



Phosphate removed from aqueous solution by electrochemical oxidation of ferrous iron

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Received 10 January 2018; Accepted 29 July 2018

ABSTRACT

The synthetic aqueous solution containing phosphate was treated using electrochemical oxidation of ferrous iron to produce the fresh precipitation of iron hydroxide or iron (oxyhydr)oxide. The results show that phosphate removal efficiency (PRE) for FPV (aqueous solution containing Fe^{2+} and phosphate, and voltage is supplied) is the highest and is 90% in 50 min. Meantime, PRE has a high correlation with iron relative consumption. Additionally, the removal mechanism on phosphate is speculated by Fourier transformed infrared analysis on the settling sludge. An optimum iron concentration of 250 mg/L is determined when initial iron concentration is increasing from 100 to 300 mg/L. Likewise, there lies an optimum phosphate concentration of 20 mg/L while initial phosphate concentration ranging from 10 to 40 mg/L. PRE increases with current density improving from 1.5 to 7.5 mA/cm². Meantime, energy for eliminating a unit mass of pollutants and energy for removing pollutants per volume unit increase from 28.08 to 188.31 kWh/kg and from 1.40 to 24.96 kWh/m³, respectively. PRE for wastewater containing Ca^{2+} is the highest and is about 100% in 50 min when wastewater contains K^+ , Na^+ , Ca^{2+} , and Mg^{2+} , respectively. However, PRE for effluent including Mg^{2+} is the lowest and is only 88% even in 90 min. The process used for removal of phosphate from wastewater is feasible.

Keywords: Phosphate; Ferrous iron; Electrochemical oxidation; Iron hydroxide; Adsorption

1. Introduction

In China, with the rapid development of national economy, a large number of pollutants from industry and agriculture have been discharged into air, surface water, and soil, and some have seeped into the groundwater and have already circulated between surface water and groundwater, which makes water body face the risk of severe deterioration. Thereinto, phosphorus, as a nutrient element to keep crops healthily growing, has been heavily supplemented by adding the fertilizer into farmland due to overcultivation of farmland [1–5]. In addition, a great deal of phosphate from

industrial wastewater and domestic sewage has been also discharged into water body, which easily makes phosphate content in surface water exceed the quality standard and leads to the eutrophication of water body [1–8]. Hence, phosphate discharged into water body has been rigidly restricted in many countries.

At present, some traditional physical, chemical, and biological methods, such as adsorption, membrane filtration, ion exchange, reverse osmosis, coagulation, and chemical precipitation, are used to remove phosphate from aqueous solution [1–6,9–12]. Among of them, adsorption is a promising process for phosphorus removal because it is simple, economical, and has less sludge production [2,3,5–7,9,11,13]. Among

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the adopted adsorbent materials, mesoporous metal oxide or hydroxide are generally applied to remove phosphate from water body [3,5–7,9]. Iron hydroxide or iron (oxyhydr)oxide, as a typical metal oxide or hydroxide, has a very strong adsorption capacity owing to their high-specific surface area [3,4,7–10,14–16] and are ordinarily employed to remove pollutants, such as phosphate, arsenic, heavy metals, and organic substance, from wastewater. In nature, iron in aqueous solution mainly exists in the form of ferrous (Fe^{2+}) or ferric (Fe^{3+}). Fe^{3+} , an oxidized state, is poorly soluble but easily hydrolyzes and produces a precipitation of iron hydroxide or iron (oxyhydr)oxide in natural water body. Similarly, Fe^{2+} , a reduced form, is moderately soluble in near-anoxic or anoxic condition and is very prone to oxidize into ferric iron which generally exists as a precipitation of iron hydroxide or iron (oxyhydr)oxide in oxygen-rich and alkaline environment [4,5,13,14,17,18]. Consequently, some researchers often utilize ferrous or ferric salts to produce the precipitation of iron hydroxide or iron (oxyhydr)oxide [4–9,14,17,18]. However, the physical and chemical properties of precipitation derived from Fe^{2+} are different from those originated from Fe^{3+} [5,13,19]. In addition, when the researchers employ Fe^{2+} to generate iron hydroxide or iron (oxyhydr)oxide, O_2 and alkaline materials are ordinarily supplemented together [4,5,13,14,17,18]. However, excessive chemical substances, especially environmental non-friendly materials, will pose a polluted risk to water body. Moreover, many researchers have used the aged iron hydroxide or iron (oxyhydr)oxide as adsorbents to remove phosphate from wastewater [6]. However, little attention is paid to using the freshly generated iron hydroxide or iron (oxyhydr)oxide to remove phosphate [9]. For that, an electrochemical process is used to produce the fresh precipitation of iron hydroxide or iron (oxyhydr)oxide. Its main ideas are as follows. Firstly, ferrous iron in aqueous solution is oxidized into ferric iron by oxygen in-situ generated from electrolyzing water, and then ferric iron forms a porous precipitation of iron hydroxide or iron (oxyhydr)oxide in a transitional acid to alkaline condition resulted from electrolyzing water. Finally, phosphate in aqueous solution is adsorbed by the fresh porous precipitation to be eliminated. In terms of the principles, the above process is a green and environmentally friendly approach. Additionally, the operation is easy owing to in-situ addition of O_2 and alkaline substances. However, its feasibility and influencing factors are seldom reported up to now.

In this paper, the synthetic aqueous solution containing phosphate is used as an investigation object, and the fresh precipitation of iron hydroxide or iron (oxyhydr)oxide, which is generated from electrochemical oxidation of ferrous iron, is employed to remove phosphate. During the trials, the feasibility of the used process will firstly be validated. Next, the effect of initial iron concentration, initial phosphate concentration, current density, and different cations on phosphate removal is explored. Additionally, analysis on energy consumption is carried out. Finally, the removal mechanism on phosphate is speculated by Fourier transformed infrared (FTIR) analysis on the settling sludge too. The aim of this work is to investigate the feasibility of phosphate removal from wastewater using the fresh precipitation, produced by electrochemical process, of iron hydroxide or iron (oxyhydr)oxide. In addition, the work will provide a green and environmentally friendly process to remove phosphate from water body.

2. Materials and methods

2.1. Experimental setup and procedure

The experimental setup is schematically demonstrated in Fig. 1. The reactor, the inner dimensions of which are $85 \times 85 \times 120$ mm, is made of transparent plexiglass plate. Two graphite electrodes with many holes of 2 mm in diameter, the size of which is $80 \times 80 \times 2$ mm, are also horizontally placed into the reactor, and their distance is 30 mm. Before a trial, a given concentration wastewater of 1,200 mL is filled in the reactor and the bottle A. Thereafter, wastewater in the bottle A is flowed through the reactor into the bottle B in 55 droplets/min by adjusting the water flow regulator and the gas regulator. Next, when water stream in tube goes steady, the graphite electrodes are connected with the DC power, and then a timer is turned on to record the reactive time. When wastewater in the bottle A is used up, the bottle B, full of treated wastewater, and the empty bottle A are swapped positions in a very short time, and this operation is carried out repeatedly until the trial is finished.

Before each run, aqueous solution containing phosphate is prepared by adding KH_2PO_4 (analytical grade) into distilled water. Simultaneously, K_2SO_4 (analytical grade) of 0.01 mol/L, as a supporting electrolyte, is also supplemented into the solution. After that, high purity nitrogen is bubbled for 10 min to eliminate the dissolved oxygen in the synthetic solution. Finally, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (analytical grade) is also added into the above solution to produce the fresh precipitation of iron hydroxide or iron (oxyhydr)oxide. During experiments, a sample of 50 mL is taken at a desired time, and then all the samples are centrifuged and filtered to remove sludge.

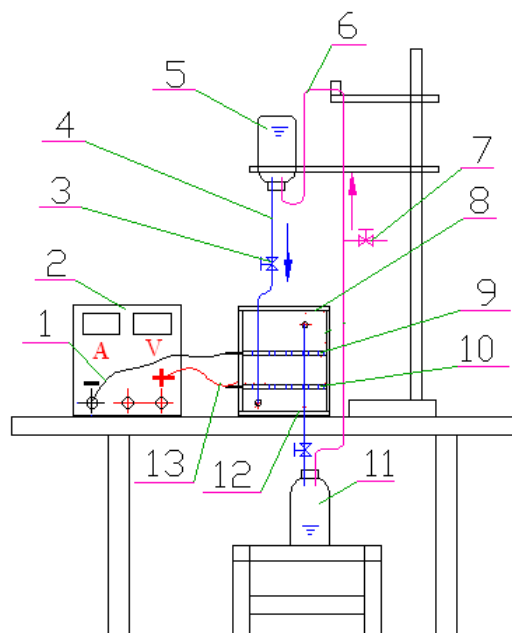


Fig. 1. Diagram of the experimental setup. (1) Negative electric wire, (2) DC power, (3) water flow regulator, (4) water tube, (5) glass bottle A, (6) inner circulating gas tube, (7) gas regulator, (8) sealing cover, (9) graphite cathode, (10) graphite anode, (11) glass bottle B, (12) reactor, and (13) positive electric wire.

In the end, the filtrate is sent to analyze physicochemical properties. For more practicability, all the tests are executed at ambient temperature and circumneutral pH value.

2.2. Analytical methods

During the experiments, total phosphorus concentration is measured according to ammonium molybdate spectrophotometric method [8,14,15]. Total iron concentration is monitored by an atomic absorption spectrophotometer (TBS-990, Beijing Purkinge General Instrument Co. Ltd., Beijing, China). Dissolved Fe^{2+} and Fe^{3+} are evaluated by colorimetry, using the ferrozine method [5,19]. pH value is measured with a pH meter (Hach 2000, Hach Company, USA). Conductivity is determined by a conductivity meter (DDS-11C, INESA Scientific Instrument Co., Ltd, Shanghai, China). Potential and current between electrodes are measured by the DC power own current and voltage meters. In addition, to analyze the structure of settling sludge, X-ray diffractometer (XRD-7000, Shimadzu, Japan) and FTIR spectrophotometer (Nicoletis10, Thermo Scientific, USA) are used.

3. Results and discussion

3.1. The feasibility of the used process

3.1.1. Removal of phosphate from aqueous solution

In order to validate the feasibility of the used process, the trials on the conditions of PV (wastewater only includes phosphate, and voltage is supplied), FV (solution only contains Fe^{2+} , and voltage is supplied), FPNV (effluent includes Fe^{2+} and phosphate, and no voltage is supplied), and FPV (wastewater contains Fe^{2+} and phosphate, and voltage is supplied) are carried out. During the experiments, if effluent contains Fe^{2+} ion, its concentration is 150 mg/L. Similarly, phosphate concentration is 20 mg/L. Additionally, if the power supply is used, voltage of 28 V is provided.

It can be seen from Fig. 2 that phosphate removal efficiencies (PREs) for PV and FPNV slowly increase with the reactive time prolonging, and PREs in 150 min are only 25% and 46%, respectively. However, PRE for FPV goes up

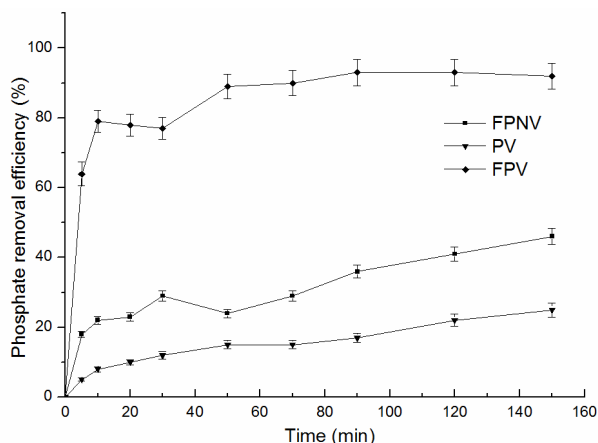
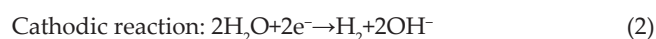
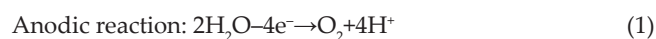


Fig. 2. Under different experimental conditions, phosphate removal efficiency changing with the reactive time.

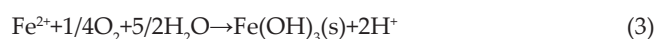
rapidly at the initial stage and then rises slowly to a steady value, and PRE of 90% can be gotten in 50 min. Additionally, at the same instant, PRE for FPV is the highest while that for PV is the lowest. These results suggest that the condition of FPV is very suitable to remove phosphate from water body and the used electrochemical process is a very feasible and promising way. Simultaneously, iron relative consumption (IRC) in aqueous solution was monitored too. Fig. 3 shows that under the abovementioned conditions, IRC in wastewater increases with the extension of time. Thereinto, IRC for FPNV is the lowest. However, IRC for FPV is slightly higher than that for FV, which also infers that iron consumption increases in the presence of phosphate. In addition, it is seen from Figs. 2 and 3 that PRE for FPV has a high correlation with IRC.

The possible reasons are as below:

When the graphite electrodes are connected with the DC power, two important reactions at the electrode surfaces are as follows:



After that, Fe^{2+} in solution is easily oxidized into Fe^{3+} by oxygen produced from Eq. (1) according to the following reaction.



It is reported that the freshly generated precipitation of iron hydroxide or iron (oxyhydr)oxide, namely $\text{Fe}(\text{OH})_3$, has a very strong adsorption capacity due to high-specific surface area [4,8–10,14–16]. Consequently, phosphate in aqueous solution is adsorbed by the porous precipitation of iron hydroxide or iron (oxyhydr)oxide to be removed. Moreover, it is thought that the following reactions are very important to phosphate removal at the presence of Fe^{2+} and H_2PO_4^- [5,8,10,14–16,18].

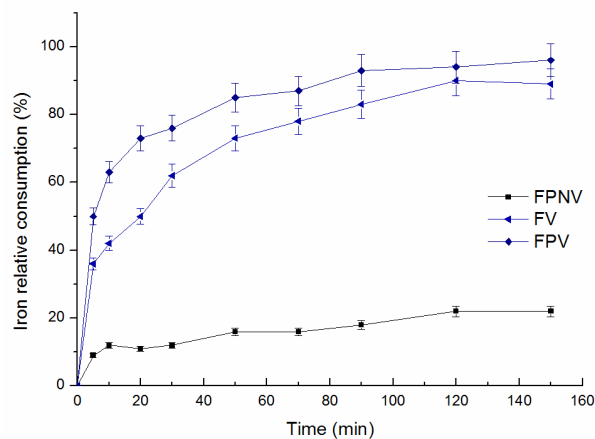
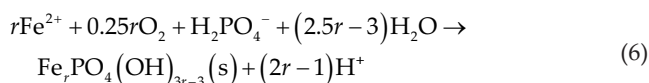


Fig. 3. Under different experimental conditions, iron relative consumption changing with the reactive time.



where $1/r$ is the stoichiometric molar P/Fe ratio of the Fe hydroxyphosphate.

As a result, when voltage is supplied and wastewater contains Fe^{2+} and phosphate, the above reactions will occur, which is also the possible reason that PRE for FPV is the highest.

3.1.2. Analysis on sludge

To analyze the structure of settling sludge, after the trials are finished, the precipitation is collected and centrifuged at 3,500 rpm for 10 min. Finally, it is air-dried at ambient temperature. XRD analysis illustrates that the precipitation has a very poor crystalline (figure is not provided). FTIR spectra analysis (see Fig. 4) demonstrates that an absorption peak is shown at around $1,653 \text{ cm}^{-1}$, which is resulted from the bending vibration distortion of H–O–H bond or the bending vibration of –OH groups in a water molecule [20–22]. Significantly, there are some slightly strong absorption peaks at approximately $1,000 \text{ cm}^{-1}$, lifting the peak at $1,014.4 \text{ cm}^{-1}$ of the O–H in plane bending vibration of lepidocrocite, which is possibly owing to the P–O and P–OH stretching vibrations of the phosphate molecules adsorbed or incorporated in the precipitation [5,9,23,24]. Moreover, there are some little peaks in the range of $690\text{--}800 \text{ cm}^{-1}$, which are assigned to bending vibration of Fe–OH [20,22]. However, the peaks at $2,900\text{--}3,000 \text{ cm}^{-1}$ are still to be explored further. Hence, analysis on sludge shows once again that phosphate in wastewater is possibly removed in the abovementioned pathways.

3.2. Effect of initial Fe^{2+} concentration

According to Figs. 2 and 3, PRE for FPV has a high correlation with IRC. Hence, the effect of initial Fe^{2+} concentration in wastewater on phosphate removal is surveyed. During the

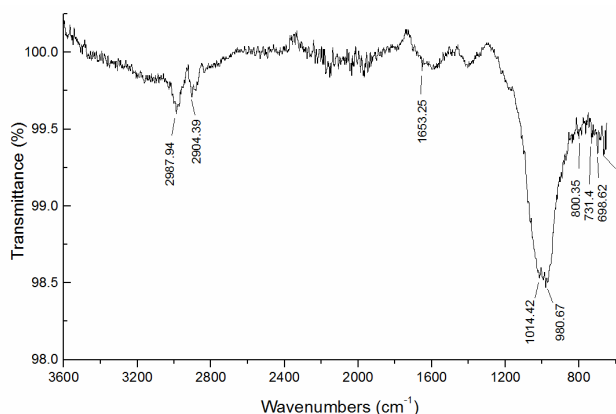


Fig. 4. FTIR spectra analysis for the settling sludge.

experiments, when Fe^{2+} concentration is changed from 100 to 300 mg/L, phosphate concentration is kept at 20 mg/L, and voltage of 28 V is provided.

Fig. 5 shows that PREs for different iron concentration are all very high, and the rates are very rapid. For instance, at the time of 10 and 30 min, PREs are 79% and 77% for 100 mg/L, 82% and 90% for 150 mg/L, 88% and 91% for 200 mg/L, 90% and 95% for 250 mg/L, and 89% and 93% for 300 mg/L, respectively. In addition, it can be also seen that PRE almost increases with iron concentration improving from 100 to 250 mg/L, and then it has a slight decrease when concentration rising to 300 mg/L, which implies that there is an optimum iron concentration of 250 mg/L. However, Fig. 6 demonstrates that IRC has a decreasing tendency with iron concentration increasing from 100 to 300 mg/L.

The reasonable interpretations are as below. During the experiments, it is found that although iron content in solution gradually improves, current, that is passed through wastewater, only slightly increases due to the supporting electrolyte of K_2SO_4 added, which infers that oxygen production in solution almost keeps constant according to Eq. (1).

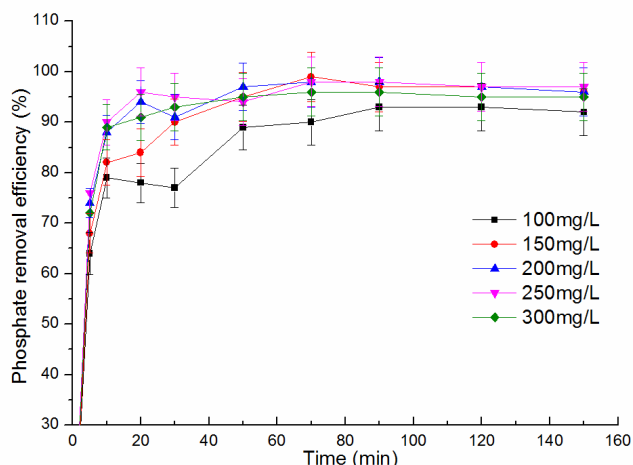


Fig. 5. Effect of initial Fe^{2+} concentration on phosphate removal efficiency.

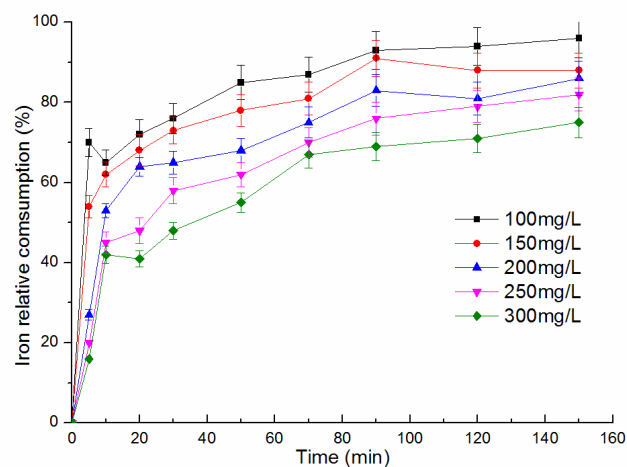


Fig. 6. Under different initial Fe^{2+} concentration, iron relative consumption changing with the reactive time.

Consequently, the consumption of Fe^{2+} in solution also remains stable according to Eq. (3) or Eq. (6). Thus, for a higher iron concentration solution, IRC becomes lower, as is perhaps a reason that IRC has a decreasing tendency with iron concentration increasing from 100 to 300 mg/L. However, if phosphate in solution is only adsorbed by the precipitation of iron hydroxide or iron (oxyhydr)oxide to be removed, PRE should still keep steady when iron concentration increases according to the forementioned explanations, but this is in contradiction with the experimental results. Considering the variation characteristics of phosphate (see Fig. 5), it is guessed that Eq. (6) is a crucial path to remove phosphate too. According to Eq. (6), iron, at the presence of H_2PO_4^- , plays a significant role in removing phosphate too. For excess H_2PO_4^- and oxygen, PRE goes higher when iron concentration becomes higher, which is in line with the varying characteristics of phosphate.

3.3. Effect of initial phosphate concentration

In fact, phosphate concentration in wastewater varies from time to time. When the effect of initial phosphate concentration on PRE is investigated, Fe^{2+} concentration remains 250 mg/L, and output voltage is still 28V. As phosphate removal rate seen from Fig. 5 is very rapid, and so the reactive time is adjusted to 90 min during the following trials.

Fig. 7 depicts that for the same phosphate concentration, PRE, especially for 30 and 40 mg/L, increases with time prolonging. In addition, at the same instant, the higher the initial phosphate concentration is, the lower the PRE is. Likewise, Fig. 8 illustrates that at the same time, IRC firstly shows a rising tendency with phosphate concentration varying from 10 to 20 mg/L, and then it decreases when phosphate concentration further increasing to 40 mg/L, which suggests that there lies an optimum phosphate concentration of 20 mg/L.

During the experiments, it is also found that current remains relatively constant when phosphate concentration varying from 10 to 40 mg/L. Thus, at the same instant, the production of oxygen, which is generated continuously by electrolyzing water, remains stable. Consequently, for a given iron concentration, the removal quantity of phosphate also maintains constant according to Eq. (6), which is probably a

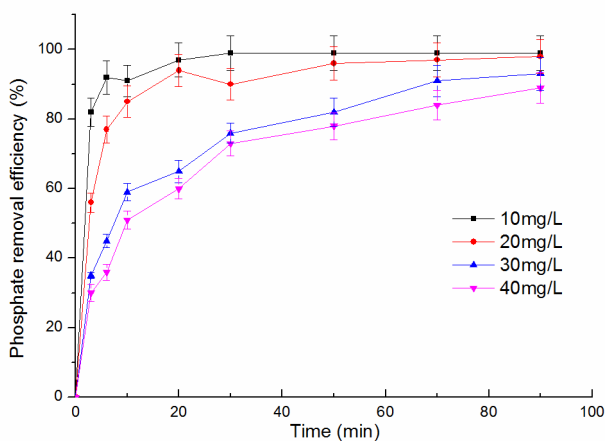


Fig. 7. Effect of initial phosphate concentration on phosphate removal efficiency.

reason that the higher the initial phosphate concentration is, the lower the PRE is.

3.4. Effect of current density

During an electrochemical reaction, current density is one of the key influencing factors, and it indicates the number of ions that are passing through solution per unit time and cross-sectional area. Hence, the effect of current density on phosphate removal performance is executed. During the experiments, current density is changed from 1.5 to 7.5 mA/cm². In addition, Fe^{2+} and phosphate concentration is 250 and 20 mg/L, respectively.

Fig. 9 illustrates that for the same current density, PRE almost increases with the reactive time extending. For example, at the time of 10, 30, and 50 min, PRE is 30%, 41%, and 75% for 1.5 mA/cm², 37%, 70%, and 87% for 3.0 mA/cm², 47%, 75%, and 90% for 4.5 mA/cm², 52%, 79%, and 91% for 6.0 mA/cm², and 59%, 91%, and 96% for 7.5 mA/cm², respectively. It is remarkable that the phosphate removal rate for current density of 7.5 mA/cm² is very fast. Furthermore, at the

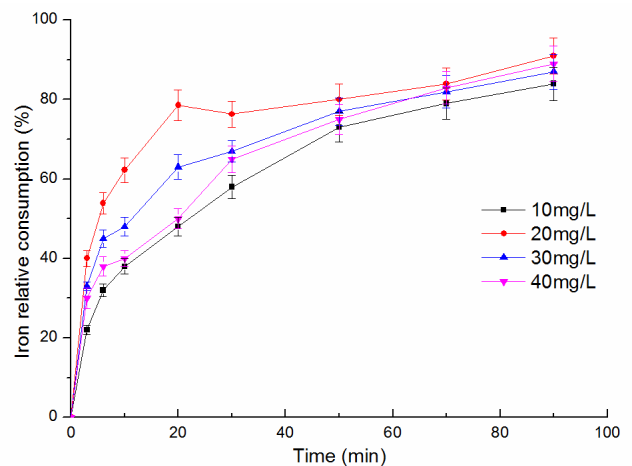


Fig. 8. Under different initial phosphate concentration, iron relative consumption changing with the reactive time.

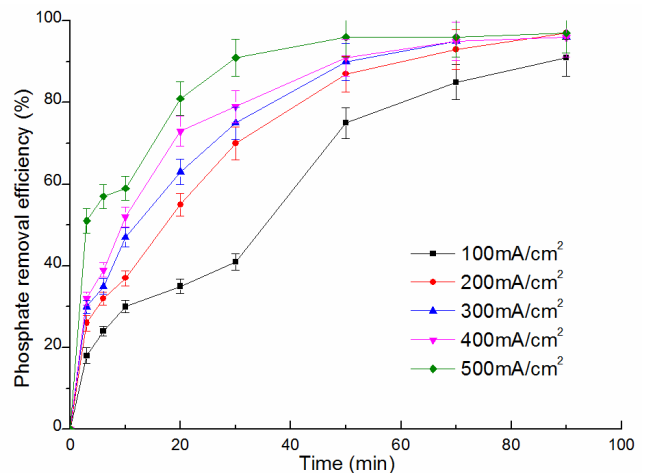


Fig. 9. Effect of current density on phosphate removal efficiency.

same instant, PRE increases with current density improving. Meanwhile, it can also be seen from Fig. 10 that the changing trend of IRC is similar with that of phosphate. However, IRC presents an upward trend all the time.

The possible reasons for the above phenomena are as below. A bigger current implies that the more O_2 is produced according to Eq. (1). Afterwards, the more Fe^{2+} and $H_2PO_4^-$ in solution react with O_2 to be removed according to Eq. (6) and/or Eq. (3). Once phosphate in solution gets less and less, the surplus Fe^{2+} will continue to react with O_2 to generate the more precipitation of iron hydroxide or iron (oxyhydr)oxide according to Eq. (3), which is the possible reason that PRE and IRC increase with current density improving.

3.5. Effect of different cations

Some common cations, such as K^+ , Na^+ , Ca^{2+} , and Mg^{2+} , often emerge in aqueous solution, and their existence affects the performance of the used process too.

For that, the effect of different cations on PRE is estimated. During the trials, Fe^{2+} and phosphate initial concentration are 250 and 20 mg/L, respectively. Additionally, current density is stabilized at 4.5 mA/cm². Moreover, to get the synthetic wastewater containing K^+ , Na^+ , Ca^{2+} , and Mg^{2+} , KNO_3 , $NaNO_3$, $Ca(NO_3)_2$ and $Mg(NO_3)_2$ (analytical grade) are also added into aqueous solution, respectively. When the above reagent is added, ion concentration in solution is all kept at 0.03 mol/L.

Fig. 11 demonstrates that as far as wastewater containing Ca^{2+} is concerned, its PRE is the highest, and removal efficiency can attain to about 100% in 50 min. On the contrary, effluent including Mg^{2+} has the lowest PRE, and its efficiency is only 88% even in 90 min. However, for solution containing K^+ and one involving Na^+ , their PREs are also very high and have a nearly similar trend. Likewise, Fig. 12 presents that IRC for wastewater containing Mg^{2+} is the lowest too. However, IRC for solution including Ca^{2+} is slightly lower than those for effluent containing K^+ and one involving Na^+ , which is seemingly no correlation with PRE.

The reasonable explanations are as follows. Ca^{2+} in wastewater easily reacts with PO_4^{3-} from ionization of

$H_2PO_4^-$ and produces the precipitation of $Ca_3(PO_4)_2$, which is a main reason that solution containing Ca^{2+} has the highest PRE.

3.6. Analysis on energy consumption

Energy consumption is one of the focus questions that the used process must pay close attention to. On the one hand, energy consumption is a key factor controlling operational cost. On the other hand, excessive energy consumption will prevent the process from widely spreading, especially in power shortage areas. For that, energy consumption for different current density is analyzed. During the experiments, energy (E_m), which is used to eliminate a unit mass of pollutants, and energy (E_v), which is done to remove pollutants per volume unit, are calculated by Eqs. (8) and (9), respectively. As iron in solution decreases, E_m includes the energy used for iron consumption too.

$$E_m = \frac{\int_0^t IV dt}{V_s (C_{Pt} - C_{P0}) + V_s (C_{Fe t} - C_{Fe 0})} \quad (8)$$

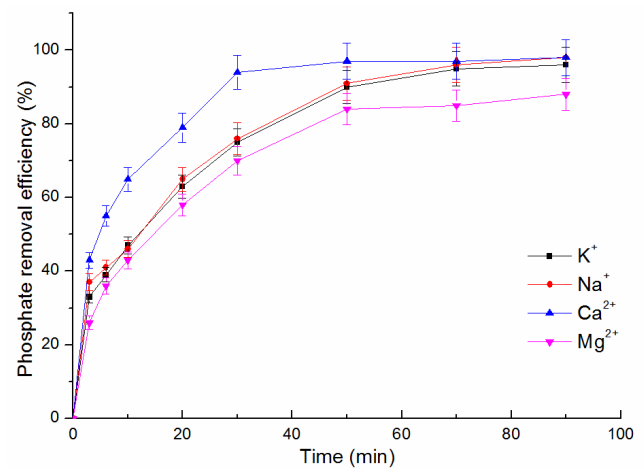


Fig. 11. Effect of different cations on phosphate removal efficiency.

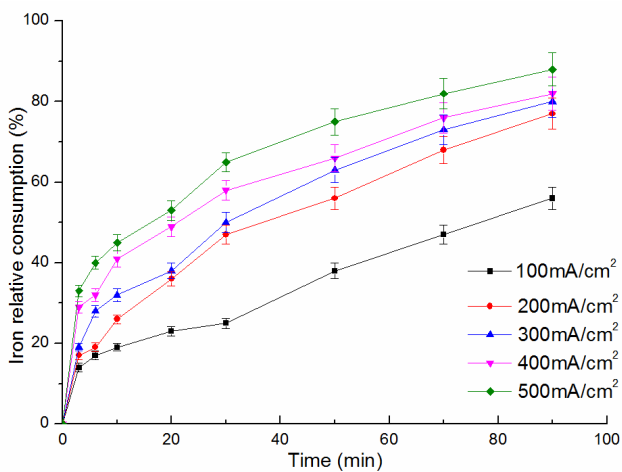


Fig. 10. Under different current density, iron relative consumption changing with the reactive time.

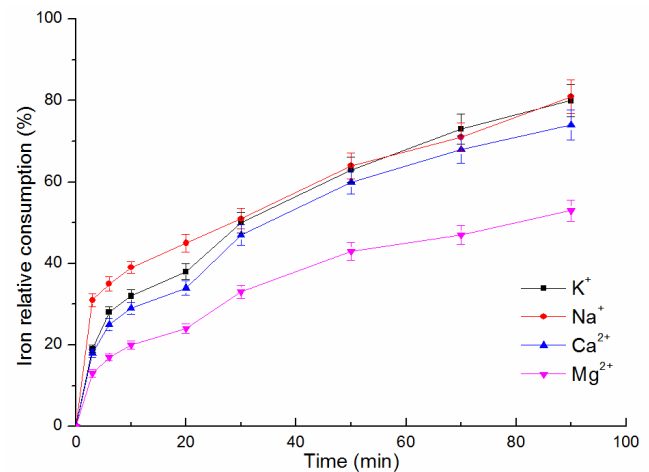


Fig. 12. Under different cations, iron relative consumption changing with the reactive time.

Table 1
Analysis on energy consumption for different current density

Current density (mA/cm ²)	1.5	3.0	4.5	6.0	7.5
E_m (kWh·kg ⁻¹)	28.08	63.42	113.68	169.27	188.31
E_v (kWh·m ⁻³)	1.40	4.49	9.36	14.33	24.96

$$E_v = \frac{\int_0^t IV dt}{V_s} \quad (9)$$

where I is the electrical current passed through the anode and the cathode (A), V is the voltage applied to the two electrodes (V), t is the treating time (S), V_s is the volume of wastewater (L), and C_{pt} and C_{Fet} are the phosphate concentration (mg/L) and iron concentration (mg/L) at t moment, respectively. Similarly, C_{p0} and C_{Fe0} are the initial phosphate concentration (mg/L) and initial iron concentration (mg/L), respectively.

During the calculations, the results from Section 3.4 are used as an example to analyze energy consumption. According to Eqs. (8) and (9), energy consumption for different current density is listed in Table 1. Table 1 shows that when current density enhances from 1.5 to 7.5 mA/cm², E_m and E_v increase from 28.08 to 188.31 kWh/kg and from 1.40 to 24.96 kWh/m³, respectively, which suggests that energy consumption sharply increases. At the same time, during the trials, it is observed that the temperature of wastewater gets higher and higher when current density becomes bigger and bigger. That is to say, the Joule heating effect goes more and more obvious, which also implies that the higher the current density is, the lower the electrical energy utilization efficiency is.

4. Conclusions

In this paper, the synthetic aqueous solution containing phosphate is successfully treated using electrochemical oxidation of ferrous iron to produce the fresh precipitation of iron hydroxide or iron (oxyhydr)oxide. Some conclusions can be drawn as below.

The condition of FPV, among PV, FV, FPNV, and FPV, is very suitable to remove phosphate from water body, and its efficiency is the highest and is 90% in 50 min, which also validates that the used electrochemical process is a very feasible and promising way. In addition, PRE for FPV has a high correlation with IRC. The removal mechanism on phosphate is speculated by FTIR spectra analysis on the settling sludge.

When iron concentration increases from 100 to 300 mg/L, an optimum iron concentration of 250 mg/L for phosphate removal is determined. Likewise, when phosphate concentration ranges from 10 to 40 mg/L, there lies an optimum phosphate concentration of 20 mg/L.

For the same current density, PRE almost increases with the reactive time extending. Remarkably, phosphate removal rate for current density of 7.5 mA/cm² is very fast. Furthermore, at the same instant, PRE increases with current density improving from 1.5 to 7.5 mA/cm².

For wastewater containing K⁺, Na⁺, Ca²⁺, and Mg²⁺, respectively, PRE for wastewater containing Ca²⁺ is the highest and is about 100% in 50 min. In contrast, effluent including Mg²⁺

has the lowest PRE, and its efficiency is only 88% even in 90 min.

When current density enhances from 1.5 to 7.5 mA/cm², E_m and E_v increase from 28.08 to 188.31 kWh/kg and from 1.40 to 24.96 kWh/m³, respectively, which suggests that energy consumption sharply increases. Meantime, it also implies that the higher the current density is, the lower the electrical energy utilization efficiency is.

Phosphate removal from wastewater using the fresh precipitation of iron hydroxide or iron (oxyhydr)oxide produced by electrochemical oxidation of ferrous iron is feasible.

Acknowledgment

This work was supported by Research and Innovation Initiatives of WHPU (No. 2017y18).

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