

Rapid Communication

Chao Wang, Changwen Wang*, Mei Xu, and Fanke Zhang

Phosphorus removal by iron–carbon microelectrolysis: A new way to achieve phosphorus recovery

<https://doi.org/10.1515/gps-2022-8120>

received October 08, 2022; accepted April 20, 2023

Abstract: Iron–carbon microelectrolysis was employed to remove phosphorus in this study. The efficiency, mechanism, influence factors, and feasibility of actual wastewater were investigated. The results showed that iron–carbon microelectrolysis had an excellent phosphorus removal ability. When the initial concentration of PO_4^{3-} –P was 19.44 mg L^{-1} , after 120 min reaction time, the remaining PO_4^{3-} –P in wastewater was 4.65 mg L^{-1} , and the removal rate was 76.05%. The precipitate formed in the reaction was mainly ferric phosphate (FePO_4), which had a high recovery value. There was a linear correlation between initial phosphorus concentrations and phosphorus removal velocity. As to actual wastewater, $88.37 \pm 0.44\%$, $89.78 \pm 1.88\%$, and $94.23 \pm 0.16\%$ phosphorus removal rates were achieved in the influent of municipal wastewater treatment plant, effluent of secondary sedimentation tank, and actual high salinity wastewater, respectively, after 120 min reaction time. This study provides a new method for phosphorus removal and recovery from wastewater.

Keywords: wastewater treatment, phosphorus removal, iron–carbon microelectrolysis, phosphorus recovery

Natural water body eutrophication is caused by wastewater discharge that contains nitrogen (N) and phosphorus (P) [1,2], while P is considered a limiting factor of eutrophication because most lakes are P limitation [3,4]. It is generally considered that eutrophication occurs when the total nitrogen and total phosphorus (TP) in water are more than 0.2 and 0.02 mg L^{-1} , respectively [5]. On the other hand, P is a necessary nutrient for the development of life, constituting one of the major nutrients vital for agriculture [6]. However, the quantities of mineral P resources (phosphate rock) are decreasing in the world, making P recovery necessary to solve the P shortage [6,7]. Therefore, many research studies are now focusing increasingly on P recovery from wastewater.

P Recovery is a feasible and valuable technique which is suited to high-strength wastewater such as anaerobic sludge digestion and high P industry wastewater [8,9]. P is easily removed by chemical precipitation. Insoluble calcium, magnesium, and iron phosphates can be formed by pH control and chemical dosing, which precipitate at the bottom of specific reactors [10,11]. However, chemical dosing means the operation cost and is not an environmentally friendly approach. Ferrous iron (Fe^{2+}) and ferric iron (Fe^{3+}) can react with phosphate to form insoluble phosphate precipitation. In recent years, iron has been developed as a promising cost-effective chemical dosage considering both its high P removal efficiency and low commercial price [12–14]. Zhang et al. reported an application of *in situ* electrochemical generation of ferrous ($\text{Fe}(\text{II})$) ions for phosphorus (P) removal in wastewater treatment; at concentrations typical of municipal wastewater, P could be removed by *in situ* $\text{Fe}(\text{II})$ with removal efficiency higher than achieved on the addition of FeSO_4 and close to that of FeCl_3 under both anoxic and oxic conditions [15]. But an electric field should be applied for *in situ* Fe^{2+} generation with direct current, which meant energy consumption.

Because of the advantages of treating waste with waste, the phosphorus removal technology of inorganic phosphorus removal filler (represented by fly ash

* Corresponding author: Changwen Wang, Institute of Architectural Engineering, Zaozhuang University, Zaozhuang Key Laboratory of Urban-Rural Water Environment Pollution Control and Ecological Restoration, Zaozhuang, Shandong, 277100, China, e-mail: 434934032@qq.com

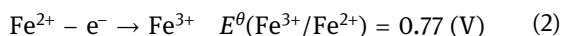
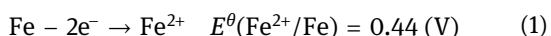
Chao Wang, Fanke Zhang: Institute of Architectural Engineering, Zaozhuang University, Zaozhuang Key Laboratory of Urban-Rural Water Environment Pollution Control and Ecological Restoration, Zaozhuang, Shandong, 277100, China

Mei Xu: Institute of Mathematics and Statistics, Zaozhuang University, Zaozhuang, Shandong, 277100, China

ceramsite, water supply sludge ceramsite, calcium-silica filter material, and so on) has developed rapidly [16,17]. Among these inorganic fillers, the iron–carbon (Fe–C) micro-electrolysis method is to treat wastewater by forming a galvanic cell reaction in the electrolyte solution through the mixture of iron chips and coke or iron–carbon composite materials under the condition of no electricity. The removal of pollutants is completed by the primary cell reaction, flocculation precipitation, oxidation–reduction, electrochemical enrichment, physical adsorption, and other processes [18,19]. The research studies of Fe–C microelectrolysis technology mostly focus on the improvement of the biodegradability of refractory organic wastewater and the treatment efficiency of some industrial wastewater as a pre-treatment unit combined with biochemical treatment process [18,19], ignoring the research of phosphorus removal of iron–carbon micro-electrolysis. In this study, iron filings acquired from a machine processing factory were used as the chemical dosage combined with activated carbon to achieve efficient P recovery via iron–carbon (Fe–C) micro-electrolysis *in situ*. The mechanism, recovery efficiency, and feasibility of actual wastewater were investigated, providing an environmental and sustainable way for P removal and recovery.

The efficiency of Fe–C microelectrolysis on P removal from synthetic wastewater is shown in Figure 1. The initial concentration of $\text{PO}_4^{3-}\text{-P}$ was $19.44 \text{ mg}\cdot\text{L}^{-1}$, then wastewater, and Fe–C fillings were contacted for reaction under agitation. The concentration of $\text{PO}_4^{3-}\text{-P}$ decreased slowly at the beginning period and then rapidly after 30 min. After 120 min reaction time, the remaining $\text{PO}_4^{3-}\text{-P}$ in wastewater was $4.65 \text{ mg}\cdot\text{L}^{-1}$, while the removal rate was 76.05%, and the average reaction rate was $0.12 \text{ mg}\cdot\text{L}^{-1}\cdot\text{min}^{-1}$. The results showed that Fe–C microelectrolysis had good P removal ability. Li et al. used electrocoagulation–ultrasound combined technology for P removal, TP decreased from 86.00 to about $0.40 \text{ mg}\cdot\text{L}^{-1}$, and the removal rate reached about 99.60% [20]. Using Fe–C microelectrolysis to remove P was based on a galvanic cell reaction, without an external power supply. Moreover, iron filings and activated carbon could be acquired from industrial waste, which were environmentally friendly and good for waste reuse.

Fe–C microelectrolysis was a common galvanic cell reaction and was explicated for many years [21–23]. Fe was the anode, and the reaction was:



C was the cathode, and the reaction was:

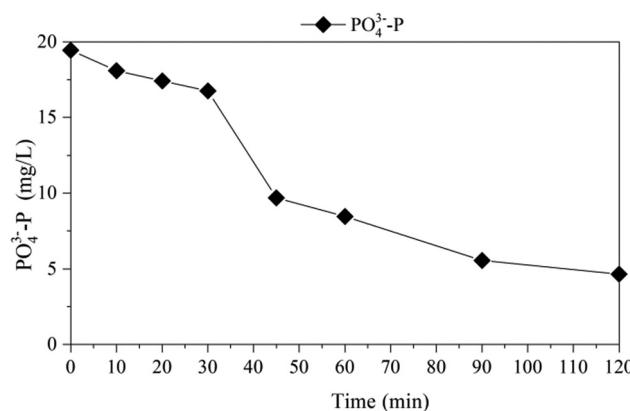
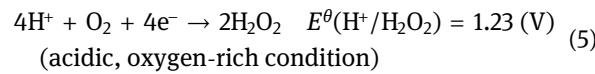
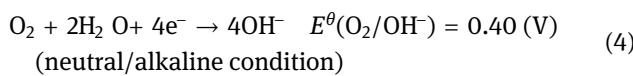
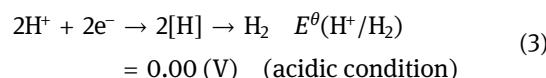
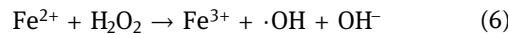


Figure 1: P Removal by Fe–C microelectrolysis.



Because the above reactions were simultaneous, Fe^{2+} from Eq. 1 and H_2O_2 from Eq. 5 could react as:



It was Fenton's reaction. Moreover, the products from the above reactions, such as $\cdot\text{OH}$, $[\text{H}]$, Fe^{2+} , Fe^{3+} , could react with many pollutants in wastewater [24,25]. Galvanic cell reaction, flocculation–sedimentation, oxidation–reduction, electrochemical enrichment, and physical adsorption were the micro-process which was with high efficiency and wide application in water treatment.

As to P removal, Fe^{2+} , Fe^{3+} could react with phosphate to form ferrous phosphate ($\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$) and ferric phosphate (FePO_4), respectively (as shown in Figure 2) [25,26]. In order to determine the main product from Fe–C microelectrolysis, X-ray diffraction analysis was employed to detect the precipitate formed after the reaction, and the diffractogram is presented in Figure 3. A number of distinct rays indicate the presence of crystalline forms. By comparison with reference spectra, most of the peaks, and in particular the bigger ones, coincided with those of ferric phosphate (FePO_4).

The above reaction provided a new way of P removal and recovery way for high P wastewater. Through Fe–C microelectrolysis pretreatment, not only could the biodegradability of raw water be improved, but also P could be removed, reducing the N and P simultaneous removal

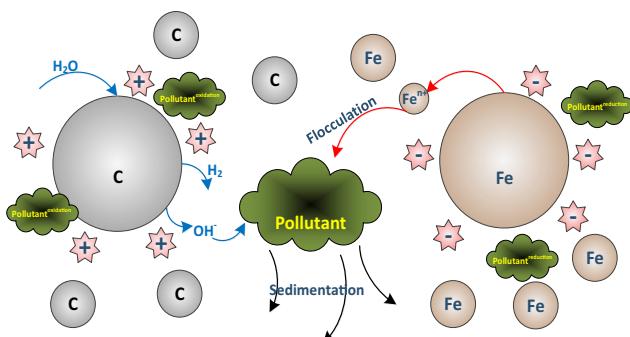


Figure 2: Schematic diagram of Fe–C microelectrolysis mechanism.

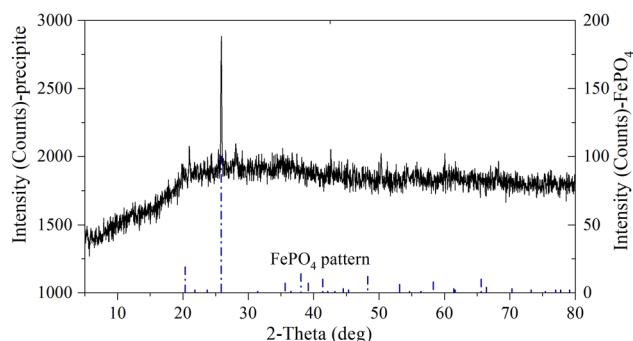


Figure 3: XRD Pattern of Fe–C microelectrolysis P removal precipitates.

pressure of subsequent biochemical treatment units. Moreover, the contradiction of N and P simultaneous removal in low C/N ratio wastewater could be relieved [27,28].

The product, FePO_4 , was a raw material to make lithium iron phosphate batteries, catalysts, and ceramics, and had a high recovery value. Nowadays, one of the most important uses of FePO_4 was to make lithium iron

phosphate batteries [29,30]. With the rapid development of the electric vehicle industry, China became the largest consumer market of lithium iron phosphate in the world. Especially from 2012 to 2013, the sales volume of lithium iron phosphate in China was about 5,797 tons, accounting for more than 50% of global sales. Therefore, FePO_4 , the precipitate of P removal by Fe–C microelectrolysis, had a high recycling value.

The initial PO_4^{3-} –P concentrations were different, but the residual PO_4^{3-} –P change curves were similar (as shown in Figure 4). All of them decreased rapidly at first and then slowly. The higher the initial PO_4^{3-} –P concentration, the higher the P removal velocity. And there was a linear correlation ($R^2 = 0.9794$). In this concentration range, the Fe–C microelectrolysis P removal was the first-order reaction.

Salinity was one of the common pollutants in industrial wastewater and also one of the limiting factors in industrial wastewater treatment [31,32]. When the initial PO_4^{3-} –P concentration was $40 \text{ mg}\cdot\text{L}^{-1}$, the influence of salinity (NaCl was added to the synthetic wastewater) on the phosphorus removal by Fe–C microelectronics is shown in Figure 5. The higher the salinity, the slower PO_4^{3-} –P the decrement rate, which indicated that the salinity inhibited the P removal by Fe–C microelectrolysis significantly. Therefore, the influence of salinity needed be considered in the application of this technology.

The influence of salinity on P removal velocity is shown in Figure 5. In the range of 0 – $10 \text{ g}\cdot\text{L}^{-1}$ salinity, the reaction rate decreased rapidly with the increment of salinity. When the salinity was $10 \text{ g}\cdot\text{L}^{-1}$, the reaction rate was $0.20 \text{ mg}\cdot\text{L}^{-1}\cdot\text{min}^{-1}$, and only 51.28% of that when the salinity was $0 \text{ g}\cdot\text{L}^{-1}$. The reaction rate was

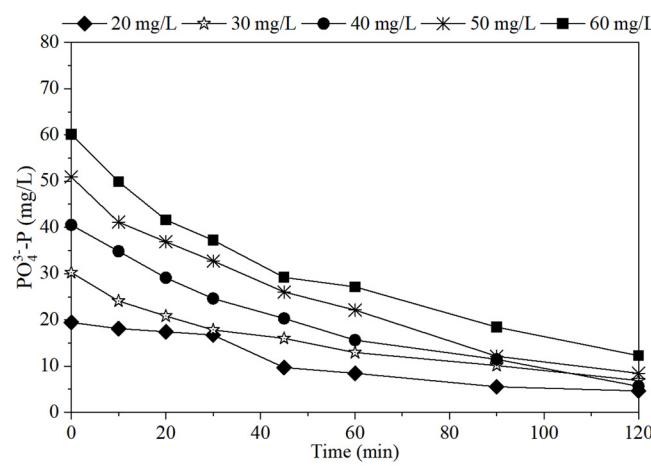
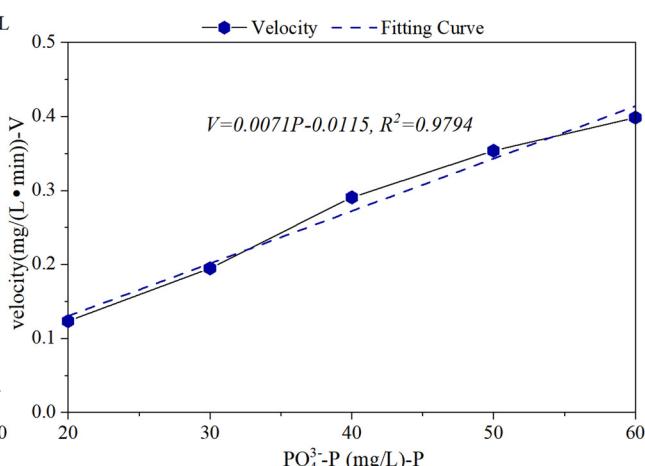


Figure 4: Influence of initial P on P removal by Fe–C microelectrolysis.



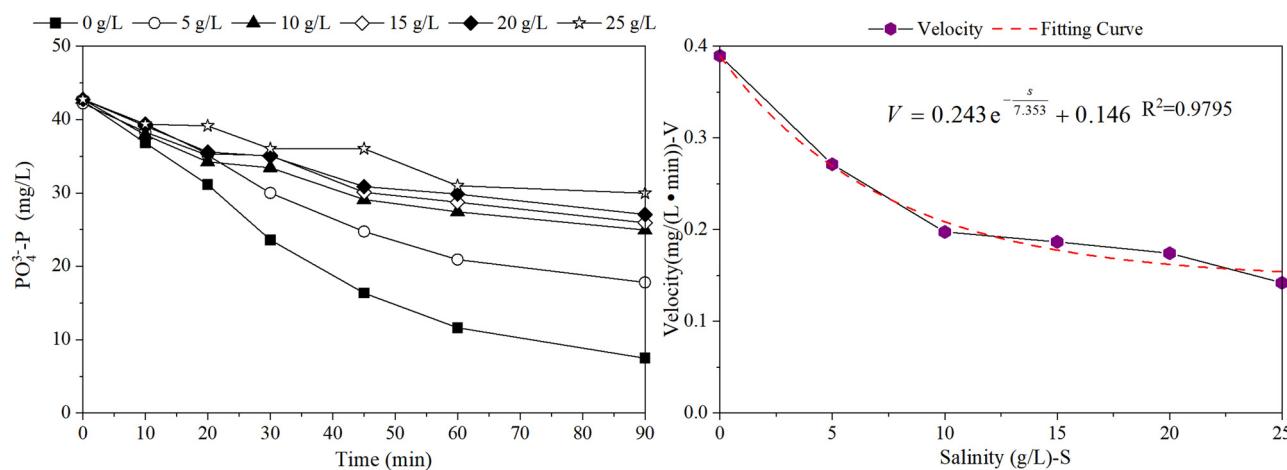


Figure 5: Influence of salinity on P removal by Fe–C microelectrolysis.

0.14 mg·L⁻¹·min⁻¹, when the salinity was 25.00 g·L⁻¹, which was 70.00% of the reaction rate when the salinity was 10.00 g·L⁻¹. The fitting curve showed that the P removal velocity by Fe–C microelectrolysis decreased exponentially under the influence of salinity ($R^2 = 0.9795$). The results showed that the salinity had an obvious inhibition on P removal by Fe–C microelectrolysis, and the salinity range of wastewater suitable for P removal by Fe–C microelectrolysis was 0–10 g·L⁻¹.

In order to verify the feasibility of P removal from actual wastewater, the influent of WWTP, effluent of SST, and actual high salinity wastewater were treated by Fe–C microelectrolysis. The results are shown in Figure 6. It can be seen that the phosphorus removal rate of Fe–C microelectrolysis for these three types of wastewaters is relatively high and stable, and the removal rate is 88.37 ± 0.44%, 89.78 ± 1.88%, and 94.23 ± 0.16%, respectively (water samples were taken every other day, and the average value of the three experiments). Even if the salinity of raw water was

greater than 20.00 g·L⁻¹, the Fe–C microelectrolysis process showed excellent TP removal capacity. The results indicated that Fe–C microelectrolysis also had a good P removal effect on the actual industrial wastewater, so it was worth further research and promotion. There was no aeration and denitrification in the reaction process, so NH₄⁺-N in raw water was unchanged. But the removal of TP from wastewater required no organic carbon and left the organic carbon to biological nitrogen removal, which was a promising way for low COD/N ratio wastewater treatment.

P Removal by microelectrolysis was achieved in this study and might be a new way to P recovery; 76.05% removal rate was achieved under the initial concentration of PO₄³⁻-P was 19.44 mg·L⁻¹ and 120 min reaction time in synthetic wastewater. The precipitate formed in the reaction was mainly ferric phosphate (FePO₄) which had a high recovery value. There was a linear correlation between initial P concentrations and P removal velocity. The salinity had an obvious inhibition on P removal by Fe–C microelectrolysis while P removal velocity decreased exponentially. As to actual wastewater, 88.37 ± 0.44%, 89.78 ± 1.88%, and 94.23 ± 0.16% phosphorus removal rate were achieved in the influent of WWTP, effluent of SST, and actual high salinity wastewater, respectively, after 120 min reaction time.

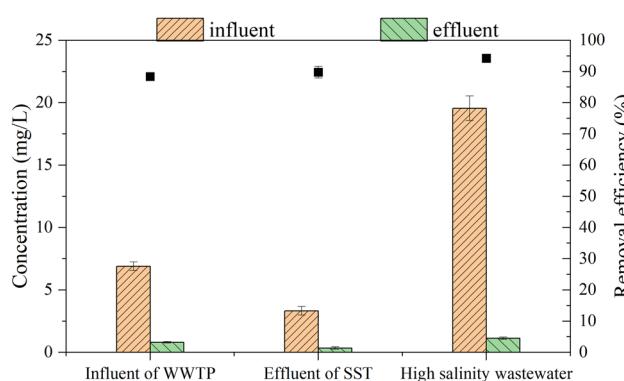


Figure 6: P removal efficiency by Fe–C microelectrolysis in different types of wastewater.

Experimental

Material preparation

Activated carbon (AR), bought from Tianjin Fuchen Chemical Reagent Factory (Tianjin, China), was washed with deionized

water, dried at 105°C, and cooled for standby. Iron filings, acquired from Linyi Taiping Machine Processing Factory (Linyi Shandong, China), were soaked in 1 mol·L⁻¹ NaOH solution for 5 min to remove the dirt on the surface and then washed to neutral with deionized water, then soaked in 1% hydrochloric acid for 5 min to remove the oxide film on the surface, and finally washed to neutral with deionized water for immediate using.

Synthetic P-containing wastewater was prepared by adding K₂HPO₄ to tap water. The mechanism, efficiency, and influencing factors of P recovery were studied with synthetic wastewater. The feasibility of P removal from actual wastewater was investigated by using the influent of municipal wastewater treatment plant (WWTP) and the effluent of secondary sedimentation tank (SST). The influent of WWTP and the effluent of SST were collected from the water inlet and the SST outlet in a municipal wastewater treatment plant in Zaozhuang City (Zaozhuang Shandong, China). High salinity wastewater (high COD and >20.00 g·L⁻¹ salinity (NaCl) on average) was collected from a pickle factory in Lanling County, Linyi City (Linyi Shandong, China).

Experiment operation

Into a 250 mL flask, 100 mL P containing wastewater was put. The flask was placed on a magnetic stirrer at room temperature (20 ± 0.5°C, 200 rpm). Added prepared iron–carbon filings to the flask according to test requirements. After the reaction, the filtrate was filtered to measure P concentration.

Measurement and analysis methods

Samples of the solution were taken at fixed times according to the experiment plan with one of these samples filtered immediately through a membrane with 0.45 µm pore size. Analysis of the filtrate was conducted immediately. The concentrations of chemical oxygen demand (COD), ammonia nitrogen, and TP were determined according to the standard method [33].

The membrane containing residual insoluble was dried in a lyophilizer (XY-FD-S40, Shanghai, China) to prevent oxidation of the Fe(II) species as much as possible and the dry solid substances present analyzed by X-ray diffraction (XRD) (XRD-6000, Shimadzu, Japan). Jade 6.0 software was used to analyze the data and determine the chemical structure of the precipitate [34].

Acknowledgments: The authors are grateful to the Natural Science Foundation of Shandong Province (Doctoral Fund, ZR2016EEB09) for financial support.

Funding information: Grants ZR2016EEB09 from the Natural Science Foundation of Shandong Province (Doctoral Fund).

Author contributions: Chao Wang: writing – original draft; Changwen Wang: writing – review and editing; Mei Xu: methodology; Fanke Zhang: formal analysis.

Conflict of interest: The authors state no conflict of interest.

References

- [1] Sun F, Liu Y. China's Ministry of Environmental Protection adopted Draft Amendment to the Law on Prevention and Control of Water Pollution. *Front Environ Sci Eng.* 2016;10(6):1–2.
- [2] Mayer T, Manning PG. Evaluating inputs of heavy metal contaminants and phosphorus to lake ontario from Hamilton Harbour. *Water Air Soil Pollut.* 1991;59(3–4):281–98.
- [3] Farmer JG. Methodologies for soil and sediment fractionation studies. *Sci Total Environ.* 2003;303(3):263–4.
- [4] Burpee B, Saros JE, Northington RM, Simon KS. Microbial nutrient limitation in Arctic lakes in a permafrost landscape of, southwest Greenland. *Biogeosciences.* 2016;13(2):365–74.
- [5] Smith VH, Tilman GD, Nekola JC. Eutrophication: impacts of excess nutrient inputs on freshwater, marine, and terrestrial ecosystems. *Environ Pollut.* 1999;100(1–3):196.
- [6] Daniel TC, Sharpley AN, Lemunyon JL. Agricultural phosphorus and eutrophication: a symposium overview. *J Environ Qual.* 1999;27(2):251–7.
- [7] Petzet S, Cornel P. Phosphorus recovery from wastewater. *Water Sci Technol.* 2013;59(6):1069–76.
- [8] Stávková J, Maroušek J. Novel sorbent shows promising financial results on P recovery from sludge water. *Chemosphere.* 2021;276(6):130097.
- [9] Yuan Z, Pratt S, Batstone DJ. Phosphorus recovery from wastewater through microbial processes. *Curr Opin Biotechnol.* 2012;23(6):878–83.
- [10] Zhang T, Ding LL, Ren HQ, Guo ZT, Tan J. Thermodynamic modeling of ferric phosphate precipitation for phosphorus removal and recovery from wastewater. *J Hazard Mater.* 2010;176(1–3):444–50.
- [11] Jordaan EM, Ackerman J, Cicek N. Phosphorus removal from anaerobically digested swine wastewater through struvite precipitation. *Water Sci Technol.* 2010;61(12):3228–34.
- [12] Yoshino H, Kawase Y. Kinetic modeling and simulation of zero-valent iron wastewater treatment process: simultaneous reduction of nitrate, hydrogen peroxide, and phosphate in semiconductor acidic wastewater. *Ind Eng Chem Res.* 2013;52(50):17829–40.
- [13] Zhang J, Abdallatif S, Chen XG, Xiao K, Sun JY, Yan XX, et al. Low-voltage electric field applied into MBR for fouling

suppression: Performance and mechanisms. *Chem Eng J.* 2015;273:223–30.

[14] Zhou YN, Xing XH, Liu ZH, Cui LW, Yu AF, Feng Y, et al. Enhanced coagulation of ferric chloride aided by tannic acid for phosphorus removal from wastewater. *Chemosphere.* 2008;72(2):290–8.

[15] Zhang J, Satti A, Chen X, Xiao K, Sun J, Yan X, et al. Low-voltage electric field applied into MBR for fouling suppression: Performance and mechanisms. *Chem Eng J.* 2015;273:223–30.

[16] Wan A, Zhao B, Dong H, Wu Y, Xie Y. Study on biological filler-coupled biological process for phosphorus removal. *Desalination Water Treat.* 2020;203:179–87.

[17] Liu S. Performance and mechanism of phosphorus removal by slag ceramsite filler. *Transactions of The Institution of Chemical Engineers. Process Saf Environ Prot Part B.* 2021;148(1):858–66.

[18] Han Y, Li H, Liu M, Sang Y, Liang C, Chen J. Purification treatment of dyes wastewater with a novel micro-electrolysis reactor. *Sep Purif Technol.* 2016;170:241–7.

[19] Xu X, Cheng Y, Zhang T, Ji F, Xu X. Treatment of pharmaceutical wastewater using interior micro-electrolysis/Fenton oxidation-coagulation and biological degradation. *Chemosphere.* 2016;152:23–30.

[20] Li JP, Song C, Wu W. A study on influential factors of high-phosphorus wastewater treated by electrocoagulation-ultrasound. *Environ Sci Pollut Res Int.* 2013;20(8):5397–404.

[21] Yuan SH, Wu C, Wan JZ, Lu XH. *In situ* removal of copper from sediments by a galvanic cell. *J Environ Manag.* 2009;90(1):421–7.

[22] Deng SH, Li DS, Yang X, Xing W, Li JH, Zhang Q. Iron [Fe(0)]-rich substrate based on iron–carbon micro-electrolysis for phosphorus adsorption in aqueous solutions. *Chemosphere.* 2017;168:1486–93.

[23] Hu SH, Wu YG, Yao HR, Lu C, Zhang CJ. Enhanced Fenton-like removal of nitrobenzene via internal microelectrolysis in nano zerovalent iron/activated carbon composite. *Water Sci Technol.* 2016;73(1):153–60.

[24] Ying DW, Peng J, Xu XY, Li K, Wang YL, Jia JP. Treatment of mature landfill leachate by internal micro-electrolysis integrated with coagulation: a comparative study on a novel sequencing batch reactor based on zero valent iron. *J Hazard Mater.* 2012;229–30:426–33.

[25] Gutierrez O, Park D, Sharma KR, Yuan ZG. Iron salts dosage for sulfide control in sewers induces chemical phosphorus removal during wastewater treatment. *Water Res.* 2010;44(11):3467–75.

[26] Ivanov V, Kuang SL, Stabnikov V, Guo CH. The removal of phosphorus from reject water in a municipal wastewater treatment plant using iron ore. *J Chem Technol Biotechnol Biotechnol.* 2009;84(1):78–82.

[27] Wu CY, Peng YZ, Gan YP. Biological nutrient removal in A~20 process when treating low C/N ratio domestic wastewater. *J Chem Ind Engineering (China).* 2008;59(12):3126–31.

[28] Chen YZ, Peng YZ, Wang JH, Zhang LC. Biological phosphorus and nitrogen removal in low C/N ratio domestic sewage treatment by a A2/O-BAF combined system. *Acta Sci Circumstantiae.* 2010;30(10):1957–63.

[29] Carter R, Huhman B, Love CT, Zenyuk IV. X-ray computed tomography comparison of individual and parallel assembled commercial lithium iron phosphate batteries at end of life after high rate cycling. *J Power Sources.* 2018;381:46–55.

[30] Lu J, Nishimura SI, Yamada A. A Fe-rich sodium iron orthophosphate as cathode material for rechargeable batteries. *Electrochim Commun.* 2017;79:51–4.

[31] Wu Y, Tam NFY, Wong MH. Effects of salinity on treatment of municipal wastewater by constructed mangrove wetland microcosms. *Mar Pollut Bull.* 2008;57(6–12):727–34.

[32] Hong J, Lu F, Yin J. Effects of salinity on treatment of aquaculture wastewater by dynamic membrane bioreactor with intermittent aeration. *Trans Chin Soc Agric Eng.* 2012;28(11):212–7.

[33] APHA. *Standard Methods for the Examination of Water and Wastewater.* 21st edn. Washington: American Public Health Administration; 2005.

[34] Huang WL, Cai W, Huang H, Lei ZF, Zhang ZY, Tay JH, et al. Identification of inorganic and organic species of phosphorus and its bio-availability in nitrifying aerobic granular sludge. *Water Res.* 2015;68:423–31.