

Aqueous Phosphate Removal and Electricity Production Using an Iron–Air Fuel Cell

Changyu Li¹ and Yanqing Sheng²

Abstract: Phosphorus (P) surplus is a key factor in water eutrophication, and aqueous phosphate removal is a concern. In this study, ferrous ions (Fe²⁺) were generated in situ by iron–air fuel cells and were used in the removal of P from synthetic P-containing wastewater. The P removal results indicated that different initial concentrations of P were more effectively removed by an in situ Fe²⁺ generation than by the addition of FeSO₄. The main P removal products of FeSO₄ were Fe hydroxides, whereas the main products with the iron fuel cell were vivianite and Fe hydroxides. These results suggested that Fe²⁺ formed in situ had a more conducive and stronger affinity to bond phosphate than FeSO₄. The maximum power density reached 1,875 mW/m² after 24 h of operation. The results indicate that the iron–air fuel cell can be used for P removal/recovery coupled with potential electricity generation. **DOI: 10.1061/(ASCE)EE.1943-7870.0001724.** © *2020 American Society of Civil Engineers*.

Introduction

Phosphorus (P) is an essential element for living organisms in aqueous ecosystems. However, the excessive emissions of P from agriculture and human activity have caused increasing crises such as eutrophication in aquatic environments (Conley et al. 2009). For P removal, the popular techniques are enhanced biological P removal and chemical P removal using Fe or aluminum salts (Wilfert et al. 2015). However, biological P removal technologies suffer from low efficiency when treating wastewater containing high concentrations of P. Based on their cost and efficiency, Febased technologies for P removal have received more attention (Molinos-Senante et al. 2011).

Currently, Fe salts are regarded as the most common method of Fe dosing. However, Fe dosing by zero-valent iron (ZVI) and Fe²⁺ generated in situ also have attracted attention for their high efficiency. Previous reports have shown that the addition of Fe salts (e.g., FeSO₄ and FeCl₃) can enhance P removal during wastewater treatment (Zhou et al. 2008; Ren et al. 2019). However, the associated anions may lead to scale formation and corrosion (Zhang et al. 2018). Furthermore, the dosage of Fe salts decreases the aqueous pH, and neutralization might be required prior to discharge. P can be effectively absorbed by ZVI for P removal (Almeelbi and Bezbaruah 2012; Sleiman et al. 2016). However, passivation prevents its reactivity due to the formation of Fe oxides on the surface, resulting in the unsustainability of the ZVI technology (Wan et al.

2018). Although nanosized sorbents have a favorable sorption capacity and removal rate, separation still is difficult, and there are concerns about their potential hazards in aqueous systems (Lefevre et al. 2016).

Particulate ZVI dissolves and generates Fe^{2+} under acidic conditions that can facilitate P removal (Yoshino and Kawase 2013). However, the Fe^{2+} generation rate and resultant dosage are difficult to control during this process. As an alternative, direct current electric field-mediated oxidative dissolution of Fe anodes can be used to produce Fe^{2+} for P removal (Zhang et al. 2018). However, conventional electrocoagulation with Fe anodes requires electrical energy consumption. As a more feasible method, fuel cells have been proposed for treating acid mine drainage (Leiva et al. 2016). Based on previous reports, air-cathode fuel cells have been widely used to convert Fe^{2+} or Fe anode to Fe oxides (Cheng et al. 2011; Zhai et al. 2013; Kim et al. 2015). In these studies, utilization of the Fe oxide was the main concern, whereas Fe^{2+} was neglected. Although ironair fuel cells can be used to treat synthetic arsenate wastewater (Kim et al. 2017), the efficacy for P removal is still unknown.

This study (1) assessed the P removal performance of in situ Fe^{2+} under different conditions compared with Fe salts, (2) identified the electricity generation characteristics of iron–air fuel cells, and (3) explored the P removal mechanism of in situ Fe^{2+} .

Material and Methods

Iron–Air Fuel Cell Setup

A single-chamber fuel cell with 1 L of a circulating synthetic solution was used for in situ Fe^{2+} generation (Fig. 1). The surface area of the electrode plates and the chamber volume were 50 cm² and 300 mL, respectively. The anode was placed at one end of the chamber and covered with a plastic end plate, and the cathode was placed at the other end and covered with a second end plate with a hole in the center (5 cm). The electrodes were connected by titanium wires (1 mm diameter). In addition, a Ag/AgCl reference electrode was used to measure the cathodic and anodic potentials. The potentials reported here were relative to the potential of the Ag/AgCl reference electrode. The Fe anode consisted of a 0.30-mm-thick plate of Fe (purity 99.5%). The cathode was an air cathode manufactured based on Cheng et al. (2006).

¹Ph.D. Student, Research Center for Coastal Environment Engineering Technology of Shandong Province, Yantai Institute of Coastal Zone Research, Chinese Academy of Sciences, Chunhui Rd. 17, Laishan District, Yantai 264003, PR China; College of Resources and Environment, Univ. of Chinese Academy of Sciences, No. 19(A) Yuquan Rd., Shijingshan District, Beijing 100049, PR China. Email: cyli@yic.ac.cn

²Professor, Research Center for Coastal Environment Engineering Technology of Shandong Province, Yantai Institute of Coastal Zone Research, Chinese Academy of Sciences, Chunhui Rd. 17, Laishan District, Yantai 264003, PR China (corresponding author). Email: yqsheng@yic .ac.cn

Note. This manuscript was submitted on October 11, 2019; approved on January 2, 2020; published online on April 8, 2020. Discussion period open until September 8, 2020; separate discussions must be submitted for individual papers. This paper is part of the *Journal of Environmental Engineering*, © ASCE, ISSN 0733-9372.



Synthetic P-Containing Wastewater Preparation and Experimental Operation

Synthetic P-containing wastewater (referred to herein as P wastewater) was prepared with ultrapure water containing NaCl and KH₂PO₄. Four kinds of P wastewater had the same NaCl concentration (500 μ M) and different KH₂PO₄ concentrations (100, 500, 1,000, and 10,000 μ M). The PO₄³⁻ concentration in P wastewater was analyzed prior to use.

In the fuel cell experiments, different concentrations of P wastewater were held in an external covered container and circulated through the reactor for 4–72 h using a peristaltic pump (flow rate 0.5 L/min). The fuel cell was operated in the open circuit mode for 5 min to measure the open circuit voltage of the anode and cathode, and then the titanium wires in the reactor were connected to an external resistance of 10 Ω . The electrode potentials and cell voltages were measured with a multimeter every 5 min. Samples consisting of 1 mL solution were taken from the external reservoir at each sampling time. Based on the different initial PO₄⁻ concentrations (100–10,000 μ M) and circulation times (4–72 h), the sampling intervals were 15, 30, 60, and 120 min, respectively.

In addition, the P wastewater containing 0.05 mM NaCl, and 500 μ M KH₂PO₄ was used for contrast experiments with FeSO₄ and FeCl₃. In the unadjusted pH experiment, 1 L P wastewater was added to each beaker, and then 250 μ mol FeSO₄ or FeCl₃ was added every 30 min with stirring (10 min) and precipitation (20 min). During the process, the pH value variations were observed to investigate the effects of acidity. In the adjusted pH experiment, 250 μ mol FeSO₄ or FeCl₃ was added every 30 min and HCl (4 M) or NaOH (4 M) were used to adjust the solution pH to 8 before stirring (10 min) and precipitation (20 min). The PO₄³⁻ in the supernatant was determined. Because the fuel cell was not an oxygen-free system, a contrast experiment was conducted under anoxic conditions (dissolved oxygen = 1.5 ± 0.5 mg/L).

Measurement and Analysis

The PO_4^{3-} in samples was measured using the molybdenum blue spectrophotometric method after vacuum filtration or syringe-driven filtration (0.45- μ m membrane, detection limit = 0.01 mg/L) (Baird et al. 2017). The Fe²⁺ and total Fe were measured using the 1,10-phenanthroline method (detection limit = 0.01 mg/L).

The filter membrane containing the retained solids was vacuum cold-dried to avoid potential oxidation of Fe²⁺. These dried solid substances were analyzed by X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). XRD data were recorded using an X-ray diffractometer (XRD-7000, Shimadzu, Kyoto, Japan) with Cu-K α radiation of 40 kV and 30 mA in the 2θ range 10°–90°. The scanning speed was 4.0°/min. The valence states of P and Fe were measured with an ESCALAB 250XI X-ray photoelectron spectrometer (Thermo Scientific, Waltham, Massachusetts).

The cell potential was calculated as the difference between the anode and cathode. The current density and power density were calculated according to the following equations:

$$i = 10000V/(RA)$$
 (1)

$$P_c = 1000iV \tag{2}$$

where *i*, *V*, *R*, *A*, and P_c = current density (mA/m²), voltage (mV), external resistance (Ω), anode surface area (cm²), and cell power density (mW/m²), respectively.

The generation of Fe^{2+} in the cells was determined by Faraday's law, and the Fe^{2+} generation in the fuel cell experiments was considered as the accumulated Fe dosage (Zhang et al. 2018). Therefore the accumulated Fe dosage was calculated as follows:

$$C_{Fe} = \frac{1000t \sum_{0}^{n} U_i}{RZFv} \tag{3}$$

where C_{Fe} , t, n, U_i , and R = accumulated Fe dosage (μ M), sampling interval time (s), sampling time, external voltage (mV), and external resistance (Ω), respectively; Z = number of electrons used (for Fe, Z = 2); F = Faraday's constant (96,485 C/mol); and v = volume of solution (1 L).

The P removal efficiency (R_e) and Fe utilization efficiency (η_{Fe}) were determined as follows:

$$R_e = \frac{C_0 - C_t}{c_0} \times 100\%$$
 (4)

$$\eta_{Fe} = \frac{C_0 - C_t}{C_{Fe}} \times 100\%$$
 (5)

where C_0 and C_t = initial P concentration (μ M) and P concentration at sampling time (μ M), respectively.

Results and Discussion

P Removal by In Situ Fe²⁺ and Fe Salts

P Removal Efficiency

In the in situ Fe²⁺-generation experiments, high P removal (>95%) was achieved under different initial P concentrations (100–10,000 μ M) studied [Fig. 2(a)]. After treatment, the PO₄^{3–} concentration in the effluent was lower than 0.2 mg/L. In the in situ process, Fe²⁺ release was an important factor for P removal, and the Fe²⁺ concentration in solution was dependent on the total passage of the electron charge through the solution. A higher initial P concentration required a larger Fe²⁺ dosage, and according to Eq. (3), it needed more reaction time.

Different initial P concentrations affected Fe utilization efficiency [Fig. 2(b)]. In the process of P removal, Fe utilization efficiency first increased and then decreased with Fe^{2+}



Fig. 2. Changes with the accumulated Fe dosage of (a) residual PO₄³⁻; and (b) η_{Fe} .

accumulation. In the dynamic system of iron fuel cells, Fe²⁺ was continually injected and was subsequently involved in solid phase formation. At the beginning of the reaction, the accumulated Fe²⁺ dosage stayed at a low level, and the reaction rate of PO_4^{3-} and Fe^{2+} was limited by Fe²⁺ availability. However, as Fe²⁺ accumulated, the P removal efficiency increased [Fig. 2(a)]. When the accumulated amount of Fe²⁺ reached approximately 500 μ M, Fe utilization efficiency decreased, indicating that a threshold of Fe²⁺ existed in the reaction. During the reaction, the Fe²⁺ released from the Fe anode exceeded an appropriate concentration (or surplus), restraining Fe utilization. These phenomena confirmed that P removal by Fe²⁺ was a dynamic unbalanced reaction (Zhang et al. 2013), which is explained partly by the requirement for a higher residual Fe²⁺ concentration to obtain a lower concentration of residual PO_4^{3-} in the solution, and partly because the generation of $Fe(OH)_2$ precipitation consumed Fe^{2+} .

In wastewater with an initial P concentration of 100 μ M, Fe utilization efficiency reached a maximum (35%) after Fe accumulated to a concentration of 250 μ M. When the initial P increased to 10,000 μ M, the maximum Fe utilization efficiency changed to 53%. When the initial P was low (<1,000 μ M), the maximum Fe utilization efficiency increased with the initial P increase (Fig. 3). There was a nonlinear positive correlation between the maximum η_{Fe} and the initial P concentration, and a maximum η_{Fe} less than 60% meant that the Fe/P molar ratio was more than 1.5. According to Eq. (6) (Wilfert et al. 2015), if the dephosphorization process consists only of the formation of ferrous phosphate, the ratio of Fe to P should be close to 1.5. This result (Fe/P > 1.5) showed that the reaction between PO₄³⁻ and Fe²⁺ not only generated ferrous



Fig. 3. Relationship between the maximum η_{Fe} and initial P concentrations.

phosphate but also was accompanied by the oxidation-hydrolysis of Fe²⁺ and dissolved Fe (Fe²⁺ and Fe³⁺). Additionally, the maximum η_{Fe} decreased with decreasing initial P concentration, indicating that an excessive amount of Fe²⁺ was required at a low initial P. Therefore, in the actual application process, for low-P sewage, P enrichment should be conducted prior to treatment by this way

$$3Fe^{2+} + 2PO_4^{3-} \rightarrow Fe_3(PO_4)_2 K_{sp} = 10^{-36}$$
 (6)

In contrast, in experiments with Fe salts, a high P removal rate was observed with in situ Fe²⁺ and FeCl₃ compared with FeSO₄ [Fig. 4(a)]. Zhang et al. (2018) used this result to justify the P removal efficiency achieved by in situ Fe²⁺ generation, which was higher than the P removal efficiency achieved with the addition of FeSO₄. This result was related to the different pH values used in the in situ and salt-dosing cases. When the final pH of the FeSO₄ dosage was adjusted to close to the in situ Fe²⁺ dosage (pH 8), the residual PO₄³⁻ concentration was significantly reduced, indicating that further comparisons need to be made under the same pH conditions.

Furthermore, in the case of adjusting the final pH to 8, η_{Fe} of FeSO₄ increased but the maximum value remained at a low level compared with in situ Fe²⁺ [Fig. 4(b)]. Fe²⁺ from Fe salt was mostly in the form of hydrated ions, which cannot directly react with PO₄³⁻. Flocs generated by Fe²⁺ hydrolysis poorly adsorb PO₄³⁻ (Wilfert et al. 2015). By contrast, the in situ Fe²⁺ released by the electrode was more likely to react with PO₄³⁻ prior to hydrolysis. Therefore, the results suggested that the activity of in situ Fe²⁺ was higher than Fe²⁺ from FeSO₄.

Variations of pH

Different Fe dosing patterns had different effects on the solution pH, which, in turn, affected the P removal. Due to continuous in situ dosing of Fe²⁺, the final pH significantly increased compared to the initial pH (Table 1). These results can be explained by reactions at the anode and cathode. At the anode, Fe was converted to Fe²⁺ by the loss of two electrons. The electron acceptors were water and dissolved oxygen, which diffused from the air cathode into the solution. These reactions required two electron transfers to produce OH⁻ or deplete H⁺, accompanied by the production of Fe²⁺ in the aqueous phase

$$Fe + 2H_2O \rightarrow Fe^{2+} + H_2 + 2OH^-$$
 (7)

$$Fe + 2H^+ + 1/2O_2 \rightarrow Fe^{2+} + H_2O$$
 (8)

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Fig. 4. P removal by in situ Fe²⁺ and Fe salts: (a) residual PO₄³⁻; and (b) η_{Fe} .

However, in the experiments in which Fe salts were added, the hydrolysis reduced the solution pH. Park et al. (2016) reported that the reduction in pH was not conspicuous after dosing with Fe salts because the low initial P concentration (<200 μ M) required a lower dosage of Fe salts. However, the pH significantly decreased at a high Fe salt dosage. Furthermore, a flocculent precipitate existed as the pH was adjusted to 8 in the experiments with FeSO₄ added and changed gradually from light green to reddish brown, indicating that part of the Fe²⁺ had been converted to Fe³⁺.

In this work, the pH effects on Fe^{2+} on P removal had three main factors: (1) the oxidation rate of Fe^{2+} ; (2) the solubility of ferrous phosphate; and (3) the side reactions of Fe^{2+} hydrolysis. Zhang et al. (2013) found an approximately 100 fold increase in the Fe^{2+} oxidation reaction for an increase of one pH unit. The increase in the Fe^{2+} oxidation rate could effectively improve the P removal efficiency (Li et al. 2009). Generally, the suitable pH range for the minimum solubility of ferrous phosphate is from 8.0 to 10.0 (Liu et al. 2018). When the pH deviates from this range, ferrous phosphate precipitation is reduced, resulting in a lower P removal efficiency. In addition, the ferrous phosphate precipitation process usually is accompanied by Fe hydroxide or ferrous hydroxide precipitates. With the pH increase, the Fe^{2+} and Fe^{3+} hydrolysis degrees is enhanced. However, the hydroxyl ion competing with P for Fe ions might result in a lower P removal efficiency when the pH exceeds these limits.

Filterable Fe

Fe ion (Fe²⁺ and Fe³⁺) coagulation and precipitation in the water phase are prerequisites for P removal. Solution samples were taken at the designated times during the contrast experiments, and the filterable Fe was measured after collection of a filter sample through a 0.45- μ m membrane filter. The filterable Fe concentration during in situ Fe²⁺ release and the addition of Fe salts varied (Fig. 5). In the case of in situ Fe²⁺ dosing, the filterable Fe concentration was 27 μ M at an accumulated Fe dosage of 235 μ M, and it increased to 56 μ M as the accumulated Fe increased to 487 μ M. However, the filterable Fe decreased to 12 μ M when the accumulated Fe increased to 1,370 μ M. These results indicated that over 95% of the Fe²⁺ released by the electric field existed in a solid precipitate form.

Compared with in situ Fe²⁺, filterable Fe increased with Fe accumulation upon FeSO₄ dosing, in which most of the Fe²⁺ passed through the filters at the different Fe accumulation levels. The formation of the Fe²⁺ solid phase was limited under this condition (pH < 7). The dissolved Fe²⁺ accounted for 90% of the total filterable Fe because the Fe²⁺ oxidation rate at this pH range was relatively slow (Li et al. 2009) (Fig. 4). However, after adjusting the solution pH to 8, filterable Fe was appreciably reduced and was accompanied by an improvement of the P removal efficiency. This result confirmed that Fe ion precipitation in aqueous solutions is a prerequisite for P removal.

Initially, the filterable Fe during FeCl₃ dosing was the lowest in all cases, which likely was caused by the high hydrolysis rate and precipitate formation rates of Fe³⁺ at circumneutral pH. However, with Fe³⁺ accumulation and hydrolysis, a substantial pH decline could hinder the subsequent precipitate formation. Hence, the filterable Fe increased with FeCl₃ continuous accumulation and was composed mostly of Fe³⁺. Generally, filterable Fe was either dissolved or present as small colloids. Dissolved Fe was expected to be almost 100% Fe²⁺ because of the low solubility of Fe³⁺ at circumneutral pH. However, substantial Fe³⁺ was present in all samples, likely due to the passage of colloidal Fe³⁺ and unavoidable oxidation of a small amount of Fe²⁺.

Characteristics of Iron-Air Fuel Cell

In the iron–air fuel cell experiment with an external resistance of 10 Ω , the cell voltage was variable, and the instant potential decreased rapidly from 1.1 to 0.94 V in 0.5 h [Fig. 6(a)]. Then the voltage gradually decreased to 0.87 V within 24 h. The Fe anode potential remained at -0.6 V for 24 h. However, the cathode potential decreased over time, which probably was related to cell voltage

Table 1.	Variations	of	pН	after	in	situ	Fe	or	Fe	salts	dosin	g
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		Initial PO_4^{3-} concentration (μM)								
Parameter	107.3	521	521	521	1,003.5	10,112				
Fe dosage (µM)	378.7	1,369.5	2,500 (FeSO ₄)	1,500 (FeCl ₃)	2,469.2	27,392				
Initial pH	6.87	5.40	5.40	5.40	5.23	4.73				
Final pH	7.61	8.2	4.94	2.96	8.56	9.42				



Fig. 5. Filterable Fe during continuous dosing of in situ Fe^{2+}/Fe salts: (a) in situ Fe; (b) $FeSO_4$, pH unadjusted; (c) $FeSO_4$, pH adjusted to 8; and (d) $FeCl_3$, pH unadjusted.

reduction. The anode potential might decrease over time due to the Eq. (9) and (10) in the Fe anode (Eliyan et al. 2015)

$$\operatorname{Fe}(\operatorname{OH})_2 + \operatorname{OH}^- \to \operatorname{Fe}(\operatorname{OH})_3 + e^-$$
 (9)

$$Fe(OH)_2 + OH^- \rightarrow FeOOH + H_2O + e^-$$
 (10)

$$2Fe(OH)_3 + Fe^{2+} \rightarrow Fe_3O_4 + 2H_2O + H^+$$
 (11)

$$2\text{FeOOH} + \text{Fe}(\text{OH})_2 \rightarrow \text{Fe}_3\text{O}_4 + 2\text{H}_2\text{O}$$
(12)

In these reactions, a passivation layer forms on the Fe anode, which may affect the cell potential stability and the P removal efficiency. However, in this study, a passivation layer of Fe hydroxide formed on the anode and then shed continually due to the sustained reaction between the electrolyte and the anode surface. The anode potential was constant during the process, indicating that Eqs. (11) and (12) occurred. Namely, Fe^{2+} in the aqueous phase prevented the formation of passive Fe hydroxide films, and Fe oxide formation in the aqueous phase was induced via reactions between Fe hydroxide on the anode surface and Fe^{2+} in the electrolyte. For the cathode, the initial actual potential (0.48 V) was lower than the theoretical value (0.804 V) under standard conditions, indicating that further improvements in the cathode performance were possible (Liu and Logan 2004).

Power density versus current density curves are shown in Fig. 6(b). The maximum power density was 1,875 mW/m², which was different from previous reports (Cheng et al. 2007; Kim et al. 2015). This maximum power density difference could be a result of multiple factors. First, changing the electrolyte increased the ionic strength in the system and induced a smaller internal resistance. The small internal resistance could result in observed increases in the working potentials. Second, the Pt catalyst on the cathode increased the efficiency of the oxygen reduction reaction. Third, NaCl affected the cell reaction. However, previous reports suggested that the effects of NaCl on the power production had both positive (increasing the ionic strength) and negative (hindered Pt catalyst performance) factors (Wang et al. 2011; Kim et al. 2015).



Fig. 6. Characteristics of the iron fuel cell: (a) electrode potentials; and (b) power density versus current density curves.

Thus, we determined that the increase in the working potential was the most likely explanation for the maximum power density difference.

The iron–air fuel cells maintained a stable output power over 24 h. Although the current can be adjusted by the external resistance, a large current may improve the formation rate of in situ Fe^{2+} , leading to fluctuation of the electrode potential. Therefore, a suitable current density (1,245–3,400 mA/m²) for stable Fe^{2+} generation is preferred for the P removal process.

Mechanisms and Applicability

Main Removal Mechanism

During the reaction process, the solution changed from colorless to light green because of Fe^{2+} production. At the beginning of the reaction, the Fe anode was oxidized to Fe^{2+} and then reacted with PO_4^{3-} . Three reactions may have occurred: (1) ferrous phosphate precipitated from Fe^{2+} and PO_4^{3-} , i.e., vivianite; (2) Fe^{2+} was transformed into ferrous hydroxide by hydrolysis, i.e., during hydrolysis a portion of the hydrolytic products underwent chemical adsorption with PO_4^{3-} to form coprecipitates of phosphate and ferrous hydroxide; and (3) a portion of Fe^{2+} was oxidized into Fe^{3+} , and the amorphous Fe oxide produced enhanced PO_4^{3-} removal by physical and chemical adsorption during hydrolysis. Because the pH in this study was close to neutral, the formation of ferric phosphate by Fe^{3+} and PO_4^{3-} was not considered (Smith et al. 2008; Zhang et al. 2010).

Compared with dosing with $FeSO_4$, the high Fe^{2+} reactivity and pH of the in situ Fe^{2+} system may result in a higher formation rate of ferrous phosphate than hydrated Fe^{2+} (FeSO₄). However, limited by the oxygen mass transfer rate of the air cathode, the



transformation from Fe²⁺ into Fe³⁺ faced some restrictions (Liu and Logan 2004). The XRD patterns of the P product removed by FeSO₄ indicated that the solid phase contained amorphous substances (Fig. 7). Presumably, the solid products were composed mainly of coprecipitation products and amorphous Fe oxides with PO_4^{3-} adsorbed. For in situ Fe²⁺ P removal products, diffraction peaks appeared in the XRD patterns, but the peaks had a slight shift compared with the standard powder diffraction file (PDF) cards; furthermore, two obvious precipitate peaks could be indexed by compounds including vivianite (ferrous phosphate) and magnetite. Magnetite could be derived from Fe hydroxide by Eqs. (11) and (12).

Furthermore, the peak in the structure of the P (2p) spectrum observed at a binding energy of 133.5 eV indicated the presence of PO_4^{3-} groups [Fig. 8(a)]. Pratt (1997) interpreted this peak to be from the PO_4^{3-} component of vivianite. The Fe (2p3/2) narrow-scan spectra were characterized by two peaks [Fig. 8(b)]; one was found near 711.6 eV and the other near 709.9 eV. According to Bae et al. (2018), fresh vivianite exhibited peaks at 709.9 eV, which were identified as being due to Fe²⁺ species. The second peak was centered at 711.6 eV and corresponded to the binding energy of Fe³⁺ with oxygen atoms. Thus, it was thought that the low energy contribution resulted from Fe²⁺, whereas the higher energy contribution resulted from Fe³⁺.

Previous studies used thermodynamic analysis to predict possible solid phase formation in aqueous solutions. Zhang et al. (2018) presumed that the reaction product was ferrous hydroxide, but vivianite formation was limited. In contrast, vivianite was the dominant product in the research by Liu et al. (2018). Combined with previous reports and experimental results, the dominant products in this study were vivianite and iron oxide-P complexes. Moreover, previous studies showed that kinetic limitations do not appear to influence the key reactions associated with P removal (Zhang et al. 2018). The P removal pathway was analyzed preliminarily based on thermodynamics. Zhang et al. (2013) calculated the priority orders for precipitation of vivianite Fe(OH)₂ according to the K_{sp} . When pH was in the range 8–9 and the PO₄^{3–} concentration was higher than 100 mg/L, vivianite precipitated first. With in situ Fe^{2+} generation, the solubility product of Fe^{2+} and PO_4^{3-} was larger than the solubility product constant, and vivianite was formed. However, the metastable zone for vivianite crystallization was supersaturated index (SI) 0-11 (Liu et al. 2018). Although the SI value in this study was not specifically calculated, the SI was less



Fig. 8. XPS spectra of elemental P and Fe in the precipitate of the iron fuel cell: (a) P; and (b) Fe.

than the lower limit with PO_4^{3-} concentration decrease, and the vivianite crystallization would be inhibited. Then ferrous hydroxide could be formed with P removal occurring via coprecipitation and/or adsorption. As stated, the main P removal mechanisms by iron fuel cells were vivianite precipitation by Fe^{2+} and PO_4^{3-} and Fe oxides adsorption.

Applicability Prospects

Compared with previous studies, electrocoagulation with an ironair fuel cell is an innovative P removal system that can simultaneously generate electricity (Zhang et al. 2018). Although the cumulative Fe dosage is limited by the cell power, this problem can be solved by improving the cell power or using a stacked iron-air fuel cell. In situ Fe²⁺ dosing could increase the effluent pH, and the continuous generation of alkalinity is likely to be advantageous for further processing. Moreover, the influence of other chemical components in wastewater (e.g., competitive anions or organic compounds) was an inevitable challenge in the actual treatment progress. Previous reports have shown that sulfate has a primary impact on vivianite formation because sulfate can be bonded to Fe to compete with P to reduce the vivianite production (Rothe et al. 2016). Clearly, adequate research was needed on the impacts of potentially interfering compounds for P removal before application.

Currently, the main relatively mature technical method for P recovery is struvite recovery (Li et al. 2019). However, some studies have shown that vivianite can be the nucleus for alternative P recovery options (Wilfert et al. 2018). Although P removed by fuel cells can be recovered in this form, enhancement of vivianite crystallization needs comprehensive and further understanding. In this study, the end products contained amounts of byproducts of iron precipitates. Therefore, optimization of the reaction conditions for a higher vivianite yield, further separation and purification of the vivianite, and feasible P recovery should be conducted under practical conditions. Cost reduction for the cell installation and maintenance is an inevitable problem in practical applications.

Conclusions

This study used a novel Fe²⁺ injection by an iron fuel cell to remove PO_4^{3-} from aqueous solutions. The P removal efficiency exceeded 95% with different initial P concentrations. In contrast to using Fe salts, after P removal by the air fuel cell, the main transition products of P were vivianite and Fe hydroxides. The output voltage of iron–air fuel cell could be kept stable over time (>24 h), and the maximum power density reached 1,875 mW/m². Further studies still are needed of high-purity vivianite formation, cost reduction, and long-term experiments.

Data Availability Statement

Some or all data, models, or code that support the findings of this study are available from the corresponding author upon reasonable request.

Acknowledgments

This study was supported by the Strategic Priority Research Program of the Chinese Academy of Sciences (Grant No. XDA23050203) and the National Natural Science Foundation of China (Grant No. 41373100). Additional support was provided by the Key Project of Research and Development Plan of Yantai, Shandong Province (Grant No. 2018ZHGY083).

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