



Highly efficient removal of perfluorooctanoic acid from aqueous solution by H₂O₂-enhanced electrocoagulation-electroflotation technique



Bo Yang^{a,*}, Yanni Han^a, Yunpan Deng^a, Yingying Li^a, Qiongfang Zhuo^b, Jinhua Wu^c

^a Department of Environmental Engineering, College of Chemistry and Environmental Engineering, Shenzhen University, Shenzhen 518060, PR China

^b South China Institute of Environmental Sciences, The Ministry of Environment Protection, Guangzhou 510655, PR China

^c School of Environment and Energy, South China University of Technology, Guangzhou 510006, PR China

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ABSTRACT

Electrocoagulation (EC) technique was used to investigate the removal performance of aqueous perfluorooctanoic acid (PFOA) with relatively high concentration as simulating the wastewater from organic fluorine industry. A comparison was done with the similar amount of coagulant between EC and chemical coagulation process. PFOA removal obtained was higher with EC process, especially for Fe anode. Several factors were studied to optimize the EC process. At the optimal operating parameters including 37.5 mA/cm² of current density, initial pH 3.77, and 180 rpm of mixing speed, 93% of PFOA could be removed with 100 mg/L of initial concentration after 90-min electrolysis. Furthermore, the remove efficiency could be obviously improved by H₂O₂ intermittent addition, which removed more than 99% of PFOA within 40-min EC. It could be attributed to that H₂O₂ facilitated the oxidative transformation from ferrous to ferric ion. In addition, the adsorptive removal of aqueous PFOA on Fe flocs during EC was also verified by fourier transform infrared spectra.

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1. Introduction

Perfluorooctanoic acid (PFOA) is exceptionally stable chemicals because of its strong C–F bonds, which with high surface activity and thermal resistance have been widely used for decades as surfactants, firefighting foams, and coatings [1]. Due to its synthesis and extensive use, PFOA have been frequently detected in environment medium, human serum, and wildlife [2]. Even high concentration PFOA was found in special point source for the emulsion polymerization of fluoropolymers. For example, wastewater produced in fluoropolymers production normally contains 50–200 mg/L PFOA [3,4]. Also, analytical studies have revealed its

toxicological properties, persistence, and bioaccumulation [5]. Therefore, the effective removal of aqueous PFOA has become new concern in environment technology [6,7]. However, PFOA is chemically stable and resistant to biodegradation. Although chemical technologies such as photochemical, sonochemical, and electrochemical decomposition were developed for PFOA degradation, harsh experimental conditions restrict their large-scale application [6–8].

Recently, physicochemical methods are also used to purify PFOA-contaminated water mainly including adsorption and coagulation, which can transfer pollutants from aqueous solution to solid phase without decomposition. But these methods possess the advantages of low energy consumption and simple operation. Schroder et al. [9] compared the conventional physical and chemical treatments for PFOA removal and found that granular activated carbon (GAC) adsorption was significantly superior to other removal techniques including reverse osmosis and some advanced oxidation processes. In addition, some synthesized adsorbents are also provided with high adsorption capacity for PFOA such as resin, mineral material, biomaterial, molecularly imprinted polymers [4,10–12]. However, they needed a long equilibrium time to finish

* Corresponding author.

E-mail address: boyang@szu.edu.cn (B. Yang).

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adsorption that continued for hours or days and were inconvenient for rapid purification of water quality. Moreover, the regeneration of spent adsorbents would increase operational complexity and difficulty in their practical application. Some reports also indicate that coagulation can effectively remove PFOA of low concentration (0.1 µg/L ~ 1 mg/L) in micro-polluted water using polyaluminium chloride or ferric chloride after about 30-min mixing [13,14]. However, to our knowledge, there is no report using coagulation to remove PFOA of relatively high concentration more than 10 mg/L from industrial wastewater.

On the other hand, electrocoagulation (EC) technology may substitute for conventional coagulation to effectively treat wastewaters containing surfactants, oil, dyes, soluble inorganic pollutants, and suspended particles [15,16]. The process generates the *in situ* active adsorbents (such as hydroxides of aluminum or hydrous ferric oxides) by the dissolution of sacrificial anode, usually using aluminum or iron. These adsorbents neutralize the electrostatic charge on adsorbates to facilitate agglomeration or coagulation and the resultant separation from aqueous solution. Meanwhile, cathodic reactions occur and H₂ evolution is involved, causing flotation of the adsorbents. However, there are a few reports to investigate the EC removal of PFOA, which are also surfactants. Baudequin et al. [17] purified firefighting water containing fluorinated surfactant (100 mg/L of Forafac 1157N, Dupont) by reverse osmosis coupled with EC-filtration. Due to firefighting water unsuitable for direct membrane processes because of high fouling, EC and filtration were employed for pretreatment using aluminum anode in their work. As a result, fluorinated surfactant removal was up to 71% and not obviously increased even by further electrolysis.

In this study, the EC technique with iron anode was explored for the removal of PFOA in aqueous solution. The removal efficiencies of PFOA were firstly compared using EC process of Al or Fe electrode as well as chemical coagulation (CC) process of aluminium sulphate or ferric chloride according to the same amount of metal cations. These factors that affected the PFOA removal were examined including applied current density, initial pH, and mixing speed. The adding operation of H₂O₂ was investigated to further improve the EC efficiency of PFOA with Fe anode. The novelty of this study is to employ Fe anode along with H₂O₂ addition to achieve the highly efficient removal of PFOA. Although the EC process of Fe electrode has been reported to remove many organic pollutants, the EC technique of Fe plate coupled with H₂O₂ addition for PFOA removal was not reported.

2. Materials and methods

2.1. Materials

The Fe and Al plates (>99%) were purchased from a local market in Shenzhen, and cut into 50 × 20 × 2 mm as electrode material. PFOA was from Fluorochem Ltd. (UK). KCl (99.5%) and H₂O₂ (30 wt %) were purchased from Aladdin Reagent Inc. (Shanghai, China). HCl (36–38%) were provided from Guanghua Reagent Co. (Shantou, China). H₂SO₄ (98%) and NaOH were from Sinopharm (Shanghai, China). All chemicals used in the study were reagent grade or higher and used as received. All solutions were prepared using water with a resistance of 18.2 MΩ cm from a Millipore-Q system.

2.2. Equipment and electrolysis

The EC reactor was a 0.5 L electrolytic cell with two parallel iron plates, each having a surface area of 8.0 cm² as submerged part. The electrodes were installed vertically in the middle of the reactor with an electrode gap of 2 cm. Before electrolysis, the electrodes were immersed in 0.1 M HCl for 1 min and then rinsed with water.

Subsequently, they were dried with absorbent paper and weighed. The electrodes were connected to a DC power supply (ATTEN APS3003Si) providing a controlled voltage or current up to 30 V or 3 A, respectively. All the runs were performed at room temperature using magnetic agitation with 1.5 g/L of KCl as supporting electrolyte. In each run, 0.4 L of PFOA solution was decanted into the electrolytic cell with the initial concentration of 100 mg/L. Then, flotation and settling proceeded simultaneously with mixing for 90 min before final pH and PFOA concentration measurements. At the end of EC, the solution was filtered and then analyzed. The solid residue collected from flotation and settling was dried until constant weight was obtained for calculation of the total sludge amounts. After each run, electrode surfaces were washed thoroughly with deionized water to remove any solid residues on surfaces and dried. All experiments were repeated twice, and the experimental error was around 5%.

2.3. Analytical methods

After the EC-electroflotation (EF) experiments, the supernatant was filtered with a 0.22 µm polyether sulphone membrane. The control experiments indicated that the adsorption of PFOA on the membrane was negligible (<1%) due to its high concentration in the range of 1–100 mg/L. The concentrations of PFOA in aqueous solution were determined by a LC-15C HPLC with a CDD-10AVP conductivity detector from Shimadzu (Japan). HPLC employed a C18 column (Diamonsil C18(2), 150 × 4.6 mm i.d., 5 µm particle size) with the mobile phase of methanol/0.02 M NaH₂PO₄ (65/35, v/v) was used as the mobile phase at 1.2 mL min⁻¹ flow rate. The sample volume injected was 50 µL. The detection limit for PFOA is 0.8 mg/L. The removal efficiency was calculated based on the difference of PFOA concentrations before and after EC-EF.

3. Results and discussion

3.1. Comparison of PFOA removal efficiency between EC and CC

Firstly, the removal efficiency of PFOA with EC are compared with that of the conventional CC, established by adding the same amount of metal cations, Al for Al₂(SO₄)₃·18H₂O, or Fe for FeCl₃·6H₂O, as the stoichiometric concentration of Al or Fe electrodisolution according to the quantity of electricity within 90-min electrolysis. This method comparatively evaluates the role of metal cations when they are electrogenerated increasingly *in situ* and when they are added at once. As shown in Table 1, EC experiments showed that the maximum removal yield of PFOA was 92% using Fe anode during 90-min reaction. It presented relatively low decrement for PFOA concentration at 58% with Al anode. However, the removal efficiency decreased further to 42% for CC with Al₂(SO₄)₃·18H₂O after 90-min agitation. As for CC using FeCl₃·6H₂O, PFOA removal efficiency was poor only at 4% and pH

Table 1
Comparison of PFOA removal efficiency, final pH, mass of sludge and operating cost between EC and CC within 90-min coagulation (initial pH = 3.8).

	EC (<i>i</i> = 37.5 mA/cm ²)		CC	
	Al anode	Fe anode	Al ₂ (SO ₄) ₃	FeCl ₃
Dosage (mM)	—	—	7 ^a	20 ^a
Y (%)	57.5 ± 1.5	91.7 ± 1.1	41.5 ± 1.5	4.1 ± 1.0
Final pH	8.1 ± 0.1	8.9 ± 0.1	3.6 ± 0.2	1.9 ± 0.1
m _s (g)	1.7 ± 0.2	2.2 ± 0.2	3.1 ± 0.1	0.4 ± 0.1
OC (\$/kg)	4.84	2.80	—	—

^a The dosages of Al or Fe salts was equal to the stoichiometric mole number of Al³⁺ or Fe²⁺ ion from anode electrodisolution according to 100% current efficiency.

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