, the more electrons were needed to convert zero-valent iron into iron ions so that the rate at which Cl\textsuperscript{-} loses electrons at the anode will decrease. The area of the RuO\textsubscript{2}-IrO\textsubscript{2}/Ti plate occupied by a greater amount of iron powder was larger than any other areas because the latter was more densely erected on the RuO\textsubscript{2}-IrO\textsubscript{2}/Ti plate after being adsorbed by the magnet.
Consequently, a smaller area was generated for the RuO$_2$-IrO$_2$/Ti plate to provide electron transfer to Cl$^-$. With increasing zero-valent iron dosage, the phosphate removal rate also increased (Fig. 4c), indicating that the higher the concentration of iron ions in the solution, the easier it is to form iron phosphate precipitate. However, increasing the amount of iron powder in the EO/EC process is not necessary because the phosphate can be completely removed within 30 min (the zero-valent iron dosage was from 0.1 g to 0.4 g), whereas the complete degradation of ammonia took longer. Hence, 0.1 g of iron powder could completely remove the phosphate in the solution, as revealed by experimental results.

### 3.1.5 Reaction temperature

Figs. 4b and 4e illustrate the removal of ammonia and phosphate at different temperatures. As the temperature increased, the removal rates of ammonia and phosphate also increased. Ammonia was completely removed within 4 h when the reaction temperature was 25 °C. Moreover, ammonia could be completely removed within 2 h when the temperature was 55 °C. For phosphate removal, the removal rate was extremely fast at each temperature. This phenomenon can be explained by the fact that the ionic strength and conductivity in the solution increased as the temperature increased, thereby accelerating the rate of electron transfer. Ammonia degradation was consistent with pseudo-zero order kinetics. Ammonia concentration decreased linearly with time at all three different temperatures (25, 35, 45, and 55 °C) in the electrochemical oxidation process (Fig. 5b). The slopes of lines were -0.96,
-1.10, -1.51, and -1.72 with correlation coefficients of 0.998, 0.983, 0.996, and 0.997, respectively. Correspondingly, the ammonia oxidation rates were 0.96, 1.10, 1.51, and 1.72 mg N L$^{-1}$ min$^{-1}$ (Fig. 5b).

### 3.1.6 Organic compounds

Organic compounds may coexist in water with ammonia and phosphate in practical applications. Wastewater discharged from various industries, such as coke plants, pharmaceuticals, textiles, distilleries, and wineries, always contains organic pollutants at high concentrations (Hu et al. 2019, Pan et al. 2018). In order to investigate the effect of organic compounds on simultaneous ammonia and phosphate removal, different concentrations of isopropanol (0, 10, 25, 50 mM·L$^{-1}$) were added to the previously solution. Fig. 4c reveals the influence of organic compounds on the ammonia removal by the mZVI-RuO$_2$-IrO$_2$/Ti anode at 25 °C in a pH 7 aqueous solution. The ammonia degradation rate was the fastest without organic compounds in the solution. When the concentration of isopropanol was increased from 0 to 25 mM·L$^{-1}$, the degradation rate of ammonia gradually decreased. This indicated when organic compounds coexist in the solution with ammonia and phosphate, the intermediate oxidant oxidizes part of the organic compounds in addition to the oxidation of ammonia. Continue to increase the concentration of isopropanol in the solution to 50 mM·L$^{-1}$, the rate of ammonia degradation was almost unchanged. Moreover, ammonia could be almost completely removed within 4 hours, regardless
of whether the system contains organic compounds. Conversely, the presence of organic compounds has no effect on phosphate removal and phosphate can be removed extremely quickly, regardless of the concentration of isopropanol (Fig. 4f).

In addition, we investigated the effect of magnetic field strength on simultaneous removal of ammonia and phosphate. From Fig S3 we find that the strength of the magnetic field in our system has no effect on the removal of ammonia and phosphate. Therefore, the magnet is only used to attract iron powder in this system. Compared to other single EO or EC processes, this electrochemical system was designed to achieve simultaneous ammonia and phosphate removal by using the mZVI-RuO$_2$-IrO$_2$/Ti anode (Table S1).

### 3.2 Characterization of precipitation

The crystallinity and structure of the samples were evaluated via the XRD technique. The XRD patterns of the precipitate obtained via reaction at different pH values are shown in Fig. 6. The vacuum-dried samples were essentially amorphous with no distinct characteristic peaks (Fig. 6a). To increase the crystallinity of the precipitate, we calcined the precipitate in a nitrogen atmosphere for 2 h (set and maintained at 600 °C for 2 h and then cooled to room temperature). The composition of the precipitate varied at different pH values (Fig. 6b). When the initial pH was 3, no apparent characteristic peak before calcination was observed, but a single broad peak appeared from 20° to 35° after calcination. This broad peak is likely to indicate
iron oxides, but this requires further analysis due to the amorphous nature of iron oxides, which are not easily detected by XRD (Yoon et al. 2016). As the pH value rose to 5, some peaks appeared from 20° to 35°; but the peak intensity was extremely low. When the initial pH of the solution was 7, the characteristic peaks of Fe$_2$(PO$_4$)O (PDF #85-2384) and Fe$_2$O$_3$ (PDF #73-2234) appeared (Fig. 6c). The appearance of iron oxide indicated that the precipitate contained Fe(OH)$_3$, which decomposed at a high temperature of 600 °C to form Fe$_2$O$_3$. When the initial pH of the solution was 9 and 11, the characteristic peaks of Fe$_2$(PO$_4$)O disappeared; when the pH increased, the intensity of the peak also increased, while the line width decreased, indicating an increase in crystallinity. Only the characteristic peak of Fe$_2$O$_3$ (PDF #73-2234) appeared when the initial pH was 11 (Fig. 6d). This finding confirmed that under higher pH conditions, Fe(OH)$_3$ was more likely to be formed, resulting in an undesirable effect of phosphate removal. This result is consistent with the conclusions we have previously obtained (Fig. 2f).

Given the different phosphate removal effects at various pH conditions, we investigated the morphology and elemental composition of the precipitate at pH 5 and 11, respectively. The morphologies of the precipitates obtained at the initial pH of 5 and 11 are shown in Figs. 7a and 7c. SEM results indicated that the precipitates were loose, without a noticeable regular shape. The elemental mapping images of the precipitate with a selected area (Figs. 7b and 7d) reveal that it contained Fe, P, and O after the EO/EC process. The atomic percentage of P was 7.6% and 2.8% in the initial
pH of 5 and 11, respectively (Table 1). The density of P on the precipitate obtained at pH 5 was higher than that on the precipitate obtained at pH 11. The atomic concentration ratio of P in the precipitate obtained at pH 5 and 11 was approximately 0.37. This result is consistent with the previously obtained phosphate removal rate of only 37.53% at pH of 11.

XPS was used to identify the chemical states of Fe, P, and O in the flocs produced during the EO/EC process. The binding energy was calibrated to adventitious carbon C 1s peak centered at 284.6 eV (Sleiman et al. 2016), and peak fittings were performed using the XPSPeak41 software. To determine the valence of iron and the form of P in the precipitate after the reaction, differentiating fitting of Fe 2p, O 1s, and P 2p was performed. In addition to Fe, P, and O, the precipitate also contained a small amount of S element (Fig. 8a). Considering that nitrogen-containing wastewater was configured using (NH$_4$)$_2$SO$_4$, flocs may adsorb trace amounts of sulfate in the solution. Fig. 8b shows the high-resolution XPS spectrum of Fe 2p$_{3/2}$, which can be deconvoluted into two peaks at 709.7 and 712.6 eV, corresponding to the ferric divalent iron and trivalent iron, respectively (Bae and Lee 2014, Chen et al. 2018). The high-resolution XPS spectrum of the O 1s (Fig. 8c) could be fitted into three peaks at binding energies of 529.9, 531.3, and 532.1 eV, which corresponded to the lattice oxygen in the metal oxide (O$^2$), the hydroxide in the surface hydroxyls (OH$^-$), and the chemically or physically adsorbed water (H$_2$O$_{ads}$) (Chen et al. 2018, Tan et al. 2018). Therefore, iron hydroxide and iron oxide were formed after the reaction. The P
2p XPS spectrum of precipitation was deconvoluted into two peaks of 132.9 and 133.7 eV, which corresponded to \( \text{PO}_4^{3-} \) and \( \text{HPO}_4^{2-} \), respectively (Yin and Kong 2014). Thus, \( \text{PO}_4^{3-} \) and \( \text{HPO}_4^{2-} \) groups existed on the surface of the precipitation after the reaction.

3.3 Energy consumption

Energy consumption is an essential aspect of electrochemical processes, and large energy consumption is an important reason for restricting electrochemical methods. Table 2 shows the energy consumption during the EO/EC process at 10 V. As the reaction progressed, the energy consumption increased. When the reaction was performed for 180 min and the ammonia removal rate reached 98.84%, the energy consumption for ammonia removal was 0.622 kWh·g\(^{-1}\) N. Meanwhile, phosphate can be completely removed by the reaction in only 30 min, and the energy consumption for phosphate removal was 0.216 kWh·g\(^{-1}\) P. In this experiment, the energy consumption was mainly determined by the energy consumed by the ammonia removal process. Methods for further reducing energy consumption are one of the issues to be studied in the future.

4. Conclusions

The mZVI-RuO\(_2\)-IrO\(_2\)/Ti electrode was designed and successfully combined with the EO/EC process to simultaneously remove ammonia and phosphate. Results of this study revealed that mZVI-RuO\(_2\)-IrO\(_2\)/Ti electrode is extremely effective in removing ammonia and phosphate. Increasing the voltage and temperature also demonstrated
positive effects. The rate of ammonia removal increased slightly with increasing initial pH. Conversely, phosphate was poorly removed under alkaline conditions. Therefore, simultaneous removal of ammonia and phosphate was suitably demonstrated at a neutral pH. In addition, zero-valent iron dosage had a minimal effect on the removal of ammonia but significantly enhanced phosphate removal by addition of iron powder. Ammonia could be completely removed within 180 min at the applied voltage of 10 V, pH of 7, zero-valent iron dosage of 0.1 g, and reaction temperature of 35 °C using mZVI-RuO$_2$-IrO$_2$/Ti anode. The phosphate removal rate was extremely fast and could be completely removed within 30 min under the same conditions. This work reports the excellent performance of the mZVI-RuO$_2$-IrO$_2$/Ti electrode in removing ammonia and phosphate. Hence, future studies should use mZVI-RuO$_2$-IrO$_2$/Ti electrode to treat actual wastewater.

Acknowledgments

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chemical oxygen demand, turbidity and hardness from biologically treated citric acid wastewater by electrochemical oxidation for reuse. Separation and Purification Technology 107, 281-288.


Profeti, D., Lassali, T.A.F. and Olivi, P. (2006) Preparation of Ir_{0.3}Sn_{(0.7-x)}Ti_{x}O_{2} electrodes by the polymeric precursor method: Characterization and lifetime study. J Appl Electrochem 36(8), 883-888.


Table 1 Surface elemental composition and atomic percentages via EDS analysis for the precipitate obtained at pH 5 and 11.

<table>
<thead>
<tr>
<th>Initial pH</th>
<th>O</th>
<th>Fe</th>
<th>P</th>
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<tbody>
<tr>
<td>5</td>
<td>65.40</td>
<td>27.00</td>
<td>7.60</td>
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<tr>
<td>11</td>
<td>62.80</td>
<td>34.40</td>
<td>2.80</td>
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</table>

Table 2 Energy consumption and removal efficiency of ammonia and phosphate at different reaction times.

<table>
<thead>
<tr>
<th>reaction time (min)</th>
<th>5</th>
<th>15</th>
<th>30</th>
<th>60</th>
<th>120</th>
<th>180</th>
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<tbody>
<tr>
<td><strong>N</strong></td>
<td></td>
<td></td>
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<tr>
<td>Energy consumption</td>
<td>0.358</td>
<td>0.463</td>
<td>0.529</td>
<td>0.506</td>
<td>0.511</td>
<td>0.622</td>
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<tr>
<td>(kWh·g⁻¹ N)</td>
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<tr>
<td>Removal efficiency</td>
<td>4.70</td>
<td>11.66</td>
<td>20.33</td>
<td>43.39</td>
<td>85.98</td>
<td>98.84</td>
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<tr>
<td>(%)</td>
<td></td>
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<tr>
<td><strong>P</strong></td>
<td></td>
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</tr>
<tr>
<td>Energy consumption</td>
<td>0.059</td>
<td>0.109</td>
<td>0.216</td>
<td>0.430</td>
<td>0.853</td>
<td>1.272</td>
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<tr>
<td>(kWh·g⁻¹ P)</td>
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<tr>
<td>Removal efficiency</td>
<td>61.60</td>
<td>99.78</td>
<td>100.00</td>
<td>100.00</td>
<td>100.00</td>
<td>100.00</td>
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<tr>
<td>(%)</td>
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</table>
Figure 1 Schematic diagram of the experimental setup.
Figure 2 Influence of different factors on ammonia removal: a) anode materials, b) voltage, and c) initial pH; and influence of different factors for phosphate removal: d) anode materials, e) voltage, and f) initial pH.
Figure 3  a) Concentrations of Cl$^-$, NH$_4^+$, NO$_3^-$, and total soluble iron ions in solution changes with time; b) pH change at different initial pH values.
Figure 4 Influence of different factors on ammonia removal: a) zero-valent dosage, b) reaction temperature, c) organic compounds; and influence of different factors on phosphate removal: d) zero-valent iron dosage, e) reaction temperature, f) organic compounds.
Figure 5 Effect of different reaction temperatures on a) ammonia concentration profiles and b) ammonia oxidation rate.
Figure 6 XRD patterns at different pH values: a) after vacuum drying; b) calcination at 600 °C; c) calcination at 600 °C, pH=7; and d) calcination at 600 °C, pH=11.
Figure 7 SEM image of precipitation at a) pH=5 and b) pH=11, and elemental mapping of precipitation at c) pH=5 and d) pH=11.
Figure 8 XPS spectra of the surface elements of the precipitation: a) survey spectrum, b) Fe element, c) O element, and d) P element of the precipitation.
Highlights:
► RuO$_2$-IrO$_2$/Ti plate combined with iron powder act as an anode of electrochemical unit.
► Iron powder were immobilized at the surface of the RuO$_2$-IrO$_2$/Ti plate by a magnet.
► The mZVI-RuO$_2$-IrO$_2$/Ti anode showed high simultaneous removal efficiency of N and P.
► N and P were synergistically removed by electro-oxidation and electrocoagulation.
Declaration of Interest Statement

We declare that we do not have any commercial or associative interest that represents a conflict of interest in connection with the work submitted.