



Efficient removal of perfluoroalkyl acids (PFAAs) from aqueous solution by electrocoagulation using iron electrode



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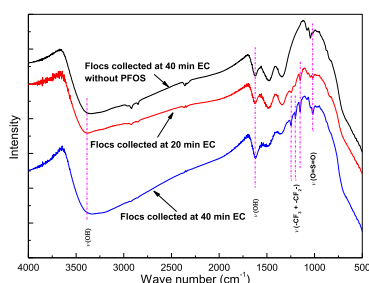
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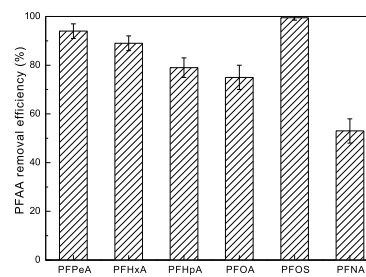
HIGHLIGHTS

- PFAAs as emerging contaminants were effectively removed by electrocoagulation.
- Iron hydroxide flocs formed *in situ* presented high removal efficiency for PFAAs.
- The important factors included current density, stirring speed, and electrolyte type.
- More than 99% PFOS was removed after 50-min electrolysis with 25.0 mA/cm².
- Further mechanistic detail of PFAA adsorptive removal on iron flocs is proposed.

GRAPHICAL ABSTRACT



Evidence of FTIR for PFOS adsorption on iron hydroxide flocs



Comparison of PFAA removal efficiency by EC with Fe anode

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ABSTRACT

Electrocoagulation (EC) technique was used to investigate the removal performance of aqueous perfluoroalkyl acids (PFAAs) with relatively high concentration as simulating the wastewater from organic fluorine industry. A comparison between iron and aluminum electrode was made to remove PFAAs with the similar electrolysis condition. Effective removal of perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) was obtained by EC process, especially for Fe anode. Several key factors were studied to optimize the EC process using Fe electrode. At the optimal operating parameters including 25.0 mA/cm² of current density, 180 rpm of stirring speed, and 2 g/L NaCl as supporting electrolyte, more than 99% of PFOS could be removed with 0.25 mM of initial concentration after 50-min electrolysis. Additionally, the adsorptive removal of aqueous PFOS on iron hydroxide flocs during EC was also verified by Fourier transform infrared spectra. The investigation of removal efficiency for PFAAs with different carbon chain length after EC and the characteristic of zeta potential on Fe flocs indicated that the electrostatic adsorption was primarily responsible for the PFAAs sorption on the iron hydroxide flocs.

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1. Introduction

Perfluoroalkyl acids (PFAAs) possess a fully fluorinated alkyl chain of different length with an acid headgroup such as sulfonic, carboxylic, or phosphoric [1]. They are exceptionally stable chemicals because of their strong C—F bonds, which with high surface

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activity and thermal resistance have been widely used as emulsifier in fluoropolymer synthesis, firefighting foams, and surfactants in textile products [2]. The industrial emission containing high concentration of PFAAs is their main pathway releasing to the environment. For example, about 0.29–3.35 mM of perfluorooctanoic acid (PFOA, C₇F₁₅COOH) appeared in the untreated wastewater after emulsifying process in fluoropolymer manufactory [3,4] and perfluorooctane sulfonate (PFOS, C₈F₁₇SO₃) concentration up to 1500 mg/L was found in wastewater of the photolithographic effluent [5]. Due to their synthesis and extensive use, PFAAs have been frequently detected in environment medium, human serum, and wildlife [1,6]. Moreover, environmental monitoring has revealed their toxicity, persistence, and bioaccumulation [1]. Among them, PFOS was listed as persistent organic pollutant in Annex B of the Stockholm Convention for strict restriction in 2009. PFOA is currently being eliminated conforming to the USA EPA. Therefore, the effective removal of aqueous PFAAs has become new concern in environment technology [6,7]. However, PFAAs is chemically stable and resistant to biodegradation. Although chemical technologies including photochemical, sonochemical, mechanochemical, and electrochemical decomposition were developed for PFOX degradation, harsh conditions restrict their large-scale application [6–8].

Recently, physicochemical methods are also used to purify PFAAs-contaminated water mainly including adsorption and coagulation, which have the advantages of low energy consumption and simple operation. Deng et al. [7] compared various adsorbents including granular activated carbon (GAC), carbon nanotubes, resin, mineral material, biomaterial, molecularly imprinted polymers to remove aqueous PFAAs at various concentrations. Generally, they need a long equilibrium time to finish adsorption that continued for hours or days and are inconvenient for rapid purification of water quality. GAC is the most widely applied adsorbent in water purification but it exhibited limited sorption capacity of less than 0.4 mmol g⁻¹ for both PFOS and PFOA [3]. The adsorbents having low sorption rates or capacities are easy to be penetrated, leading to difficulty in application. In addition, the regeneration of spent adsorbents would increase operational complexity in real-life scenarios. Some reports indicate that coagulation can partly remove PFAAs of low concentration (0.1 µg/L–1 mg/L) in micro-polluted water using polyaluminium chloride or ferric chloride [9,10]. Xiao et al. [9] found that 10–40% removal of PFOS/PFOA could be achieved with an enhanced coagulation at high coagulant dosages (60–110 mg/L). However, to our knowledge, there is no report using coagulation to remove PFAAs of relatively high concentration more than 5 mg/L from industrial wastewater. Therefore, these above limitations promoted a great interest in developing novel cheap technologies or adsorbents with fast adsorption rate and high sorption capacity to remove PFAAs from wastewater.

On the other hand, electrocoagulation (EC) technology may substitute for conventional coagulation to effectively treat wastewaters containing surfactants, oil, dyes, and soluble inorganic pollutants [11]. The process generates the *in situ* active adsorbents (such as hydrous ferric oxides or hydroxides of aluminum) by the dissolution of sacrificial iron or aluminum anode. These adsorbents neutralize the electrostatic charge on adsorbates to facilitate agglomeration or coagulation and the resultant separation from water. 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 PFAAs. Only Lin et al. [11] reported that an EC process using Zn anode can effectively remove PFOS/PFOA (1.5 µM–0.5 mM) by the formed zinc hydroxide flocs. However, this method would be restricted due to relatively high cost of Zn material and ecological toxicity of Zn²⁺ released into environment.

In this study, the EC technique with common iron anode was explored for the effective removal of aqueous PFAAs. The removal

efficiencies of PFOX were firstly compared by EC process using iron or aluminum electrode. These factors that affected PFAA removal were examined including current density, stirring speed, and electrolyte type. Furthermore, the possible mechanism was proposed by exploring the interactions between PFAAs and iron hydroxide flocs. To the best of our knowledge, there is no report on systematically evaluating the removal efficiency and mechanisms of PFAAs in aqueous solution by the EC process of iron electrode.

2. Materials and methods

2.1. Materials

The Fe and Al plate (>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). PFOS was provided from J&K Scientific Ltd. (China). PFAAs (C5–C9) standards were obtained from Wellington Laboratories Inc. (Canada). Ferron reagents (8-hydroxy-7-iodoquinoline-5-sulfonic acid) were from Shanghai Crystal Pure Industrial Co. Ltd. NaCl, Na₂SO₄, NaNO₃, and NaH₂PO₄ were purchased from Aladdin Reagent Inc. (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 600 mL electrolytic cell with two parallel metal 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 to remove oxides. Subsequently, they were dried with absorbent paper and weighed. The electrodes were connected to a DC power supply (ATTEN APS3003Si) providing a controlled current up to 3 A. All the runs were performed at room temperature using magnetic agitation. In each run, 500 mL solution containing 0.25 mM of PFAAs was decanted into the electrolytic cell with 2 g/L NaCl as electrolyte. During EC, 2 mL of the suspending liquid was extracted for analysis at each sampling time. After each run, electrode surfaces were washed again to remove any solid residues on surfaces, dried with absorbent paper and re-weighed. All experiments were repeated twice.

2.3. Analytical methods

After the EC experiments, the suspending liquid was filtered through a vacuum suction filter with a 0.22 µm glass fiber membrane (Whatman™, UK), which possesses a negligible adsorption for PFAAs (<1%). The solid residue was dried in air until constant weight was obtained to analyze its characterizations. The concentrations of aqueous PFAAs 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 (70/30 for PFOS, 65/35 for PFOA, v/v) was used as the mobile phase at 1.2 mL min⁻¹ flow rate. The sample volume injected was 50 µL. More details about the analysis of PFAAs could be found in our previous study [12].

3. Results and discussion

3.1. Effect of anode materials

This study firstly explored the two common anodes of EC including iron and aluminum for PFOS/A removal. As shown in

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