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Preparation of high concentration polyaluminum chloride with high content of Al_b or Al_c

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Abstract

A novel membrane distillation concentration method was used to prepare high concentration polyaluminum chloride (PACl) with high content of Al_b or Al_c. 2.52 mol/L $PACl_1$ with 88% Al_b and 2.38 mol/L $PACl_2$ with 61% Al_c were successfully prepared. Three coagulants, $AlCl_3$, $PACl_1$ and $PACl_2$ were investigated on their hydrolysis behavior and speciation under different conditions. The effects of pH and dilution ratio on Al species distribution were investigated by ferron assay. Experimental result showed that pH had a significant effect on Al species distribution for the three coagulants. Dilution ratio had little effects on Al_b and Al_c distribution in whole dilution process except the beginning for $PACl_1$ and $PACl_2$. The results indicated that transformation of Al depends largely on their original composition. $AlCl_3$ was the most unstable coagulant among these three coagulants during hydrolysis process. $PACl_1$ and $PACl_2$ with significant amounts of highly charged and stable polynuclear aluminum hydrolysis products were less affected by the hydrolysis conditions and could maintain high speciation stability under various conditions.

Key words: polyaluminum chloride; membrane distillation; Al species distribution

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Introduction

Coagulation is a common process in water and wastewater treatment process. Among many coagulants, polyaluminum chloride (PACl) is the most widely used coagulant (Liu *et al*., 2003) and has been paid attention by researchers (Edzwald, 1993; Hu *et al*., 2006; Qu and Liu, 2004; Tang and Luan, 1995; Wang *et al*., 2002; Yan *et al*., 2008). Many studies have confirmed that the content of Al_b and Al_c in PACl are correlated closely to Al_{13} and Al_{30}, respectively (Akitt and Farthing, 1981; Chen *et al*., 2005; He *et al*., 2003; Yan *et al*., 2007). It has been generally demonstrated that Al_{13} or Al_b is regarded as the active species responsible for coagulation or precipitation (Bottero *et al*., 1988; Gao *et al*., 2005; Hu *et al*., 2005; Huang *et al*., 2006b; Qian *et al*., 2008; Wang and Hsu, 1994). As we know, high Al_b content more than 70% is found stable at total Al concentration (Al_T) below 0.5 mol/L; but the content of Al_b would be less than 30% with Al_T above 2 mol/L (Huang *et al*., 2006a; Xu *et al*., 2003). Therefore, how to prepare the high concentration PACl with high Al_b content has become the primary goal for the research and production industry of PACl. Previous reports on hydrolysis process mainly focused on PACl solutions of low concentration (10^{-4}–10^{-1} mol/L), and few concerned with the high concentration above 2 mol/L. Huang *et al*. (2006a) investigated Al species distribution and transformation at high PACl concentration at 2 mol/L, but the content of Al_b was lower than 18.3%.

Al_{30} polymer is regarded as another polycation in hydrolytic polyaluminum solutions (Allouche and Taulelle, 2003; Casey, 2006; Chen *et al*., 2005; Zhang *et al*., 2008). Our previous research indicated that Al_{30} was another high active species in solutions responsible for coagulation/flocculation besides Al_{13} (Chen *et al*., 2006). But there were few reports on the hydrolysis and coagulation performance of Al_{30} or Al_c at high Al_T. Therefore, it is necessary to further investigate the preparation and property of high concentration PACl with high Al_c content.

Membrane distillation (MD) is a thermally driven process involving transport of water vapor through a porous hydrophobic membrane (Lawson and Lloyd, 1997). During MD process only water vapor can be transferred through the membrane in the feed system. MD process enables the production of pure water from natural water. In addition, it is less dependent on the initial salinity of the feed as well as a higher salt rejection ratio. Thus, MD is widely proposed for desalination and other concentration applications (Alklaibi and Lior, 2005; Guo *et al*., 2007; Obaidani *et al*., 2008; Qtaishat *et al*., 2009; Qu *et al*., 2009; Wang *et al*., 2008).

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In this article, it is the first time to prepare the high concentration PACl at $Al_T > 2.3$ mol/L containing high content of Al_b or Al_c respectively using a chemical synthesis-membrane distillation process. This work is intended to investigate the hydrolysis property of high content of Al_b or Al_c under different conditions. The effects of pH and dilution ratio on Al species distribution are discussed in detail. The results would provide further insight into the understanding of the transfer characteristics of high concentration PACl with high content of Al_b or Al_c.

1 Materials and methods

1.1 Preparation of PACl

The reagents used in this study were all of analytical grade. The coagulant with Al_T 2.5 mol/L containing high content of Al_b ($PACl_1$) was prepared by chemical synthesis-membrane distillation method. First, 0.2 mol/L PACl was prepared by chemical synthesis process: a certain amount of 1 mol/L $AlCl_3$ solution was added into a 1000-mL glass reactor equipped with a Teflon anchor stirrer and a reflux condenser. The solution was kept at 65°C using a thermostatic apparatus, a certain amount of 0.6 mol/L NaOH solutions was pumped into the reactor through peristaltic pump under rapid stirring until the hydrolysis ratio reached a prearranged value.

After chemical synthesis, membrane distillation (MD) process was used to concentrate 0.2 mol/L PACl. As shown in Fig. 1, feeding and permeate thermostatic cycles were connected to the membrane module, respectively. The membrane module was equipped with a flat-sheet membrane module with the efficient area of 70 cm^2. The flat-sheet membrane material was a hydrophobic microporous PVDF (IPVH00010, Millipore, USA) with 0.45 μm pore size and was placed between the two identical chambers. The temperature of the feed and the permeate were controlled at 55 and 20°C, respectively, through a water bath. In the experiment, the initial feeding of 0.2 mol/L PACl solution in the stirred tank with an initial volume of 3000 mL was pumped into the feed side of membrane module, then returned to the stirred tank for circulating. Another permeate side with pure water was also pumped into the permeate side of membrane module to provide heat exchanger. When the liquid in the feed tank and the flow volume of the total remaining was about 250 mL, experiment process was stopped. At the same time, the conductivity of permeate was detected by the conductivity meter (CO150, HACH, USA) to confirm the intact membrane hydrophobicity.

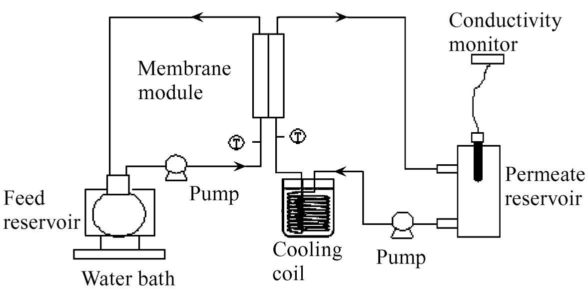

Fig. 1 Schematic view of membrane distillation process.

The coagulant with $Al_T = 2.38$ mol/L containing high content of Al_c ($PACl_2$) was prepared based on $PACl_1$. First, $PACl_1$ solution was added into a glass reactor equipped with a Teflon anchor stirrer and a reflux condenser. Then, that $PACl_1$ solution was heated to a predetermined temperature 90°C and maintained using a thermostatic apparatus. The reaction was controlled for 12 h.

1.2 Analytical methods

The Al species was measured by ferron assay with a timed colorimetric reaction with ferron reagent to provide speciation based on chemical reactivity on UV-Vis spectrophotometer (DR/4000U, HACH, USA). Based on dissociation and complex reaction kinetic rates between ferron reagent and hydrolyzed Al species (Chen *et al*., 2006; Huang *et al*., 2006a; Wang *et al*., 2005), the hydrolyzed Al species were divided into monomeric species (Al_a) (reacting with ferron from 0 to 1 min), planar oligomeric and medium polymeric species (Al_b) (reacting with ferron from 1 to 120 min), and three dimensional species or sol-gels (Al_c) (reacting with ferron after 120 min and non-reacting with ferron). The Al_T concentration was measured based on titrimetric method (Chen *et al*., 2006; Guo *et al*., 2007). The pH value of the solutions was also measured.

2 Results and discussion

2.1 Al species distribution during membrane distillation

Different concentration PACl solutions from 0.2 to 2.52 mol/L were obtained by membrane distillation. As shown in Table 1, the content of Al_b is almost stable even though Al_T reached 2.5 mol/L during the MD process. The results showed that we could synthesize the PACl containing as high as possible percentage of Al_b in high Al_T by MD. That is to say, MD concentration process is very effective method for preparing high concentration PACl with high content of Al_b.

2.2 Effect of pH on Al species distributions during hydrolysis process

Hydrolysis behavior and transformation mechanism are different for different coagulants in coagulation process when coagulant was added into water. Owing to the complexity species of PACl in solutions, it is necessary to investigate the species transformation of different

Table 1 Al concentration and species distribution during membrane distillation

Al_T (mol/L)	pH	Al_a (%)	Al_b (%)	Al_c (%)
0.200	5.20	1.4	86.6	12.0
0.489	4.66	2.3	86.2	11.5
0.884	4.32	2.3	88.1	9.6
1.613	4.04	3.1	87.0	9.9
1.925	3.87	4.2	88.4	7.4
2.521	3.61	4.5	88.2	7.3

coagulants and supply some information for actual coagulant process. In this article, two new coagulants 2.52 mol/L PACl ($PACl_1$), 2.38 mol/L PACl ($PACl_2$) with different Al speciation distributions and $AlCl_3$ were selected to compare their hydrolysis behavior and speciation under different conditions. Al species distributions of the three different coagulants are summarized in Table 2.

Table 2 Characterization of coagulants by ferron assay

Coagulant	Al_T (mol/L)	pH	Al_a (%)	Al_b (%)	Al_c (%)
$AlCl_3$	0.50	2.21	96.20	3.80	0.00
$PACl_1$	2.52	3.61	4.50	88.20	7.30
$PACl_2$	2.38	3.72	3.34	35.32	61.34

In order to get more insight into the mechanism of the effect of pH on the speciation transfer of PACl, hydrolysis tests with different pH control were carried out. Synthetic water containing 2×10^{-4} mol/L $NaHCO_3$ and $NaNO_3$ in deionized water was prepared for control experiments. A predetermined amount of 0.2 or 0.05 mol/L NaOH or HCl solution was added to control pH.

The effect of pH on Al species distributions during dilution process was studied in the pH range 4–11, and corresponding results are shown in Fig. 2. The results indicated that pH significantly affected Al species distribution. Al species distributions of $AlCl_3$ during hydrolysis and dilution process were greatly changed compared with the initial species distributions. With the increase of pH in acidic region, the content of Al_a decreased rapidly and reached a minimum at near neutral pH, while the content of Al_b increased rapidly and reached a maximum at near neutral pH; the distribution of Al_c was similar to that of Al_b but at a reduced scale. In alkaline region, with the increase of pH, the content of Al_a increased rapidly, while a rapid decrease of the content of Al_b occurred, the content of Al_c decreased after pH exceeded 8.5. For $PACl_1$, the contents of Al_a and Al_b decreased while the content of Al_c increased with the increase of pH in acidic region. In alkaline region with the increase of pH, the content of Al_a increased while the content of Al_c decreased. For $PACl_2$, the content of Al_a decreased while the content of Al_c increased with the increase of pH in the acidic region. The contrary trend occurred in the alkaline region. The content of Al_b was almost unchanged and stable through the investigated pH range.

From the above results, it can be indicated that pH control could change Al species distributions. The Al_a fraction in the primary coagulants is the most unstable species for every coagulant; the Al_b fraction in the primary coagulants is the most stable species for $PACl_1$ and $PACl_2$.

2.3 Effect of dilution ratio on Al species distributions

In order to test the stability of $PACl_1$ and $PACl_2$, a series of dilution ratio experiments was carried out and determined after dilution 30 min. Dilution ratio referred that $PACl_1$ and $PACl_2$ were diluted into different multiples using deionized water. It can be seen that dilution ratio has little effect on the species distribution of PACls (Fig. 3). For $PACl_1$, the content of Al_b decreased from 88% to 78% and transfered into Al_c, which resulted in the content of Al_c increased with fractions 10% during dilution process. The contents of Al_b and Al_c were relatively stable with the increase of dilution ratio; the content of Al_b can be above 70% at any concentration for $PACl_1$ during dilution process. The content of Al_a was stable and about equal to original content during dilution process. For $PACl_2$ the content of Al_c increased from 61% to 71% but the content of Al_b decreased 10% when dilution began. The contents of Al_b and Al_c were stable with the increase of dilution ratio. The content of Al_a was stable during whole dilution process. The reason may be that dilution increased the pH of PACl solution and enhanced its basicity, which resulted in the conversion from part of Al_b in the role of OH^- to the high polymerization species Al_c. The above results indicated that the coagulants of $PACl_1$ and $PACl_2$ were relatively stable in different concentrations during dilution process. It is feasible to prepare high concentration PACl with high content of Al_b or Al_c.

3 Conclusions

Membrane distillation method was first employed to prepare high concentration PACl with high content of Al_b or Al_c. The effects of pH and dilution ratio were investigated to determine Al species distribution during hydrolysis process. It has been proved that solution pH plays an important role in hydrolysis process. The effect of dilution ratio on the speciation distribution of PACls is

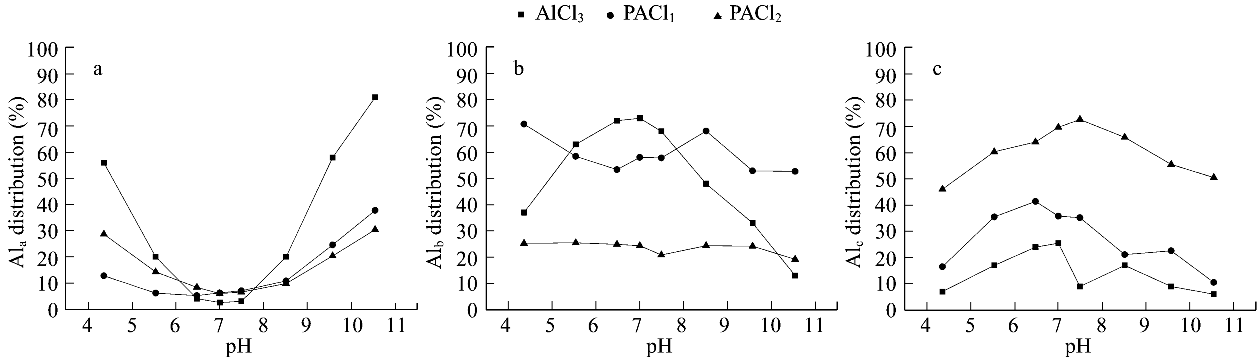

Fig. 2 Al speciation characterization after dosing 2×10^{-4} mol/L of PACl under various pH conditions.

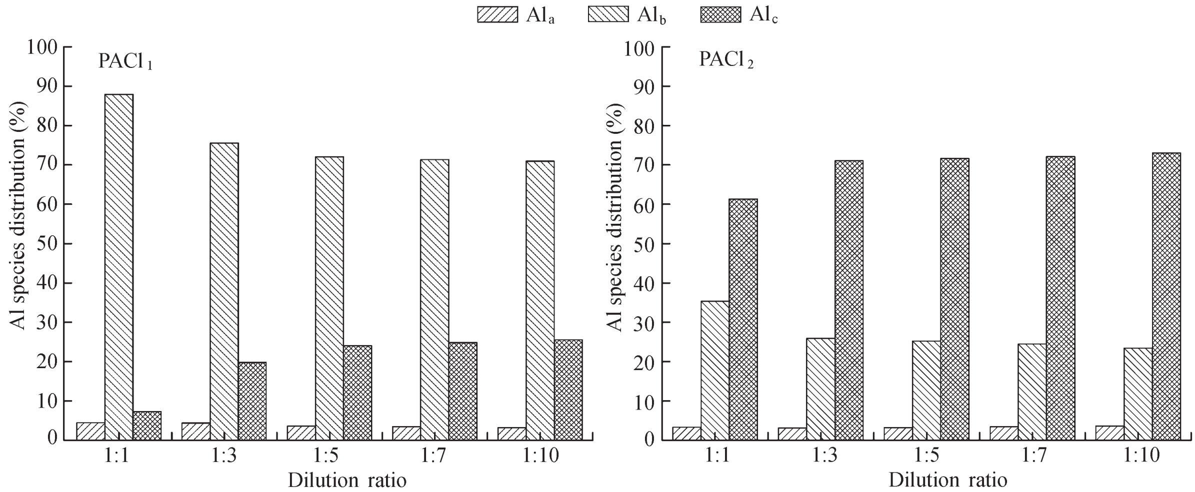

Fig. 3 Al species distribution of $PACl_1$ and $PACl_2$ as a function of dilution ratio.

relatively little. Al species change for $PACl_1$ and $PACl_2$ was relatively stable during dilution process.

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