Energy efficient electrocoagulation using an air-breathing cathode to remove nutrients from wastewater

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Highlights

• First application of an air-breathing cathode for electrocoagulation (EC).
• Energy reduced for treatment due to lack of a need for wastewater aeration.
• High efficiency in the removal of nutrients from wastewater.
• Design allows for a compact, stackable and modular configuration.

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Abstract

Electrocoagulation (EC) can be used to remove nutrients as well as suspended solids and organic carbon from wastewaters, but the high energy requirements (pumping air) and the use of precious metals in some processes has hindered widespread application of EC technologies. The use of a thermodynamically favorable activated carbon air cathode and a sacrificial aluminum anode was examined to reduce the energy needed for EC for nutrient removal. Performance of the air cathode electrocoagulation (ACEC) process was tested using raw wastewater, and a carbon-free synthetic solution (nitrogen:phosphorus ratio of 1:10 in deionized water) to simulate nutrient removal of a wastewater treated for organic matter removal. ACEC treatment of wastewater removed up to 99% of both ammonia and phosphorus, along with 72–81% COD and 78–89% TSS in 4 h (1.5 cm electrode spacing, current density of 8 A m⁻²). Nearly total removal of the nutrients required 1.8 kWh m⁻³, which is lower than that previously reported for some EC processes for this application (0.4–22 kWh m⁻³). Nutrient removals using synthetic solutions (no organic matter) ranged from 74% to 93% for nitrogen (47–370 mg-N/L) and 44–76% for phosphorus. These results indicate that the ACEC can achieve good levels of nutrient removal with reduced energy demands compared to previous EC systems.

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1. Introduction

In recent years, there has been great interest in the development of completely anaerobic treatment processes, such as anaerobic fluidized bed reactors, anaerobic membrane bioreactors [1–3] and microbial fuel cells (MFCs) [4]. While these processes can be used to remove organic matter, there is little nutrient (nitrogen and phosphorus) removal in these processes. Therefore, effective processes that can be coupled to these anaerobic systems are needed in order to achieve nutrient removal [5].

Electrocoagulation (EC) is an electrochemical process that can be used to treat wastewaters in terms of both organic matter and nutrient removal [6,7]. The process is based on the use of sacrificial electrodes such as aluminum, iron, and zinc [8–11] that are oxidized to produce metal ions that can be used to coagulate and react with organic matter and nutrients in the wastewater. When current is applied, the metal ions that are produced react with primary hydroxides and produce polyhydroxy-metallic flocs [12]. When aluminum is used as the sacrificial electrode material, the primary chemical species that are produced under typical alkaline (pH of 7.5–9) or acidic (pH 3.5–6) conditions at the anode (20 °C) are:
where applied voltages are typically <0.81 V, and the temperatures are usually in the range of 25–50 °C reported. The flocs that form have a large surface area that can adsorb soluble organic compounds and trap colloidal particles in the wastewater [10]. Various metals have been examined to improve process performance [13], but commonly aluminum or iron is used [8,14–18] due to the good performance of these metals for domestic and textile wastewaters, as well as for pesticides and arsenic [18–20].

While EC processes are effective for treatment of many types of wastewaters, applications have been limited due to high energy demands and high current densities. Examples include: oil in wastewater at 25 mA cm$^{-2}$ [21] and 4–30 mA cm$^{-2}$ [22], berberine hydrochloride removal from a pharmaceutical factory wastewater at 19 mA cm$^{-2}$ [23], food wastes from restaurants at 30–80 A m$^{-2}$ [24], 50–200 A m$^{-2}$ for hexavalent chromium treatment in an industrial wastewater [25], heavy metal ions removal from a metal plating wastewater at 4 mA cm$^{-2}$ with 6.3 kWh m$^{-3}$ energy consumption [26], EC has also been used for drinking water treatment to remove hardness and fluoride, but at very high applied voltages of 24 V, with 22 A m$^{-2}$ and a treatment time of 1 h [27,28]. The advantage of the EC process is that treatment can be accomplished without the need for additional chemicals or pre-treatment, but energy costs need to be reduced for EC processes to become more applicable.

The cathodic reaction in an EC process is usually hydrogen evolution, or oxygen reduction supported by wastewater aeration. Both of these approaches require energy that is not intrinsically part of the treatment process. Hydrogen evolution is thermodynamically unfavorable, and requires a cathode potential of −0.414 V under standard conditions [29]. While oxygen reduction is thermodynamically favorable, the production of dissolved oxygen requires aeration, which is an energy consuming process. For example, wastewater aeration in an activated sludge process consumes about 0.6 kWh m$^{-3}$ [30]. Air cathodes are commonly used in many types of electrochemical systems such as hydrogen fuel cells and microbial fuel cells (MFCs) [31,32], to provide oxygen to the cathode. The use of an air cathode avoids energy losses due to aeration, while providing a favorable reaction at the cathode. However, air cathodes have not been previously examined for nutrient removal from wastewater using an air cathode electrocoagulation (ACEC process). Air cathodes developed for MFC applications do not need to use precious metal catalysts. Instead, inexpensive activated carbon can be used, with the cathode made using various press or rolling methods [33,34]. The impact of the reactor configuration, such as electrode spacing, operational conditions, and treatment time, were examined using two solutions: domestic wastewater, which contains high concentrations of residual organic matter; and a simulated treated wastewater, prepared by adding ammonia and phosphorus to deionized water, to examine the impact on nutrient removal in the absence of organic matter. Aluminum mesh anodes were used to produce a higher active surface than flat plate electrodes. Power requirements were examined for different operational conditions to achieve high nutrient removals while minimizing power consumption.

2. Materials and methods

2.1. Reactor construction

Cube-shaped ACEC reactors were constructed based on a previous design [35] and contained a 3 cm diameter electrolyte chamber and an air cathode. Reactor lengths of 0.5, 1, 1.5, and 2 cm were used to examine the impact of electrode spacing on performance, with the electrodes placed on opposite ends of the chamber (Fig. 1). The reactive surface area of each electrode was 7 cm$^2$.

2.2. Solutions

Wastewater was collected from the primary clarifier of the Penn State Wastewater Treatment Plant and stored at 4 °C. The wastewater had a pH of 7–7.2, and contained 490 ± 10 mg L$^{-1}$ COD, 200 ± 6 mg L$^{-1}$ TSS, an ammonia concentration of 52 ± 4 mg-N L$^{-1}$, and a total phosphorus concentration of 3 ± 0.1 mg-P L$^{-1}$. The ratio of N:P in this wastewater was 17:1, and many wastewaters often have a total nitrogen concentration about ten times that of phosphorus. The solution used to simulate treated wastewater was prepared by adding NH$_4$Cl and NaH$_2$PO$_4$·H$_2$O (Sigma Aldrich) to deionized water at an initial N:P ratio of 10:1, at four different
initial concentrations of 50, 125, 250, 500 mg-N L\(^{-1}\) (5, 12.5, 25, 50 mg-P L\(^{-1}\)).

2.3. Reactor operating conditions

To select an appropriate operation time based on stable current, the reactor was operated in continuous flow at a hydraulic retention time (HRT) of 1 h using a peristaltic pump (Cole Parmer, USA), at a voltage of 0.5 V set using a potentiostat (VMP3; BioLogic, Claux, France), at an electrode spacing of 1.5 cm. In all other tests, the reactor was operated in fed-batch mode. To evaluate the impact of electrode spacing distance on performance, the electrode spacing was varied from 0.5 to 2 cm (based on electrode distances used in previous studies) [37–39].

Treatment of domestic wastewater was examined at electrolysis times ranging from 0.5 to 6 h (0.5 V applied voltage, 1.5 cm electrode spacing). Treatment efficiency was further examined at various current densities at a fixed electrolysis time under constant current density operation mode. Synthetic wastewater without the electrode spacing). Treatment efficiency was further examined at various current densities at a fixed electrolysis time under constant current density operation mode. Synthetic wastewater without the presence of other ions and suspended solids was examined for the current density operation mode. Synthetic wastewater without the presence of other ions and suspended solids was examined for the current density operation mode. Synthetic wastewater without the presence of other ions and suspended solids was examined for the current density operation mode. Synthetic wastewater without the presence of other ions and suspended solids was examined for the current density operation mode. Synthetic wastewater without the presence of other ions and suspended solids was examined for the current density operation mode.

2.4. Solution measurements and calculations

Total suspended solids (TSS) were measured using standard methods [40]. Total COD was measured using method 5220 (HACH Company, Loveland, CO). For nutrient measurements, all samples were filtered through 0.45 µm pore diameter syringe filters (polyvinylidenedifluoride, PVDF, 25 mm diameter; Restek Corporation) and analyzed using Method 10031 (HACH Company, Loveland, CO) for NH\(_4\)–N, and Method 10127 (HACH Company, Loveland, CO) for P–PO\(_4\)\(^3\) [40]. 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.

Energy consumption \(W\) (kWh m\(^{-3}\)) for EC treatment of wastewater was calculated as \(W = UIt/v\), where \(U\) is the voltage (V), \(I\) the current (A), \(t\) the electrolysis time (h), and \(v\) the volume (m\(^3\)).

3. Results and discussion

3.1. Current generation as a function of time and electrode spacing

Current production examined over time in continuous flow mode (1.5 cm electrode spacing, 1 h HRT) showed that there was an initial rapid decrease in current from 7.5 to 5.8 mA over the first 0.6 h, and that current was relatively constant at 6.0 ± 0.5 mA for the next 6.4 h (Fig. 2A). The subsequent decline in current at longer treatment times was likely due to losses of aluminum from the small mesh anode used in these tests (Fig. 2A). Therefore, a working time of 4 h was chosen for subsequent fed-batch tests to ensure uniform operational conditions.

Changing the electrode spacing from 0.5 to 1 cm improved the current density, but larger electrode distances (1.5 and 2 cm) reduced current (applied voltage of 0.5 V) (Fig. 2B). The stability of the current generated was also affected by the electrode spacing, with the smallest variation in current (±0.5 mA) obtained with a 1.5 cm electrode spacing. As a result, an electrode spacing of 1.5 cm was used in all subsequent tests to minimize variations in anode performance. Salt precipitates were observed on the cathode following these tests. These salts were removed by intermittent soaking of the cathode in an acid solution.

3.2. Wastewater treatment at a fixed applied voltage

The effectiveness of the ACEC for nutrient, COD, and TSS removal was examined using domestic wastewater at electrolysis times ranging from 0.5 to 6 h (fixed applied voltage of 0.5 V). There was a nearly linear decrease in ammonia, COD, and TSS with electrolysis time, while phosphate removal increased more rapidly, with smaller changes in concentrations at the longer treatment times (Fig. 3). Overall changes in concentrations varied from: 15–88% for NH\(_4\)–N, 50–99% for PO\(_4\)\(^3\)–P, 51–71% for COD, and 22–77% for TSS. The current densities varied over a relatively small range of 6–6.7 A m\(^{-2}\) in these fixed-voltage tests. These results show that there was an increase in the total nitrogen and phosphorus removal over time, with nearly complete phosphorus removals at the longer treatment times. Thus, after only 2 h there was nearly 93% removal of phosphorus to a concentration of only 0.2 mg L\(^{-1}\), compared to 40% of nitrogen removal to 31 mg L\(^{-1}\). After 6 h, there was 88% removal of nitrogen.

3.3. Wastewater treatment at constant current

Treatment was further examined under conditions of a fixed current density over the cycle of 6 A m\(^{-2}\) (similar to that obtained at a fixed voltage) to 12 A m\(^{-2}\) (Fig. 4). Higher current densities...
improved removal of all wastewater constituents, with phosphate removal increased from 95% to 99% when the current density was increased from 6 to 8 A m\(^{-2}\), and NH\(_4^+\)-N removal increased from 79% to 96%. Lower removals were achieved for organic matter and solids, with 81% removal of COD, and 89% removal of TSS. The use of current densities in the range of 8–12 A m\(^{-2}\) did not substantially improve removals. Therefore, these results showed that a current density of 8 A m\(^{-2}\) was sufficient for achieving good nutrient removals from domestic wastewater at a treatment time of 4 h.

Fig. 3. Removals as a function of electrolysis time using domestic wastewater at a set voltage of 0.5 V, for: (A) NH\(_4^+\)-N, (B) PO\(_4^{3-}\)-P, (C) COD, and (D) TSS (1.5 cm electrode spacing).

Fig. 4. Performance of the ACEC at different fixed current densities using domestic wastewater for: (A) NH\(_4^+\)-N, (B) PO\(_4^{3-}\)-P, (C) COD, and (D) TSS (1.5 cm electrode spacing, 4 h electrolysis time).
3.4. Nutrient removal using synthetic wastewater

In order to examine possible impacts of COD and TSS on performance, nutrient removal was examined using nutrients added at different concentrations to deionized water, at a fixed N:P ratio of 10:1 (50–500 mg-N L\(^{-1}\), 5–50 mg-P L\(^{-1}\)). All other experiment conditions were similar to the experiments with the wastewater treatment (0.5 V voltage, 1.5 cm electrode spacing and 4 h electrolysis time). The lowest nutrient concentrations were similar to that of the domestic wastewater examined here (52 mg-N L\(^{-1}\), 3 mg-P L\(^{-1}\)). Ammonia removal (93%) at the lowest NH\(_4^+\)-N concentration was significantly higher than that achieved using the actual wastewater (75%), showing that the organic matter and TSS in the wastewater negatively affected nitrogen removal (Fig. 5). In addition to the removal of ammonium ions by the Al(OH)\(_3\), the fluid near the cathode can reach a high pH, which results in the conversion of NH\(_4^+\) to NH\(_3\) [41]. This formation of ammonia can therefore result in volatilization and loss of ammonia from the solution, which may have resulted in improved nitrogen removal here. This possible loss of ammonia by this mechanism will require further study.

Phosphorus removal (76%) at the lowest nutrient loading was much lower than that achieved with the wastewater (99%), indicating the presence of COD and TSS improved phosphorus removal. The greater removal of phosphorus in the wastewater samples suggests that the presence of suspended solids in the flocs was important for increasing removal of phosphorus. The higher removal of phosphate in wastewater compared to synthetic water indicates phosphate was present largely in insoluble form and the soluble phosphate was mainly removed by precipitation followed by inclusion into the flocs containing TSS.

Higher initial nutrient concentrations resulted in lower removal (Fig. 5), with ammonia removals decreased from 93% to 75% and phosphorus removal decreased from 76% to 45%. Due to higher conductivity at higher nutrient concentration, flocs were more readily formed and accumulated at the bottom of the reactor, creating a larger local current between anode and cathode. As a result, more anode mass was consumed to generate precipitates depositing on air cathode, hindering oxygen transfer. In addition, future improvement on reactor configuration can be made to increase the removal efficiency for high nutrient loading wastewater.

3.5. Energy consumption

Nutrient removal increased with applied current, although this increased the energy consumed. The energy used for treating domestic wastewater in the set current tests ranged from 0.4 kWh m\(^{-3}\) (6 A m\(^{-2}\)) for 79% N removal and 95% P removal, to 9.9 kWh m\(^{-3}\) (12 A m\(^{-2}\)) for 99% removal of both N and P (Fig. 6). Considering the balance of energy consumption and nutrient
removal, a current density of 8 A m$^{-2}$ provided a good balance in nutrient removal (96% ammonium ion removal, and 98% phosphate removal), and energy demand (1.8 kWh m$^{-3}$).

For tests without high concentrations of organic matter, at nutrient concentrations (52 mg-N L$^{-1}$ and 3 mg-P L$^{-1}$) similar to wastewater, the energy demand was 0.4 kWh m$^{-3}$ (fixed applied voltage of 0.5 V, average current density of 6.2 A m$^{-2}$). Nutrient removals (93% N and 76% P removal) in this test were similar to that obtained in the fixed current tests at 6 A m$^{-2}$. Energy demands increased with higher initial nutrient concentrations, with 0.5 kWh m$^{-3}$ for 125:12.5 mg L$^{-1}$ tests (N:P), up to 2.33 kWh m$^{-3}$ for the 500:50 mg L$^{-1}$ nutrient concentrations (Fig. 7). The higher energy demands were likely due to higher electrode overpotentials with the increased concentrations of precipitates formed in the tests.

These energy requirements of the ACEC using air cathodes at the lower current densities were generally less than those reported in other studies using Al and Fe or Al and Al electrodes (Table 1). When using a synthetic wastewater, which contained only phosphate, the percentages of nutrients removed here were similar to those obtained in these previous studies at similar initial nutrient concentrations. However, the ACEC system required less energy than these other studies with synthetic solutions. When the experiments were conducted using an actual wastewater the ACEC system removed more phosphorus, and at the same time removed ammonia, than that reported by others [42]. While phosphorus removals were high here and in previous studies (99%), the ACEC system consumed much less energy and had lower current densities than previous studies [9,43]. Moreover, the ACEC system showed excellent removal of ammonia, TSS, and COD in addition to phosphorus removal. In order to take into account all the relevant variables that impact power production and nutrient removal, it will be necessary in future studies to examine a wider range of variables, using a multivariate analysis, as done by others for evaluating other technologies [44–46].

4. Conclusions

The ACEC process based on using an air-breathing cathode achieved a nearly linear removal of nitrogen over time (up to 6 h), with a final removal of 88% of nitrogen, when operated at a fixed applied voltage of 0.5 V, average current density of 6.2 A m$^{-2}$. Phosphorus was removed to a greater extent, with 99% of P removed within 2 h. When the system was operated at a set current density of 8 A m$^{-2}$, rather than a fixed voltage, there was up to 99% PO$_4^{3-}$-P and NH$_4^+$-N removal, and 73% COD and 72% TSS removal, at a fixed operation time of 4 h. The energy requirement of 1.8 kWh m$^{-3}$ was lower than that reported in most previous studies, as the ACEC process did not require wastewater aeration or mechanical mixing. These results demonstrate that the ACEC system is a promising technology to remove nutrients from treated wastewater, as the process has both a high efficiency of nutrient removal, and low energy requirements.

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