Characteristics of nanosized polyaluminum chloride coagulant prepared by electrolysis process

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Received 17 June 2002; accepted 11 November 2002

Abstract

Polyaluminum chloride (PAC) has become a focus of many studies involving coagulation because of its advantages over traditional coagulants. In this study, a novel method involving an electrolysis process for preparing of PAC was developed. The products were characterized using ^{27}Al NMR spectroscopy, dynamic light scattering (DLS) and transmission electron micrograph (TEM). Results indicated that the electrolysis process provided favorable conditions for the formation of significant quantities of active species (Al_{13} polymer) at relatively high concentrations of total Al (Al_T) ($0.2\text{--}2.0\text{ mol l}^{-1}$). For each concentration of Al_T , there was an optimum molar ratio of OH/Al (n) for formation of Al_{13} . The Al_{13} species was stable for more than 6 months in solution when the n value was <2.0 . However, in solutions with n values above 2.2, the Al_{13} species gradually converted to other polynuclear forms that were not detectable by ^{27}Al NMR spectroscopy. The results of DLS and TEM showed that the particles existing in PAC prepared by the electrolysis process were in the nanometer size range.

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Keywords: Preparation; Polyaluminum chloride; Electrolysis process; Al_{13} polymer; Stability

1. Introduction

Concentrated solutions of partially prehydrolyzed aluminum salts such as polyaluminum chloride (PAC) are commonly used as flocculants for water treatment and other coagulation–flocculation applications [1–3]. Much attention has been paid to partially prehydrolyzed Al salt in recent

years because of their higher efficiency and relatively lower costs compared with the traditional coagulants. A good understanding of the characteristics of PAC is of benefit in optimizing operational conditions of water treatment. It is generally thought that the higher efficiency of these flocculants depends on characteristics such as the content of active species and the particle size distribution. 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 [4–8]. Al_{13} is composed of one tetrahedral center

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surrounded by 12 octahedral Al units [9–14]. Besides the characteristic of higher positive charge (+7) and resultant strong ability to bind to particles, Al_{13} polymer possess fairly stable structure against hydrolysis before adsorption to particle surfaces. These properties contribute to their superior behavior in coagulation.

PAC is an intermediate product in the hydrolysis, polymerization, gelation and precipitation process of aluminum. The tendency for Al_{13} formation in partially neutralized aluminum solutions has been shown to be a function of solution composition and synthesis conditions [15–18]. Bertsch et al. [15] presented a tenable model wherein the formation of Al_{13} depends critically on an interfacial disequilibrium between the acidic, Al-containing solution and the base being injected into it. Ordinarily, the main PAC preparation processes include acid hydrolysis [19] utilizing aluminum and alumina refined from clay and coal stone as the raw material, acidifying aluminum hydrate from sodium aluminate in inadequate hydrochloric acid [19], and neutralization, electrolysis [20], and heat decomposition using aluminum chloride as the raw material [19]. Recent research has shown that the electrolysis process could produce effective PAC [21–24]. However, the role of their physical properties, especially the content of active species, the stability of the active species and the particle size distribution, remains unclear. It is believed that the active species and the particle size distribution are of particular importance in the behaviour and efficiency of PAC.

The first purpose of this work is to ascertain the optimum parameters for preparation of high-content, stable active species (Al_{13}) in the electrochemical preparation of PAC at relatively high Al concentration ($\sim 2.0 \text{ mol l}^{-1}$). The second purpose is to characterize the particle size distribution of the PAC prepared by the electrochemical process. In this preliminary study, we aim to obtain some important insights into the electrochemical formation of nanosized PAC. In a late study, we focus on the coagulation mechanisms and efficiency of flocculation using electrochemically generated PAC.

2. Materials and methods

2.1. Electrochemical preparation of PAC

The schematic view of the electrochemical reactor used for PAC preparation is illustrated in Fig. 1. It consists of an electrolytic rectifier (GCA12-16, China) and an electrolytic cell made of organic glass. Five sheets of Al ($110 \times 60 \text{ mm}^2$) were used as anodes while five sheets of Fe ($110 \times 60 \text{ mm}^2$) were used as cathodes. A 700 ml AlCl_3 aqueous solution of designated concentration was added to the electrolysis reactor. Electrolysis was then carried out at a constant current density of 1.1 A dm^{-2} as recommended by Lu et al. [23]. A pump was used to circulate the solution and to increase mass transfer. Finally, the product was aged for 48 h to stabilized the PAC. The final product was a clear aqueous solution with the

Fig. 1. The schematic view of electrochemical reactor for PAC preparation.

following characteristics: $Al_T = 0.2\text{--}2.0 \text{ mol l}^{-1}$, $n = 0\text{--}2.8$. PAC prepared at n values from 0 to 2.2 were stable with no sign of sedimentation after 6 months.

2.2. Analytical methods

2.2.1. NMR spectrometer

^{27}Al NMR spectroscopy was used to characterize the Al species with ^{27}Al NMR spectra obtained on a VARIAN^{UNITY} INOVA (500 MHz) spectrometer. Samples were placed in 5 mm tubes and the spectra generated at 20 °C. 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 concentration's corresponding signals. There were three signals in the ^{27}Al NMR spectra (Fig. 2). The intensities of the 0 ppm resonance represented quantitative determinations of the monomeric Al in 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} . 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 [1,15].

2.2.2. Dynamic light scattering

The particle size distribution in the final electrolyte solution was measured using a servomotor-controlled light scattering goniometer (Brookhaven BI200SM, USA). The incident light source was a 35 mW He–Ne laser operating at a 623.8 nm wavelength with vertical polarization. Prior to dynamic light scattering (DLS) determination, PAC samples were purified by filtering with 0.45 μm Whatmann membranes 4–5 times. The purified samples were then transferred into the sample cell for further determination.

The pH value of the solutions was measured with a pH meter (Orion 720A, USA). Al_T and the

Fig. 2. ^{27}Al NMR spectra of PAC prepared by electrochemical process.

n value were determined by titrimetric methods, and details of the analytical procedure are given elsewhere [19]. Transmission electron micrographs (TEMs) were obtained using a HITACHI H-600 instrument.

3. Results and discussion

3.1. Active species formation in PAC preparation

Lu et al [23] illustrated the principles of PAC preparation by the electrolysis process. When the electrolysis is carried out with direct current in the reactor, Al^{3+} and OH^- are generated at the anode and cathode, respectively. The reaction, which then takes place in the electrolysis cell, is:

$\text{Al}_m(\text{OH})_n\text{Cl}_{(3m-n)}$ represents the intermediate product which continues to hydrolyze to $\text{Al}(\text{OH})_3$ (Eq. (2)). If the generation and reaction of ionized OH^- and Al^{3+} are regulated at a proper rate, it is possible to control the ensuring processes of hydrolysis, polymerization, gelation and precipitation of aluminum species in order to obtain PAC containing as much Al_{13} as possible.

It is assumed by several authors [18,25] that the process of Al_{13} formation requires the presence of $\text{Al}(\text{OH})_4^-$ as a precursor. Akitt and Farthing [25]

assumed a very rapid $\text{Al}(\text{OH})_4^-$ production under the inhomogeneous conditions at the solid–solution interface. During the electrolysis, OH^- was generated at the surface of the cathode sheets that were arranged throughout the electrolysis reactor, leading to formation of $\text{Al}(\text{OH})_4^-$ at the metal–solution interface with subsequent formation of Al_{13} polymers.

As the reaction continued, the Al_{13} polymer units gradually formed tenuous linear aggregates with Cl^- acting to bridge the units. The proposed mechanism of forming Al_{13} aggregates through anion bridging is illustrated in Fig. 3 [26]. Small Al_{13} aggregates could transform to condensed aggregates with the transformation from $[\text{Al}_{13}]_n$ to the poorly ordered solid phase(s) highly dependent on the concentration of Al_T and neutralization ratio and the concentration of anions which act to neutralize the charge on the Al_{13} units and facilitate bridging. It is, therefore, important to confirm the optimum n value associated with certain Al_T concentrations. With optimal parameters, the PAC prepared by electrochemical process not only exhibited high Al_{13} content but was also stable with time.

3.2. Al_{13} content of PAC

A series of PAC with total aluminum concentrations (Al_T) of 0.2, 1.0 and 2.0 mol l^{-1} at different n were prepared by the electrolysis process. The percentage of Al_{13} in the solutions of varying of Al_T as a function of n is shown in Fig. 4. At the same concentration of Al_T , the

Fig. 3. Suggested structure of the small Al_{13} aggregates where individual units are bridged via anions.

amount of Al_{13} increased as a function of n , and passed through a maximum before decreasing at the higher n value. For different concentrations of Al_T , the optimum n value yielding a high content of Al_{13} was slightly different. At $\text{Al}_T = 2.0 \text{ mol l}^{-1}$ the maximum Al_{13} yield (70.2% of Al_T) was obtained at $n = 2.2$. The maximum Al_{13} yield (79.8% of Al_T) was obtained at $n = 2.4$ when $\text{Al}_T = 1.0 \text{ mol l}^{-1}$, whereas the maximum Al_{13} yield (83.5% of Al_T) was obtained at $n = 2.5$ when $\text{Al}_T = 0.2 \text{ mol l}^{-1}$. When n was above these optimum values, the formation of Al_{13} rapidly decreased due to the formation of a colloidal, amorphous precipitate.

Inspection of the Al_{13} data reveals that formation of Al_{13} was favored by decreasing Al_T (from 2.0 to 0.2 mol l^{-1}). This tendency is not consistent with the trend of Al_{13} formation at more dilute Al concentrations. Most other studies [18,27,28] of Al_{13} formation have utilized Al_T concentrations below 0.01 mol l^{-1} and proved that lowering Al_T tended to produce lesser quantities of Al_{13} . Parker and Bertsch [27] offered two possible explanations for the reduced quantities of Al_{13} at lower Al_T values. First, concentrations of necessary precursors for formation, perhaps including the aluminate ion as well as a small oligomer, would likely be diminished in more dilute solutions, thus favoring colloidal Al formation over that of Al_{13} . Alternatively, abundant Al_{13} forms initially but more rapidly aggregates and begins conversion to the colloidal form. These possible explanations are also suitable for the concentrated Al concentration. In concentrated Al solution, the quantity of small oligomers is abundant, so the precursor generation is the key parameter in the formation of Al_{13} . The $\text{Al}(\text{OH})_4^-$ precursor will produce at the solid–solution interface as in the following reaction:

$\text{Al}^{3+} + 4\text{OH}^- \rightarrow \text{Al}(\text{OH})_4^-$

$$K = \frac{[\text{Al}(\text{OH})_4^-]}{[\text{Al}^{3+}][\text{OH}^-]^4} \quad (3)$$

Since the formation rate of OH^- is determined by the current density, we can know that higher concentrations of Al can yield higher quantities of $\text{Al}(\text{OH})_4^-$ as precursor of Al_{13} . But it also tends to exhibit suboptimal yields of Al_{13} because increasing Al_T results in greater degrees of supersaturation of $\text{Al}(\text{OH})_4^-$ that might favor direct formation

Fig. 4. Percentage of Al_{13} in PAC solutions of varying concentration of Al_T (0.2, 1.0, or 2.0 mol l^{-1}) as a function of n .

of amorphous $\text{Al}(\text{OH})_3$ and/or gibbsite. These effects become much more pronounced with increasing concentrations of Al_T and n values.

3.3. Stability of PAC

PAC with high stability is appropriate for long-term storage and accelerating its potential for large-scale use. Although hydroxy aluminium polymers are metastable with respect to precipitation, they persist in solution for at least a few months [29]. Turner [30,31] demonstrated that the rate of neutralization played a critical role in the subsequent reactions taking place during aging. With rapid neutralization, the initial $\text{OH}-\text{Al}$ polymers gradually transformed to gibbsite, whereas slow neutralization led to the formation of stable polymers of similar n . Lu et al [23] has shown that the rate of base addition in the electrolysis process lies between the “one shot” addition and sequential “micro-injection”.

Table 1 shows the results of Al species distribution with aging time for an Al_T concentration of

2.0 mol l^{-1} and n values of 1.2, 2.0, 2.2, and 2.5, respectively. For $n = 1.2$ PAC, the content of Al_{13} polymer accounted for 36.9% of the Al_T at the end of the electrolysis (0 day). The increase of Al_{13} at the beginning of the aging time (0–2 days) is mainly due to further hydrolysis of the aluminum dissolved from anode but does not react with OH^- completely in the electrolysis process. After 2 days aging, the content of Al_{13} polymer was stable and nearly no change with time was observed until 208 days of aging. For a fresh (0 day) PAC solution of $n = 2.0$ and 2.0 mol l^{-1} in Al_T , about 65.6% of the Al_T was in the Al_{13} form. In the stages of aging, the content of Al_{13} increased a little, as found for $n = 1.2$ solution. After 303 days of aging, some Al_{13} polymer rearranges into large polymers unobserved with the NMR technique. Formation of other polymers was evident from the increase in the amount of undetectable Al, the disappearance of Al_{13} , and the decrease of monomeric Al in solution. Even so, the content of Al_{13} was stable and accounted for above 60% of Al_T after 302 days aging.

Table 1
Distribution change of various Al species in PAC ($\text{Al}_\text{T} = 2.0 \text{ mol l}^{-1}$) with aging time

n	Aging time per day	pH	% of Al_T		
			Monomeric	Al_{13}	Undetected
1.2	0	2.78	55.2	36.9	7.9
	2	2.82	54.8	37.2	8.0
	30	2.71	51.3	35.4	13.3
	208	2.79	50.5	34.3	15.2
2.0	0	3.01	22.2	65.6	12.2
	2	3.12	19.7	67.2	13.1
	30	3.28	18.9	62.1	19.0
	255	3.25	19.2	61.6	19.2
	302	3.16	16.8	60.8	22.4
2.2	0	3.26	10.8	70.2	19.0
	2	3.31	7.2	72.3	20.5
	30	3.42	7.9	60.6	31.5
	281	3.38	7.7	42.1	50.2
	373	3.50	7.0	33.6	59.4
2.5	0	3.68	8.1	55.3	36.6
	2	3.74	7.2	42.1	50.7
	10	3.79	6.5	20.6	72.9
	30	3.76	6.5	10.4	83.1

Several studies [15,32–35] have shown that upon aging, structural rearrangements take place within the Al_{13} structure without the involvement of further hydrolysis and with the rate of rearrangement dependent on the concentration of Al and the n value. Parthasarathy and Buffle [28] suggested that 0.01 M solutions of Al_{13} seem to be stable for up to a year if the neutralization ratio, n , does not exceed a value of 2.5. Furrer et al [36] found from ^{27}Al NMR studies that homogeneous solutions of 1 mmol l^{-1} Al_{13} at $n = 2.46$ and pH 5 could be stored at room temperature for at least 6 months without any noticeable transformations. If n was increased above 2.5, the dissolved Al_{13} units tend to aggregate, and at $n = 3$, the precipitated Al_{13} was transformed into amorphous Al hydroxides within a few days [37].

From Table 1, it can be seen that when n values were higher than 2.0, the Al_{13} was not stable, and transformed into colloidal aggregates. For the solutions of $n = 2.2$, despite the high content of Al_{13} formed in the preparation process (70.2%), the content of this species decreased to 42.1% after 281 days and to 33.6% after 373 days of aging. For the PAC of $n = 2.5$, after 30 days of aging, only 10.4% of Al_T remained as Al_{13} .

3.4. Particle size distribution of PAC prepared by electrochemical process

A TEM of PAC ($\text{Al}_T = 2.0 \text{ mol l}^{-1}$, $n = 2.0$) is shown in Fig. 5 and shows that the particles are distributed homogeneously in PAC prepared by the electrochemical process.

The particle size distribution of PAC ($\text{Al}_T = 2.0 \text{ mol l}^{-1}$, $n = 1.5$, 2.0 and 2.5) prepared by the electrolysis process was analyzed by DLS after 3 days of ageing. During the measurement, we found that the scattered intensity of samples with n value of 1.5 was too low to obtain reasonable results. The PAC with larger n values (2.0 and 2.5) exhibited intensities of between 1 and 50 Kcps. Distinct “size bands” were observed with the proportion of particles within observed size ranges and the mean diameter of the samples given in Table 2. For the $n = 2.0$ sample, a small size band between 3 and 5 nm, a second size band between 8 and 15 nm, and a third band of large aggregates of

Fig. 5. TEM of particle distribution of PAC prepared by electrolysis process ($\text{Al}_T = 2.0 \text{ mol l}^{-1}$, $n = 2.0$).

size more than 100 nm with a broad distribution were observed. With the same concentration of Al_T and larger n value (2.5), the particle size distribution changed to a two band distribution. They were of sizes 8–15 and 192–425 nm, respectively. In addition, the mean diameters were 47 and 62 nm when the n values were 2.0 and 2.5, respectively.

The mean diameter of the Al_{13} polymer has been measured by small-angle X-ray scattering (SAXS) and found to be about 12 Å [37]. Many researchers [26] have suggested that the Al_{13} polymer units could gradually form tenuous linear aggregates with Cl^- acting to bridge the units (Fig. 3). They suggested that these aggregates could form rapidly and predominate if the rate of neutralization was rapid. Thomas et al. [38] provided evidence that, at least under some conditions, small aggregates of Al_{13} form that still produce a visible 63 ppm resonance, albeit quite broad. Bertsch and Parker [39] have also made this observation in very dilute, partially neutralized solutions. In this paper, the particles sized in the 3–5 nm range analyzed by DLS might be Al_{13} and those of 8–15 nm might be small Al_{13} aggregates, while those of 110–220 nm were probably Al_{13} aggregates of chain-like cluster. The results of Table 2 also demonstrate that the percentage of particles sized 3–5 and 8–15 nm were 18.5 and 45.6% respectively. The particles sized 110–220 nm only accounted for 21.8% of the

Table 2
Particle size distribution by DLS ($Al_T = 2.0 \text{ mol l}^{-1}$)

Samples (<i>n</i>)	Size distribution	Particle size distribution (nm)	Proportion of particles (%)	Mean diameter (nm)
2.0	Trimodal distribution	3–5	18.5	47
		8–15	45.6	
		110–220	21.8	
2.5	Bimodal distribution	8–15	45.5	62
		192–425	45.3	
1.5	Scattered intensity was too low to obtain reasonable result			

particles present. Thus, in the PAC of $n = 2.0$, most of the hydroxy aluminium polymers existed as Al_{13} polymer or small aggregated Al_{13} . From Table 2, it is observed that when the n value increased from 2.0 to 2.5, the particles sized 3–5 nm disappeared and the proportion of larger particles increased. We conclude that more Al_{13} aggregates of chain-like cluster were formed under these conditions.

4. Conclusions

The electrolysis process was employed to prepare nanosized PAC. The results of ^{27}Al NMR spectroscopy showed that significant quantities of the active species— Al_{13} polymer—were formed in PAC solutions at relatively higher concentrations of Al_T (0.2 – 2.0 mol l^{-1}). For PAC of $Al_T = 2.0 \text{ mol l}^{-1}$ and $n = 2.0$, the content of Al_{13} accounted for 65.6% of Al_T and they were stable in the PAC solution for more than 6 months. Although more Al_{13} was formed at higher n values, they did not persist in solution and gradually transformed to other polynuclear forms that were not detectable by ^{27}Al NMR spectroscopy.

The results of DLS and TEM analysis showed that most of particles existing in PAC prepared by the electrolysis process were in the nanometer size range. The particle size of PAC with $n = 2.5$ was larger than that of $n = 2.0$. For PAC of $Al_T = 2.0 \text{ mol l}^{-1}$ and $n = 2.0$, the particle sizes exhibited a trimodal distribution with most of the Al_{13} present as single Al_{13} molecules and small aggregates of Al_{13} .

Acknowledgements

The work was supported by the National Natural Science Foundation of China (Grant No. 50108016).

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