Optimum conditions for Al_{13} polymer formation in PACl preparation by electrolysis process

Jiuhui Qu^{*}, Huijuan Liu

State Key Laboratory of Environmental Aquatic Chemistry, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, P.O. Box 2871, Beijing 100085, China

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Abstract

This paper introduces a new and effective method for preparation of PACl-electrolysis process. A series of PACl with high content of Al_{13} polymer was successfully prepared by electrolysis process. The amount of Al_{13} polymer formed in electrolysis process was found to be highly influenced by current density (d_i), the distance between the electrodes, electrolysis time and the stirring rate of the electrolyte. For the Al_T (total aluminum concentration) of 2.0 M PACl obtained by electrolysis process, the optimal d_i and distance between the electrodes were 1.1 A dm^{-2} and 10 mm respectively. The optimum circulating rate was 5.5 h^{-1} . Because of the inhomogeneous pH between the surface of cathode and the bulk solution, the electrolysis process has the advantage to form more $\text{Al}(\text{OH})_4^-$ as precursor of Al_{13} polymer. At the optimum condition, Al_{13} polymer accounted for above 70% of Al_T (PACl of $\text{Al}_T = 2.0 \text{ M}$ and $B = 2.0$), which was much higher than that of PACl prepared by other method.

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1. Introduction

Polyaluminum chloride (PACl) is commonly used as flocculants for water treatment and other coagulation–flocculation applications. Much attention has been paid to PACl in recent years because of its higher efficiency and relatively lower costs compared with the traditional coagulants (Buffle et al., 1985; Edzwald, 1993; Tang and Luan, 1995; Wang et al., 2002). It has been demonstrated that the active species responsible for coagulation or precipitation is the highly charged polymeric aluminum Al_{13} ($[\text{AlO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+}$) species

(Stumm and O'Melia, 1968; Wang and Hsu, 1994). Al_{13} is composed of one tetrahedral center surrounded by 12 octahedral Al units (Johansson, 1960; Akitt and Farthing, 1981a,b; Bottero et al., 1987). Besides the characteristic of higher positive charge (+7) and resultant strong ability to bind to particles, Al_{13} polymer possesses fairly stable structure against hydrolysis before adsorption to particle surfaces. These properties contribute to their superior behavior in coagulation.

PACl is an intermediate product in the processes of hydrolysis, polymerization, gelation and precipitation of aluminum species. Many investigations (Bertsch et al., 1986; Bertsch, 1987; Klopogge et al., 1992; Parker and Bertsch, 1992) suggested that synthesis methodology was very important in determining the relative distribution of Al between monomeric and Al_{13} polymeric forms. Bertsch et al. (1986) found that base injection rate was an important parameter influencing Al_{13} polymer formation at high OH/Al molar ratios (B) for Al

^{*} Corresponding author. Tel.: +86-10-62849151; fax: +86-10-62923558.

E-mail addresses: jhqu@mail.rcees.ac.cn (J. Qu), hjliu@mail.rcees.ac.cn (H. Liu).

solutions of 3.34×10^{-2} M. The drawbacks of such a preparation are tedious, time consuming and impossible for the industrial production.

Recent research has shown that the electrolysis process could produce effective PACI (Liu et al., 2002). Lu et al. (1999) illustrated the principle of PACI preparation by electrolysis and demonstrated the electrolysis process could provide favorable conditions for polyaluminum formation. The purpose of this investigation is to optimize the Al_{13} yield conditions in the electrolysis process for PACI preparation.

2. Materials and methods

2.1. Characteristics of electrochemical reactor

A schematic view of electrolysis reactor for PACI formation is illustrated in Fig. 1. It consisted of an electrolytic rectifier (MPS3220, made in China), an electrolytic cell made of organic glass. Five sheets of Al (110×60 mm) were used as anodes while the cathodes were five sheets of Fe (110×60 mm). The distance between the anode and the adjacent cathode could be regulated from 30 to 10 mm, and circuit arranged in parallel. AlCl_3 aqueous solution was used as electrolyte. A pump was used to circulate the solution to increase mass transfer.

2.2. Experimental method

2.0 M Al stock solutions were prepared by dissolving reagent grade $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ in deionized water, and further diluted to various concentrations in the experiments. A 700 ml volume of AlCl_3 aqueous solution was added to the electrolysis reactor. The electrolysis was then carried out at constant d_i . After the reaction started, some samples were withdrawn at regular intervals. Then the pH value, the concentration of Al_T , the distribution of Al species and the B value of the samples were analyzed.

Fig. 1. A schematic view of electrolysis reactor. (1) DC power supply; (2) electrolytic cell; (3) Fe cathode; (4) Al anode; (5) electrolyte; (6) pump; (7) pH meter.

Fig. 2. ^{27}Al -NMR spectra of PACI.

2.3. Analytical methods

The method used to characterize the Al species was ^{27}Al -NMR spectroscopy (VARIAN^{UNITY} INOVA, 500 MHz, USA). To estimate the distribution of various species in solution, selected samples and standard solutions of known monomeric Al concentration were run using a coaxial sample tube, with a 0.2 M Na aluminate solution in the inner insert as reference. The intensities for ^{27}Al signals relative to the aluminate reference were used for calculating the Al concentrations corresponding signals. PACI commonly showed two signals in ^{27}Al -NMR spectra (Fig. 2). The intensities of 0 ppm resonance represented quantitative determinations of the monomeric Al (Al_m) of aluminum solution, that of 63 ppm resonance represented quantitative determinations of the Al_{13} polymer of alum solution. The 80 ppm resonance represented Na aluminate. The concentration for the 63 ppm signal was multiplied by 13 to obtain the concentration of Al_{13} (Buffle et al., 1985; Bertsch et al., 1986). It has been generally accepted that for the Al_{13} complex, only the tetrahedrally coordinated Al at the center of the structure yields the signal at 63 ppm.

The pH value of the solutions was measured with a pH meter (Orion 720A, USA). Al_T concentration and the B value were determined by titrimetric methods, and details of the analytical procedures were given elsewhere (Li, 1981).

3. Results and discussions

3.1. Al_{13} formation in electrolysis process

The principle of PACI preparation by the electrolysis process is illustrated in Fig. 3. When the electrolysis is carried out at direct current in the reactor with aluminum as the anode, iron as cathode and AlCl_3 aqueous solution as the electrolyte, some reactions will bring out on the anode and cathode.

Fig. 3. The simple principle scheme of Al₁₃ formation in electrolysis process.

It is assumed by several authors (Akitt and Farthing, 1981a; Bertsch et al., 1986), the process of Al₁₃ formation requires the presence of Al(OH)₄⁻ as a precursor. Akitt and Farthing (1981a) assumed a very rapid Al(OH)₄⁻ production under the heterogeneous conditions at the interface of solid and the solution. During the electrolysis, OH⁻ homogeneously evolved on the surface of the cathode sheets that were more fully arranged in the whole space of electrolysis reactor, leading to the formation of Al(OH)₄⁻ at the metal-solution interface as reaction (3).

So the concentration of Al³⁺ and Al(OH)₄⁻ near the anode-solution interface and cathode-solution interface respectively were higher than those of bulk solution. Using an effective circulating method, Al³⁺ and Al(OH)₄⁻ will be transferred to the bulk solution, followed the further reaction (Eq. (4)) in the electrolysis cell:

In Eq. (4), Al_m(OH)_nCl_(3m-n) represents the intermediate product of Al species and it can also continue to hydrolyze into Al(OH)₃ (am). If the generation and reaction of ionized OH⁻ and Al³⁺ are regulated at a proper rate and the transfer rate is optimized, it is possible to control the following processes of hydrolysis-polymerization-gelation-precipitation of aluminum species in order to obtain PACl containing as much of Al₁₃ as possible.

According to the reactions (1) and (2), the molar ratio of Al³⁺ and OH⁻ produced in electrolysis process is 1:3, so the following relation is approximated for preparing PACl with desired values of *B*:

$$B = \frac{\text{OH}^-}{\text{Al}^{3+}} = \frac{3\text{Al}_i}{\text{Al}_i + \text{Al}_0} \quad (6)$$

Al₀: quantities (mol) of Al³⁺ coming from AlCl₃ before electrolysis; Al_i: quantities (mol) of Al³⁺ coming from Al sheets during electrolysis.

In Eq. (6), the hydrolysis of Al³⁺ itself can be neglected (Tang, 1995). And then based on the current intensity through the electrolysis reactor and Faraday Law, the electrolysis time can be calculated.

3.2. Effect of *d_i* on Al₁₃ formation

According to the reactions (1) and (2), *d_i* is a key factor to control the dissolved rate of Al³⁺ and OH⁻ in the electrolysis process for keeping the reaction of Al³⁺ and OH⁻ in the stage of Al₁₃ (Eq. (5)). The percentage of Al₁₃ in the solutions of different Al_T concentrations as a function of *d_i* is shown in Fig. 4. All the *B* values of the PACl solutions are 1.8. At the same concentration of Al_T, the amount of Al₁₃ increased as a function of *d_i*, and passed through a maximum before decreasing at the higher *d_i*. For different concentration of Al_T, the optimum *d_i* for high content of Al₁₃ was different. At Al_T = 0.2 M, the optimum *d_i* was 0.59 A dm⁻² and the content of Al₁₃ accounted for 72% of Al_T. The maximum Al₁₃ yield (66% of Al_T) was obtained at *d_i* = 1.1 A dm⁻² when Al_T = 2.0 M. These data revealed that each concentration of Al_T corresponding with an optimum *d_i*,

Fig. 4. Percentage of Al₁₃ in PACl of different Al_T concentrations as a function of *d_i* (aging time: 48 h).

and the formation of Al_{13} was favored by decreasing Al_T from 2 to 0.2 M.

As mentioned before, the formation rate of Al^{3+} and OH^- in electrolysis process depended on the current intensity passing through the electrolysis reactor. At higher d_i , more OH^- generated at the cathode–solution interface, so did the $\text{Al}(\text{OH})_4^-$. When the precursor of $\text{Al}(\text{OH})_4^-$ was forming in large enough quantities, the content of octahedral component that interacting with the $\text{Al}(\text{OH})_4^-$ to form Al_{13} species was the key factor to form more Al_{13} . When $\text{Al}(\text{OH})_4^-$ generated more than can be consumed by the formation of Al_{13} . The excess $\text{Al}(\text{OH})_4^-$ re-equilibrated with the bulk solution resulting in colloidal or precipitated $\text{Al}(\text{OH})_3$ (Bertsch, 1987). So there is an optimum d_i for the Al_{13} formation according to a certain Al_T concentration.

3.3. Effect of electrolysis time on Al_{13} formation

The Al species distribution and B value changes as a function of the electrolysis time are illustrated in Fig. 5. Lower polymers such as dimeric Al ($\text{Al}_2(\text{OH})_2^{4+}$) were formed at the lower B values. When B value was increased to 1.3–1.8, Al_{13} formed rapidly and became the main species of the PACl. However, with the prolonged reaction time (>10 h) a little of colloidal and precipitated $\text{Al}(\text{OH})_3$ which undetected by ^{27}Al NMR (Al_u) were formed at B values higher than 1.8. These results suggested that the optimum reaction time associated with a highest Al_{13} content in PACl is 10 h. Beyond that, the content of Al_{13} was decreasing and the concentration of Al_u was increasing with electrolysis time prolonged. The content of Al_{13} in the final electrolyte reached to the maximum value of 70% with $\text{Al}_T = 1.8$ M at the electrolysis time of 10 h. But with the electrolysis time extended to 12 h, the content of Al_{13} content decreased to 66% with Al_T of 2.0 M.

Fig. 5. Al species distribution and B values change as a function of the electrolysis time.

Table 1

The influence of the distance between the electrodes on Al_{13} formation ($\text{Al}_0 = 0.7$ M; Current density: 1.1 A dm^{-2} ; aging time: 48 h)

Distance (mm)	Al_T (M)	Al_m (%)	Al_{13} (%)	Al_u (%)
10	1.9	25	66	9
15	1.8	20	59	21
20	1.8	21	55	24
30	1.7	21	54	25

3.4. Effect of the distance between electrodes on Al_{13} formation

The distance between anode and the adjacent cathode was varied to examine its effect on the Al_{13} formation (Table 1). All the experiments were carried out at the same d_i , stirring rate, Al_0 and electrical amperage through the electrolysis reactor. It was apparent that the content of Al_{13} prepared at the distance of 10 mm was higher than that of prepared at other distances. As a result, 66% of Al_{13} polymer in the final electrolyte was achieved when the distance between electrodes was 10 mm. However, only 59% and 55% of Al_{13} polymer in the final electrolytes were prepared when the electrodes distances were 15 and 20 mm respectively.

As the results of Table 1, when the distance between the adjacent electrodes decreased, more electrodes would be applied in the reactor. According, the total area of the electrodes would increase in the same reactor, and then more $\text{Al}(\text{OH})_4^-$ would created at more interface of metal–solution, so more Al_{13} was formed.

3.5. Circulating rate on Al_{13} formation

The formation of Al_{13} has also been shown to be sensitive to the stirring rate when base was injected into the solution containing aluminum. During the electrolysis process, OH^- was generated on the whole metal surface and more Al_{13} precursor ($\text{Al}(\text{OH})_4^-$) was formed on the metal–solution surface. A pump was used to circulate the electrolyte to increase the interaction chance between $\text{Al}(\text{OH})_4^-$ and aluminum oligomer to form Al_{13} polymer. The distribution of Al_m , Al_{13} polymer and Al_u in $\text{Al}_T = 0.2$ and 2.0 M, $B = 1.8$ PACl solutions at different circulating rates is shown in Table 2. When there were no stirs during the preparation processes, Al_u was the optimum species in the PACl solution, the Al_{13} species only accounted for 23% and 7% when Al_T were 0.2 and 2.0 M respectively. The content of Al_{13} polymer improved rapidly with increasing circulating rate from 0 to 2.8 h^{-1} and 0 to 5.5 h^{-1} for PACl of 0.2 and 2.0 M respectively. Beyond that, increasing the circulating rate could not be found the content of Al_{13} polymer considerably enhanced. Hence

Table 2
Circulating rate on Al_{13} formation (aging time: 48 h)

Circulating rate (l h^{-1})	Al_{13} account for Al_T (%)	
	PACl ($\text{Al}_T = 0.2 \text{ M}$, $B = 1.8$)	PACl ($\text{Al}_T = 2.0 \text{ M}$, $B = 1.8$)
0	23	7
1.5	41	15
2.8	74	35
4.2	75	68
5.5	76	70
9.5	75	67
12.3	75	66

2.8 and 5.5 l h^{-1} were considered as the optimum circulating rates for Al_{13} polymer formation for PACl of 0.2 and 2.0 M respectively. A further increasing the circulating rate would not realize much economical advantage because of little increase in Al_{13} polymer formation.

This behavior can be mainly explained as the kinetic process of Al_{13} polymer formation in the electrolysis process. High circulating rate will cause high mass transfer rate and more $\text{Al}(\text{OH})_4^-$ formed on the cathode surface will be transferred to the bulk solution. Moreover, when the $\text{Al}(\text{OH})_4^-$ transfer rate is high enough, the content of aluminum oligomer is the key step. It can also be concluded that high Al_T concentration of PACl need high circulating rate for Al_{13} polymer formation.

3.6. Al_{13} formation at optimum condition in electrolysis process

According to the optimum conditions ascertained above, the PACl of 2.0 M Al_T with $B = 1.8$ was prepared as following parameters: 700 ml AlCl_3 aqueous solution (0.7 M) in electrolysis reactor was electrolyzed for 10 h under $d_i = 1.1 \text{ A dm}^{-2}$, circulating rate = 5.5 l h^{-1} , and the distance between adjacent electrodes was 10 mm. At the end of electrolysis process, the PACl solution was suspended aqueous because some dissolved aluminum from anode sheet was not reacted with OH^- completely. The aluminum would continue to hydrolyze in acidity solution after the electrolysis and the solution was becoming clear along with aging time (to start after electrolysis process). The concentration of Al_T and the distribution of Al species aged for 0 and 48 h respectively are illustrated in Table 3.

Table 3 showed that the concentration of Al_T in the electrolyte increased from 0.7 to 1.9 M after electrolysis. The Al_{13} species accounted for 70% of the Al_T . After 48 h aging, the concentration of Al_T increased from 1.9 to 2.0 M and the content of Al_{13} increased to 74%.

Table 3
Distribution of Al species in PACl prepared by electrolysis process

Aging time (h)	pH	B	Al_T (M)	Al_m (%)	Al_{13} (%)	Al_u (%)
0	3.01	2.0	1.9	21	70	9
48	3.20	2.0	2.0	16	74	10

3.7. Comparison of different method on formation of Al_{13}

The rate of base injection into the Al-containing solution has been shown to influence the amount of measurable Al_{13} (Akit and Farthing, 1981a,b; Bertsch, 1987; Furrer et al., 1992; Parker and Bertsch, 1992). Many reports (Bertsch, 1987; Furrer et al., 1992; Parker and Bertsch, 1992) suggested that “slow” neutralization favor Al_{13} formation, and that “rapid” neutralization tend to favor Al_u . Table 4 shows the distribution of Al_m , Al_{13} , Al_u in PACl prepared with different approaches. For the preparation of PACl with base micro-injection, a solution of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ was titrated slowly with NaOH, using a syringe pump under rapid stirring conditions. The rate of adding OH^- to aluminum solution by micro-injection was adjusted to the same as that of by electrolysis process. The results in Table 4 showed that using the method of micro-injection could form relatively high content of Al_{13} at lower Al_T (0.2 M), 41% and 44% of Al_{13} were formed when the B values were 2.0 and 2.5 respectively. With increasing Al_T (2.0 M), the content of Al_{13} was decreased and only 35% and 32% of Al_{13} were formed when B values were 2.0 and 2.5 respectively. But for electrolysis process, high content of Al_{13} polymer formed even at high Al_T concentration (2.0 M). The content of Al_{13} polymer were 73% and 68% when B values were 2.0 and 2.5. So high content of Al_{13} was produced using electrolysis process with an easily regulated condition. In addition, the electrolysis process can practice in industrial application easily.

Table 4
Distribution of Al species in PACl prepared by different approaches

Preparation method	Al_T (M)	B	Al_m (%)	Al_{13} (%)	Al_u (%)
Base micro-injection	0.2	2.0	23	41	36
	0.2	2.5	13	44	43
	2.0	2.0	21	35	44
	2.0	2.5	13	32	55
Base addition by electrolysis	0.2	2.0	13	80	7
	0.2	2.5	6	89	5
	2.0	2.0	17	73	10
	2.0	2.5	13	68	19

4. Conclusions

The electrolysis process was employed to prepare PACl with high content of Al_{13} polymer. The effect of the d_i , the distance between anode and the adjacent cathode, the electrolysis time and the circulating rate were investigated to determine their optimum conditions on Al_{13} formation. It has been observed that Al_{13} formation was dependent on the interaction of all these parameters. For obtaining as much as Al_{13} polymer by electrolysis process, the optimal d_i , the optimal distance between anode and the adjacent cathode were 1.1 A dm^{-2} and 10 mm respectively when the concentration of Al_T in the final electrolyte was the 2.0 M . As well, the circulating rate should be controlled at 2.8 and 5.5 l h^{-1} for PACl of $\text{Al}_T = 0.2 \text{ M}$, $B = 1.8$ and $\text{Al}_T = 0.2 \text{ M}$, $B = 1.8$ respectively. At these conditions the content of Al_{13} polymer in the electrolyte could reach to above 70% of Al_T .

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