An effective method for improving electrocoagulation process: Optimization of Al_{13} polymer formation

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HIGHLIGHTS

- Al_{13} polymer formation in EC process are investigated.
- Al_{13} species fraction positively correlated with removal of turbidity and organic.
- pH 5–7 and lowering j favored the formation of Al_{13} polymer.
- Al_{13} fraction can reach more than 60% under optimal EC conditions.

GRAPHICAL ABSTRACT

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ABSTRACT

Al_{13} polymer has been believed to be the most active species responsible for coagulation. The character of Al species distribution and the formation of Al_{13} polymer in electrocoagulation (EC) process were investigated in order to provide insight into optimizing EC operation and design. The results indicated that predominant Al species shifted from monomer toward medium polymer then to larger polymer or $Al(OH)_s$ with increasing EC time. The in-situ Al_{13} polymer could be generated in EC process, and became the dominant species during 5–15 min. In EC process, Al_{13} species fraction positively correlated with the removal of turbidity and organic. The increase of pH and current density could accelerate the hydrolysis-polymerization process of Al^{3+} . pH 5–7 and lowering current density favored the formation of Al_{13} polymer during EC process. EC process with bipolar electrodes had a higher yield of monomeric and Al_{13} species, while EC process with monopolar electrodes facilitated the formation of larger polymer or $Al(OH)_s$. The content of Al_{13} polymer can reach more than 60% under optimal conditions.

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1. Introduction

Electrocoagulation (EC) is gaining recognition as an alternative process to conventional chemical coagulation (CC). The advantages

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of EC include a compact treatment facility, relatively low cost, less sludge production, minimum requirement of chemicals, and the possibility of complete automation [1–4]. During the last few decades, EC technology has undergone a rapid development, and has been proved to be competitive and effective in the treatment of drinking water and wastewater to remove heavy metals [5–7], anions [8,9], organic compounds [10–13], oil [14,15], and particulates [16,17].

In EC process, active coagulant species are generated in-situ by anodic dissolution of sacrificial Al or Fe electrode. Dissolved anode produces various Al or Fe hydrolysis species, which involve charge neutralization and sweep flocculation of particles or adsorption of pollutants onto Al or Fe hydroxides [1,12]. Many researchers have demonstrated that Al species distribution during CC and EC process determined the performance of both Al based coagulants [18–21] and EC with Al electrode [22]. Therefore, the character of Al species distribution in CC [18,23,24] and EC [25,26] process has been extensively studied.

Al hydrolysis reactions during CC and EC process are very complicated depending on coagulant type, water quality and Al concentration [23,25–27]. According to the analysis method of ferron colorimetric and ^{27}Al nuclear magnetic resonance, Al species are usually divided into monomeric species (e.g., $\text{Al}(\text{OH})_2^+$, $\text{Al}_2(\text{OH})_2^{4+}$, $\text{Al}_3(\text{OH})_4^{5+}$), medium polymer species (i.e., $\text{AlO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}^{7+}$, Al_{13}), and colloidal or solid species [28–30]. Previous studies indicated that with high positive charge and strong binding ability [31–33], both pre-formed and in-situ formed Al_{13} polymer are the most active species in Al based coagulants responsible for coagulation [21,34,35]. Thus, researchers paid more attention to the regulatory method of Al_{13} formation and subsequent efficiency enhancement during CC process.

Most previous studies about EC have focused on the removal efficiency of a specific pollutant, manipulating parameters, and electrode materials, but few study the Al species distribution during EC process. Recently, Jimenez et al. [26] confirmed the formation of some polymeric species at pH range of 4–6, although the polymers concentration was low. In addition, our previous study [36,37] demonstrated that high content of Al_{13} polymer could be generated during an electrolysis process with sacrificial Al anodes, whose principle is similar with that of EC process. However, so far no study has focused on the formation of Al_{13} species in EC process. Moreover, in EC process the influence of electrochemical parameters and aquatic chemical conditions on Al_{13} species formation need be clarified.

The purpose of this study is to investigate the character of Al species distribution and its influence on pollutant removal in EC process. Particular emphasis was paid to understanding the formation mechanism of Al_{13} polymer in term of electrochemical reactions. The effect of current density (j), pH conditions, and electrodes arrangement pattern were investigated. The present study provided insight into optimizing EC operation from the viewpoint of the formation of active Al species.

2. Materials and methods

2.1. Experimental apparatus

EC experiments have been carried out in an electrochemical cell. Fig. 1 shows a schematic diagram of the experimental apparatus. Al electrodes were used as the anode and cathode. The electrodes were square in shape with a geometric area of 54 cm^2 ($6 \times 9\text{ cm}$) each and with an electrode gap of 10 mm. The electrical current was applied using a DC power supply (DH1720A-6, Dahua, China). The electrolyte was prepared with deionized water containing 0.05 M NaCl and 0.5 mM NaHCO_3 . Electrolyte was stirred by a stainless

steel rod stirrer. All of the chemicals used were at the least reagent grade. Fig. 1 shows the electrode arrangement of monopolar electrodes and bipolar electrodes, which were conducted in EC system in order to study the effect of electrode arrangement.

2.2. Characterization of Al speciation during EC process

Ferron colorimetric method was used to monitor Al species distributions during EC process. The reagents preparation and procedures for the Ferron colorimetric method are illustrated in the literature [23,29]. Absorbance increase was monitored for 120 min such that three fractions could be operationally defined: Al_a , Al_b and Al_c , corresponding to monomeric species, medium polymer species and larger polymer species and/or solid phase $\text{Al}(\text{OH})_3$, respectively. The reaction time of Al_a -Ferron was 1 min, and the Al species reacting with Ferron reagent before 120 min represented $[\text{Al}_a + \text{Al}_b]$, then Al_c was obtained by total aluminum concentration (Al_T) minus Al_a and Al_b . Many investigations [29,38] proved that the Al_b species could be regarded as the Al_{13} species that identified by ^{27}Al nuclear magnetic resonance.

Electrospray ionization mass spectrometer (ESI-MS) was also used to detect Al species distribution in EC process. The ESI-MS spectra was recorded with a micromass hybrid quadrupole time-of-light mass spectrometer (2695XE micro, Water, U.S.) equipped with an electrospray ion source with a positive ion mode. The solutions were introduced into the spectrometer at a flow-rate of $10\text{ }\mu\text{L}/\text{min}$. The instrumental conditions were as follows: capillary voltage 3500.0 V, sample cone voltage 70 V, Ff lens 200 V, extraction cone voltage 5 V, source temperature 120°C , cone gas (N_2) flow rate $300\text{ L}/\text{h}$, and mass range 80–1000.

2.3. Experimental procedure and analysis

Before each experiment, the electrodes were polished with sandpaper to remove the scale build-up and then dipped in a 1.3 mol/L HCl solution for 10 min, and then finally cleaned with successive rinses of deionized water. During each test run, the electrolyte solution of 1.0 L was placed into the reactor. The initial pH of electrolyte solution was adjusted by adding 0.2 mol/L NaOH or 0.05 mol/L HCl. After that, the magnetic stirrer was turned on and set at 300 rpm. The DC power source was operated with a constant j of 1.0, 5.0, or $10.0\text{ mA}/\text{cm}^2$. The samples were taken at certain time in a 10 mL test tube respectively and then analyzed immediately by ferron colorimetric method or ESI-MS. The solution pH was measured on-line by pH meter (720A, Thermo Orion, USA). Al_T were determined by dilution 50:50 v/v of samples with HNO_3 4 N, and measured using an inductively coupled plasma optical emission spectrometer (ICP-OES) (Optima 2000, PerkinElmer, UK). According to Faraday's law, theoretical Al concentration (in g/L) dissolved from Al sheet was calculated using the following equation (Eq. (1)):

$$[\text{Al}] = \frac{nItM_{\text{Al}}}{ZFV} \quad (1)$$

$[\text{Al}]$, theoretical Al concentration (g/L); n , cells number; I , current (A); t , reaction time (s); Z , valence (3 for aluminum); M_{Al} , molecular weight of aluminum (26.98 g/mol); F , faraday constant, (96,487 C/mol); V , solution volume ($V=1\text{ L}$)

For the experiments of water treatment efficiency by EC, water samples were synthesized by spiking humic acid (Sigma-Aldrich) and kaolin (Sinopharm) into deionized water containing 0.05 M NaCl and 0.5 mM NaHCO_3 . The initial dissolved organic carbon (DOC) and turbidity of water samples were 5 mg/L and 8.3 NTU, respectively. During EC process, a small amount of sample was taken immediately to measure the zeta potential (Malvern, Zetasizer 2000, UK). At the same time, 15 mL water samples were taken into test tube at certain time, after a 30 min settling period the

Fig. 1. Schematic diagram of the electrocoagulation equipment.

Fig. 2. Characterization of Al species distribution in EC process by ESI-MS. Initial pH was 7.0. Current density was 50 A/m².

supernatants were collected to measure residual turbidity using a HACH 2100N turbidimeter. The filtrates by 0.45 μ m pore size membrane filter were tested for DOC using a total organic analyzer (TOC-Vcph, Shimadzu, Japan).

3. Results and discussion

3.1. Al₁₃ polymer formation

When Al is used as anode, release of Al³⁺ is known to be produced according to Eq. (2). Electrochemically generated Al³⁺ can undergo hydrolysis in aquatic solution to produce a series of hydrolysis products. Monomeric (Al(OH)²⁺, Al(OH)₂⁺) and dimeric (Al₂(OH)₂⁴⁺) species are primarily generated in bulk solution. Meanwhile, part of Al³⁺ moves into the metal-solution interface

of cathode under the imposed electric field. OH[−] is homogeneously generated from the hydrogen evolution on the surface of cathode (Eq. (3)), leading to the formation of Al(OH)₄[−] at the metal-solution interface. Base (i.e., OH[−]) from the cathode reaction has been continuously added into bulk solution. It has been believed that the process of Al₁₃ formation requires the presence of Al(OH)₄[−] as a precursor [39]. The hydrogen evolution on the cathode provides a localized zone of high pH at the interface of metal-solution, which would favor the formation of Al(OH)₄[−]. Al(OH)₄[−] interacts with Al monomers and dimers to form Al₁₃ polymer. Al₁₃ polymer is an intermediate species in the processes of hydrolysis, polymerization, gelation and precipitation of Al³⁺ in aqueous solution (Eq. (4)).

Fig. 3. Quantitative characterization of Al speciation in EC process by Al-Ferron method (a) and removal of TOC and turbidity, and Zeta potential of flocs during EC process (b). Initial pH was 7.0. Current density was 50 A/m².

ESI-MS was used to characterize Al species distribution and monitor Al₁₃ formation during EC process. The ESI-MS spectra of Al species distribution in EC process at 2, 30 and 60 min are shown in Fig. 2. The results indicated that the polymerization degree of Al species gradually increased with increasing EC time, and Al₁₃ polymer generated during EC process. At 2 min (Fig. 2a), the most intensive peaks are at *m/z* 259 and 81, which are assigned to tetrameric Al species. Monomeric Al at *m/z* 97, dimers (*m/z* 121 and 139), trimers (*m/z* 199) and Al₁₃ species at *m/z* 328 were also observed in the spectra. Except the signal of monomer, low polymers (i.e., dimer, trimer and tetramer) and Al₁₃ polymer, higher polymeric Al species (Al₁₅ species at *m/z* 379 and Al₂₁ species at *m/z* 373) also appeared in the ESI/MS spectra at 2 min. At 30 min (Fig. 2b), the most intensive peaks were assigned to Al₁₃ species at *m/z* 213, 225, 337 and 355. At 60 min (Fig. 2c), the peak intensity of Al₁₅ species (*m/z* 379) and Al₂₁ species (*m/z* 373) were strongest ever before.

The Al species distribution during EC process has been quantitatively measured by Al-Ferron method which shown in Fig. 3a. Predominant Al species shifted from monomer (Al_a) to medium polymer (Al_b) then to larger polymer or Al(OH)₃ (Al_c) with increasing EC time. At the primary period of EC process, Al_a formed rapidly and became the predominant species during the first 2 min. Al_a decreased sharply while Al_b kept rise after 2 min. Al_b fraction reached the maximal value of about 55% at the EC time of 10 min, after which it was in decline. The distribution trend of Al_a and Al_b were similar during EC process. With the increase of EC time, Al_c increased continuously.

Fig. 4. Influence of initial pH on Al species distribution in EC process. Current density was 50 A/m².

The removal of turbidity and DOC during EC process was examined (Fig. 3b) to illuminate the effect of Al speciation on EC efficiency. Comparison of the Al₁₃ species distribution (Fig. 3a) with the EC efficiency (Fig. 3b) gave an obvious finding. Al₁₃ species fraction in the EC process corresponded well to turbidity and DOC removals. The Al₁₃ content positively correlated with the EC efficiency. At the EC time of 10 min, Al₁₃ species reached the maximal value. Meanwhile, for turbidity and DOC removal, the optimal EC time also was about the 10 min. Noted that zeta potential also corresponded well to turbidity and DOC removals, and was close to the isoelectric point at the EC time of 10 min, indicating charge neutralization might be responsible for turbidity and DOC removal before and at the EC time of 10 min. At slightly longer EC time, charge reversal caused the destabilization of particles. Thus, the removal of turbidity and DOC slightly decreased from the EC time of 10–20 min. After the EC time of 20 min, the removal of turbidity and DOC reincreased, resulting from the sweep flocculation of bulk hydroxide precipitation.

3.2. Effect of pH adjustment

Effect of pH adjustment on Al₁₃ formation in EC process was examined at the initial pH of 4, 5, 6, 7 and 9, respectively. Fig. 4 showed that pH had a significant influence on Al species distribution, and high pH could accelerate the hydrolysis process of Al³⁺. The largest amount of Al_a species occurred at pH 4 (Fig. 4a). At the EC time of 2 min for example, the content of Al_a species decreased

Fig. 5. Change of Al_T during EC process under various initial pH (a). Change of pH during EC process under various initial pH (b). Current density was 50 A/m^2 .

with the increase of initial water pH. The maximum of Al_c in EC process was observed at pH 9 (Fig. 4c). There are more hydroxyl ions that are available to the process of Al^{3+} hydrolysis-polymerization-gelation-precipitation at a high pH condition. Thus, at high pH larger polymers and $Al(OH)_3$ may account for higher ratio in Al species distribution. On the contrary, the Al species at low pH tends to remain monomer and oligomer. Fig. 4b indicated that weak acidic condition was optimal for the formation of Al_b species. At pH 6, Al_b content reached more than 60% at the EC time of 10 min. The present study demonstrated that near neutral pH region (pH 5–7) was an ideal pH range for in-situ formation of Al_{13} during EC process. The character of Al species distribution in EC process was consistent with that in CC process [20,23].

The effect of pH adjustment on Al dissolution from anode was also studied, since it has been believed that Al concentration could produce significant influence on Al species transformation and distribution [27]. The results indicated that dissolution rate of Al anode was independent of the pH of bulk solution. Fig. 5a showed that the Al_T at various pH values were almost same. Therefore, it can be concluded that the difference (Fig. 4) of Al species distribution at various pH did not result from Al concentration. Fig. 5b presents the changes of pH vs. time during EC process at different initial pH values. The results showed that, regardless of initial pH value, the pH change vs. time followed two consecutive stages: a stage of rapid pH change before 15 min then followed by a stage in which pH values were close to a constant value of about 8.5. It is noted that, in Fig. 4, there are almost no differences in Al species distribution at various initial pH after the EC time of 15 min, which can be well supported by the pH change since the pH values are almost same at that period.

3.3. Effect of j regulation

Effect of j regulation on the formation of Al_{13} in EC process was investigated at pH 7, 10, 50 and 100 A/m^2 , which are quite common

Fig. 6. Influence of j on Al species distribution in EC process. The initial pH was 7.0.

j values of EC in practice according to the report of Emamjomeh and Sivakumar [2], were applied in this study. Fig. 6 shows that lowering j favored the formation of Al_{13} polymer. For example, 10 A/m^2 yielded as much as 65% Al_b , while maximal content of Al_b was about 50% when the 100 A/m^2 was employed (Fig. 6b). The content of Al_{13} generated in EC process was negatively correlated with the applied j value. In addition, increasing j shortened the EC time to gain the maximum Al_b content. The times for gaining the maximal Al_b fraction at 10, 50 and 100 A/m^2 were about 5, 8 and 10 min, respectively.

j is an important factor that strongly regulates the electrochemical reaction rate, and it determines the coagulant dosage in the EC process. As j increases during EC process, the amount and rate of base injection due to the hydrogen evolution reaction also increases. So, the pH of bulk solution rose greater when a higher j was applied. The pH values at a certain moment were positively related to the applied j . With increasing solution pH, the net positive charge is likely to be reduced, as are the repulsive forces between individual Al_{13} polymer units. This in turn could favor aggregation of units to form Al precipitates [40]. It has been also demonstrated that at more rapid rates of base injection into Al^{3+} solution, less Al_{13} polymer is formed, presumably to the advantage of colloidal precipitate formation [41]. Meanwhile, as the applied j is increased, the dissolved Al from anode increases according to Eq. (1). With a high Al_T concentration in solution, the opportunity of collision between Al_{13} polymer units could be increased, which may accelerate the formation

Fig. 7. Al species distribution (a) and Al_T change (b) in EC process with monopolar electrodes (ME) and bipolar electrodes (BE) under a consistent j (50 A/m^2). Initial pH was 7.0.

of large polymer and Al precipitates. Furthermore, previous study [42] about polyaluminum chloride synthesis by electrolysis method indicated that higher Al_T concentration tended to exhibit inferior yields of Al_{13} because increasing Al_T results in greater degrees of supersaturation of $Al(OH)_4^-$ that might favor direct formation of $Al(OH)_3(s)$.

3.4. Effect of electrode arrangement

Electrode arrangement in EC reactor can be classified as monopolar and bipolar pattern [1]. The Al species distribution of EC with monopolar electrodes and bipolar electrodes were analyzed, respectively. The numbers of sacrificial anodes for monopolar and bipolar pattern in this study were 2 and 3, respectively. In order to fundamentally understand the effect of electrode arrangement on Al_{13} formation, 0.092 A and 0.138 A were used for monopolar and bipolar pattern, respectively, to insure a same Al concentration and j during the two different EC process. As shown in Fig. 7a, Al_{13} formation has been shown to be sensitive to the arrangement of electrode. EC process with bipolar electrodes had a higher yield of Al_a and Al_b species, while EC process with monopolar electrodes facilitated the formation of Al_c species. The EC processes with monopolar electrodes and bipolar electrodes had a similar Al_T (Fig. 7b), which was consistent with the theoretical value according to Eq. (1). Meanwhile, the same j led to a same rate of base injection for the two EC processes. Although the total amount of electrodes was same (Fig. 1), the cell numbers (a pair of anode and cathode) of the monopolar and bipolar pattern were 2 and 3, respectively. The EC with bipolar electrodes could provide a larger solution-electrode interface for electrochemical reactions. It implied that Al^{3+} and OH^- more homogeneously evolve from the surface of bipolar electrodes that are more fully arranged in bulk solution, which may present

more bearing points of $Al(OH)_4^-$, leading to the advantage of Al_{13} formation.

4. Conclusion

Predominant Al species shifted from monomer to medium polymer then to larger polymer or $Al(OH)_3(s)$ with increasing EC time. With respect to the optimization of Al_{13} formation in EC process, pH adjustment, j regulation, and electrode arrangement are the critical parameter of water quality, operation, and design, respectively. In addition, hydraulic retention time of EC was also an important factor to Al_{13} formation. The content of Al_{13} polymer can reach more than 60% under optimal conditions.

Al_{13} polymer could in-situ form in EC process, and became the dominant species during 5–15 min. pH 5–7 was an ideal pH range for the formation of Al_{13} polymer during EC process, which was consistent with that in CC process. Lowering j favored the formation of Al_{13} polymer. With an increase of j , the proceeding of Al hydrolysis and polymerization was promoted, resulting in fewer yields of monomeric and Al_{13} species and more large and precipitated Al species. EC process with bipolar electrodes tended to produce more monomeric and Al_{13} species, while EC process with monopolar electrodes facilitated the formation of larger polymer or $Al(OH)_3(s)$.

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