

Original Paper

Study on Efficiency and Mechanism of Advanced Fluoride Removal by Electrocoagulation Process

Wei Xie^{1*} & Hua Fang¹

¹ School of Environmental Science and Engineering, Nanjing University of Information Science & Technology, Nanjing, Jiangsu, China

* Corresponding Author

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Abstract

In this study, the effects of current density, electrolysis time, pH value, and sodium chloride (NaCl) electrolyte dosage on fluoride removal efficiency were systematically investigated. The results showed that the optimal operating parameters were determined as follows: current density of 10 mA/cm², electrolysis time of 30 min, pH value of 6, and NaCl dosage of 1 g/L. Under these optimal conditions, the fluoride removal efficiency could stably exceed 85%. Calcium, magnesium, and sulfate ions at an appropriate concentration of 50 mg/L significantly enhanced the fluoride removal efficiency, whereas nitrate ions exhibited a pronounced inhibitory effect. In the current density range of 5–15 mA/cm², the advanced fluoride removal process via electrocoagulation was better fitted to the pseudo-first-order adsorption kinetics model, indicating that the adsorption process was dominated by physical adsorption. The Zeta potential showed a trend of initial increase followed by a gradual decrease. The generated flocs had an average particle size of 146.4 μm and underwent significant directional aggregation, forming a large number of irregular dendritic and star-shaped flocculent aggregates.

Keywords

Fluorine-containing wastewater, Electrocoagulation, Advanced defluorination, Defluorination mechanism

1. Introduction

Industrial fluoride-containing wastewater, as a typical category of toxic and hazardous industrial wastewater, is extensively generated in various high-end manufacturing industries, including semiconductors, electronic component manufacturing, photovoltaics, lithium batteries, and fine chemicals. Among these, with the continuous expansion of production capacity in the photovoltaic

industry, the volume of fluoride-containing wastewater produced during photovoltaic manufacturing has increased rapidly, making this industry a key regulatory focus in the field of industrial fluoride wastewater treatment in China. Throughout the entire production chain of the photovoltaic industry, key wet processes such as texturing, etching, and cleaning continuously generate large quantities of fluoride-containing wastewater. This type of wastewater is characterized by complex water quality components, high concentrations of characteristic pollutants, and poor biodegradability, representing a major challenge and priority in wastewater treatment for the photovoltaic sector. Fluoride, as the primary characteristic pollutant in such wastewater, is non-biodegradable. If discharged without meeting standards, it poses significant dual risks to both the ecological environment and human health. Jiangsu Province of China officially implemented the new local standard Discharge Standard of Pollutants for Municipal Wastewater Treatment Plants (DB32/4440-2022) on March 28, 2023, which significantly tightened the discharge limit for fluoride from the national standard of 10 mg/L to 1.5 mg/L, providing a 3-year transition period for existing wastewater treatment plants to carry out retrofitting. Conventional fluoride removal processes currently in use can no longer meet the requirements for stable compliance, creating an urgent need to develop and screen efficient advanced fluoride removal technologies that are both adaptable to the water quality characteristics of photovoltaic fluoride-containing wastewater and economically viable.

Electrocoagulation, as an emerging water treatment process, offers significant advantages including high automation, no requirement for additional chemical dosing, and high treatment efficiency (PRIYADARSHINI, AHMAD, DAS et al., 2022), and has demonstrated promising application prospects in the field of fluoride removal from groundwater and drinking water. Its fundamental principle involves the oxidative dissolution of soluble metal anodes under the action of an external electric field, generating metal hydroxides and polynuclear hydroxyl complexes with strong adsorption and flocculation capabilities. Simultaneously, microbubbles generated by hydrogen evolution at the cathode synergistically achieve the entrapment, coprecipitation, and flotation separation of pollutants.

Aiming at the deficiencies of existing advanced fluoride removal water treatment technologies, this study selected the electrocoagulation process for advanced fluoride removal research. The optimal process conditions, fluoride removal efficiency, and underlying mechanisms were investigated, providing a reference for the development of new advanced fluoride removal technologies for industrial fluoride-containing wastewater.

2. Experiment

2.1 Experimental Setup and Experimental Procedure

The experimental setup consisted of a DC regulated power supply, an electrolytic cell, aluminum electrodes, and a stirring device. A 1 L beaker was used as the electrolytic cell. 1 L of prepared simulated fluoride-containing wastewater was added to the electrolytic cell. An appropriate amount of NaCl was added as the electrolyte to enhance electrical conductivity. Aluminum electrodes were

inserted into the solution in parallel with an inter-electrode distance of 2 cm. The power supply was turned on to set the required current intensity, and the stirring device was activated to commence the experiment. After the experiment, the solution was allowed to settle, and the supernatant was collected for fluoride concentration measurement.

2.2 Materials

All reagents used were of analytical grade and employed without further purification. The aluminum electrodes had dimensions of 11 cm (length) \times 5 cm (width) \times 0.2 mm (thickness), with an effective working dimension of 10 cm (length) \times 5 cm (width) \times 0.2 mm (thickness). Fluoride-containing wastewater was prepared by dissolving sodium fluoride (NaF) in deionized water. The initial fluoride ion (F^-) concentration of the simulated wastewater was 10 mg/L, and the initial pH value was adjusted to 6. Sodium chloride (NaCl) was added to the simulated wastewater as the supporting electrolyte. Hydrochloric acid (HCl) and sodium hydroxide (NaOH) solutions were used for pH adjustment.

2.3 Analytic Methods

Water samples were filtered through a 0.45 μ m membrane filter prior to analysis. Fluoride ion (F^-) concentration was determined using the ion-selective electrode (ISE) method.

Zeta potential variations during the electrocoagulation process were measured at different time intervals using a Zetasizer Nano ZS90 instrument. Floc morphology was observed under an optical microscope at a magnification of 40 \times , and floc particle size distribution was analyzed using ImageJ software.

3. Results and discussion

3.1 Single-Factor Experiments of Electrocoagulation

3.1.1 Effect of Current Density on Fluoride Removal

As shown in Fig 1, the fluoride removal efficiency of all groups increased rapidly during the initial 5–15 min of electrolysis, which was mainly attributed to the rapid formation of abundant $Al(OH)_3$ flocs near the aluminum electrodes that rapidly adsorbed and coprecipitated fluoride ions. As the electrolysis time extended to 15–35 min, the growth rate of removal efficiency gradually slowed down, indicating that the adsorption sites on the flocs were gradually saturated and the reaction gradually shifted from mass transfer control to adsorption equilibrium.

At an electrolysis time of 30 min, the removal efficiency of the 5 mA/cm² experimental group was approximately 62.2%, while that of the 15 mA/cm² experimental group reached approximately 88.5%. This was because a higher current density could accelerate the dissolution rate of the electrodes, promote the generation of more $Al(OH)_3$ flocs, and simultaneously enhance the mass transfer efficiency within the system, thereby improving the binding efficiency between fluoride ions and flocs. However, considering the economic feasibility of the process in practical applications, 10 mA/cm² was finally selected in combination with the discharge standards.

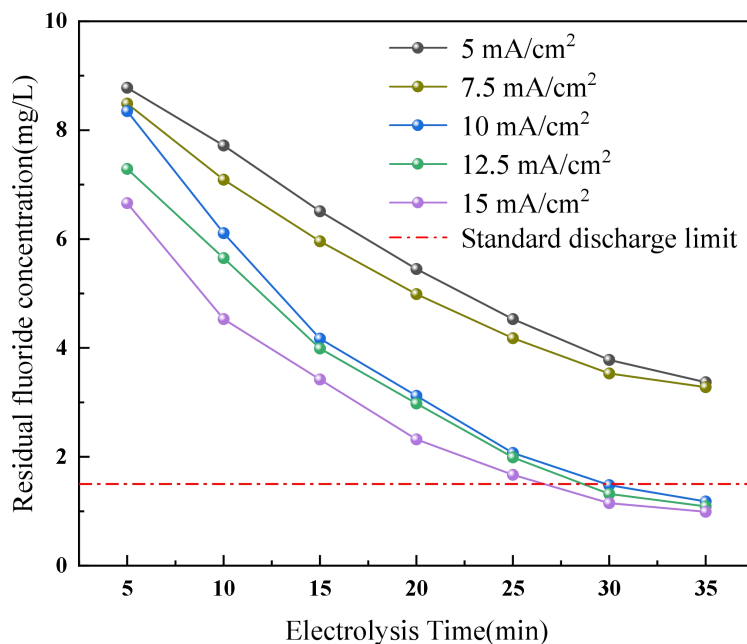


Figure 1. Effect of Current Density on Fluoride Removal

3.1.2 Effect of Electrolysis Time on Fluoride Removal

As shown in Figure 2, the fluoride removal efficiency increased progressively with electrolysis time, rising continuously as the reaction time extended from 10 min to 60 min. After 10 min of electrolysis, the residual fluoride concentration was approximately 5.86 mg/L, corresponding to a removal efficiency of 41.4%. When the electrolysis time reached 30 min, the residual concentration decreased to 1.48 mg/L, and the removal efficiency increased to 85.2%.

This stage was the core period for fluoride removal enhancement, during which the electrodes dissolved rapidly, generating a large amount of highly active $\text{Al}(\text{OH})_3$ flocs in-situ that rapidly captured fluoride ions through adsorption, coprecipitation, and ion exchange. After 30 min of electrolysis, the growth rate of removal efficiency slowed down significantly, with an increase of only 10 percentage points within the subsequent 30 min. This phenomenon was attributed to the gradual saturation of adsorption sites on the flocs and the increased mass transfer resistance for fluoride ions diffusing into the interior of the flocs. Consequently, the reaction gradually shifted from rapid adsorption control to a stage dominated by surface complexation and diffusion equilibrium. Considering the discharge standards and economic feasibility comprehensively, an electrolysis time of 30 min was selected as the optimal condition (EMAMJOMEH, SIVAKUMAR, & VARYANI, 2011).

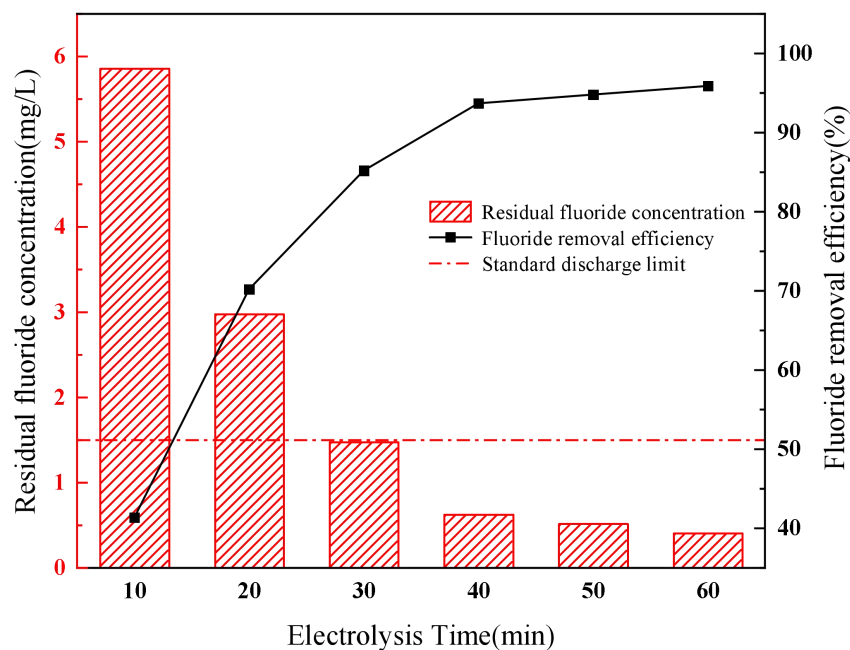


Figure 2. Effect of Electrolysis Time on Fluoride Removal

3.1.3 Effect of pH Value on Fluoride Removal

As shown in Figure 3, the fluoride removal efficiency was higher under acidic and neutral conditions but lower under alkaline conditions. When the pH value ranged from 5 to 7, the fluoride removal efficiency remained at a high level, reaching 87.7%, 85.6%, and 82.9%, respectively. In contrast, when the pH value increased to 8 and 9, the fluoride removal efficiency decreased significantly to 79.3% and 75.5%, respectively.

This phenomenon can be explained as follows: under weakly acidic to neutral conditions, the in-situ generated $\text{Al}(\text{OH})_3$ flocs from electrocoagulation possess a positively charged surface, which can efficiently adsorb negatively charged fluoride ions through electrostatic attraction. Meanwhile, the ion exchange reaction between hydroxyl groups and fluoride ions is also more favorable under these conditions. However, under high pH conditions, the increased OH^- concentration in the solution exerts two adverse effects: on the one hand, OH^- competes with F^- for adsorption sites on the floc surface; on the other hand, it promotes the transformation of $\text{Al}(\text{OH})_3$ into negatively charged hydroxyl complexes, thereby weakening the electrostatic adsorption capacity for F^- . Therefore, considering the fluoride removal efficiency, a pH value of 6 was finally selected as the optimal condition.

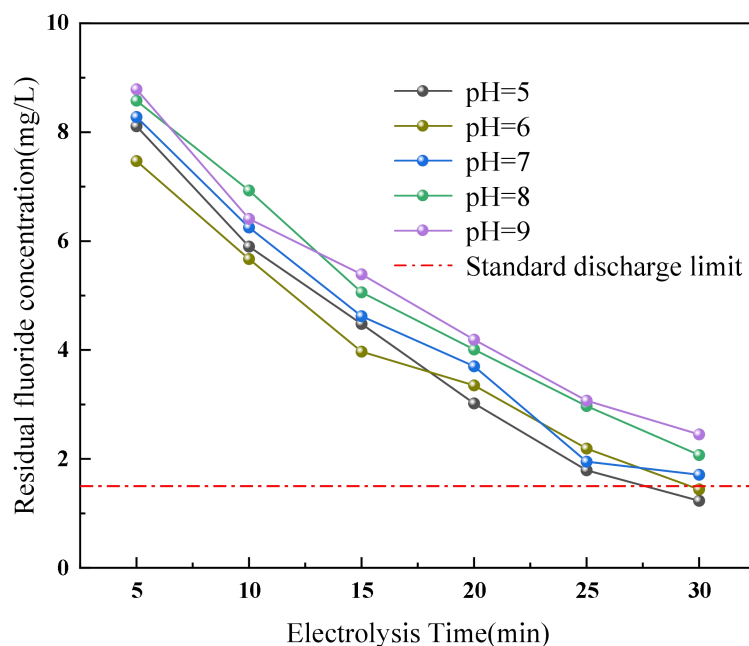


Figure 3. Effect of pH Value on Fluoride Removal

3.1.4 Effect of Electrolyte Dosage on Fluoride Removal

As shown in Figure 4, the fluoride removal efficiency exhibited a trend of initial increase followed by a decrease with increasing electrolyte dosage. When the electrolyte dosage ranged from 0.25 to 1 g/L, the removal efficiency increased significantly, while it began to decline when the dosage reached 1.5 g/L. An appropriate amount of electrolyte can increase the electrical conductivity of the solution and reduce the resistance, accelerate the electrode dissolution and electron transfer rates, and simultaneously enhance convective diffusion within the system, promoting the migration of fluoride ions to the floc surface, thereby improving the fluoride removal efficiency. When the dosage exceeded 1 g/L, the residual fluoride concentration sharply increased from 1.26 mg/L to 1.96 mg/L, and the removal efficiency decreased from 87.4% to 80.4%, resulting in a significant decline in fluoride removal performance.

This decline can be attributed to two main mechanisms. First, with the continuous increase in Cl⁻ concentration, more acidic substances such as HCl and HClO are generated in the solution, which hinder the precipitation and adsorption of fluoride ions by flocs. Second, excessive ionic strength compresses the electric double layer, leading to floc agglomeration and a decrease in specific surface area, thereby weakening the adsorption and coprecipitation effects. Additionally, an appropriate electrolyte dosage can reduce power consumption and inhibit anode passivation during the electrocoagulation process (THAKUR & MONDAL, 2017). Therefore, an electrolyte dosage of 1 g/L was selected as the optimal condition.

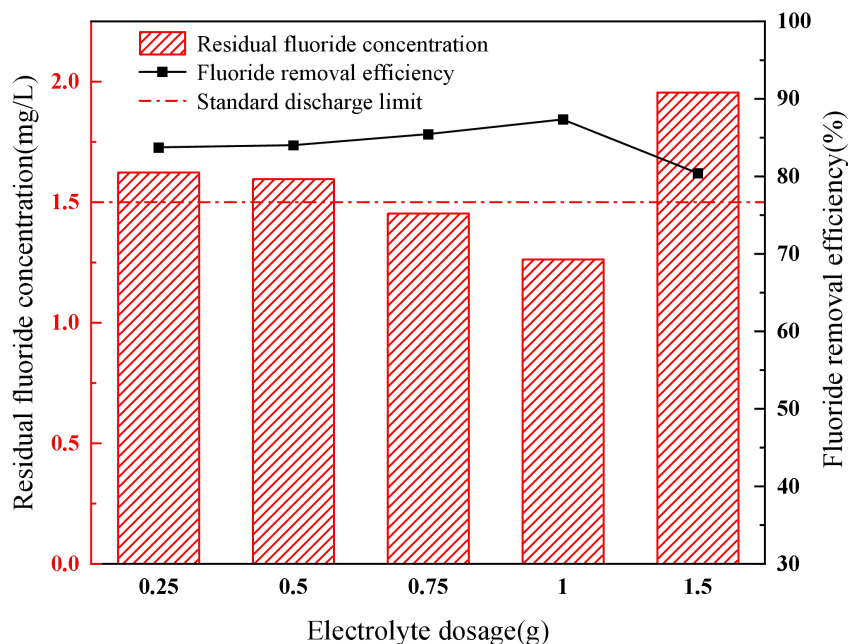


Figure 4. Effect of Electrolyte Dosage on Fluoride Removal

3.2 Effect of Coexisting Ions on Fluoride Removal

3.2.1 Effect of Calcium and Magnesium Ions on Fluoride Removal

As shown in Figure 5 (a), the fluoride removal efficiency increased with electrolysis time, and it was evident that the fluoride removal efficiency of the three groups with calcium sources added was higher than that of the control group. Furthermore, the maximum fluoride removal efficiency of 97.6% was achieved at a calcium ion concentration of 50 mg/L, indicating that an appropriate amount of calcium ions is beneficial for fluoride removal. Calcium ions can react with fluoride ions in water to form calcium fluoride (CaF_2) and hydroxide precipitates, thereby enhancing the defluoridation performance of the process (ZUO, CHEN, LI et al., 2008).

As shown in Figure 3-6(b), the fluoride removal efficiency increased with increasing magnesium ion concentration within a certain range. The maximum fluoride removal efficiency of 95.6% was obtained at a magnesium ion concentration of 50 mg/L, suggesting that an appropriate amount of magnesium ions can also improve fluoride removal efficiency. Moderate magnesium ions react with fluoride ions to form magnesium fluoride (MgF_2) and hydroxide precipitates for removal (SHEN, CHEN, GAO et al., 2003).

However, when the concentrations of calcium and magnesium ions reached 100 mg/L, the fluoride removal efficiency decreased in both cases. This is because excessive calcium ions form stable $\text{Ca}(\text{OH})_2$ precipitates prematurely with fluoride ions, consuming part of the adsorption sites on the flocs and leading to a slight decrease in performance. Excessive magnesium ions generate $\text{Mg}(\text{OH})_2$ precipitates, which coat the floc surface and block adsorption sites, while competing with fluoride ions for hydroxyl sites, significantly inhibiting the removal efficiency (NYANGI, CHEBUDE, KILULYA et

al. , 2022). Additionally, the excessive formation of calcium and magnesium precipitates may cause anode passivation and reduce electrolysis efficiency.

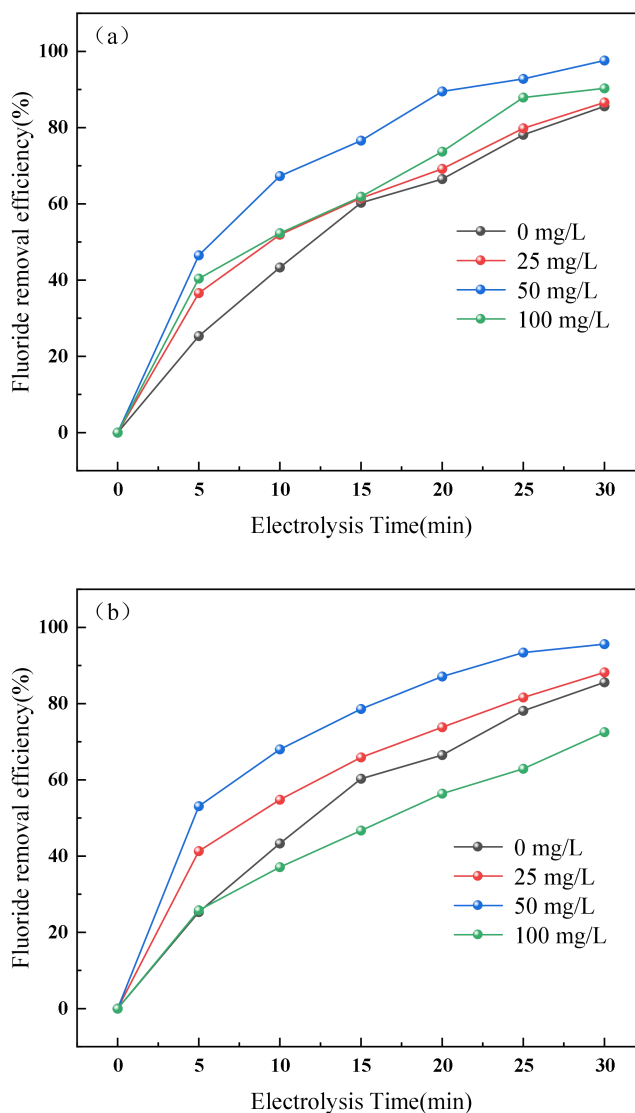


Figure 5. Effect of Calcium and Magnesium Ions on Fluoride Removal (a)Calcium;(b) Magnesium

3.2.2 Effect of Sulfate and Nitrate Ions on Fluoride Removal

As shown in Figure 6 (a), sulfate ions had a significant effect on fluoride removal. Within a certain concentration range, sulfate ions assisted fluoride removal through ion exchange and electrostatic adsorption, simultaneously increasing solution conductivity, accelerating electrode reactions, and inhibiting plate passivation via pitting corrosion to improve electrolysis efficiency. The maximum fluoride removal efficiency of 97.8% was achieved at a sulfate concentration of 50 mg/L. However, when the concentration increased to 100 mg/L, the removal efficiency decreased significantly. This was

attributed to the intense competition between excess sulfate and fluoride ions for hydroxyl adsorption sites on flocs, compression of the electric double layer leading to floc agglomeration and reduced specific surface area, and accumulation of sulfate on the electrode surface reducing flocculant release, ultimately inhibiting defluoridation performance.

As shown in Figure 6 (b), nitrate ions exhibited an obvious inhibitory effect on fluoride removal. Nitrate ions have higher charge density and adsorption energy, making them more likely to compete with fluoride ions for active sites on flocs. High concentrations of nitrate also increase solution ionic strength, destroying the colloidal stability of $Al(OH)_3$ flocs and causing floc fragmentation and reduced effective adsorption sites. Additionally, the reduction reaction of nitrate ions produces OH^- , which increases the solution pH and decreases the formation of $Al(OH)_3$ under alkaline conditions, further reducing fluoride removal efficiency (VASUDEVAN, KANNAN, LAKSHMI et al., 2011).

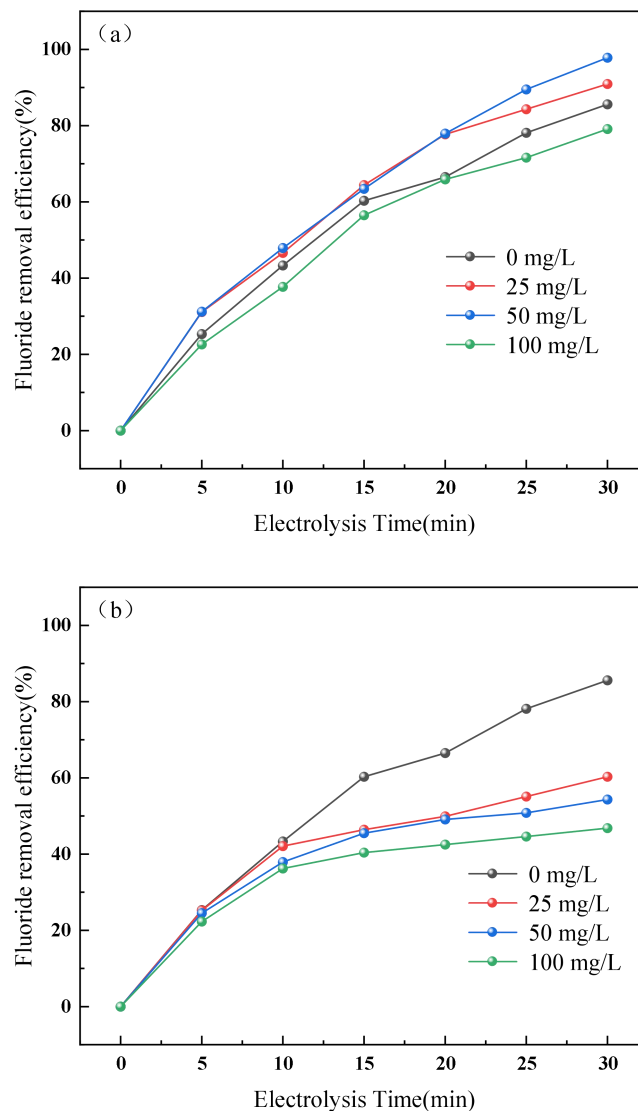


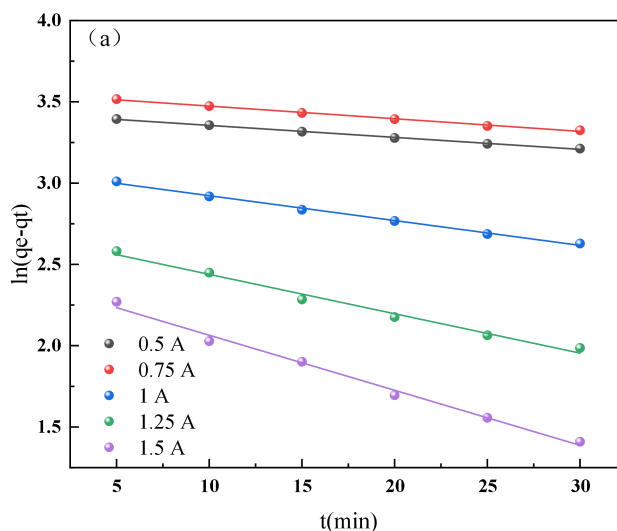
Figure 6. Effect of Sulfate and Nitrate Ions on Fluoride Removal (a) Sulfate;(b) Nitrate

3.3 Adsorption Kinetics

As shown in Figure 7 and Table 1, among the five groups of experiments with current densities ranging from 5 to 15 mA/cm², the R² values of the pseudo-first-order adsorption kinetics fitting equations for the first four groups were consistently higher than those of the pseudo-second-order adsorption kinetics fitting equations. It can be inferred that under the same current density conditions, the goodness of fit of the pseudo-first-order adsorption kinetics is better than that of the pseudo-second-order adsorption kinetics equation.

The reaction rate constant in the pseudo-first-order kinetic equation exhibited a trend of initial decrease followed by increase. This is because at the early stage of advanced fluoride removal by electrocoagulation, low current densities could not electrolyze sufficient flocculant components, resulting in low removal efficiency, which then increased rapidly with electrolysis time. When the current density was appropriately increased, a high removal efficiency was already achieved in the early reaction stage, so the reaction rate slowed down with time. When the current density was sufficiently high, the excessive current density caused the anode to generate a large amount of flocculant, leading to a continuous increase in the reaction rate.

In summary, the advanced fluoride removal process by electrocoagulation is more consistent with the pseudo-first-order adsorption kinetics, and the adsorption process of this reaction is dominated by physical adsorption.



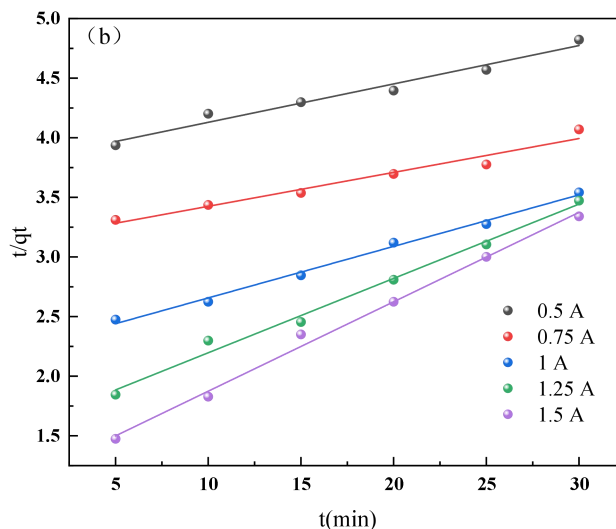


Figure 7. Adsorption Kinetics Fitting Curves for Fluoride Removal by Electrocoagulation at Different Current Densities (a) Pseudo-First-Order Kinetic Model; (b) Pseudo-Second-Order Kinetic Model

Table 1. Kinetic Parameters for Fluoride Removal by Electrocoagulation at Different Current Densities

Current density (mA/cm ²)	Pseudo-first-order kinetic model		Pseudo-second-order kinetic model	
	k ₁	R ²	k ₂	R ²
5	0.06884	0.99003	0.00027	0.96355
7.5	0.01697	0.99729	0.00026	0.95402
10	0.01792	0.99495	0.00084	0.99218
12.5	0.03519	0.99478	0.00247	0.98797
15	0.05578	0.98424	0.00499	0.99282

3.4 Zeta Potential Analysis

Figure 8 shows the variation of Zeta potential during the electrocoagulation defluoridation process. The Zeta potential exhibited a trend of initial increase followed by a gradual decrease, which is consistent with previous studies. It rose from an initial negative potential to a positive potential and then decreased slowly. This is because the surfaces of particles in water are negatively charged at the initial stage, and the system is in a relatively stable state. After a period of electrolysis, the anode releases Al³⁺ ions, which adsorb and neutralize the negative charges on the particle surfaces. In the later stage of the reaction, the potential decreases slowly and tends to stabilize.

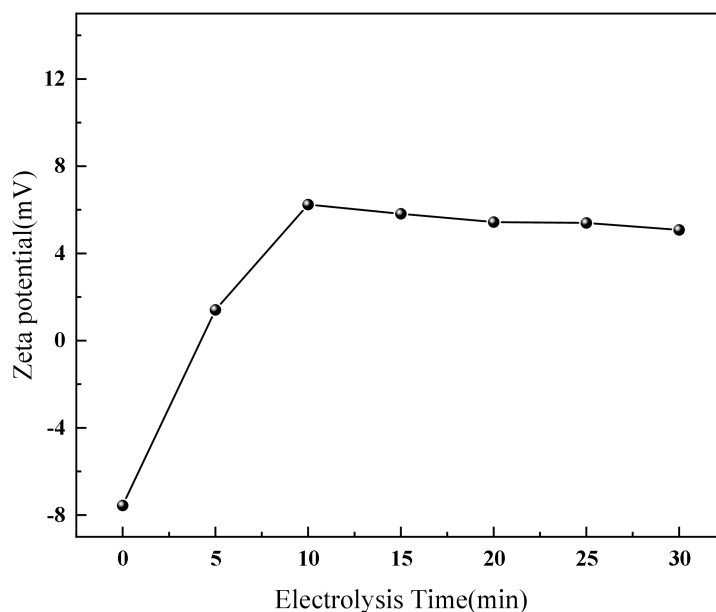


Figure 8. Zeta Potential Variation During Electrocoagulation Process

3.5 Floc Morphological Analysis

As shown in Figure 9(a), the flocs in the electrocoagulation system exhibited obvious oriented aggregation, forming a large number of dendritic and star-shaped irregular flocculent aggregates. The overall particle size of the flocs was relatively large, with only a small number of incompletely agglomerated fine particles dispersed in the system. Electrocoagulation generates highly active hydroxyaluminum complexes through the hydrolysis of Al^{3+} ions in-situ dissolved from the anode. These complexes have much higher specific surface area and adsorption activity than the hydrolysis products of externally dosed aluminum salts in conventional coagulation, and thus possess stronger complexation and adsorption capacity for fluoride ions. Meanwhile, the electric field in the system drives electrophoretic movement of charged particles, significantly increasing the collision frequency and efficiency between particles and promoting the agglomeration and growth of flocs.

As shown in Figure 9(b), the average floc size in electrocoagulation was $146.4 \mu m$. The main peak of the particle size distribution curve was concentrated in the range of $0-200 \mu m$, and the upper limit of particle size extended to over $1800 \mu m$. This indicates a wide particle size distribution of flocs. Although the proportion of large-sized floc aggregates was low, they still had a significant distribution, which is fully consistent with the floc morphology observed in Figure 9(a).

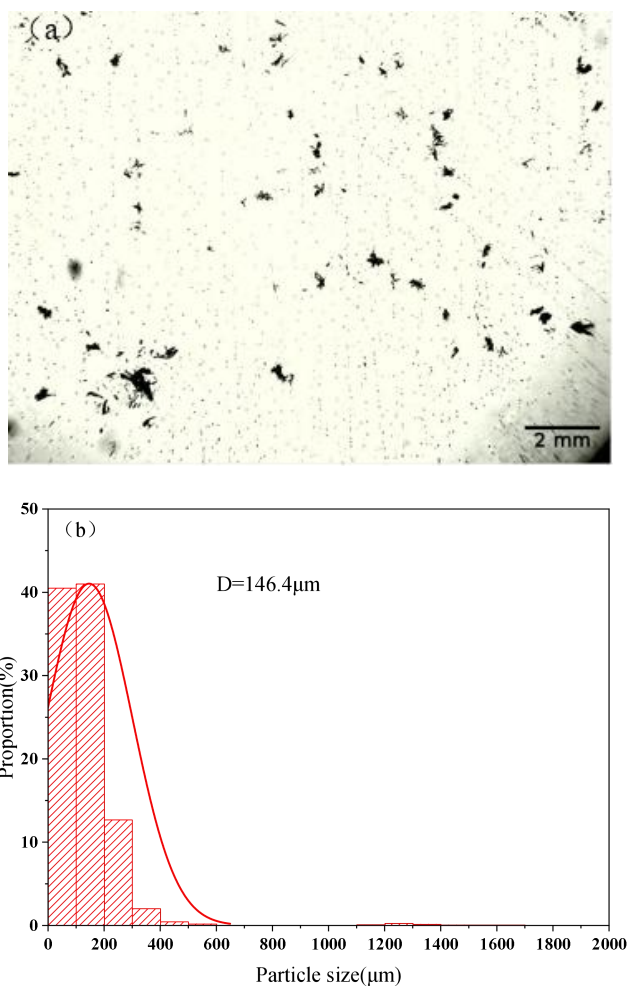


Figure 9. Microscopic Floc Morphology and Particle Size Distribution (a) Electrocoagulation Floc Morphology; (b) Electrocoagulation Floc Particle Size Distribution

4. Conclusion

Single-factor experiments were conducted to investigate the effects of current density, electrolysis time, pH, and NaCl dosage on fluoride removal by electrocoagulation. The optimal conditions were 10 mA/cm², 30 min, pH 6, and 1 g/L NaCl, achieving a stable fluoride removal efficiency of over 85%.

Coexisting ions experiments showed that Ca²⁺, Mg²⁺, and SO₄²⁻ at 50 mg/L significantly enhanced defluoridation, while NO₃⁻ exhibited a notable inhibitory effect.

Adsorption kinetics fitting revealed that the pseudo-first-order model provided a better fit than the pseudo-second-order model within 5–15 mA/cm², indicating that the advanced fluoride removal process was dominated by physical adsorption.

Zeta potential increased initially and then gradually decreased, as Al³⁺ released from the anode neutralized the negative charges on particle surfaces, eventually stabilizing at a lower potential.

Floc morphology analysis showed that electrocoagulation flocs had an average size of 146.4 μm and formed dendritic and star-shaped aggregates through oriented aggregation.

This study has systematically elucidated the efficiency laws and action mechanism of advanced fluoride removal by electrocoagulation process. It can stably achieve a fluoride removal efficiency of over 85%, and the effluent meets the latest drinking water fluoride standard of 1.5 mg/L in Jiangsu Province.

The electrocoagulation process has broad application prospects in the field of industrial fluorine-containing wastewater treatment, and provides important experimental basis and theoretical support for the design and operation of advanced fluorine-containing wastewater treatment projects. Future research can be improved and optimized from the perspective of process economy to further increase the possibility of practical application.

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