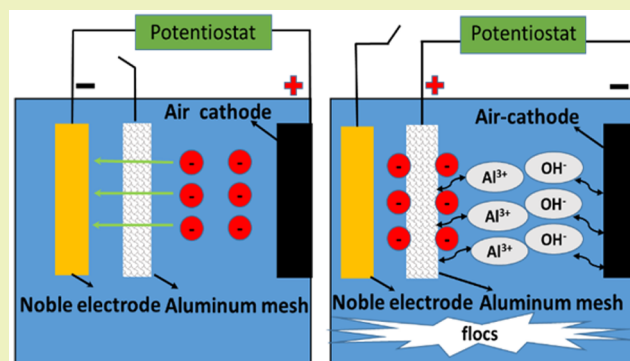


## Improved Electrocoagulation Reactor for Rapid Removal of Phosphate from Wastewater

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**ABSTRACT:** A new three-electrode electrocoagulation reactor was investigated to increase the rate of removal of phosphate from domestic wastewater. Initially, two electrodes (graphite plate and air cathode) were connected with 0.5 V of voltage applied for a short charging time (~10 s). The direction of the electric field was then reversed, by switching the power supply lead from the anode to the cathode, and connecting the other lead to a sacrificial aluminum mesh anode for removal of phosphate by electrocoagulation. The performance of this process, called a reverse-electric field, air cathode electrocoagulation (REAEC) reactor, was tested using domestic wastewater as a function of charging time and electrocoagulation time. REAEC wastewater treatment removed up to 98% of phosphate in 15 min (inert electrode working time of 10 s, current density of 1 mA/cm<sup>2</sup>, and 15 min total electrocoagulation time), which was 6% higher than that of the control (no inert electrode). The energy demand varied from 0.05 kWh/m<sup>3</sup> for 85% removal in 5 min, to 0.14 kWh/m<sup>3</sup> for 98% removal in 15 min. These results indicate that the REAEC can reduce the energy demands and treatment times compared to conventional electrocoagulation processes for phosphate removal from wastewater.

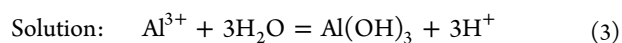
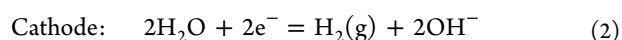
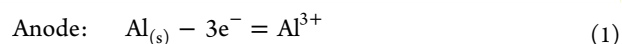
**KEYWORDS:** Energy efficiency, Wastewater Treatment, Electrocoagulation, Air cathode, Aluminum electrode, Ion mobility



## ■ INTRODUCTION

Anaerobic bioreactors, such as anaerobic fluidized bed reactors, anaerobic membrane bioreactors, and microbial fuel cells (MFCs), are being increasingly investigated for removal of the organic matter from wastewater.<sup>1–4</sup> However, effluents from these reactors still have high phosphorus concentrations in the form of orthophosphate, polyphosphate and organic phosphate.<sup>5</sup> The wastewater must be further treated to remove the phosphorus to low levels to avoid stimulating eutrophication of receiving water bodies.<sup>6,7</sup> These anaerobic systems will therefore require additional treatment processes in order to achieve nutrient removal.<sup>8</sup>

Electrocoagulation (EC) has been successfully applied to removal of nutrients and other pollutants from different types of wastewaters,<sup>9–16</sup> such as orthophosphate and boron from synthetic wastewater,<sup>17–19</sup> degradation of disperse red 167 in textile industry wastewater,<sup>20</sup> and remediation of hydrofluoric wastewater.<sup>21</sup> EC is a process where metallic hydroxide ion flocs are produced by electrocoagulation of sacrificial anodes typically made of iron or aluminum<sup>11,22–27</sup> because these materials are cheap, readily available, and effective coagulants. When aluminum ions are released into the water, they form hydroxides that can then react with phosphate to form precipitates of AlPO<sub>4</sub>, according to the following:<sup>28</sup>

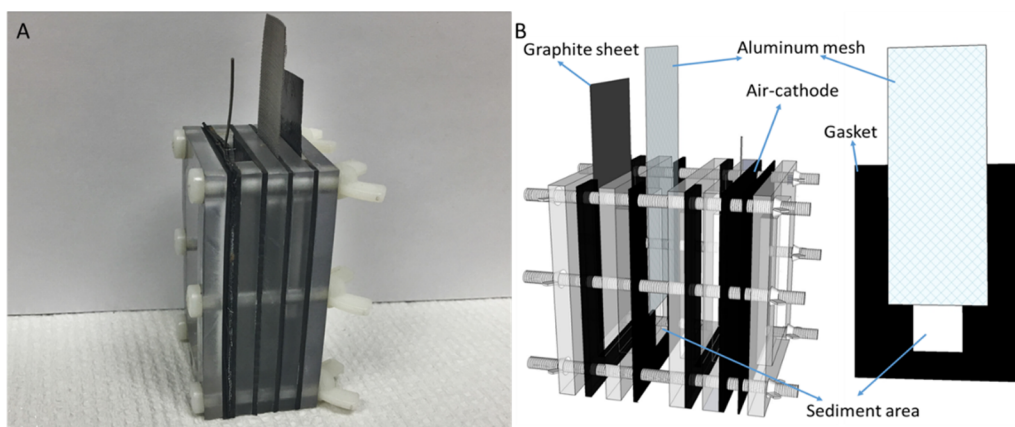


The high energy requirements of EC is one of the main disadvantages of this process.<sup>15,16,29,30</sup> Using an air cathode instead of a metal electrode has been shown to reduce the energy requirements for EC, as the reaction at the cathode is favorable due to oxygen reduction rather than hydrogen evolution. The use of a passive air cathode also uses less energy than that needed for oxygen reduction based on electrodes using dissolved oxygen due to the high energy demands needed for gas sparging.<sup>27</sup> Inexpensive air cathodes have been developed for MFC applications due to the use of activated carbon as the catalyst.<sup>30,31</sup>

**Received:** July 12, 2016

**Revised:** October 23, 2016

**Published:** November 1, 2016



**Figure 1.** (A) Photo and (B) schematic diagram of the electrocoagulation reactor with an air cathode.

A new type of EC process, called a reverse-electric field, air cathode electrocoagulation (REAEC) process was developed to improve removal and energy efficiencies of EC nutrient removal. The REAC process is different from a conventional EC process as it contains a graphite plate electrode that is charged prior to treatment, so that less time and energy is subsequently needed for EC treatment. The REAC reactor also contained an aluminum mesh electrode as the sacrificial anode, and an air cathode that has been shown to reduce energy demands compared to that needed for hydrogen evolution at the cathode. The reactor was operated by applying a voltage of 0.5 V across the graphite plate anode and air cathode for a short time to polarize the electrodes and draw positively charged ions to the graphite electrode, and negatively charged ions to the cathode (charging phase). The direction of the electric field was then reversed, by switching the anode lead to the air cathode, and then connecting the other end of the circuit to the sacrificial aluminum mesh anode (EC treatment phase). During this subsequent EC treatment time, aluminum was oxidized to produce aluminum hydroxides and aluminum phosphate particles that subsequently settled out and were removed. The impact of inert electrode working time and subsequent electrocoagulation was examined relative phosphate removal, and compared to a control lacking the inert electrode. To reduce the impact of particles on the electrodes, the reactor was designed with a sedimentation zone to remove particles produced during the electrocoagulation process.

## MATERIALS AND METHODS

**Electrode Materials and Reactor Construction.** REAC reactors were constructed based on a previous EC system design that<sup>29</sup> consisted of a 40 mL electrolyte chamber and an air cathode, but no charging (graphite) electrode. The sacrificial anode was a single piece of aluminum mesh (mesh size 200 per 2.54 cm, wire diameter 0.053 mm, opening 0.074 mm; TWP Corporation). Cathodes contained an activated carbon catalyst, and were made by a continuous rolling and press process, using a polytetrafluoroethylene (PTFE) binder, and a PTFE/carbon black diffusion layer to avoid water leakage, as previously described.<sup>30</sup> The surface areas of the electrodes were: cathode, 18 cm<sup>2</sup> (6 cm × 3 cm); aluminum mesh anode, 15 cm<sup>2</sup> (5 cm × 3 cm), and graphite plate, 21 cm<sup>2</sup> (7 cm × 3 cm). The charging electrode was a graphite sheet (>99% carbon, <1000 ppm sulfur, <10 ppm leachable chloride, 0.127 mm thick; Beyond Materials, Inc.).

REAEC reactors were built from polycarbonate plates (0.5 cm × 5 cm × 8 cm) cut to produce an inner chamber (6 cm × 3 cm), with the plates separated by rubber gaskets 0.1 cm wide (Figure 1). The

distance between the aluminum mesh anode and the air cathode was set at 1.5 cm based on previous optimization tests.<sup>27</sup> The aluminum mesh was inserted into a u-shaped polycarbonate plate with a reaction area (6 cm × 3 cm) and a sedimentation zone (1 cm × 1 cm) on the bottom. The inert electrode was inserted in a u-shape polycarbonate plate (7 cm × 3 cm) 2 cm from the air cathode. The plates were connected using plastic screws.

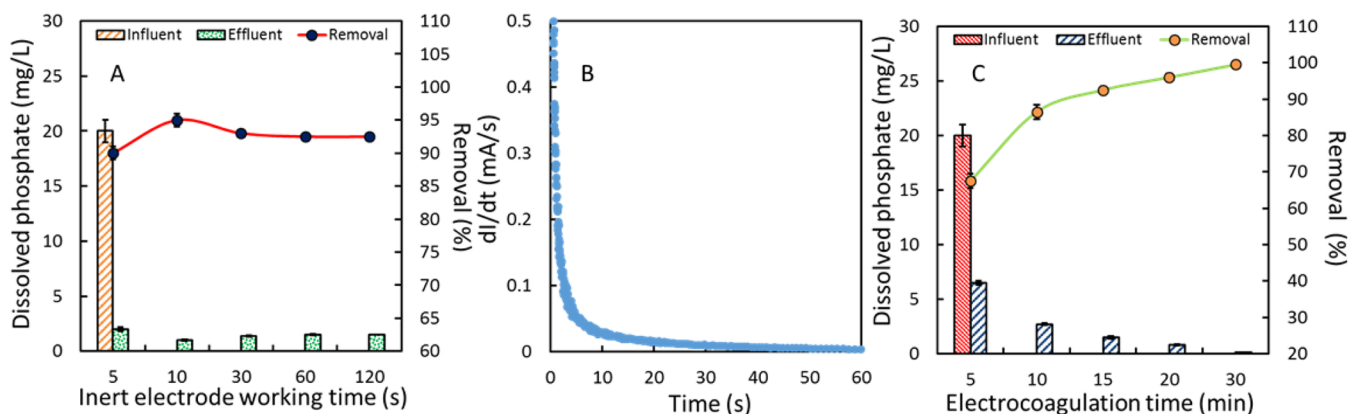
**Reactor Operating Conditions.** Wastewater was collected from the primary clarifier at the Penn State Wastewater Treatment Plant and stored at 4 °C. The wastewater had a pH of 7 ± 2, conductivity of 1.2 ± 0.1 mS/cm, and a dissolved phosphate concentration of 20 ± 1 mg/L. All reactors were operated in fed-batch model.

Treatment of domestic wastewater was examined as a function of different inert electrode working times (inert electrode connected to the air cathode) and electrocoagulation times (aluminum anode connected to the air cathode), with voltages or current set using a potentiostat (VMP3; BioLogic, Claix, France). Voltage was applied during to the inert electrode circuit with the inert electrode connected to the negative lead of the power supply. The direction of the current was then switched during the electrocoagulation period with the positive lead from the power supply connected to the cathode. Inert electrode working times were set at 10, 30, 60, and 120 s with a constant applied voltage of 0.5 V, followed by a fixed electrocoagulation time of 10 min at 1 A/cm<sup>2</sup>. Control tests (no inert electrode operation) were conducted using wastewater with only electrocoagulation times of 5, 10, 15, 20, and 30 min to determine the time needed to achieve similar removals compared to inert electrode tests.

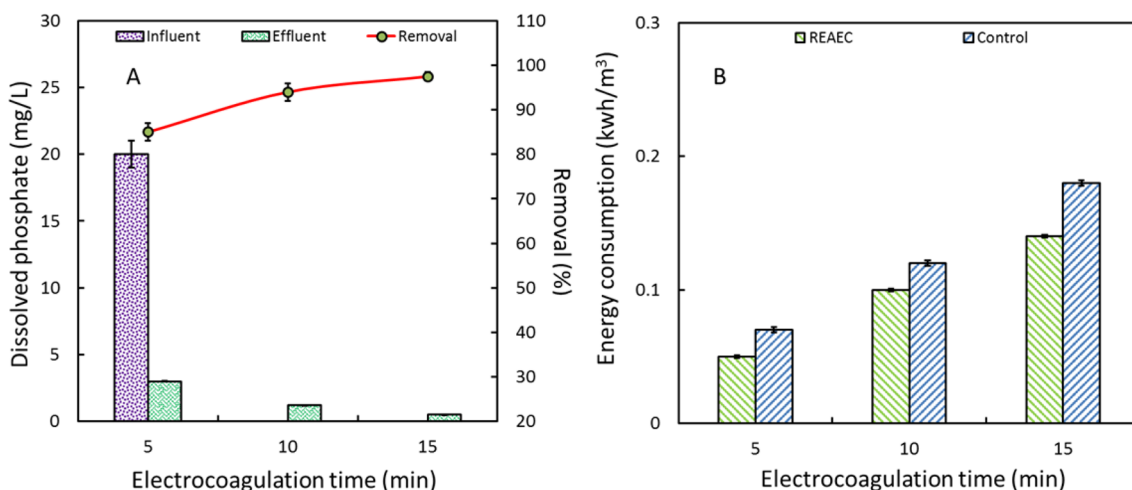
The impact of electrocoagulation on phosphate removal and energy utilization was compared with a set inert electrode time of 10 s, with electrocoagulation times of 5, 10, and 15 min. Following each electrocoagulation period, the particles were allowed to settle in the reactor for 1 h (no applied current). Cathodes were cleaned after 20 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 30 °C, with averages reported ± a standard error.

**Solution Measurements and Calculations.** All samples were filtered through 0.45 μm pore diameter syringe filters (polyvinylidene difluoride, PVDF, 25 mm diameter; Restek Corporation) and analyzed for phosphate using standard methods (method 8190, HACH Company, Loveland, CO).<sup>32</sup> Removals were calculated based on initial and final concentrations. A probe (SevenMulti, Mettler-Toledo International Inc.) and meter (SevenMulti, Mettler-Toledo, OH) were used to measure solution pH and conductivities.

Voltage and the counter electrode potentials were recorded at 10 s intervals, and analyzed using the potentiostat software (EC-Lab V10.02). Energy consumption,  $W$  (kWh/m<sup>3</sup>), was calculated for the electrocoagulation period as  $W = UIt/\nu$ , where  $U$  is the voltage (V),  $I$  the current (A),  $t$  the electrocoagulation time (h), and  $\nu$  the volume



**Figure 2.** (A) Phosphate removal using the REAEC system, as a function of the inert electrode working time for a fixed 10 min electrocoagulation time (current density 1 mA/cm<sup>2</sup>). (B) Derivative of the current as a function of the inert electrode working time at a fixed applied voltage (0.5 V). (C) Phosphate removal in the control lacking an inert electrode, at different electrocoagulation times at a fixed current density of 1 mA/cm<sup>2</sup>. (Phosphate concentrations shown are after 1 h of settling time.)



**Figure 3.** (A) Phosphate concentration and (B) energy requirements for REAEC system (10 s fixed inert electrode working time) versus the control (no inert electrode) as a function of electrocoagulation time (fixed current density of 1 mA/cm<sup>2</sup>; phosphate concentrations shown are after 1 h of settling time).

(m<sup>3</sup>). The power ( $P = UI$ ) to polarize the inert electrode was not included in this calculation, as there was only a minor current.

## RESULTS AND DISCUSSION

Polarization of the inert electrode for 5 s, followed by a fixed 10 min electrocoagulation time and settling, resulted in removal of  $90 \pm 1\%$  of the phosphate in the wastewater, and  $95 \pm 2\%$  for 10 s. Phosphate removal was not further improved by using longer inert electrode polarization times of up to 120 s (Figure 2A). The lack of an impact of longer inert electrode operation times was likely due the nearly constant circuit potentials after  $\sim 10$  s, as shown by a plot of the first derivative of the current (Figure 2B). The energy used to polarize the inert electrode was very low, as the current in the inert electrode circuit after 120 s was only 0.01 mA/cm<sup>2</sup>.

The performance of the REAEC system was compared to a control reactor lacking an inert electrode, at the same fixed current density of 1 mA/cm<sup>2</sup>. Phosphate removals increased from  $67 \pm 2\%$  with a 5 min treatment time to  $87 \pm 1\%$  for the same 10 min period used in the REAEC tests (Figure 2C). Longer treatment times increased removals, with  $98 \pm 1\%$  phosphate removal achieved after 30 min of electrocoagulation. Based on the percentage removal line shown in Figure 2C,

approximately twice the treatment time (20 min) would be needed to achieve the same removal as the REAEC reactor in 10 min.

These results indicate that a short period of only  $\sim 10$  s was needed to polarize the inert circuit electrodes, and greatly improved performance of the REAEC system compared to a typical electrocoagulation process. By switching the direction of the ionic current flow in the electrolyte, the subsequent electrocoagulation process was more effective, likely due to the migration of the negatively charged phosphate ions toward the aluminum electrode.

**Treatment Times and Energy Requirements.** Treatment of the REAEC process was further examined at two other total electrocoagulation times, with a fixed inert electrode time of 10 s. The phosphate removal was  $85 \pm 2\%$  for a shorter treatment time of 5 min, and  $95 \pm 2\%$  for a 10 min time (Figure 3A). Phosphate removal further increased to  $98 \pm 1\%$  when for a 15 min treatment time (Figure 3A), which was about half the time needed by the control (Figure 2C) for the same percentage of phosphate removal.

The energy used for treating domestic wastewater using the REAEC ranged from 0.05 kWh/m<sup>3</sup> for 85% phosphate removal at a 5 min electrocoagulation time, to 0.14 kWh/m<sup>3</sup> for 98%

**Table 1. Energy Consumption of Electrocoagulation and Removals of Phosphorus, Nitrogen, COD, and TSS Reported in Different Studies Using Fe or Al Electrodes**

electrode type	wastewater type	energy (kWh/m <sup>3</sup> )	current density (mA/cm <sup>2</sup> )	phosphate removals (%)	reference
Al and Fe	synthetic solution	22	1	97	33
Al and Al	urban wastewater	4.5	1	99	34
Al and Fe	synthetic solution	0.76	16	98	35
Al and air cathode	domestic wastewater	0.4–9.9	0.6–1.2	97–99	27
graphite sheet, Al and, air cathode	domestic wastewater	0.05–0.14 0.07–0.18 (control)	1 1	85–98 67–92	this study this study

removal of phosphate for a 15 min electrocoagulation time (Figure 3). The energy requirement of the REAEC with a 10 s inert electrode working time was generally less than those reported in other studies using two metal electrodes (Al and Fe, or Al and Al), or an Al anode and air cathode (Table 1). In addition, the REAEC system required lower energy consumption compared to the controls, with 0.1 kWh/m<sup>3</sup> required for the control 0.12 kWh/m<sup>3</sup> in 10 min, and 0.14 kWh/m<sup>3</sup> for the control with 0.18 kWh/m<sup>3</sup> in 15 min (Figure 3B). Thus, the use of this system reduced the time and energy needed for phosphate removal using an electrochemical reactor with a sacrificial aluminum electrode.

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### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

This work was supported in part by the Strategic Environmental Research and Development Program (SERDP), Award OSR-2015-SEED-2450-01 from the King Abdullah University of Science and Technology (KAUST), the State Key Laboratory of Urban Water Resource and Environment (Harbin Institute of Technology) (No. 2013DX01), and a scholarship from the China Scholarship Council (CSC).

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