

Influence of operating parameters on ammonia nitrogen removal from micro-polluted water by electro-coagulation-flotation with aluminum electrodes

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Abstract

Due to the eutrophication and pollution of urban water supply sources, the traditional treatment techniques can no longer satisfy the requirement of the micro-polluted water treatment. The efforts have been made to explore the ammonia nitrogen removal efficiency from the micro-polluted water with electro-coagulation-flotation (ECF) which is one of the most promising techniques for practical application. The effect of operating parameters, such as the electrolysis time, current density, initial pH value and precipitation time in the solution have been extensively studied in a wide range of values. And the optimum operation parameters are determined with the current density of 3.42 mA/cm^2 , electrolytic time of 40 min and the initial pH of weak alkalinity from 7 to 9. When the chloride ions exist, the ECF exhibits better ammonia nitrogen removal through the generation of active chlorine and the enhancement of Al^{3+} release.

Keywords

Ammonia nitrogen; Electro-coagulation-flotation; Aluminum electrodes

1 INTRODUCTION

With the process of industrialization, the pollution of water resource becomes quite serious. Not only the organics concentration increases in the water, but also the concentration of ammonia nitrogen is raised. However, the traditional water purification processes cannot effectively remove ammonia nitrogen. Studies have shown that (Rogalla et al. 1992) 0.25 mg/L of NH_4^+ was enough to make the nitrifying bacteria grow in the water supply network, and then nitrifying bacteria would release a smelly smell in the metabolic process. Excessive amounts of nitrate nitrogen will be converted into nitrite nitrogen in the stomach, which further forms carcinogenic substance nitrosamines with secondary amine in the stomach. Therefore, ammonia nitrogen ($\text{NH}_3\text{-N}$) in drinking water is stipulated at 0.5 mg/L or less in France and Germany and 0.2 mg/L in Netherlands. According to the new drinking water health standards (GB5749-2006) in China, 0.5 mg/L of $\text{NH}_3\text{-N}$ or less is required. The ammonia nitrogen has been a major impact on the environment since it is one of the major causes for the eutrophication. Therefore, effective removal of ammonia nitrogen with low concentration has become a hot topic in the field of micro-polluted water source treatment.

With regards to the drinking water treatment technologies, conventional coagulation is still the main treatment process. However, due to the small size and low specific gravity, it is difficult to get rid of ammonia nitrogen effectively with the traditional water treatment processes. The electro-coagulation-flotation (ECF) method, a quite promising technology, has been applied in some wastewater treatment with the rapid development of power industry and shown a better performance of ammonia nitrogen removal with relatively low energy consumption.

The available literature reveals that the ECF with aluminum electrodes could achieve better ammonia nitrogen removal compared with that of iron electrodes. Some researches have been done to validate the reliability of EFC in terms of phosphate (Attour et al. 2014) and algae (Alfajara et al. 2002), fluoride (Hu et al. 2003), oil (Canizares et al. 2008), etc. In the case of aluminum, main reactions are as follows:

Al^{3+} ions released from the anode:



The oxidation of water at the anode:



The reduction of water at the cathode:



The electrochemical reduction of O_2 at the cathode:



Firstly, the ammonia nitrogen was subjected to electro-coagulation by Al^{3+} ions generated from the anode in the ECF process with aluminum electrodes. And then the flocs were floated after being captured by the micro bubbles (H_2 and O_2) released at electrode.

In this study the influence of operating factors on ammonia nitrogen removal from micro-polluted water using ECF process have been investigated, such as electrolysis time, current density, initial pH and precipitation time, and the optimal operating conditions were proposed. As we know, the anion ubiquitously exists in natural waters and it has been reported that anion has much influence on the wastewater treatment in the ECF process, especially the chloride ions which display a positive role. However, the effect of chloride ions on ECF for ammonia nitrogen removal has not been studied up to now. Thus, the performance of ECF using aluminum electrodes for ammonia nitrogen removal in the presence of chloride ions and other anions was also explored and the fundamental mechanism was further discussed.

2 Materials and methods

2.1 Experiment device

The experimental device is shown in Figure 1. The electro-coagulation experiments have been carried out in a batch reactor (125 mm length, 100 mm width and 125 mm height). The mixed liquor was stirred continuously by a magnetic stirrer at a speed of 200 rpm and the stirring speed was kept low enough to avoid the destruction of the flocculating constituent. The two sets of aluminum electrodes were vertically immersed in the liquid with the effective electrode area of 11250 mm^2 ($90 \times 1125 \text{ mm}^2$). The electrode gap was set at 1.0 cm. Current was supplied with a digital direct current power (WYY 30V 3A, China) and all the experiments were carried out under constant-current mode with a voltage ranging from 0 to 30 V. Electrochemical coagulation experiments were conducted under constant-current mode in the range 0.1–0.9 A.

Each experiment was performed with 1000 mL of synthetic water at room temperature with initial ammonia nitrogen concentration of 1.0 mg/L which was prepared by ammonium chloride and similar with those in Suzhou creek and Huangpu River. The pH value was adjusted by using 0.1 M NaOH or 0.1 M H_2SO_4 solution. NH_4Cl and $(\text{NH}_4)_2\text{CO}_3$, $(\text{NH}_4)_2\text{SO}_4$ were added to explored the influence of different anion with the same initial $[\text{NH}_3\text{-N}]$ of 1.0 mg/L. After the scheduled time, the sample was taken at 4.0 cm under the liquor and taking on a clear liquid test. Prior to the next experiment, the electrodes were pumiced and degreased with 400 grit sandpaper and then rinsed

with 0.1 M HCl and clean water to avoid any effect of the used electrodes.

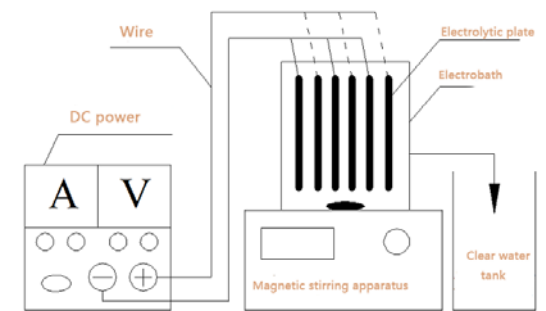


Figure 1. Electro-coagulation-flotation device

2.2 Analysis methods

In the experiments, the surface morphology and elemental composition of aluminum anode after ECF treatment with different anion were determined by SEM-EDX (scanning electron microscopy with energy dispersive X-ray) analysis. The conductivity was measured continuously using a consort conductivity meter (DDS-307A). The pH and temperature measurements were performed continuously using a pH meter (HACH). The concentrations of ammonia nitrogen in samples were determined by the nessler's reagent spectrophotometry method.

Ammonia nitrogen removal rate = $(C_0 - C_1) / C_0 \times 100\%$

In which, C_0 is initial concentration of ammonia nitrogen solution, mg/L; C_1 is solution concentration of ammonia nitrogen in the sample, mg/L.

3 Results and discussions

3.1 Effect of electrolysis time and current density

Electrolysis time and current density are the most sensitive operating parameters in ECF process. And the two factors are also in relation to energy consumption which is the key to the wide application. The influence of the electrolysis time and current density on ammonia nitrogen removal is shown in Figure 2 at the conditions of the pH 8, precipitation time 20 min and initial concentration of ammonia nitrogen 1.0 mg/L.

Electrolysis time affects the efficiency of the electrolytic flocculation treatment mainly by influencing the generation of aluminum ion and determining the contact time between pollutants and hydroxyl aluminum compound. It could be seen from Figure 2 that at same current density, the removal of ammonia nitrogen improved a lot with the extension of time. However, removal rate was relatively slow after 30 min, because metal oxide film on the surface of aluminum anode hampered the reaction rate. With longer duration of electricity, the water temperature was also rising and the side effects appeared at the same time which inhibited further oxidation degradation, thus removal rate of ammonia nitrogen began to flatten out.

Current density decides not only the discharge of flocculants but also the producing rate of air bubbles, and even affects the solution mixing and mass transferring between the electrodes. With the increase of current density, ammonia nitrogen removal efficiency increased. This phenomenon could be attributed to the following two reasons. Firstly, the fast production of small bubble of hydrogen facilitated the flotation. Secondly, the increasing of current density, strengthened the impetus of a charged particle movement, electrode plates on the operation of the conductive ion activity increased significantly. One side effect induced by using aluminum as electrode metal was

the formation of a passive oxide film. But the higher current density was, the thinner the oxide layer was. When there was Cl^- in the system, more hypochlorite was produced with higher current density, which would oxidize the ammonia nitrogen with higher removal efficiency. Thus, current density determined the amount of hypochlorous acid and affected the removal efficiency of ammonia nitrogen. Taking the energy consumption into consideration, the current density of 3.42 mA/cm^2 and electrolytic time for 40 min were recommended.

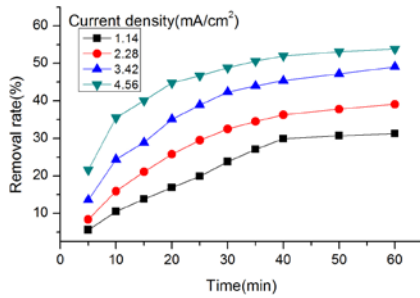


Figure 2. Effect of electrolysis time and current density on ammonia nitrogen removal ($\text{pH} = 8$, $[\text{NH}_3\text{-N}]_0 = 1.0 \text{ mg/L}$, precipitation time = 20 min).

3.2 Effect of initial pH

It is well known that pH plays a crucial role in the ECF process, because the variation of aluminum chemical valence depends directly on the pH level. pH value mainly affects the hydroxyl aluminum iron compounds form in the solution, and then decides the removal pathway of pollutants. The pH value will also influence the formation of colloid on the surface of the anode. Effect of initial pH on ammonia nitrogen removal was shown in Figure 3.

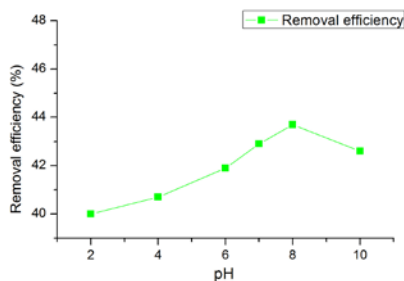


Figure 3. Effect of initial pH on ammonia nitrogen removal ($[\text{NH}_3\text{-N}]_0 = 1.0 \text{ mg/L}$, precipitation time = 20 min, electrolytic time = 40 min, current density = 3.42 mA/cm^2).

When the pH is too low, H_2 reduced form the cathode. At the mean time the amount of OH^- decreased. In addition, too low value of pH, aluminum electrode corrosion is serious, metal hydrolysis reaction is detected. Impertinent acid-base properties produce escaping fluid loss and secondary environmental pollution. Under acid atmosphere, O_2 and Cl_2 is the main oxidant in the system. But $\text{Cl}^- \rightarrow \text{Cl}_2 \rightarrow \text{OCl}^- \rightarrow \text{Cl}^-$ is only produced in weak alkali conditions. Therefore, in order to guarantee the effective generation and utilization of hypochlorite, too low pH is undesirable for the practical application.

But strongly alkalinity is unwise, either, which is different from the conditions for phosphate removal. High concentration of OH^- in the solution leads to strong oxidation ability of oxygen, which reacts with aluminum on the surface of the anode. The metal oxide film hindered the normal

dissolution of metal and alkali conditions, and moreover could produce ClO_3^- ion in the anode, which is stable with low reactivity. Thus the increased pH value reduced oxidation efficiency. Besides, Al^{3+} in the electrolyte would be in the form of hydroxide precipitation which reduced the oxidation abilities.

3.3 Effect of precipitation time

At the condition of 40 min electrolytic time, 3.42 mA/cm^2 current density, 1.0 mg/L initial concentration of ammonia nitrogen, and initial pH of 8, the relationship between ammonia nitrogen removal rate and the precipitation time was explored and the result was shown in Figure 4.

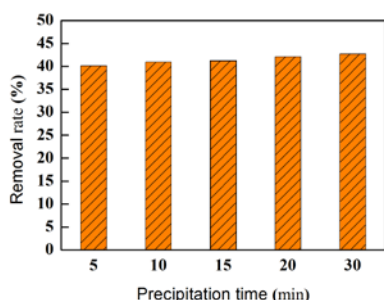


Figure 4. Effect of precipitation time on ammonia nitrogen removal ($\text{pH} = 8$, $[\text{NH}_3\text{-N}]_0 = 1.0 \text{ mg/L}$, electrolytic time = 40 min, current density = 3.42 mA/cm^2).

With regards to other contaminants removal in the micro-polluted water treatment using the ECF process, precipitation time has been frequently investigated. It is illustrated above that the effect of precipitation time on ammonia nitrogen removal rate is not very obvious. Compared to the electrolysis time, current density and initial pH, precipitation time could be considered as the secondary factor.

3.4 Effect of the anion

3.4.1 Effect of anion on ammonia nitrogen removal. The influence of different anions on the ammonia nitrogen removal was studied and three typical anions were chosen which are common and exist widely in the natural water. As shown in Figure 5, the removal of ammonia nitrogen increased with the electrolysis time. It was obvious that the removal efficiency reached maximum after 60 min. It is interesting to find that there is difference between the Cl^- and CO_3^{2-} , SO_4^{2-} on the ammonia nitrogen removal. The chloride anion contributed to the ammonia nitrogen removal. Nevertheless, the carbonate and sulfate anions had the negative impact.

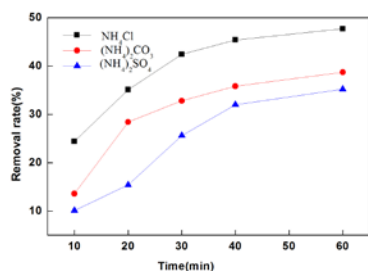
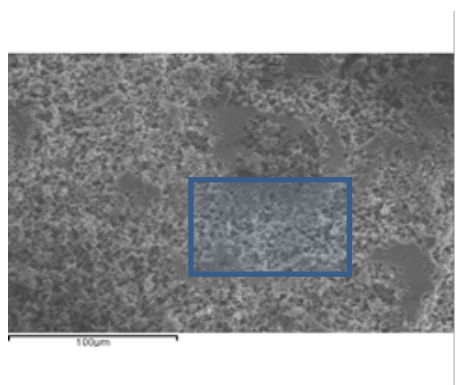
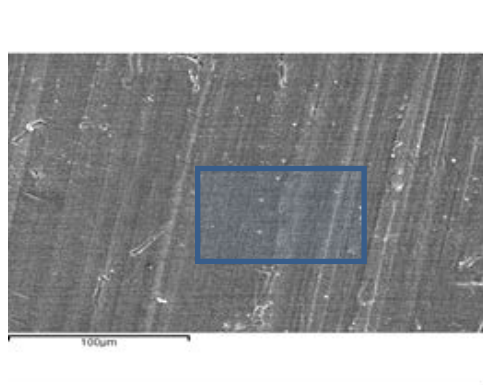
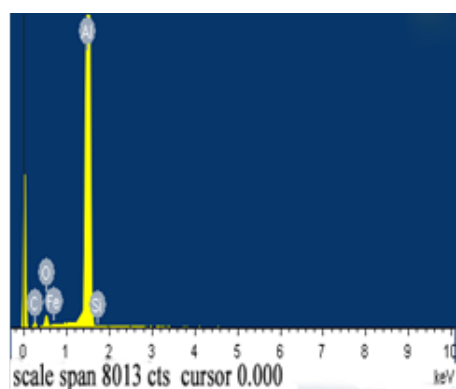
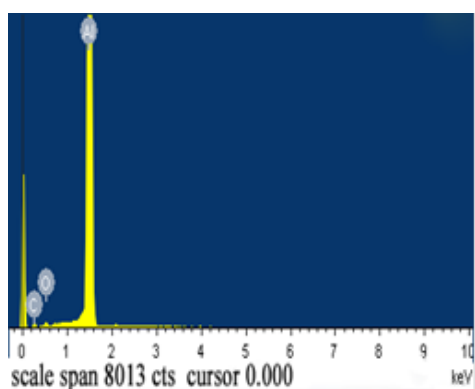


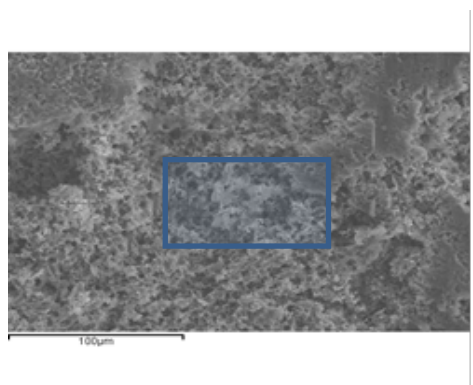
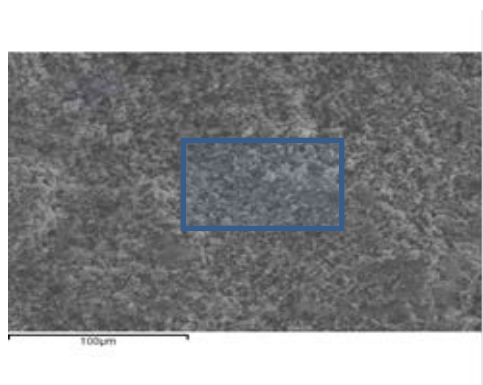
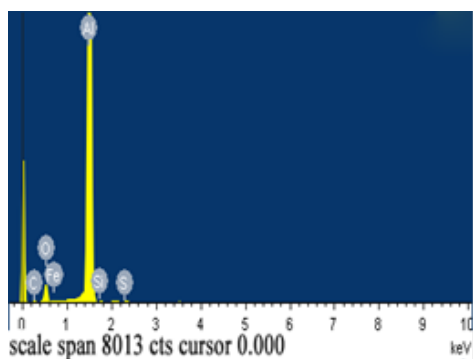
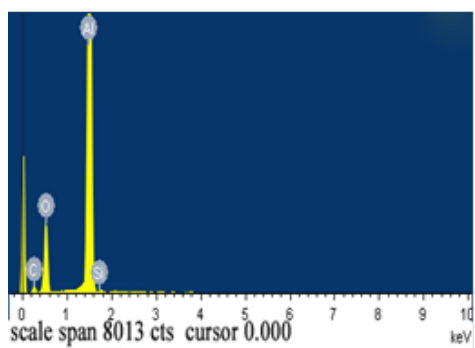
Figure 5. Effect of different anions on ammonia nitrogen removal rate ($\text{pH} = 8$, $[\text{NH}_3\text{-N}]_0 = 1.0$

mg/L, electrolytic time = 40 min, current density = 3.42 mA/cm²).



a. The original plate

b. The chloride ion



c. Carbonate ions

d. Sulfuric acid ion

Figure 6. SEM-EDX analysis of aluminum anode surfaces

3.4.2 Reaction mechanism. It is necessary to figure out the reason why chloride ion performances a positive effect, as anions are contained in many drinking water sources. In order to explore the mechanism of different anion on ammonia nitrogen removal, the subtle variation of aluminum plates was concerned. When using aluminum as plates, the electrochemical reactions would happen as shown in Eqs. 1, 2, 3, 4 (Hu et al. 2003).

The anode corrosion and passivation process on the aluminum anodes surface could be understood better by using SEM-EDX analysis. The SEM images and EDX analysis of the aluminum anode surfaces affected by different anions after 40 min in the ECF process were displayed in Figure 6.

Figure 6(a) is the result of the original aluminum anodes and it can be seen that the metal texture of electrode plate surface was obvious without any sign of corrosion. It could be seen from Figure 6(b) that there was a number of deep corrosion pits on the surface of electrode plate with addition of Cl^- . From EDX analysis (Table 1) of corrosion pit, it was known that oxygen element (O) accounted for only 7.68% of the total element content which was almost the same as that in the new aluminum plate, and this result indicated that the formation of oxide film on the surface of aluminum anode was slowed down in presence of Cl^- and aluminum electrode plate could be dissolved more smoothly (Mouedhen et al. 2008). The evolution of Cl^- could be shown below:



As shown in Figure 6(c) and (d), when CO_3^{2-} , SO_4^{2-} were added into the electro bath, respectively, a bit of corrosion pits were distributed on the surface of plate. However, compared to the presence of Cl^- , the formation of corrosion pits were shallow and oxygen element percent were 35.93% and 16.05%, respectively (Table 1), which were significantly higher than that in the original aluminum plate. It was inferred that corrosion pits were formed on the surface of the oxide film with a layer of Al (or hydrogen oxidation film), which covered the effective area of aluminum anodes and inhibited the dissolution of aluminum and the transferring of aluminum ion. Thereby the reaction rate was decreased in the existence of CO_3^{2-} , SO_4^{2-} (Hu et al. 2003).

Table.1 Aluminum anode surface composition and relative content of atomic elements analysis

Element	C%	O%	Al%	Si%	S%	Total
Spectra1-a	13.99	3.33	82.68	0.00	0.00	100
Spectra1-b	18.11	7.68	73.65	0.30	0.00	100
Spectra1-c	16.81	35.93	46.92	0.34	0.00	100
Spectra1-d	12.06	16.05	71.07	0.27	0.27	100

4 CONCLUSIONS

1. The electro-coagulation-flotation using aluminum electrode has better ammonia nitrogen removal from micro-polluted water and the removal efficiency was affected by some operating parameters. Ammonia nitrogen removal rate increased with the increase of current density and electrolytic time. The slightly alkaline initial pH value was optimum. Precipitation time has little effect on removal rate. The optimal process conditions were the current density of 3.42 mA/cm^2 , electrolytic time of 40 min and the initial pH from 7 to 9.

2. The effect of anion in the solution on ammonia nitrogen removal was obvious. Al^{3+} was remarkably increased from the electrodes in the presence of Cl^- ions. It was demonstrated that the enhancement of Al^{3+} release could be partially ascribed to the pitting corrosion and the alleviation of passivation through SEM-EDX analysis. As Cl^- ions are widespread in natural waters, the effect of Cl^- ions on ECF for ammonia nitrogen removal is of great importance, and should be taken into account in practical applications.

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