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Electrolytic degradation of polyacrylamide in aqueous solution using a three-dimensional electrode reactor

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ABSTRACT

In this study, electrochemical treatment of a synthetic solution containing 2,000 mg/L of polyacrylamide (PAM) was studied using a three-dimensional electrode reactor, which received granular activated carbon (GAC) as particle electrodes. Air and ferrous salt were introduced into the system to electrogenerate hydrogen peroxide and Fenton's reactions. The effect of operating conditions such as solution pH, current density, ferrous concentration and GAC amount on the efficacy of the process was investigated. The experimental results showed that the effluent with a satisfied chemical oxygen demand removal efficiency (84%) was obtained after 60 min of electrolysis when the initial pH was 3.0, current density was 40 mA/cm^2, air flow = 1.5 L/min, pH = 3, [Fe^{2+}] = 1.5 mM, and temperature = 28℃. The analyses of five-day biochemical oxygen demand and Microtox® toxicity indicated that the optimum electrolysis duration was 30 min, at which satisfied biodegradability of wastewater was achieved. The three-dimensional electrode method can be selected as an effective alternative to PAM wastewater pretreatment before subjected to the biological process.

Keywords: Fenton's reaction; Ferrous salt; Nitrate; Microtox® toxicity

1. Introduction

Polyacrylamide (PAM) is widely used as soil conditioning agents, water purification flocculants, in crude oil production, etc. In China, PAM is widely used to enhance oil recovery; therefore, a large quantity of wastewater containing PAM is produced every year [1].

Due to the high viscosity and high oil content, some conventional treatments cannot give good results for oilfield wastewater containing PAM. Hence, effective treatment of wastewater containing PAM becomes a bottleneck in production and development in oilfields. Presently, advanced oxidation processes (AOPs) are usually used to degrade PAM and/or reduce the molecule weight of PAM so as to increase the bioavailability of pollutants. EL-Mamouni et al. [2] oxidized PAM with ultraviolet ray, finding that the treated PAM still has low characteristics of biologically chemical reactivity upto 17–29%. Lu et al. [1] compared the degradation efficiency of PAM by eight AOPs and found that the UV/Fenton with the addition of sodium tartrate was the optimum process for chemical oxygen demand (COD) removal in PAM solution. Moreover, the addition of NaCl in PAM solution has an adverse effect on the COD removal, but to a varying degree depending on the salt used. A zerovalent iron/EDTA/air system

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was applied by Lu et al. [3] to pretreating oilfield wastewater containing PAM, followed by the activated sludge treatment. The results showed that total removal efficiencies of 96 and 92% were obtained for PAM and COD, respectively.

Recently, as an important branch of AOPs, advanced electrochemical oxidation processes (AEOPs) have been chosen as a pretreatment or mineralization process for remediating wastewater containing bio-refractory or toxic organics. AEOPs based on three-dimensional electrode, put forward by Backhurst [4], have drawn many interests for the treatment of a variety of wastewaters such as refinery wastewater [5], dye wastewater [6], urban wastewater [7], and 2,4-dichlorophenol [8].

In this study, the feasibility of electrochemical oxidation of PAM in aqueous solution was studied using a three-dimensional electrode reactor. Influencing factors including filling amount of particle electrodes, current density, solution pH, and ferrous concentration on treatment efficiency were investigated.

2. Materials and methods

2.1. Materials

PAM was purchased from Beijing Chemical Reagent Co., Ltd., China, with an average molecule weight of 1.6×10^7 g/mol. Granular activated carbon (GAC) with a specific surface area of 900 m^2/g and an average pore diameter of 2.0 nm was purchased from Delong Chemical Plant, Hebei, China and used as the particle electrodes in the present study. Other reagents were of analytical grade. All solutions were prepared with high purity water.

2.2. Apparatus and procedure

The electrolytic treatment of PAM was conducted in an electrode reactor, whose schematic diagram is shown in Fig. 1. The reactor was made of polymethyl methacrylate with an effective volume of 9 L (30 cm × 20 cm × 15 cm). The main electrodes (30 cm × 10 cm) consisted of two anodes and one cathode, positioned vertically and parallel to each other with an inter-electrode gap of 5 cm. $Ti/SnO_2 + Sb_2O_3$ DSA®-type anodes ($Ti/Sb0.10Sn0.90O_2$) were employed as working electrodes, and the cathode was a 304-stainless steel mesh plate with a hole diameter of 2 mm. A certain amount of GAC was packed between the anode and cathode to form a three-dimensional electrode. Before treatment, GAC was exposed to 10 cycles of a batch experiment to preclude PAM removal due to its adsorption on the GAC. The average particle size and surface area of GAC were 2–4 mm and 985.3 m^2/g, respectively. Direct current was supplied from a regulated ZY200591BS power supply (Yongfeng Electronic Company, China), and the voltage was set to 18 V. Air was introduced into the reactor when needed. The reactor received 5 L of 0.2 wt% PAM solution (COD = 2,200 mg/L, containing a certain amount of $FeSO_4$), continuously stirred by means of a magnetic stirrer. The temperature was controlled at 28 ± 2°C during the experiment. The initial solution pH was adjusted to 3.0, 5.0, 7.0, and 9.0, respectively. At regular intervals, water samples were collected, filtered through 0.45 μm membrane filters (Millipore, USA), and analyzed. A summary of treatment is listed in Table 1. Each treatment was carried out in triplicate.

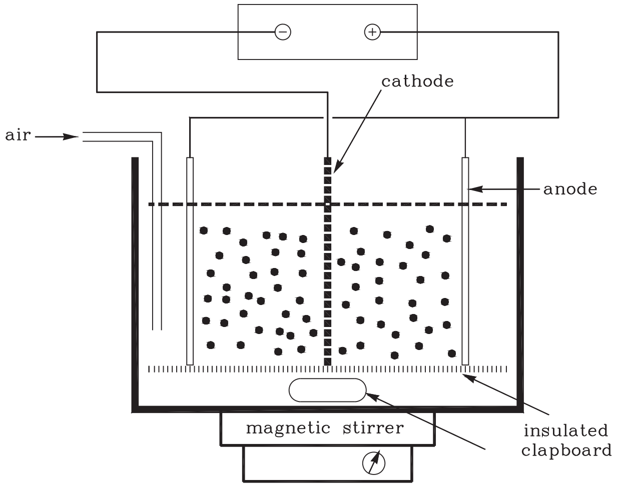

Fig. 1. Schematic diagram of the electrochemical reactor.

Table 1
Experimental set-up for the treatment of PAM-containing wastewater

Units	GAC	Stirring	Aeration
A	No	Yes	No
B	No	Yes	Yes
C	Yes	Yes	No
D	Yes	Yes	Yes

2.3. Analytical methods

The concentration of H_2O_2 was measured by a photometric DPD (N,N-diethyl-p-phenylenediamine) method ($\lambda = 551$ nm, $\in = 21{,}000\ M^{-1}$), in which the DPD reagent is oxidized by H_2O_2 based on the peroxidase-catalyzed reaction in a phosphate buffer (pH 6.8) [1].

To exclude the interferences of hydroxyl radicals and H_2O_2 in the following measurements, the pH of the collected effluents was increased above 11 with the addition of 6 M NaOH solution, and then an appropriate amount of Na_2SO_3 was added to the solution to decompose residual H_2O_2 and hydroxyl radicals in the treated solution [1,3]. Then the solution was shaken at 100 rpm for 1 h, to allow the oxygen in the air to dissolve into the solution and consume residual Na_2SO_3. COD was determined with $K_2Cr_2O_7$ and H_2SO_4 by the open reflux method with $AgSO_4$ as a catalyst. Excess dichromate was titrated with Fe^{2+} using phenanthroline as an indicator. The five-day biochemical oxygen demand (BOD_5) was determined via the oxygen consumption of bacteria breaking down organic matter in the sample over a five-day period under standardized conditions. The ratio of BOD_5 to COD (B/C) was adopted as a biodegradability index. The released NO_3^- ions were determined by ion chromatography with a Shim-pack IC-A3 chromatographic column.

Microtoxicity of effluents from the treatment process was measured by an SDI M500 analyzer (SDI, USA). Results were expressed as EC_{50} (15 min, 15°C), which was defined as the effective concentration of pollutant for a 50% reduction of the luminescence of the bacterium *Photobacterium phosphoreum*.

2.4. Energy consumption and instantaneous current efficiency

Energy consumption (EC) was calculated using Eq. (1) [5]:

$$\mathrm{EC} = \frac{UI\Delta t}{3.6V(\mathrm{COD}_t - \mathrm{COD}_{t+\Delta t})} \tag{1}$$

where EC is the energy consumption (KWh/kg COD), U is the cell voltage (volt), I is the current (amp), V is the volume of wastewater (L), COD_t and $\mathrm{COD}_{t+\Delta t}$ are the COD (g/L) at treatment time = t and $t + \Delta t$ (s), respectively.

2.5. Data analysis

All tests in this study were performed in triplicate, and results represented the average of three parallel experiments.

3. Results and discussion

3.1. Comparison of different treatment units

The effect of aeration on two- and three-dimensional systems for COD removal was investigated and the results are shown in Fig. 2(A). As can be seen, the highest COD removal was obtained for the three-dimensional aerated system, indicating that both GAC and aeration had influences on the electrochemical process. After 60 min, the COD removal efficiency reached 84% for unit D, whereas it was only 21, 25, and 62% for units A, B, and C, respectively. Compared with units A, B, and C, the COD removal efficiency for unit D was enhanced by 300, 236, and 35%, respectively. It can be found that, when air was introduced into both the two- and three-dimensional electrode reactors, the COD removal efficiency could be obviously enhanced.

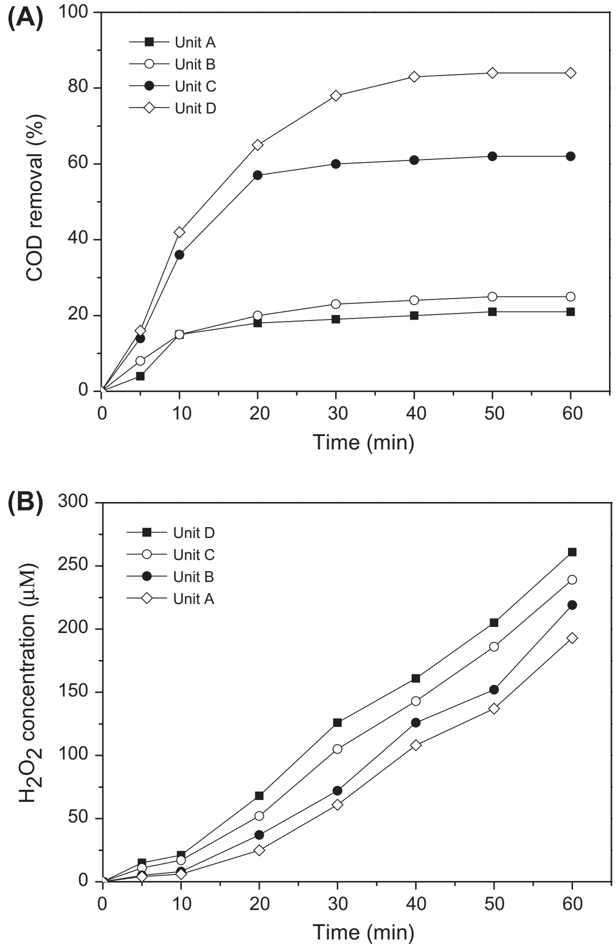

Fig. 2. Time course of (A) COD removal and (B) H_2O_2 concentration under different treatment conditions. Experimental conditions: filling amount of GAC = 100 g/L, initial COD = 2,200 mg/L, current density = 40 mA/cm^2, temperature = 28°C, air flow = 1.5 L/min, [Fe^{2+}] = 1.5 mM, and pH = 3.0. Unit A: two-dimensional system without aeration; unit B: two-dimensional system with aeration; unit C: three-dimensional system without aeration; and unit D: three-dimensional system with aeration.

Compared with two-dimensional electrode, three-dimensional electrode can provide larger interfacial electrode surface areas and high current density during treatment process [9]. This is because many small particles like active carbon can perform as charged microelectrodes in the presence of electric field.

3.2. Electrogeneration of hydrogen peroxide using different treatment units

The concentration of H_2O_2 generated is shown in Fig. 2(B). Comparing the four lines in Fig. 2(B), it is evident that there was a distinct difference in the H_2O_2 concentrations. H_2O_2 concentrations increased with time. However, the concentration of H_2O_2 increased much quicker after 10 min. This is because that the decomposition rates of H_2O_2 declined due to the decrease in the dissolved fraction of iron species with increasing pH as the reactions proceeded [10]. In general, the H_2O_2 concentrations were higher in the three-dimensional and/or aerated systems than those in the two-dimensional and/or non-aerated systems.

The reason why the COD removal efficiency in aerated system was higher than that in the non-aerated system is proposed as follows: hydrogen peroxide is electrogenerated in acidic solutions by two-electron reduction of oxygen on the cathode surface by the reaction [10]:

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \qquad (2)$$

or in alkaline solutions by the reaction:

$$O_2 + H_2O + 2e^- \rightarrow HO_2^- + OH^- \qquad (3)$$

Hydrogen peroxide decomposes catalytically by Fe^{2+} (known as the Fenton's reagent) and generates hydroxyl radicals by the reaction:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^\bullet + OH^- \qquad (4)$$

In this reaction, hydroxyl radicals are produced efficiently, but one molecule of Fe^{2+} only produces one hydroxyl radical. The hydroxyl radicals formed initiate the oxidative destruction of organics in solution which may lead to a total mineralization of the pollutants:

$$RH + HO^\bullet \rightarrow R^\bullet + H_2O_2 \qquad (5)$$

The organic radical generated in reaction (5) reacts instantaneously with dissolved oxygen to yield a peroxyl radical, thus initiating subsequent oxidation by chain reactions [1]:

$$R^\bullet + O_2 \rightarrow RO_2^\bullet \qquad (6)$$

$$2RO_2^\bullet \rightarrow R - O - O - O - O - R \qquad (7)$$

$$R - O - O - O - O - R \rightarrow 2RO^\bullet + O_2 \qquad (8)$$

$$RO^\bullet \rightarrow F^\bullet + F \qquad (9)$$

where RH is the polymer molecule with H representing the extractable proton and F and F are fragment polymer radical and stable fragment polymer molecule, respectively. These reactions appear with high yield and satisfactory rate only at a three-dimensional carbon-based cathode due to limited solubility of oxygen in aqueous solutions [10]. Hence, by the application of aeration, the COD removal was only increased by 4% points in the two-dimensional system compared with 22% points in the three-dimensional system (Fig. 2(A)). It has also been reported that the presence of dissolved oxygen was necessary for the chain scission of PAM [11].

3.3. Effect of pH

The electrochemical degradation of PAM by three-dimensional electrode process with air assistance was investigated under different experimental conditions in order to explore the influence of operative parameters on COD removal.

To clarify the effect of pH, PAM solutions with initial pH of 3.0, 5.0, 7.0, and 9.0 were electrolyzed and the degradation efficiency of COD as a function of electrolysis time is illustrated in Fig. 3. A notable pH effect was observed for the process, reaching its faster degradation at pH 3.0 with a maximum COD removal of 84% at 60 min. This result is in agreement with the one reported by other authors [6,12,13], for the degradation of organic pollutants by three-dimensional electrode reactors.

At $pH > 3.0$, the decomposition rate of H_2O_2 declined due to the decrease in oxidation potential of hydroxyl radicals and the dissolved fraction of iron species with increasing pH [10]. It is known that the optimum pH for Fenton's reaction is 2.8 [14]. While at very acidic pH ($pH < 2.8$), the electrogenerated hydrogen peroxide solvates a proton to form an oxonium ion that enhances its stability and reduce the reactivity with ferrous ions and consequently less hydroxyl radicals are produced by reaction (4) [15]. In addition, the acidic solution easily controls the oxygen evolution so as to enhance the overall current efficiency for both direct and indirect

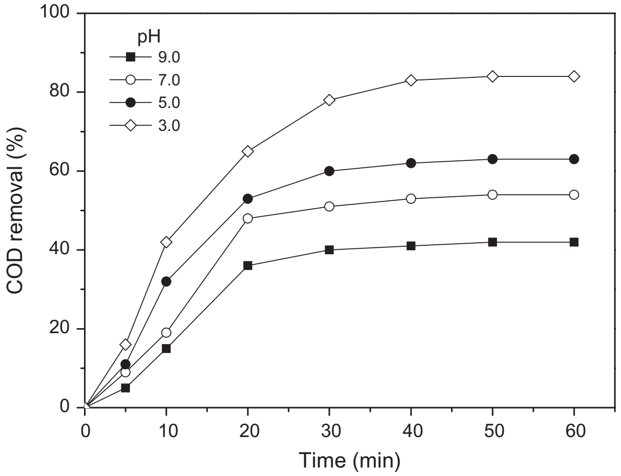

Fig. 3. Time course of COD removal at different initial pH values. Experimental conditions: filling amount of GAC = 100 g/L, initial COD = 2,200 mg/L, current density = 40 mA/cm^2, temperature = 28℃, air flow = 1.5 L/min, and [Fe^{2+}] = 1.5 mM.

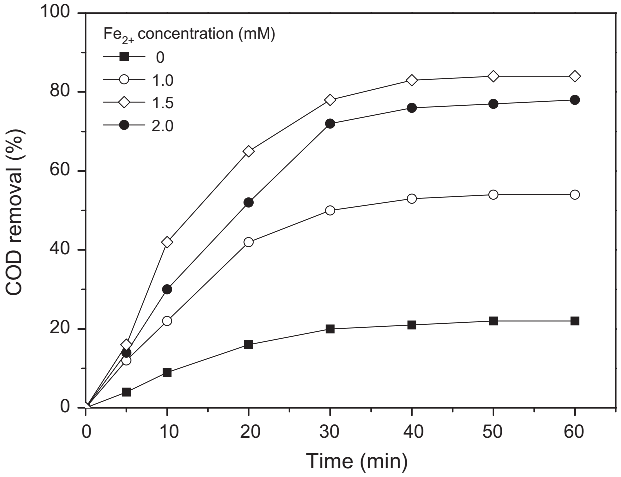

Fig. 4. Time course of COD removal at different initial [Fe^{2+}] concentrations. Experimental conditions: filling amount of GAC = 100 g/L, initial COD = 2,200 mg/L, current density = 40 mA/cm^2, temperature = 28℃, air flow = 1.5 L/min, and pH = 3.0.

oxidation of organic pollutants on the anodes [16]. Moreover, alkaline solution conduces to forming carbonate and bicarbonate which are well-known scavengers for hydroxyl radical [17]. Consequently, pH = 3.0 was used for further experiments.

It was also found that pH increased to > 8 after 30-min treatment. This is attributed to the accumulation of OH^- generated by reaction (4), which resulted in the formation of $Fe(OH)_3$. It can also explain the reason why the degradation rate obviously declined in three-dimensional system after 20-min treatment.

3.4. *Effect of Fe^{2+} concentration*

Fig. 4 shows the influence of Fe^{2+} ions on the evolution of COD. The COD removal efficiency was poor (22%) in the absence of ferrous ions after 60 min of electrolysis because the main oxidant was the electrogenerated H_2O_2 which has limited oxidation ability. In contrast, in the solution containing Fe^{2+} ions, PAM oxidation was accelerated because of the formation of hydroxyl radicals according to Eq. (4). A gradual increase in COD reduction was observed when Fe^{2+} level increased, leading to a final mineralization of 54% and 84% for 1.0 and 1.5 mM Fe^{2+}, respectively. However, the COD removal did not increase further as the dosage of Fe^{2+} increased from 1.5 to 2.0 mM.

When [Fe^{2+}] and [$HO^\bullet$] are high, the Fe^{2+} can react with the [$HO^\bullet$] according to Eq. (10).

$$Fe^{2+} + HO^\bullet \rightarrow Fe^{3+} + OH^- \tag{10}$$

Hence, the excess Fe^{2+} consumed the $HO^\bullet$. In addition, the active sites on the electrode surface might be occupied by the excess Fe^{2+} [13]. Consequently 1.5 mM of Fe^{2+} was used for the further experiments.

Panizza and Cerisola [10] demonstrated that the addition mode of Fe^{2+} had no influence on treatment efficiency of electro-Fenton process due to the increased propagation of Fenton's reaction by electrochemical regeneration of Fe^{2+} ions on cathode surface according to the reaction [18]:

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \tag{11}$$

3.5. *Effect of current density*

Fig. 5 plots the effect of current density on COD removal. Increasing the current density increased the production rate of hydrogen peroxide on the cathode. Therefore, the COD removal efficiency increased with the current density. In this study, the removal efficiencies of COD were 27, 46, 84, and 87% for the current densities of 10, 20, 40, and 50 mA/cm^2, respectively. The increase in COD removal efficiency was insignificant when the current density exceeded 40 mA/cm^2, indicating that the production rate of hydrogen peroxide was controlled by mass transfer at a high current density. Since the consumption of electric energy increased with the applied current, the optimal applied current density in this system was 40 mA/cm^2. In this case, the removal efficiency was 84% and the energy consumption was 46 kWh/kg COD after 60 min.

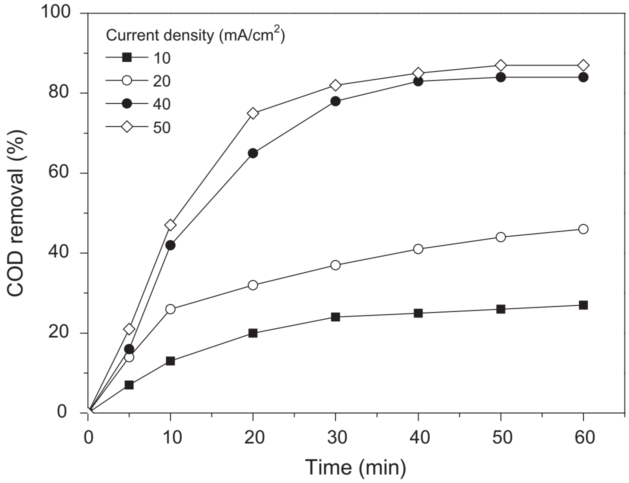

Fig. 5. Influence of current density on COD evolution during the electrolysis of PAM. Experimental conditions: filling amount of GAC = 100 g/L, initial COD = 2,200 mg/L, temperature = 28℃, air flow = 1.5 L/min, pH = 3.0, and [Fe^{2+}] = 1.5 mM.

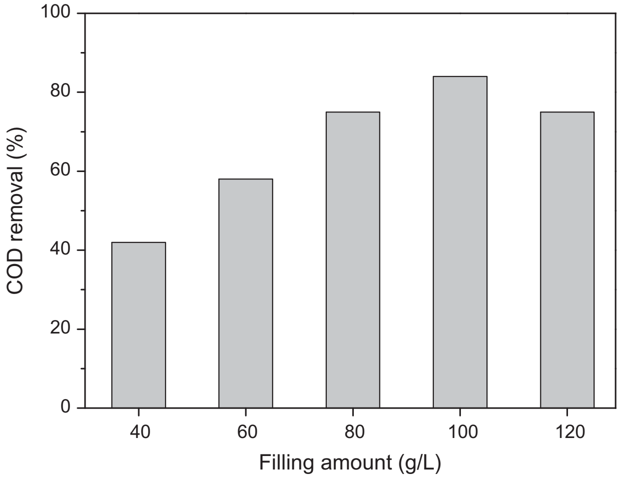

Fig. 6. Influence of filling amount of GAC on COD removal after 60 min of electrolysis. Experimental conditions: initial COD = 2,200 mg/L, current density = 40 mA/cm^2, temperature = 28℃, air flow = 1.5 L/min, pH = 3.0, and [Fe^{2+}] = 1.5 mM.

3.6. Effect of filling amount of GAC

The influence of GAC filling amount on PAM oxidation was investigated and the results are reported in Fig. 6. These data show a gradual increase in COD removal with raising GAC amount. This enhancement of PAM oxidation is associated with larger interfacial electrode surface areas with increasing amount of GAC. However, further increase in the amount of GAC to 120 g/L brought about a decrease in COD removal, which is attributed to the low permeability, high resistance and choking of granular electrodes caused by high concentrations of GAC.

3.7. Changes in nitrate concentration

Based on the above results, the optimum conditions for COD removal of PAM solution were: current density = 40 mA/cm^2, pH = 3.0, [Fe^{2+}] = 1.5 mM, GAC filling amount = 100 g/L. In this case, further analyses were conducted.

The concentration of released nitrate can be used as an indicator of the mineralization degree of PAM, as nitrogen is one of the constituents in the molecule of PAM. Fig. 7 shows the evolution of nitrate concentration during the electrochemical process. It can be found that the release rate of nitrate was slow during the first 10 min of electrolysis, after that nitrate release was enhanced significantly. This is because most reactions involved polymer chain rupture instead of PAM mineralization in the initial period of reaction [1]. After a certain degree of chain scission, mineralization reaction began to dominate and nitrate release was increased. The concentration of released nitrate was 1,439 mg/L after 60 min of electrolysis. Theoretical nitrate value is about 1,700 mg/L, according to the total nitrogen molar content in the initial PAM molecule. Therefore, it can be inferred that there existed a large amount of PAM intermediates containing nitrogen. The mineralization degree of PAM was calculated as 85%.

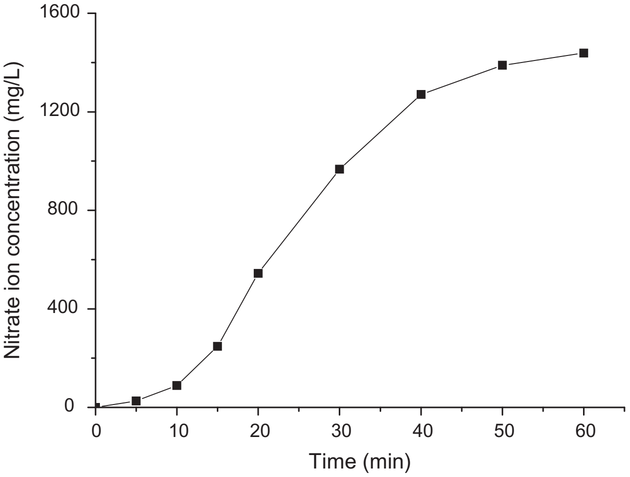

Fig. 7. Time course of [NO_3^-] in solution during the electrolysis of PAM. Experimental conditions: filling amount of GAC = 500 g, PAM concentration = 2,000 mg/L, current density = 40 mA/cm^2, temperature = 28℃, air flow = 1.5 L/min, pH = 3.0, and [Fe^{2+}] = 1.5 mM.

3.8. Biodegradability and Microtox® toxicity during electrolysis

Fig. 8 illustrates the effect of treatment time on the changes of B/C ratio and Microtox® toxicity. As can be seen, there was a similar variation trend between B/C ratio and EC_{50}. The B/C ratio increased from 0.10 to 0.37 after the initial 10 min and increased rapidly to 0.16 at the 20th min, and then increased quickly to 0.38 at the 30th min and kept stable until the 60th min with some small fluctuation. As far as Microtox® toxicity is concerned, ecotoxicity decreased substantially after the first 10 min of electrolysis, suggesting that some toxic compounds were removed. The EC_{50} value was significantly decreased at the 20th min, implying generation of some toxic intermediates such as acrylamide monomer. After 20 min of treatment, microtoxicity decreased again.

From an economic point of view, a 30-min electrochemical treatment is suitable for pretreating PAM wastewater, because the biodegradability of wastewater has been increased to a reasonable level. Further electrolysis is not economical due to high energy consumption. Partial oxidation of bio-refractory organic pollutants to readily biodegradable intermediates requires less energy consumption than complete mineralization.

3.9. Kinetic analysis of PAM degradation

According to Fig. 2(A), the results fitted a pseudo-first-order reaction well in the first 20 min of electrolysis. The kinetic equations and parameters are shown in Table 2, from which it can be seen that the kinetic constant of PAM degradation was apparently greater in the aerated three-dimensional system than in other processes.

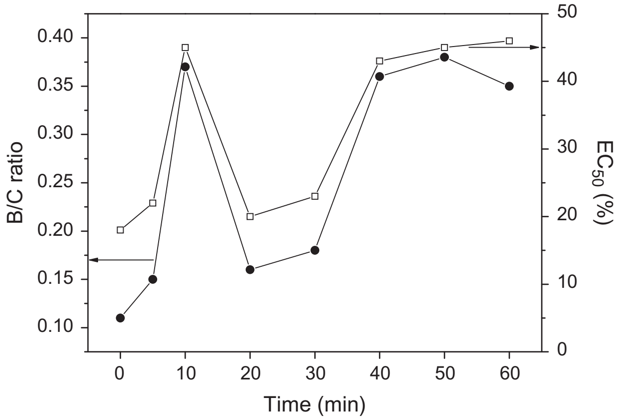

Fig. 8. Effect of reaction time on the changes of BOD_5/COD ratio and Microtox® toxicity. Experimental conditions: filling amount of GAC = 100 g/L, PAM concentration = 2000 mg/L, current density = 40 mA/cm^2, temperature = 28℃, air flow = 1.5 L/min, pH = 3.0, and $[Fe^{2+}]$ = 1.5 mM. (•) B/C ratio; (□) EC_{50}.

Table 2
The apparent rate constants for PAM degradation using different processes

Treatment	Rate constant (min^{-1})	Regression coefficiency
Unit A	0.0196	0.9624
Unit B	0.0218	0.9753
Unit C	0.0621	0.9842
Unit D	0.0735	0.9816

4. Conclusions

In this study, the electrochemical treatment of a synthetic solution containing 2,000 mg/L PAM was conducted using electro-Fenton process. The results showed that the wastewater can be effectively depolluted by the three-dimensional electrode reactor using GAC as particle electrodes. The reactor was fed with air and ferrous salt to electrogenerate hydrogen peroxide and Fenton's reactions. The results of the bulk electrolysis under different experimental conditions demonstrated that the COD removal was influenced by the concentration of ferrous, current density, solution pH, and GAC amount. The BOD_5 and Microtox® toxicity analysis indicated that the optimum electrolysis duration was 30 min, at which a good biodegradability of solution had been obtained.

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