



# Effective phosphate removal for advanced water treatment using low energy, migration electric–field assisted electrocoagulation

Yushi Tian<sup>a,1</sup>, Weihua He<sup>b,1</sup>, Dandan Liang<sup>a</sup>, Wulin Yang<sup>c</sup>, Bruce E. Logan<sup>a,c,\*</sup>, Nanqi Ren<sup>a,\*\*</sup>

<sup>a</sup> State Key Laboratory of Urban Water Resource and Environment, Harbin Institute of Technology, No.73 Huanghe Road, Nangang District, Harbin 150090, China

<sup>b</sup> School of Environmental Science and Engineering, Tianjin University, No. 92 Weijin Road, Nankai District, Tianjin 300072, China

<sup>c</sup> Department of Civil & Environmental Engineering, Penn State University, 231Q Sackett Building, University Park, PA 16802, USA

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## ABSTRACT

A migration electric–field assisted electrocoagulation (MEAEC) system was developed to increase phosphate removal from domestic wastewater, with reduced energy consumption, using a titanium charging (inert) electrode and a sacrificial iron anode. In the MEAEC, an electric field was applied between the inert electrode (titanium) and an air cathode to drive migration of phosphate anions towards the sacrificial anode. Current was then applied between the sacrificial anode (Fe or Al mesh) and the air cathode to drive electrocoagulation of phosphate. A MEAEC with the Fe electrode using primary clarifier effluent achieved 98% phosphate removal, producing water with a total phosphorus of 0.3 mg/L with <6 min total treatment time (five cycles; each 10 s inert electrode charging, and 1 min electrocoagulation), at a constant current density of 1 mA/cm<sup>2</sup>. In the absence of the 10 s charging time, electrocoagulation required 15 min for the same removal. With an aluminum anode and the same phosphorus removal, the MEAEC required 7 cycles (7 min total treatment, 1 min 10 s total charging), while conventional electrocoagulation required 20 min. The energy demand of Fe-MEAEC was only 0.039 kWh/m<sup>3</sup> for 98% phosphate removal, which was 35% less than with the Al-MEAEC of 0.06 kWh/m<sup>3</sup>, and 28% less than that previously obtained using an inert graphite electrode. Analysis of the precipitate showed that a less porous precipitate was obtained with the Al anode than with the Fe anode. The phosphorus in precipitate of Fe-MEAEC was identified as PO<sub>4</sub><sup>3-</sup> and HPO<sub>4</sub><sup>2-</sup>, while the Fe was present as both Fe<sup>2+</sup> and Fe<sup>3+</sup>. Only HPO<sub>4</sub><sup>2-</sup> and Al<sup>3+</sup> were identified in the precipitate of the Al-MEAEC. These results indicated that the MEAEC with a titanium inert charging electrode and iron anode could achieve the most efficient phosphate removal with very low energy demands, compared to previous electrochemical approaches.

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## 1. Introduction

In recent years, avoiding pollution of water bodies has become even more important due to further industrialization and urbanization, but the costs of aerobic treatment of wastewaters remain high. Anaerobic wastewater treatment can be a less expensive and

more effective approach to remove organic matter in the wastewater, using processes such as anaerobic fluidized bed reactors, anaerobic membrane bioreactors (Kim et al., 2010; Ren et al., 2014; Yoo et al., 2012), and microbial fuel cells (MFCs) (He et al., 2016a; Kim et al., 2015). However, only a small fraction of nutrients (nitrogen and phosphorus) are removed in these anaerobic processes. Therefore, additional nutrient removal processes are needed following these anaerobic systems to achieve efficient nutrient removal (Delgado Vela et al., 2015). Phosphorus removal is particularly needed as it is often the controlling factor in the eutrophication of natural water bodies.

Electrocoagulation (EC) is an electrochemical process that can be used to treat wastewaters in terms of both organic matter and

\* Corresponding author. State Key Laboratory of Urban Water Resource and Environment, Harbin Institute of Technology, No.73 Huanghe Road, Nangang District, Harbin 150090, China.

\*\* Corresponding author.

E-mail addresses: [blogan@psu.edu](mailto:blogan@psu.edu) (B.E. Logan), [mq@hit.edu.cn](mailto:mq@hit.edu.cn) (N. Ren).

<sup>1</sup> The authors contributed equally to the work.

nutrient removal (Gao et al., 2017). The process is based on the use of a sacrificial electrode such as aluminum (Gharibi et al., 2010; Irdemez et al., 2006a; Kobya et al., 2003) that is oxidized to produce metal ions that coagulate and react with organic matter and nutrients, removing them from wastewater by chemical precipitation. While many different metals have been examined for electrocoagulation (Gatsios et al., 2015), aluminum or iron are most commonly used due to their good flocculation performance, as shown for domestic and textile wastewaters (Abdel-Gawad et al., 2012; Gomes et al., 2007; Hu et al., 2003; Kobya et al., 2003), as well as wastewaters containing boron (Chorghe et al., 2017) or arsenic (Delaire et al., 2017; Katal and Pahlavanzadeh, 2011; Wan et al., 2011). When current is applied, metal ions that are produced react with primary hydroxides and produce polyhydroxides and polyhydroxy-metallic flocs (Pulkka et al., 2014). The sacrificial anode (aluminum or iron), cathode (with oxygen reduction), and pH-dependent coagulation reactions are:



Cathode:  $2\text{H}_2\text{O} + 2e^- = \text{H}_2(\text{g}) + 2\text{OH}^-$  (3) Coagulation at alkaline pH:



Coagulation at acidic pH:



Most previous work research on the EC of wastewaters has focused on the effects of materials and operational conditions on nutrient removal (Tian et al., 2016), including electrode materials (Chen et al., 2014; Si et al., 2016), pH (Gatsios et al., 2015; Gharibi et al., 2010), current density (Bektaş et al., 2004), treatment time, and initial nutrient concentration of the influent wastewater (Gharibi et al., 2010; Irdemez et al., 2006c). The major advantages of EC are convenient operational procedures, high pollutant removal performance, and no requirement of chemical addition into the wastewater. However, the high electricity and anode material costs have limited more widespread applications of EC processes for wastewater treatment.

One method recently developed to reduce energy costs was based on using an air-breathing cathode to directly reduce oxygen, as opposed to aerating the wastewater or driving electrochemical hydrogen production at the cathode (Tian et al., 2016). The use of this cathode was shown to provide effective EC wastewater treatment using an aluminum anode. A second recent advance to reduce energy demands and improve the efficiency of phosphate removal was the application of an electric field, applied for a short period of time (10–120 s), between an additional inert anode (graphite) positioned in between the sacrificial anode and the cathode (Tian et al., 2017). This charging process drove phosphate ion migration to the sacrificial anode and subsequently improved phosphate ion removal in the subsequent EC process. The lower energy and material consumption were found to improve the overall removal of phosphate compared to sustained EC without the initial charging cycle. While the energy needed for EC was reduced to 0.14 kWh/m<sup>3</sup>, which was among the lowest yet reported for EC processes, this energy demand was still considered to be higher than that desired for a process for

phosphate removal from wastewater (Tian et al., 2017).

In order to further improve the electrochemical removal of phosphate from domestic wastewaters, the migration electric-field assisted electrocoagulation (MEAEC) system was modified to use new materials in order to reduce energy production, improve nutrient removal, and produce a more environmentally friendly precipitate. First, to reduce energy consumption by increasing current when applying a fixed voltage (0.5 V), a titanium plate was used instead of graphite sheet, as the inert electrode situated between the sacrificial anode and air cathode. Second, a sacrificial iron electrode was used to avoid the production of an aluminum sludge that would be a more toxic byproduct. To demonstrate the improved performance of the system with the iron anode, experiments were conducted with both the iron and aluminum mesh anodes and the Ti inert electrode (MEAEC), and without the applied electric field (EC control), using both primary and secondary clarifier effluents. The morphologies of the titanium and graphite inert electrodes, and the precipitates formed in the process with these anodes, were studied with a scanning electron microscope (SEM). The chemical composition of the precipitates were further investigated with energy dispersive spectrum analysis (EDS), and X-ray photoelectron spectroscopy (XPS).

## 2. Materials and methods

### 2.1. Electrode materials and reactor operating conditions

MEAEC reactors were constructed as previously described (Tian et al., 2017), except different inert and sacrificial anode materials were used here. A titanium plate (3 × 7 cm<sup>2</sup>) was used as the inert electrode, and its charge-discharge current and durability was compared to a graphite sheet used in previous studies (3 × 7 cm<sup>2</sup>). The sacrificial anodes were either iron mesh (mesh size 100 per 2.54 cm, wire diameter 0.017 mm, opening 0.03 mm; Yingkai corporation, China) or aluminum mesh (mesh size 200 per 2.54 cm, wire diameter 0.05 mm, opening 0.07 mm; TWP Corporation, USA). The projected surface areas of the sacrificial anodes were 15 cm<sup>2</sup> (3 × 5 cm<sup>2</sup>). Cathodes used an activated carbon catalyst for oxygen reduction, and were made by a continuous rolling and pressing process, with polytetrafluoroethylene (PTFE) as the binder, and an outer PTFE diffusion layer to avoid water leakage through the cathode (Dong et al., 2012; He et al., 2016b).

All reactors were operated in batch mode. The MEAEC reactors consisted of an inert electrode (titanium plate), a sacrificial anode (aluminum/iron mesh) and an air cathode, while the control EC reactor was made using only the sacrificial anode and air cathode. The sacrificial anode was placed between inert anode and cathode, with 1.5 cm between the sacrificial anode and air-cathode, and 2 cm between inert anode and air-cathode. A potentiostat (VMP3; Bio-Logic, Claix, France) was used to set voltages or current. For the MEAEC reactors, a constant voltage of 0.5 V was first applied between inert anode and air cathode for 10 s. Then, the sacrificial anode was connected with air cathode in electric circuit and operated with constant current density of 1 mA/cm<sup>2</sup> for 1 min, while the inert anode was disconnected with cathode. These two steps formed a single working cycle and the cycles repeated until the phosphorus concentration was lower than the detection limit (0.1 mg/L). The control EC reactor was operated continuously at a constant current density of 1 mA/cm<sup>2</sup> between anode and cathode.

The durability of the two inert electrodes (titanium plate or graphite sheet) over time was compared in charging and discharging tests with an air-breathing cathode and a synthetic nutrient solution. The charge and discharge times were both set at 90 s with an applied voltage of 0.5 V, for 400 cycles for both types of electrodes. The surface structure of Ti and graphite electrodes were

then examined using a scanning electron microscope (SEM) to evaluate changes in the electrode surfaces due to oxidation or corrosion. The charge transfer efficiency of different electrode materials was evaluated by the current produced over 400 charging-discharging cycles.

The effectiveness of the Ti electrode on phosphate removal was further compared to that obtained using a graphite electrode with aluminum mesh as the sacrificial anode for the advanced treatment of both primary (high phosphorous concentration) and secondary (low phosphorus concentration) clarifier effluent. The inert electrode working time (10 s) and total electrocoagulation times (1, 3, 5 and 7 min) were selected based on detectable final concentrations of phosphate.

The impact of EC on phosphate removal and energy utilization was also compared with a fixed inert electrode time of 10 s. The control EC was operated with a continuous working time of 3, 5, 10, 15 and 20 min for primary clarifier effluent, and 1, 3, 5 and 10 min for secondary clarifier effluent, based on obtaining a final phosphate concentration below the limit of detection (0.1 mg/L). For MEAEC tests, the total treatment times were 1, 3, 5 and 7 min for primary clarifier effluent, and 1, 2, 3 and 5 min for secondary clarifier effluent. Following each electrocoagulation period, particles were allowed to settle in the reactor for 1 h (no applied current). Cathodes were cleaned after every 100 batch cycles by soaking the cathode in a diluted (10%) hydrochloric acid solution (BDH ARISTAR PLUS, VWR) for 2 min to remove salt deposits. All tests were conducted using duplicate reactors at 25 °C, with results reported based on the average and standard deviations ( $\pm$ SD).

## 2.2. Wastewater and synthetic nutrient solution

The two wastewater sources, primary clarifier effluent, and secondary clarifier effluent, were both obtained from the Wenchang Municipal Wastewater Treatment (Harbin, China) and stored at 4 °C prior to use. The primary clarifier effluent had a pH of 6.8–7.1, a conductivity of 900  $\mu$ S/cm, an ammonia concentration of  $48 \pm 2$  mg/L, a total nitrogen concentration of  $65 \pm 3$  mg/L, and a phosphate concentration of  $17 \pm 1$  mg/L. The secondary clarifier effluent had a pH of 7–7.2, a conductivity of 600  $\mu$ S/cm, an ammonia concentration of  $8 \pm 0.5$  mg/L, a total nitrogen of  $22 \pm 1$  mg/L and a phosphate concentration of  $2.4 \pm 0.1$  mg/L. The synthetic nutrient solution contained 1200 mg/L  $\text{NaH}_2\text{PO}_4$  (Sigma Aldrich) in order to produce the same conductivity as the primary clarifier wastewater.

## 2.3. Solution measurements and calculations

Before phosphate measurements, all samples were filtered using 0.45  $\mu$ m pore diameter syringe filters (polyvinylidenedifluoride, PVDF, 25 mm diameter; Restek Corporation). Samples were analyzed using Method 10031 (HACH Company, Loveland, CO) for phosphate, Method 10127 (HACH Company, Loveland, CO) for ammonia, and Method 10071 for total nitrogen. The removal efficiencies were calculated from the initial and final concentrations.

Voltage and the counter electrode potential were recorded at 1 s intervals, and analyzed using the potentiostat software (EC–Lab V10.02). Energy consumption ( $E$ , kWh/m<sup>3</sup>) for EC wastewater treatment was calculated as  $W=UIt/v$ , where  $U$  is the voltage (V),  $I$  the current (A),  $t$  the electrolysis time (s), and  $v$  the volume of reactor (m<sup>3</sup>). In charge and discharge tests, the total inert electrode charge ( $Q$ , C) was calculated by summing the total charge transferred over both the charging and discharging cycles based on the current, where  $Q=It$ . The power ( $P=UI$ ) to polarize the inert electrode was not included in this calculation as there was only a tiny current.

## 2.4. Characterization techniques

Microstructural study tests were conducted on the precipitates and electrodes using a scanning electron microscope (SEM; QUANTA200, FEI Co.) equipped with energy dispersive spectroscopy (EDS). The particles sizes in the SEM images were calculated by image analysis using the open platform software of Image J. Surface chemical characterization was performed by X-ray photoelectron spectroscopy (XPS) using a Thermo Scientific Escalab 250Xi spectrometer with a six-channel (Channeltron) detector. High-resolution spectra of the elements identified were corrected using the C1s signal (285 eV) as a reference, and then the percentages of each element presented in the generated sediment were calculated relative to this signal. The precipitates produced from the EC process were dried overnight and ground up for XPS analysis, and prepared for SEM analysis after the gold sputtering treated. After 400 cycles, the Ti and graphite electrodes were dried at 80 °C overnight prior to SEM analysis.

## 3. Results and discussion

### 3.1. Comparison of titanium and graphite inert electrodes

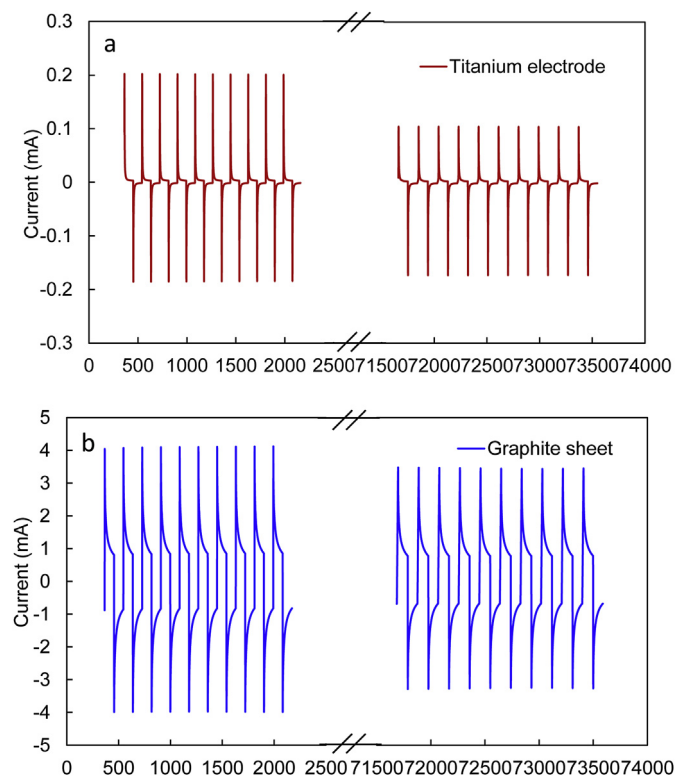
To demonstrate that using a titanium electrode could improve electrochemical performance, titanium plate and graphite sheet electrodes were compared in charge and discharge tests using a synthetic nutrient solution (no sacrificial anode installed). After 400 cycles, the graphite electrode absorbed 29% more charge (69,600 C) than the Ti electrode (49,516 C). Therefore, the Ti electrode was relatively more inert in wastewater due to less current transferred, which would result in a longer service time and less energy consumption compared to graphite. The maximum current produced with the Ti electrode (Fig. 1a) was 0.2 mA which was only 5% of that compared to graphite (4 mA) (Fig. 1b), which also indicated the titanium was less active than graphite. The surfaces morphologies obtained using SEM of the Ti and graphite electrodes indicated the more stable structure of Ti than graphite. The surface morphology of Ti was not noticeably altered after 400 cycles, while holes, cracks and obvious deformations were observed on graphite electrode surface after the charging and discharging tests (Fig. 2). The large changes in surface morphologies of the graphite electrodes suggested that they were oxidized during electrochemical tests.

### 3.2. Treatment of primary clarifier effluent using MEAEC

Phosphate removal using primary clarifier effluent was examined in MEAEC reactors using iron sacrificial anodes (Fe-MEAEC), with each cycle consisting of an applied voltage of 0.5 V between the inert and air-cathode for 10 s, followed by a constant current density of 1 mA/cm<sup>2</sup> between the sacrificial anode and air cathode for 1 min. Phosphate removals increased with treatment time, with  $76 \pm 5\%$  removal using primary clarifier effluent for one cycle, and  $88 \pm 5\%$  for three cycles. After 5 cycles, there was nearly complete phosphate removal (98%), with an effluent phosphate concentration of 0.3 mg/L, and no detectable phosphate (<0.1 mg/L) in the effluent after 7 cycles (Fig. 3a).

The performance of the Fe-MEAEC system was further compared to the control reactor without an inert electrode (Fe-EC) (Fig. 3b). After the first 3 min of electrocoagulation, the phosphate removal of primary clarifier effluent was  $88 \pm 5\%$ , which was very similar with that of MEAEC. However, after 5 min of electrocoagulation, the phosphate removal was only  $93 \pm 5\%$ , compared to  $98 \pm 6\%$  for the MEAEC after 5 min. After 10 min of electrocoagulation, the phosphate removal of Fe-EC was 97%, and



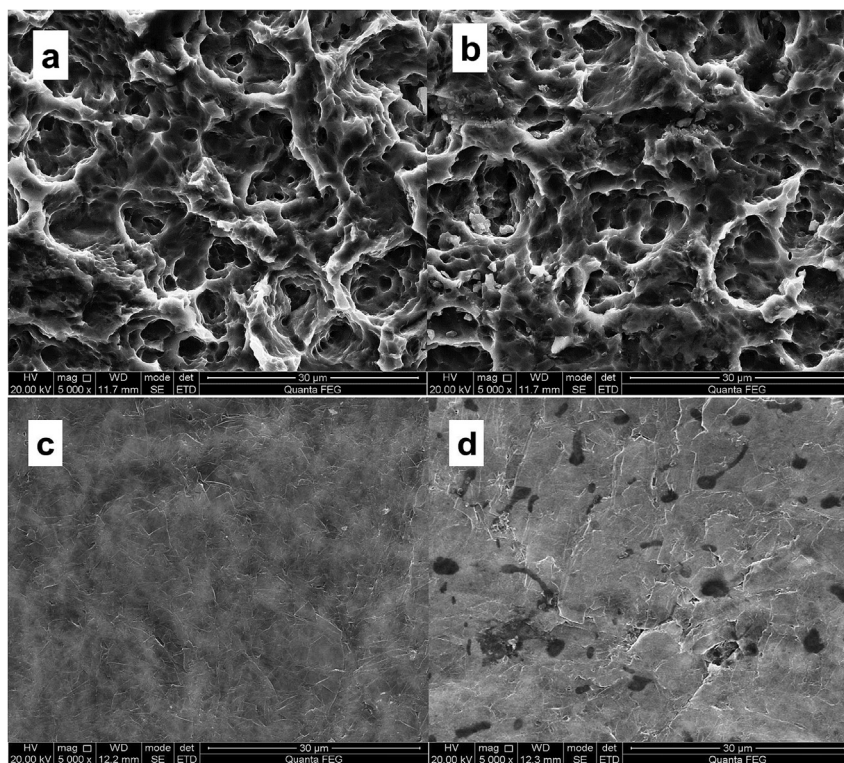


**Fig. 1.** Current produced using a (a) titanium electrode ( $Q_T = 49,516$  C) and (b) graphite electrode ( $Q_T = 69,608$  C) over 400 charging and discharging cycles with a synthetic nutrient solution. (Shown are only the first 10 and last 10 cycles).

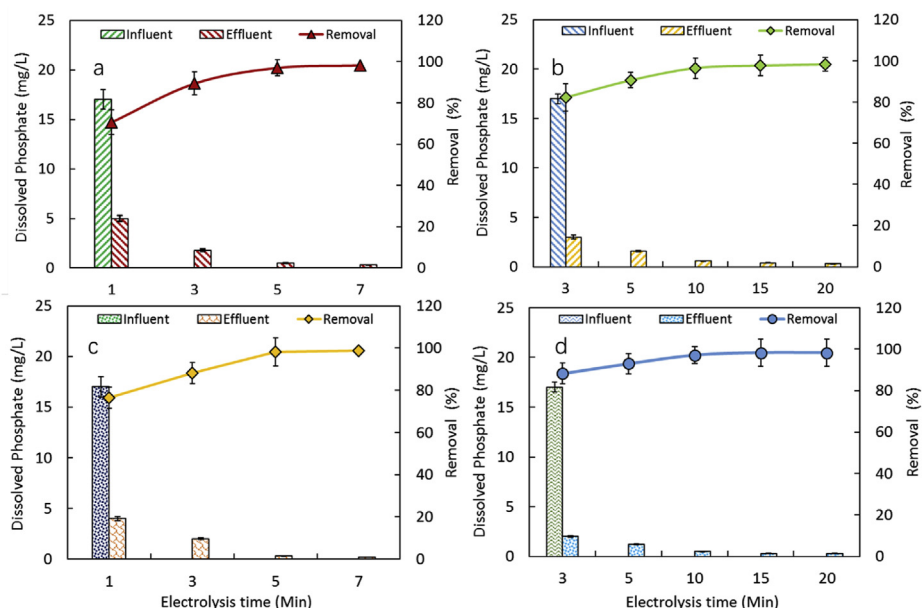
15–20 min was required to reach a comparable phosphate removal of 98% obtained using the MEAEC after <6 min (5 min 50 s). The differences between Fe-MEAEC and control Fe-EC indicated that the MEAEC greatly improved phosphate removals for wastewaters with low nutrient concentrations. The localized accumulation of target ions near the sacrificial anode by charging (inert) electrode was considered to be the primary reason, which allowed for a greater opportunity for the phosphate ions to be attracted to the sacrificial electrode and thus to more rapidly form precipitates with metal ions or to be absorbed by the flocs.

For the MEAEC using the Al sacrificial anode, phosphate removal of the primary clarifier effluent was  $71 \pm 6\%$  with one working cycle (10 s migration process, 1 min electrolysis time), and it increased to  $89 \pm 5\%$  after 3 working cycles reached (Fig. 3b). This was much better than the phosphate removal for the control reactor using an Al electrode without an inert electrode (Al-EC), which was only  $82 \pm 6\%$  after 3 min. A total of 10 min of working time was needed for the Al-EC reactor to obtain a similar phosphate removal (97%) as that of the Al-MEAEC for the same working time of 5 min (<6 min including inert electrode charging times). The Al-EC required 15–20 min of treatment to achieve the same as that with the Al-MEAEC using only 7 min of treatment time (not including inert electrode charging).

A comparison of the Fe-MEAEC and Al-MEAEC systems show that they obtained similar phosphate removals of 89% in the first 3 working cycles. However, after 7 working cycles the effluent phosphate concentration of Fe-MEAEC was near the detectable level ( $0.1 \text{ mg L}^{-1}$ ), while that of Al-MEAEC was still  $0.3 \text{ mg L}^{-1}$ . This indicated the Fe-MEAEC had a slight advantage in reducing phosphate more rapidly to low concentrations. Both the Fe-MEAEC and Al-MEAEC required only ~50% of the working time compared to the controls for achieving a phosphate removal of 97%. The major factor



**Fig. 2.** Surface micrographs of the (a, b) titanium plate and (c, d) graphite sheet before and after 400 charging and discharging cycles in the synthetic nutrient solution.



**Fig. 3.** Phosphate removals using primary clarifier wastewater as a function of electrolysis time, using Fe sacrificial anodes and (a) MEAEC and (b) control EC, and Al sacrificial anodes using the (c) MEAEC system and (d) control EC (fixed current density of 1 mA/cm<sup>2</sup>).

leading to better performance of MEAEC was the use of the inert anode and its impact on ion migration due to the assisted electric field, which localized accumulated target phosphate ions and enhanced the precipitate forming with metal ions.

The performance of the Al-MEAEC system using a titanium inert electrode was compared to the graphite electrode used in previous tests, using primarily clarifier effluent over multiple cycles. Phosphate removals were similar for the two inert materials (Fig. S1), with 70%–98% removal using the titanium electrode as the inert electrode (Fig. S1a), and 72%–97% using the graphite electrode (Fig. S1b). Thus, while the phosphate removals are similar for both Ti and graphite inert electrodes under these conditions, the much greater stability of the Ti electrode made it a better choice as the inert electrode.

### 3.3. Treatment of secondary clarifier effluent using the MEAEC

Secondary clarifier effluent that had lower organic matter and phosphate concentrations was also tested with both MEAEC and control EC reactors (Fig. 4). The phosphate removal for the Fe-MEAEC reactor increased rapidly in the first 1–3 working cycles from  $71 \pm 5$  to  $96 \pm 1\%$  ( $0.1 \text{ mg L}^{-1}$  in effluent). After that, the phosphate removal was essentially constant after 5 working cycles since the phosphate was nearly completely removed. Phosphate removal by the control (Fe-EC) was much lower with  $46 \pm 6$  to  $85 \pm 2\%$  removals for 1 and 5 min (Fig. 4a). With up to a 10 min working time, the control Fe-EC (Fig. 4b) achieved only  $88 \pm 2\%$  phosphate removal, with an effluent phosphate concentration of  $0.3 \text{ mg L}^{-1}$ . The Fe-MEAEC, however, required only 2 working cycles to achieve a higher phosphate removal of  $92 \pm 2\%$  with an effluent phosphate concentration of  $0.2 \text{ mg L}^{-1}$ .

Similar trends were observed between the reactors using Al electrodes for the Al-MEAEC (Fig. 4c) and control Al-EC (Fig. 4d). The phosphate removal of the Al-MEAEC increased from  $67 \pm 5$  for 1 working cycle to  $94 \pm 2\%$  with 3 working cycles, with 96% removal and an effluent phosphate concentration of  $0.2 \text{ mg L}^{-1}$  after 5 working cycles. However, the control Al-EC had a phosphate removal of only  $85 \pm 2\%$  with a 5 min working time, and  $88 \pm 2\%$

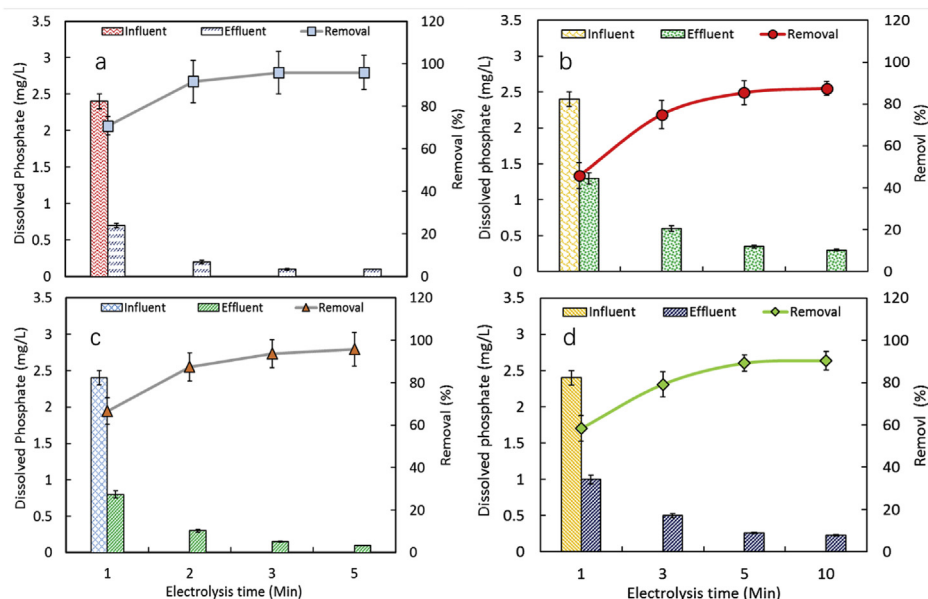
with a 10 min working time ( $0.3 \text{ mg L}^{-1}$  in effluent), compared to only 2 cycles needed for  $88 \pm 2\%$  phosphorus removal using the Al-MEAEC.

Both control reactors (Fe-EC and Al-EC) were inefficient in removing phosphorus from the secondary clarifier effluent due to the lower initial phosphate concentrations ( $2.4 \text{ mg/L}$ , compared to  $17 \text{ mg/L}$  for the primary clarifier effluent). The minimum concentration of phosphate that could be achieved with these two processes was  $\sim 0.3 \text{ mg L}^{-1}$  for both primary and secondary clarifier effluents. However, by using the inert electrode in the MEAEC, it was still possible to reduce the effluent phosphate concentration to  $< 0.1 \text{ mg L}^{-1}$ . Considering other possible conditions that could impact phosphate removals, such as suspended solids and CODs, the MEAEC performance was still excellent and thus it demonstrated good performance even for secondary clarifier effluent treatment. Based on the comparison of the Fe and Al sacrificial anodes, the Fe-MEAEC was slightly better in performance than the Al-MEAEC for 3 working cycles, indicating the advantages of the Fe electrode with low phosphate concentrations in secondary effluent.

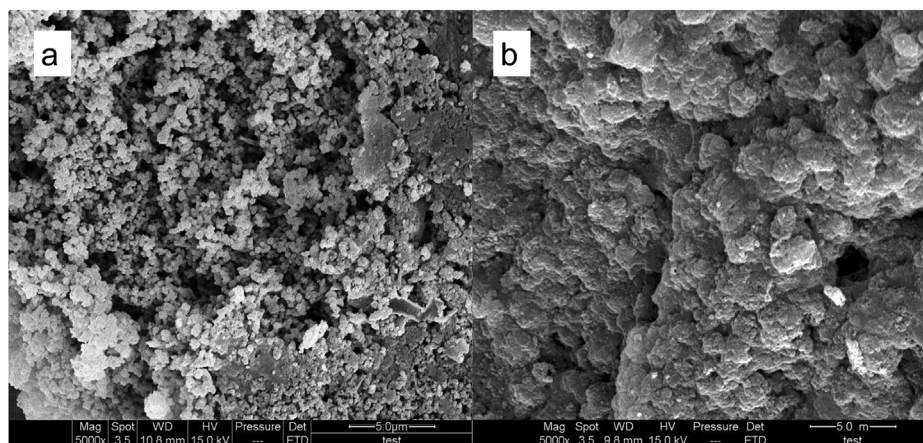
### 3.4. Chemical and morphological analysis of precipitates and electrodes

#### 3.4.1. Morphology and composition of the sediment by SEM-EDS

The morphologies of the precipitate collected from the control EC with both Fe and Al electrode after treating primary clarifier effluent were examined by SEM (Fig. 5). The particles in the precipitate from the control Fe-EC were  $0.45 \pm 0.07 \mu\text{m}$  (range of  $0.2$ – $0.6 \mu\text{m}$ ), which were relatively smaller and more spherical than those collected from control Al-EC ( $1.69 \pm 0.33 \mu\text{m}$ ). Unlike the loosely organized particles of control Fe-EC precipitate, the particles of control Al-EC were closely packed together and formed a bulk precipitate. Although there is direct reaction of the metal with phosphate ions to form flocs, sweep and adsorption effects are considered as the main mechanisms for conventional electrocoagulation processes to remove nutrition ions (Lacasa et al., 2011; Moreno-Casillas et al., 2007). Therefore, the smaller particles and loose structure of the precipitate from Fe-EC may contribute to its



**Fig. 4.** Phosphate removals in secondary clarifier effluent as a function of electrolysis time, using Fe sacrificial anodes and (a) MEAEC and (b) control EC, and Al sacrificial anodes using the (c) MEAEC system and (d) control EC (fixed current density of 1 mA/cm<sup>2</sup>).



**Fig. 5.** Micrographs of the precipitate collected from control reactors with sacrificial (a) Fe and (b) Al electrodes, using primary clarifier effluent.

better phosphate removal compared to the Al-EC (Fig. S2).

The surface elemental composition and atomic number percentage of the sediments obtained by EDS showed that the most abundant elements in the sediment were C, N, and P for both electrodes, with a higher content of Fe or Al depending on the specific electrode (Table 1). The surface elemental composition and atomic percentages of the precipitate from the control Fe-EC and Al-EC tests were obtained by EDS analysis. The most abundant elements in both precipitates were Al (or Fe), C, O, N, and P, while

differences were observed in the atomic number percentages (Table 1). The electrocoagulation system has been proven to contribute to COD and nitrogen removal (Lacasa et al., 2011; Lin et al., 2017), therefore, the elements of C, O, N were also observed in precipitates. However, at treatment times of 1–20 min, there was little effective total nitrogen removal, with an influent TN of  $65 \pm 2$  mg/L and an effluent TN of  $62 \pm 2$  mg/L. The atomic ratio of Fe

**Table 1**

Surface elemental composition and atomic percentages obtained by EDS for the aluminum or iron electrode generated sediment samples using primary clarifier wastewater (collected from the control tests).

| Electrode material | Element (atomic%) |      |     |      |     |
|--------------------|-------------------|------|-----|------|-----|
|                    | C                 | N    | P   | Al   | Fe  |
| Al                 | 5.1               | 18.6 | 1.8 | 19.9 | 0.6 |
| Fe                 | 24                | 18.3 | 3.4 | 0.4  | 23  |

**Table 2**

Surface elemental composition and atomic percentages obtained by XPS for the aluminum or iron electrode generated sediment samples using primary clarifier wastewater (collected from MEAEC and control tests).

| Experiment group | Element (atomic %) |     |     |      |      |
|------------------|--------------------|-----|-----|------|------|
|                  | C1s                | N1s | P2p | Al2p | Fe2p |
| Fe MEAEC         | 68                 | 4   | 2   | —    | 1.7  |
| Fe control       | 64                 | 3.5 | 1.9 | —    | 3.2  |
| Al MEAEC         | 59                 | 2.8 | 1.9 | 8.9  | —    |
| Al control       | 52                 | 2.6 | 1.7 | 12.5 | —    |



elements was 23% from the precipitate of control Fe-EC system, while that of Al elements was similar at 20%. The atomic percentage of phosphorus was 3.4% for the precipitate from the control Fe-EC system, which was almost twice than that of control Al-EC system (1.8%), indicating the higher efficiency of Fe as a sacrificial electrode without the assistance of inert electrode. The results of the elemental composition are consistent with the better performance of the Fe electrode than Al electrode in treating the primary clarifier effluent (Fig. 3).

### 3.4.2. Determination of surface elemental composition of precipitates by XPS

In order to identify the valences of the composite elements in the precipitates of the primary clarifier effluent treatment, XPS analyses were performed for the MEAEC and the control, with both Fe and Al electrodes. Nitrogen was detected in the precipitate of from the MEAEC and control EC reactors, consistent with the above results and previous studies (Lacasa et al., 2011). The phosphorus signals in the control EC and MEAEC with Fe electrode were identified as  $\text{PO}_4^{3-}$  and  $\text{HPO}_4^{2-}$ , while the Fe elements existed in both  $\text{Fe}^{2+}$  (709.5–709.6 eV) and  $\text{Fe}^{3+}$  (711.8 eV) oxidation states. However, only  $\text{HPO}_4^{2-}$  and  $\text{Al}^{3+}$  (73.8 eV) were identified in the systems with Al electrode. The pH with Fe electrode electrocoagulation was near-neutral while that of Al electrode electrocoagulation was higher due to the longer working times (Lacasa et al., 2011). This change in pH was likely the reason for the existence of the  $\text{HPO}_4^{2-}$  signal. In the comparison of control EC and MEAEC, the atomic proportion of Fe from sacrificial anode was reduced from 3.2% to 1.7% by applying inert electrode, while that of Al was reduced from 12.5 to 8.9%. However, with the reduction in the atomic proportion of Fe and Al from the control EC to MEAEC tests, the atomic proportion of phosphorus was slightly increased for both the Fe electrode (from 1.9 to 2%) system and the Al electrode (from 1.7 to 1.9%) system. These data indicated that the migration electrical field and inert electrode could effectively reduce the consumption of sacrificial anodes in MEAEC, with the improved efficiency more notable for the Fe-MEAEC.

XPS results further demonstrated that there was more efficient phosphate removal with the MEAEC using Fe instead of the Al. Compared to the XPS results of the controls with MEAEC, there was no change in the chemical composition of the generated precipitate due to the use of MEAEC, but the decreased elemental content of Fe and Al in the precipitate demonstrated that the MEAEC played a role of increasing local phosphate concentrations near the sacrificial electrode. Comparing the Fe precipitate composition using the Fe or Al electrode, the generated flocs containing iron would have less toxicity than those containing high concentrations of aluminum, and the iron rich material could easily be safely recycled (Cheng et al., 2012). There were no appreciable nitrogen and ammonia removals from solution, although nitrogen was detected using XPS in the sediment, suggesting minimal nitrogen removal by adsorption.

### 3.5. Energy consumption

Phosphate removals increased with treatment time, although more time resulted in greater energy consumption. When the iron electrode was used as the sacrificial anode treating primary clarifier wastewater, the MEAEC used only  $0.007 \text{ kWh/m}^3$  for a 1-min treatment with  $76 \pm 5\%$  phosphate removal, and up to  $0.039 \text{ kWh/m}^3$  for a 7-min treatment to achieve  $98 \pm 2\%$  removal. These energy requirements were much less than those for the control (Fe-EC) with no Ti inert electrode, which was  $0.024 \text{ kWh/m}^3$  for  $88 \pm 5\%$  phosphate (3 min), to  $0.16 \text{ kWh/m}^3$  for  $98 \pm 3\%$  removal (20 min), due to the increased treatment times. Energy requirements using the aluminum electrode and the Ti electrode were slightly higher, with a range of  $0.009 \text{ kWh/m}^3$  for  $70 \pm 6\%$  removal (1 min) to  $0.06 \text{ kWh/m}^3$  for  $98 \pm 2\%$  (7 min) treatment time. These energy requirements also increased in the absence of the Ti electrode, with  $0.028 \text{ kWh/m}^3$  for  $82 \pm 6\%$  P (3 min) to  $0.19 \text{ kWh/m}^3$  for  $98 \pm 3\%$  removal (20 min). Considering the balance of energy consumption and nutrient removal, a 5-min treatment provided the best balance in phosphate removal (98%), and energy demand ( $0.0039 \text{ kWh/m}^3$ ) for the Fe-MEAEC.

For treatment of the secondary clarifier wastewater, phosphate removals using the iron sacrificial electrode and Ti inert electrode in MEAEC system were all improved relative to the controls (no Ti electrode) or with the aluminum electrode. For example, at an initial phosphate concentrations  $2.4 \pm 0.1 \text{ mg/L}$ , 98% P removal was achieved with an energy consumption of  $0.023 \text{ kWh/m}^3$  for iron electrode in 3 min using the iron electrode in the MEAEC, compared to  $0.043 \text{ kWh/m}^3$  for a longer 5 min tests using the Al electrode. The energy demand of the controls was much larger, for example,  $0.08 \text{ kWh/m}^3$  for 87.5% phosphate removal using the Fe electrode in 10 min, compared to  $0.09 \text{ kWh/m}^3$  for 90% phosphate removal using the Al electrode (see Table 2).

These energy requirements of MEAEC system to treat primary clarifier wastewater with the iron sacrificial anode and the Ti inert electrode were all less than those reported in other EC studies using Al or Fe electrodes (Table 3). For secondary clarifier wastewater treatment, which contained lower concentrations of phosphate and organic matter, the MEAEC system also achieved a good level of phosphate removal as it required much shorter treatment times than those reported in previous studies (Irdemez et al., 2006a, 2006b, 2006c; Rodrigo et al., 2010).

## 4. Conclusions

A low energy consumption, high phosphate removal efficiency MEAEC process was developed by using a three electrodes reactor, containing a sacrificial Fe anode, air cathode, and an inert Ti electrode. The inert electrode material comparison showed that the Ti electrode was more durable and stable than a graphite electrode. By setting inert electrode potentials to drive phosphate ions toward the reactor sacrificial anode, electrocoagulation times were reduced using the MEAEC process compared to electrocoagulation

**Table 3**

Energy consumption of electrocoagulation and removals of phosphorus, nitrogen, COD and TSS reported in different studies using Fe or Al electrodes.

| Electrodes                      | Wastewater type | Energy ( $\text{kWh/m}^3$ ) | Current density ( $\text{mA/cm}^2$ ) | Phosphate Removals (%) | Reference               |
|---------------------------------|-----------------|-----------------------------|--------------------------------------|------------------------|-------------------------|
| Al and Fe                       | Synthetic       | 22                          | 1                                    | 97                     | (Irdemez et al., 2006a) |
| Al and Al                       | Urban           | 4.5                         | 1                                    | 99                     | (Rodrigo et al., 2010)  |
| Al and Fe                       | Synthetic       | 0.76                        | 16                                   | 98                     | (Chen et al., 2014)     |
| Al, Air–cathode, Graphite sheet | Domestic        | 0.4–9.9                     | 0.6–1.2                              | 97–99                  | (Tian et al., 2016)     |
| Al, Air–cathode, Graphite sheet | Domestic        | 0.05–0.14                   | 1                                    | 85–98                  | (Tian et al., 2017)     |
| Al, Air–cathode, Titanium sheet | Domestic        | 0.009–0.06 Al–MEAEC         | 1                                    | 71–98                  | This study              |
| Fe, Air–cathode, Titanium sheet | Domestic        | 0.007–0.039 Fe–MEAEC        | 1                                    | 76–98                  | This study              |

with an air cathode in the absence of the inert electrode. The electric-field generated using the inert electrode achieved a localized accumulation of target ions near the sacrificial anode, which subsequently improved phosphate ion removal, especially for low influent phosphate concentrations. The iron electrode produced better phosphate removals than the aluminum electrode for treating both primary and secondary clarifier effluents. Based on a balance of treatment time, energy usage, and P removal, the optimal MEAEC system operation would be using the iron electrode with a 5-min treatment time (and five 10 s intervals for the inert electrode working time), at a fixed current density of 1 mA/cm<sup>2</sup>. These conditions could achieve 98% phosphate removal with a low energy consumption of 0.039 kWh/m<sup>3</sup>, which was substantially lower than that reported in previous studies. In addition, the production of the sediment enriched in Fe would be preferred than that containing the more toxic Al species. The use of the Fe sacrificial anode also decreased the cost of treatment because the price of Fe (910 RMB/t) is over 20 times less than that of Al (19000 RMB/t) in China. Based on the success of this laboratory study, it is recommended that a MEAEC system be further investigated at larger scales to see if the low energy consumption could be maintained with larger electrode dimensions.

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## Appendix A. Supplementary data

Supplementary data related to this article can be found at <https://doi.org/10.1016/j.watres.2018.03.037>.

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