



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



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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

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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.

decline was obvious with that a few solid flocs were formed. So pH evolution appeared as the key restriction of CC, where high acidity hindered the formation of ploy-ferric floc. It was in agreement with Chafi's report where there was no sludge formation for $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ addition at pH below 2.0 [18]. Conversely, EC presents a neutralizing effect, especially with Fe, and avoids the addition of co-anions.

Additionally, after the floc was efficiently formed, EC exhibited less sludge production than that of CC (1.7 or $2.1 < 3.1$ g in Table 1). Moreover, sludge produced after EC can be separated by flotation or settling spontaneously in this study. Therefore, EC was faster and more economic, consumed less material and formed less sludge, and pH of the medium was more appropriate for EC than CC to higher PFOA removal levels. As a conclusion, the superiority of EC over CC is clearly established for PFOA removal. Table 1 also illustrates that more sludge generation for Fe anode than Al anode could be attributed to the electro-dissolution of 1 mol Fe requires only 2 mol electrons, while 1 mol Al needs 3 at constant current. At the same quantity of electricity, it could provide more floc area to adsorb PFOA for Fe anode than Al anode. Moreover, ferric ion could also form complex with PFOA to improve its removal efficiency during EC with Fe anode. It is well known that ferric ion easily forms complex with carboxylate, which is just the functional group at one end of PFOA molecule. Wang et al. [19] reported that ferric ion could coordinate with PFOA to generate a complex, which was proved by UV-Vis absorption spectra of PFOA solution, and thus achieve PFOA photolysis by 254 nm UV light. Therefore, EC using Fe anode presented the high removal efficiency for PFOA.

On the other hand, the operation costs (OC) [\$/kg PFOA removed] associated with current and others are compared for the above EC process, which includes material, mainly electrodes, electrical energy and supporting electrolyte in Eq. (1).

$$OC = a \times C_{\text{energy}} + b \times C_{\text{electrode}} + c \times C_{\text{supporting electrolyte}} \quad (1)$$

$$C_{\text{energy}} = (U \times I \times t) / (60 \times m) \quad (2)$$

where C_{energy} (consumption kWh energy per kg PFOA), $C_{\text{electrode}}$ (consumption kg electrode per kg PFOA) and $C_{\text{supporting electrolyte}}$ (consumption kg electrolyte per kg PFOA) of wastewater treated. Unit prices, a, b and c given for Chinese Market, April 2016, are as follows: (a) electrical energy prices 0.10 US \$/kWh, (b) electrode material price 2.50 US \$/kg for Al and 0.60 US \$/kg for Fe, respectively, (c) KCl price about 0.55 \$/kg. In Eq. (2) U is the applied voltage (V), t = treatment time (min), and m is the mass of the removed PFOA (kg). Based on the initial/final concentrations of the PFOA, OC per kg of PFOA can also be readily evaluated according to Eqs. (1) and (2). The economic values of the EC process for each electrode in this work are presented in Table 1, which indicated that Fe electrode presented a lower cost to remove PFOA than Al electrode as 2.80 and 4.84 \$/kg PFOA removed, respectively.

3.2. Effect of current density

During the electrochemical processes, current density is the most important parameter for controlling the reaction rate within the electrochemical reactor [20]. For EC, it determines the production rate of coagulant, adjusts also bubble production on cathode, and thus affects the growth of flocs [21]. So EC processes were carried out using various current densities for PFOA removal. The data monitored for 90 min electrolysis is presented in Fig. 1. An increase in current density from 6.25 to 37.5 mA/cm² led to an obvious increase in the efficiency of PFOA removal from 35 to 93%. It could be due to that the increase of current density resulted in the increases of Fe^{2+} cations released by anode dissolution and

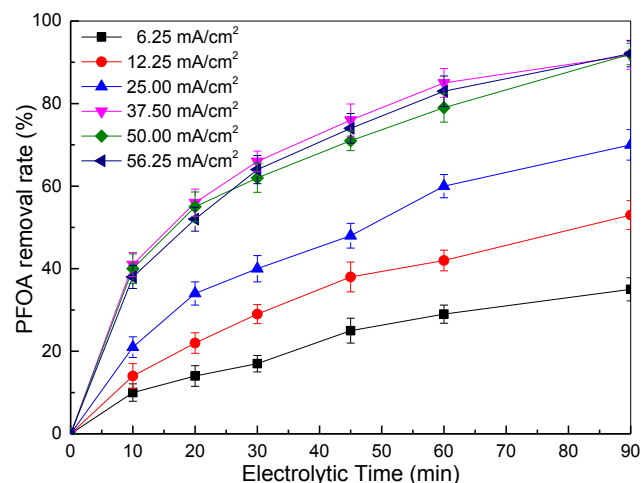


Fig. 1. Effect of current density on PFOA removal during the electrocoagulation using Fe anode. Applied current density is shown in the figure ($C_0 = 100$ mg/L, initial pH = 3.8, mixing speed = 180 rpm).

therefore of iron hydroxides. However, the difference between the curves corresponding to different current densities became small rapidly when it was higher than 37.5 mA/cm². An optimum current density can therefore be defined. Indeed, when the increase of PFOA removal efficiency with current density became slight, the disadvantages of working at high current densities prevail including the increase of energy and anode material consumption. Fig. 2 indicates that energy consumption almost doubled from 119.1 Wh/g to 190.4 Wh/g with the similar removal efficiency of PFOA while current density increased from 37.5 to 56.25 mA/cm². It can be also seen that obtaining a PFOA relative removal of up to 20% had similar energy requirements using current densities of 25.0 and 37.5 mA/cm², but that more energy was consumed when the current density was 50.0 mA/cm². In addition, increasing the current would increase the amount of metal oxidized, causing more precipitate to be formed. However, the anode consumption per g PFOA should be minimized because it can constitute up to 80% of the total operating costs for anodes, according to Bayramoglu et al. [22].

On the other hand, compared with these data already reported in the literature for the removal of metal ion such as Cu^{2+} , Cr^{6+} , and

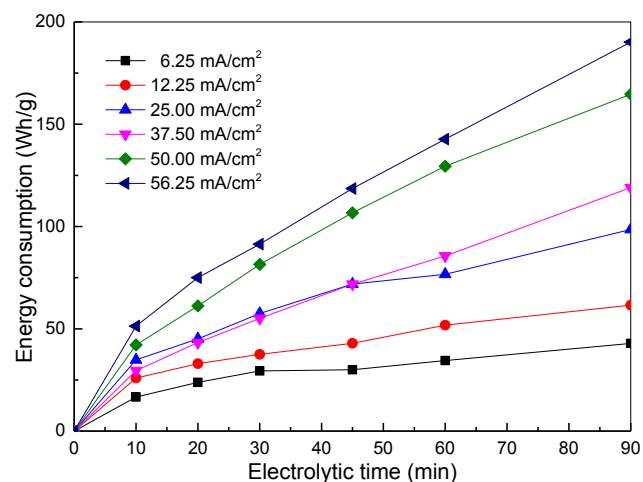


Fig. 2. Effect of current density on energy consumption during the electrocoagulation using Fe anode. Other conditions are the same as those in Fig. 1.

Ni^{2+} by EC with iron electrode [23,24], longer electrolytic time was needed to remove PFOA in this study. It was probably due to the relatively weak ionic intensity and adhesive force of PFOA to Fe flocs, which be only provided with a limited adsorption site at the small carboxylic end of its whole molecule as electrostatic interaction. In fact, the electrostatic negativity is still principally originated from PFOA functional head, while the tail of PFOA molecule mostly presents the hydrophobic effect overwhelming the charged effect [7]. Additionally, during EC, increasing the current density will increase the bubble density and decrease the bubble size [21,25]. This would promote an upward momentum flux to transfer coagulants from the solution to the surface so that it was not adequately prepared for adsorption equilibrium between PFOA molecules and Fe flocs. So higher current values could lead to a high turbulence in the system and consequently the particles responsible for coagulation did not have enough time to agglomerate themselves and continuously remove PFOA. As a result, excessive bubble could also cause that further increase of the current density more than 37.5 mA/cm^2 only results in negligible increase of PFOA removal efficiency.

3.3. Effect of initial pH

The aqueous pH is the important parameter in the EC process, since the solubility of the metal floc formed is dependent on pH and ionic strength [26]. The removal efficiency of PFOA was evaluated for eight initial pH values, the raw pH 3.77, followed by pHs 2.96, 5.04, 6.02, 7.04, 8.16, 9.10, and 10.04, which were adjusted with NaOH or H_2SO_4 , when the initial formulation was fixed. Fig. 3 illustrates the decrease of PFOA concentration over time and as can be observed the similar removal efficiencies were achieved from initial pH 5.04 (89%) to initial pH 8.16 (83%) after 90 min of electrolysis. While for the experiment at pH 9.1 and 10.04, there are the relatively low removal efficiency for PFOA as 73% and 70%, respectively. In addition, the test with pH 2.96 also led to a slightly low PFOA removal (79%) up to 90 min. The above results were approximately in agreement with Fe Pourbaix diagram. For pH value of $4 < \text{pH} < 7$, Fe undergoes hydrolysis and Fe^{3+} hydroxide begins to precipitate as floc with yellowish color. As $\text{pH} < 6.5$, the oxidation rate of Fe^{2+} into Fe^{3+} is extremely slow [27]. For $\text{pH} 6 < \text{pH} < 9$, precipitation of Fe^{3+} hydroxide continues, and Fe^{2+} hydroxide precipitation also occurs presenting a dark green floc. Fe

floc is formed due to the polymerization of iron oxyhydroxides, which performs the coagulation with the aggregation of the pollutants, reducing the organic load and the concentration of pollutants in wastewater [28]. So when the aqueous pH is too low at 3, the dissolution of the electrode could occur to the solution in the form of Fe^{2+} , which only reacted with the small quantity of hydroxyl anion formed in the cathode in strongly acidic condition. It restricted the formation of Fe(II) hydroxides and reduced the PFOA removal during early stage of EC at initial pH 3.03 as shown in Fig. 3. For initial pH 9.1 and 10.04, the hydroxide ions would be oxidized at the anode to reduce anode dissolution; moreover, $\text{Fe}(\text{OH})_6^{3-}$ and $\text{Fe}(\text{OH})_4^-$ ions may be generated at high pH values [26]. These ions are not capable of removing the contaminants from the wastewater due to weak flocculation effect. Additionally, when pH is more than 8.5, transformation of Fe^{2+} into Fe^{3+} is very fast in seconds [27]. So there is almost not the existence of Fe^{2+} in stronger alkaline solution. But coexisting divalent cations have the bridging effect for PFOA adsorption, which can form a bridge between negatively charged groups (carboxyl or hydroxyl groups) and PFOA anions [28]. The deficiency of Fe^{2+} as divalent cation in stronger alkaline solution may reduce the adsorption removal of PFOA by flocculation.

Fig. 4 illustrates the pH change for the above experiments followed over time. As can be observed, the pH increased for all tests. This increase could be explained by the electrolytic reaction occurring at the cathode. During the electrolysis, at this electrode, water molecules receive electrons and dissociate into hydrogen bubbles and hydroxyl ions, causing the pH values increase. Even for the process with initial pH 3.03, the solution rose to neutral pH finally, whose PFOA removal efficiency obviously increased after 10-min electrolysis due to the rapid increase of aqueous pH. For the initial pH 3.77 as raw PFOA solution without pH adjustment, the aqueous pH rose to weak alkaline lasted for a long time, which is in the ideal range, not needing pH adjusting, to be directly discharged or even to be subsequently treated in biological processes. Additionally, based on the results of Fig. 4, it can be concluded that the PFOA removals were not favorable at higher basic pH values because the final pH values after electrolysis have not retained the neutral or weak alkaline level as the appropriate pH value range for EC using Fe electrode. Therefore, pH 3.77 was the optimal value for PFOA removal in this system with the highest removal efficiency of PFOA at 93% within 90-min electrolysis.

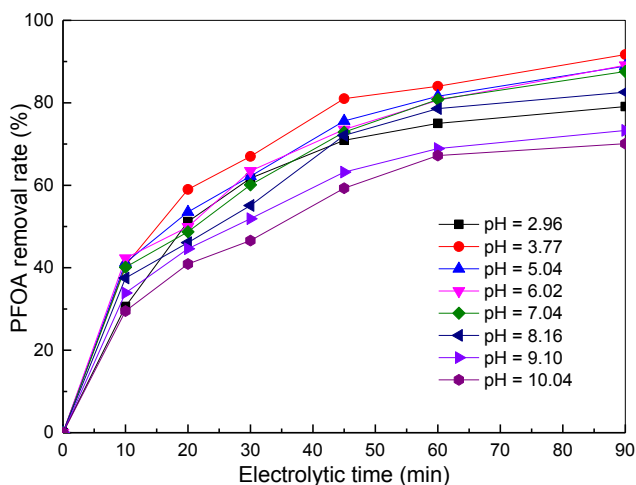


Fig. 3. Effect of initial aqueous pH on PFOA removal during the electrocoagulation using Fe anode. Applied pH is shown in the figure ($i = 37.5 \text{ mA/cm}^2$). Other conditions are the same as those in Fig. 1.

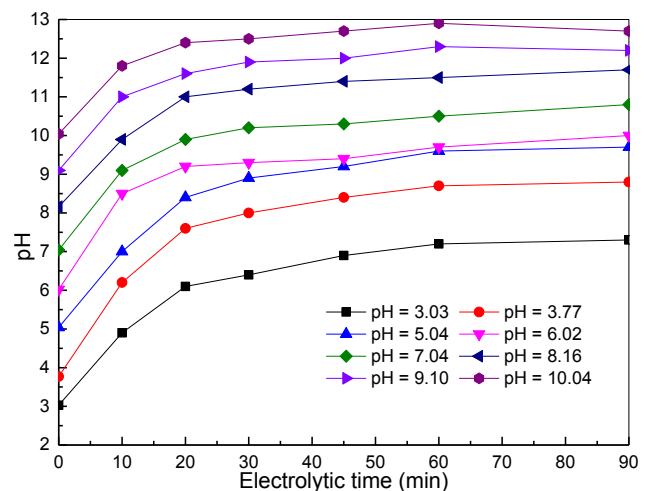


Fig. 4. Variation of pH values with time for different initial pH during the electrocoagulation removal of PFOA using Fe electrode. Other conditions are the same as those in Fig. 3.

3.4. Effect of mixing speed

PFOA molecule access to the floc surface is essential for the efficient utilization of electrogenerated adsorption sites in bulk solution. To determine whether the mass transfer of PFOA molecules did affect EC efficiency, electrolysis were performed as mixing speed of rotor varying from 120 to 360 rpm. As shown in Fig. 5, the mixing speed had a pronounced effect on PFOA removal. Increasing mixing speed from 120 to 180 rpm result in an increase of 11% for removal efficiency after 90-min electrolysis. However, continuing to increase mixing speed from 180 rpm to 300 rpm actually led to the decrease of PFOA removal efficiency from 92% to 76%. Subsequently, PFOA removal declined into 71% while still increasing mixing speed from 300 rpm to 360 rpm. In fact, for coagulation, some kind of agitation is essential because the small flocs must be random motion and brought into contact with one another so that they may agglomerate to form large flocs. Without mixing or agitation the flocculating effect is exceedingly slow and uncontrollable. However, too intensive mixing was accompanied with high shear force so the size and strength of primary flocs generated by the coagulation of Fe ion and the broken particles were small and molecular chains were easy to be damaged [29,30]. Therefore the removal efficiency of PFOA declined for excessive agitation since the little incompact flocs were not prone to bridging for net catching and sweep flocculation.

On the other hand, PFOA as strong acid mainly existed in the deprotonated form in the above experimental conditions. Its anions could be adsorbed onto the positive surface of the coagulants and the flocs via electrostatic interaction and then removed with the formed precipitate. The mechanisms related to PFOA removal contain the following: (i) binding of polymeric cationic species into flocs; (ii) anionic sites of PFOA adsorbing on the flocs, which were superficially positively charged; and (iii) enmeshment in a precipitate. However, the tiny particles derived from excessive agitation could be carried up to the surface of solution due to the EF effect, which actually reduced the retention time of flocs in bulk solution. In this study, the weight of flotation sludge is about 20%–50% of total sludge amount. It obviously shortened the adsorption time of PFOA on the flocs and thus restricted PFOA removal since the anionic site of PFOA is limited only in its molecule end. But for the removal of many metal ions in EC reports, mixing speed is not an important factor for their removal efficiencies due to the relatively

rapid adsorption equilibrium between metal ion and Fe flocs [23,24]. As a result, 180 rpm was identified as the recommended mixing speed for Fe flocs during treatment of PFOA, at which a balance between particle distribution and floc shear was properly achieved.

3.5. Effects of H₂O₂ addition and dosing interval

H₂O₂ as green oxidant in aqueous solution could regulate the oxidation process of Fe and subsequently coagulation of Fe ion. So the effect of H₂O₂ addition was explored as coagulant-aid for PFOA removal. Considering the duration of H₂O₂ reactivity, the pattern of intermittent addition was adopted in this test. Fig. 6 shows the PFOA removal versus time at different H₂O₂ dosing interval, in which each H₂O₂ (30 wt%) dosage was 2 ml (0.66 g H₂O₂) per liter of solution. When the EC was conducted with H₂O₂-aid, a higher removal of PFOA was obviously achieved. 5-min H₂O₂ dosing interval could improve the removal efficiency of PFOA from 74% (no H₂O₂ dosing) to more than 99% within 40-min electrolysis. Increasing the length of the testing interval from 5 to 10 min did not appear to a major impact on PFOA removal. But while increasing to 15 min of interval, PFOA removal efficiency decrease to 90%. So a 10 min of dosing interval for PFOA removal was chosen as the optimum addition pattern of H₂O₂. In fact, H₂O₂ addition could rapidly promote ferrous ion produced at the anode to be oxidized into ferric ion according to: $\text{H}_2\text{O}_2 + \text{Fe}^{2+} \rightarrow \cdot\text{OH} + \text{OH}^- + \text{Fe}^{3+}$. Although EC allows the formation of $\text{Fe}(\text{OH})_n$ ($n = 2$ or 3) coagulant and $\text{Fe}^{3+}/\text{Fe}^{2+}$ ions, the desired $\text{Fe}(\text{OH})_3(\text{s})/\text{FeOOH}(\text{s})$ derived from ferric ion undertake the main role of coagulation and flocculation [27,31]. So more ferric ion formed due to H₂O₂ addition resulted in the higher removal efficiency of PFOA compared with that without H₂O₂ addition. In addition, H₂O₂ addition could lead to the formation of hydroxyl radical as the above equation, which is attributed to the mechanism of Fenton reagent [32]. The removal of PFOA was not ascribed to the oxidation of hydroxyl radical but flocculation because $\cdot\text{OH}$ is very difficult to oxidize highly stable PFOA [6,33].

To better understand the adsorption process of PFOA during the EC, Fourier transform infrared (FTIR) spectra were recorded to show the variation of functional groups in PFOA as shown in Fig. 7. In FTIR spectra, the typical peak band for PFOA is around 1200–1350 cm^{-1} , which corresponds to the vibrations of $-\text{CF}_3$ and $-\text{CF}_2-$ groups and could be used as the identification of organic fluorine [34,35].

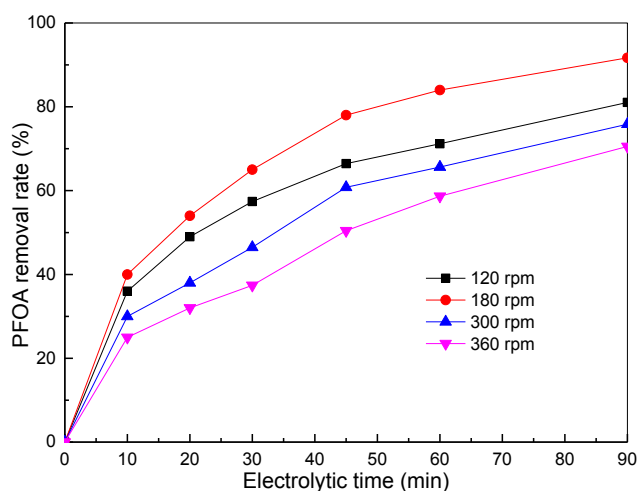


Fig. 5. Effect of mixing speed on PFOA removal during the electrocoagulation using Fe anode. Applied mixing speed is shown in the figure ($i = 37.5 \text{ mA/cm}^2$). Other conditions are the same as those in Fig. 1.

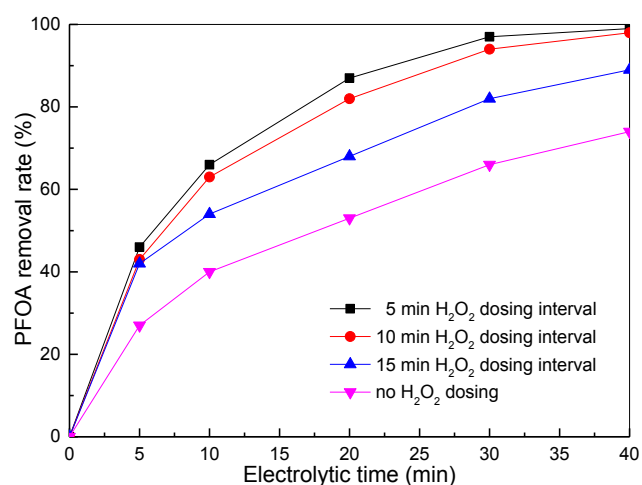


Fig. 6. Effect of H₂O₂ dosing interval on PFOA removal during the electrocoagulation using Fe anode. Applied dosing interval is shown in the figure (each H₂O₂ dosage: 0.66 g/L, $i = 37.5 \text{ mA/cm}^2$). Other conditions are the same as those in Fig. 1.

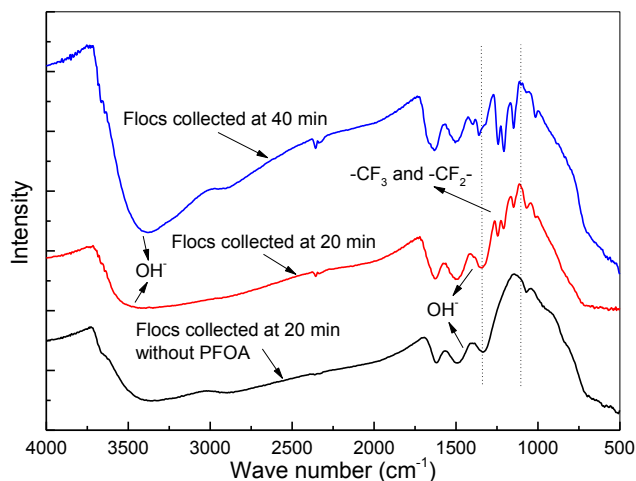


Fig. 7. FTIR spectra of dry Fe flocs collected at different electrocoagulation time for the solution with PFOA or without PFOA as blank.

During the EC of PFOA with Fe electrode, the peak intensity of $-\text{CF}_3$ and $-\text{CF}_2-$ group strengthened remarkably from 20 to 40 min electrolysis. There was no peak of $-\text{CF}_3$ and $-\text{CF}_2-$ after 20-min electrolysis when no PFOA adding in the raw solution as blank. It indicates that PFOA, which contains a large amount of C-F bonds, was removed gradually into Fe flocs by adsorption. The other peak bands shown in $1400\text{--}1500\text{ cm}^{-1}$ and $3250\text{--}3350\text{ cm}^{-1}$ could be assigned to the vibrations of $-\text{OH}$, which imply the formation process of Fe flocs containing hydroxyl group. Additionally, The PFOA solution after EC was filtered; and the trapped iron hydroxide flocs from flotation and settling were collected and then dissolved by 0.1 M HCl solution. The results showed that the recovery efficiency of the adsorbed PFOA was $96 \pm 3\%$ in triplicated experiments. The raw PFOA solution in this study was prepared in purified water without suspended solids. Therefore, the soluble PFOS was certainly removed by sorption on the flocs.

4. Conclusions

In this study, EC is proven as an efficient method to remove relatively high concentration PFOA from wastewater, especially for Fe anode. Comparison of EC using Fe or Al electrodes with chemical coagulation indicated that Fe anode possessed the highest removal efficiency for PFOA based on the similar coagulant dosage. Several key operation parameters were investigated to optimize the EC process including current density, initial aqueous pH, and mixing speed. Using the optimal conditions, 100 mg/L of PFOA could be removed with the efficiency of up to 93% by 37.5 mA/cm^2 at initial pH 3.77 using 180 rpm of mixing speed after 90-min electrolysis. Furthermore, the PFOA removal efficiency could be obviously improved by H_2O_2 addition during EC, which promoted the oxidative transformation from Fe^{2+} to Fe^{3+} and thus the generation of $\text{Fe}(\text{OH})_3(\text{s})/\text{FeOOH}(\text{s})$ as the main components of Fe flocs. More than 99% of PFOA could be removed by the intermittent addition of H_2O_2 at 10 min of dosing interval using 2 mL/L dosage. After electrolysis, the characteristic peaks of PFOA in FTIR test remarkably appeared, demonstrating the adsorption removal of organic fluorine with generation of Fe flocs. For the future work, it should address a better understanding of the above EC mechanisms and more perfluorinated compounds need to be tested for their removal efficiency by EC in order to improve scale-up methodology.

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