

A novel method to synthesize polyaluminum chloride with a membrane reactor

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Abstract: Al_{13} or Al_b is usually regarded as the most efficient species of polyaluminum chloride (PAC), the performance flocculant for water treatment. This paper was intended to report a new method to synthesize PAC with high content Al_b , by using the membrane reactor. NaOH solutions were managed to permeate slowly through the micropores of ultrafiltration membrane into $AlCl_3$ solutions under the suitable transmembrane pressure (TMP). Meanwhile NaOH drops size was limited to nano-scale, resulting in dramatical reduction of the characteristic diffusion time and great increment of contact interface between the strong base and Al ions in solution to favor the formation of $Al(OH)_4^-$, the precursor of Al_{13} , so few precipitates and much Al_b are produced. When the initial concentration of $AlCl_3/NaOH$ is 0.40/2.0 (mol/L), $MWCO = 10000$, $TMP = 0.0085$ MPa, $T = 305$ K and B (molar ratio of OH^-/Al^{3+}) = 2.25, the quantity of Al_b attains about 80%. The results of ^{27}Al -NMR determination showed that the Al_{13} content is equal to Al_b content. And our PAC product has shown better flocculation effects than the commercial product.

Keywords: membrane reactor; polyaluminum chloride

Introduction

When $AlCl_3$ solutions are partially neutralized via addition of base, polynuclear hydroxo-Al complex, i. e. polyaluminum chloride (PAC), a kind of important flocculants in potable and wastewater treatment, is prepared. As the most efficient species of polyaluminum for its higher positive charge and stability (Tang, 1995), the Al_{13} species of Keggin structure (tridecameric polycation, $[AlO_4Al_{12}(OH)_{(24-n)}(H_2O)_{(12-n)}]^{(7-n)+}$) has frequently been assumed to be the dominant complexes in solutions, which structure has been directly confirmed using NMR spectroscopy (Thompson, 1987). Meanwhile, reaction with the Ferron reagent has also been used to separate the partially neutralized Al solutions into three fractions (Bersillion, 1980): the " Al_a " fraction (mononuclear Al, including the hexaaqua, mono- and dihydroxo monomers and in solutions of higher pH value the tetrahydroxo aluminate ion), " Al_b " (polynuclear Al), and " Al_c " (larger polynuclear and/or solid phase aluminum trihydroxides). Among them, Al_b fraction corresponds to Al_{13} in freshly prepared solutions according to previous ^{27}Al NMR reports (Bertsch, 1986).

The tendency for Al_{13} formed in partially neutralized solutions depends critically on an interfacial disequilibrium between the acidic, Al-containing solution and the base being injected into it (Bottero, 1987; Parker, 1992). A localized high pH at the base injection point would favor the formation of the aluminate ion, $Al(OH)_4^-$, which would provide the requisite tetrahedral coordination for the core atom of the tridecamer (Akitt, 1978; Bertsch, 1987). Generally speaking,

at higher reactants concentrations, lower adding rate of base favors the synthesis of PAC with higher Al_b content, which has been proven by the synthesis methods, such as adding base by capillary (I. D. 0.1 mm) (Vermeulen, 1975), electro dialysis, electrolysis (Akitt, 1981; Lu, 1999) and so on. However, there are still some limitations for these methods to increase Al_b content at relatively higher basicity.

Here a novel method is proposed for the synthesis of PAC, in which NaOH solution permeated through the micropores of hollow fiber (HF) ultrafiltration (UF) membranes gradually into the fiber lumina to react with $AlCl_3$ solution under the transmembrane pressure (TMP). Since the micropores of HF UF membranes are very small, e.g. several or tens of nanometer in mean diameter, the drop size of NaOH solutions and the characteristic diffusion time can be dramatically reduced; with the proper sheer force to disperse the injected base homogeneously, the micro-mixing conditions can be improved greatly. Besides, due to a larger contact interface between the strong base drop and Al ions, more $Al(OH)_4^-$ ions are presumed to be formed (Bottero, 1987), leading to the increase in the Al_b content.

In this paper, PAC with high content Al_b was synthesized by using the membrane reactor. The composition of PAC was analyzed with the Ferron spectrophotometric assay and ^{27}Al -NMR method. Besides, the hydrodynamics condition and the flocculation test were discussed.

1 Materials and methods

1.1 Membrane reactor

The membrane module was fitted with 10 pieces of hollow

fibers UF membranes (PS/PDC, MWCO '10000 Dalton, produced by RCEES), each with 1.0 mm in inner diameter and 0.13 m in length.

1.2 Preparation method

The reaction was operated in semi-batch as shown in Fig. 1a. NaOH solution in the graduated glass tube gradually permeated into the lumens of the HF membrane through the micropores from the shell side of the module under the transmembrane pressure. At the same time, AlCl_3 solution in the stirred tank, with the initial volume of 100 ml, was pumped into the lumens of the HF UF and reacted with NaOH to form PAC, then returned into the stirred tank for circulating.

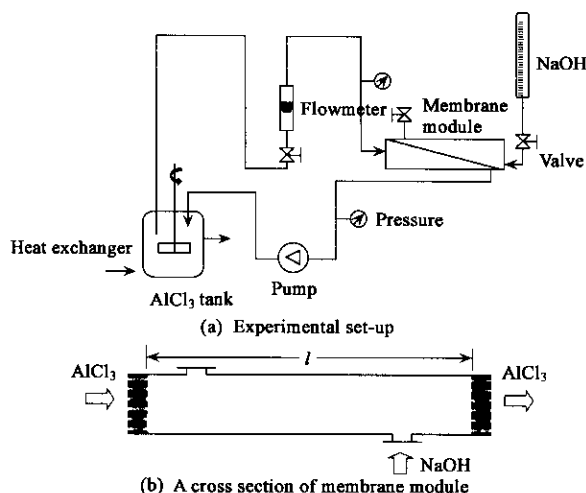


Fig.1 Experimental set-up and membrane module

The initial flow rate of AlCl_3 solution and trans-membrane pressure were adjusted by the valves. The temperature of the solutions in the reactor was strictly controlled by a heat exchanger. The liquid level of NaOH solution in the graduated glass tube was kept unchanged by elevating the tube continually with the permeation. Then the average transmembrane pressure, TMP , can be expressed as follows:

$$TMP = P_{vac} + \rho_B g \Delta h, \quad (1)$$

where, P_{vac} is the average vacuum at the entrance and exit of the module, ρ_B is the density of NaOH solution, g is the acceleration of gravity, Δh is the liquid level difference between the NaOH solution and the membrane module.

1.3 Ferron timed-colorimetric assay

After aging for 24 h, the partially neutralized solutions were analyzed by the Ferron timed-colorimetric assay. In this experiment, 0.2% Ferron (Sigma Chem. Co.), 20% NaAc solution and 1:9 HCl solution (in which the volume ratio of pure water/hydrochloric acid was 1/9), with the volume ratio of 2.5:2:1, were combined to yield the mixed working Ferron reagent. The solid NaAc and hydrochloric acid were the analysis grade reagents.

Volumes of the PAC sample and Ferron reagent were selected so that the $\text{Ferron}_T/\text{Al}_T$ molar ratio was always about

10. After sufficient mixing of the sample and reagent with the magic stirrer at 600 r/min for 30 s, the specimen was transferred into a 1 cm path-length glass cuvette and placed in a UV754 UV-vis spectrophotometer (Spectrum Apparatus Ltd. of Shanghai). Absorbance increments were monitored for 120 min at 370 nm. Considering absorbance increments after 120 min were negligible, the Al reacted at 120 min was assumed to represent $[\text{Al}_a + \text{Al}_b]$, and $[\text{Al}_c]$ was thought to completely react within 1 min.

Before determination of the total Al, $[\text{Al}_T]$, the sample was diluted with aqueous HCl (pH = 1.5) and heated at 85°C for 3 h. When it was cooled down, the absorbance was detected with Ferron assay at 370 nm. Then, $[\text{Al}_c]$ was computed as the difference between $[\text{Al}_T]$ and $[\text{Al}_a + \text{Al}_b]$.

1.4 ^{27}Al -NMR method

To compare with the results from Ferron assay, the ^{27}Al -NMR spectra were measured by a BRUKER-AM300 NMR spectrometer with a sample tube of 10 mm diameter. Standard curves of Al solution were constructed using the integrated intensities of measured resonances for the 0 ppm hexaaquaaluminum resonance. Quantitative determinations of Al species in hydroxy-Al solutions were made by referencing the integrated intensities of their respective peaks to the standard curve. To each sample D_2O was added quantitatively to provide an external field-frequency lock. The resonance frequency was 78.2 MHz, the angle of pulse 90°, pulse delay time 0.1 s, 4 k data point and the spectrum width 600 ppm.

1.5 Flocculation experiments

The effects of coagulation were compared between our preformed PAC product and the commercial PAC, which noted as syn-PAC and D-PAC, respectively. Kaolinite suspension with the concentration of 100 mg/L was used as colloids to be coagulated. The synthetic medium was made up by 50% tap water and 50% distilled water. Prior to the addition of coagulants, the target pH was adjusted with NaOH and HCl until the pH values of the suspension maintained constant. The coagulation tests were carried out at room temperature (20–23°C). A six-place paddle stirrer (JTY-6 type, Daiyuan Center, China) with 1 L glass beakers was used for the tests, which allows for 1 min of rapid mixing at 150 r/min, together with the subsequent 15 min of slow stirring at 50 r/min, to be preset. After the mixing and coagulation, the flocs were settled for 10 min. Samples for analysis were withdrawn 1 cm below the water surface with a plastic syringe. And the residual turbidity (RT) was measured with a microprocessor turbidimeter (Hanna Instruments Pte Ltd., Singapore).

2 Results and discussion

2.1 The principle of PAC synthesis with membrane reactor

For the formation of Al_{13} , the localized high pH values to

provide the precursor, $\text{Al}(\text{OH})_4^-$, are required. However, at the point of NaOH introduction, the formation of "clusters" is unavoidable when Al^{3+} and OH^- ions are pulled together. Fortunately, most "clusters" are unstable and incline to dissolve in the Al solution; or they could rapidly dissociate into constituent ions if the rapid stirring is possible. When traces of the "clusters" have reached the critical size and structure of nuclei, they aggregate due to the high surface energy.

So in order to provide much more chances for the formation of $\text{Al}(\text{OH})_4^-$, instead of the nuclei of $\text{Al}(\text{OH})_3$, at the point of base introduction, superior micro-mixing condition is critical. To enhance the acid dissolution of nuclei, the large interface between base drops and Al ions is necessary, which depends on the homogeneous distribution of the base drops and the decrease in the base drop size. On the other hand, the strong stirring force is favorable for the physical abrasion, which can be obtained by the slow base injection rate and the strong mixing in the Al solution.

With the employment of the membrane reactor, the

superior micro-mixing conditions are easy to be realized. The micro pores, several to decades of nanometer, distribute homogeneously at the working surface of the membrane. By lowering the permeate flux under the suitable TMP and meanwhile raising the flow rate of Al solution, a larger interface to bear more $\text{Al}(\text{OH})_4^-$ and higher shear force to disturb the nuclei formation is available. Thus, PAC with high content Al_b are obtainable.

The species distributions of PAC prepared with membrane reactor and other methods were compared in Table 1. Due to the small base drops and superior micro-mixing between the base drops and Al ions, the results from membrane method is similar to that from the micro-titration method, so the approach of base injection through membrane micropores should belong to the micro-titration method. And by using the membrane reactor, the PAC production efficiency can be increased greatly. Compared with electro dialysis and electrolysis methods, our product has shown great advantage with much higher Al_b content.

Table 1 Species distribution of PAC prepared with different methods

Methods	Al_T , mol/l	Basicity	Al_a , %	Al_b , %	Al_c , %	Base injection rate, ml/min	References
Micro-titration	0.1	2.5	12.55	82.8	4.7	0.04—0.05	Luan, 1995
Slow-injection	1.0×10^{-4}	1.6	28.1	62.1	9.8	0.33	Parker, 1988
Electro dialysis	0.26	1.8	17.1	61.2	21.7		Zheng, 1989
Electrolysis	0.225	2.5	17.0	71.7	11.3		Lu, 1999
Membrane reactor ^a	0.28	2.25	10.2	79.0	10.8	~ 0.3	
Membrane reactor ^b	0.26		13.2	84.6	2.2		

Notes: ^a PAC was synthesized with AlCl_3 and NaOH; ^b PAC was synthesized with AlCl_3 and Na_2CO_3

2.2 PAC synthesized with NaOH

In this experiment, PAC was synthesized with the strong base. The preparation conditions include: $C_{A0} = 0.40$ mol/L, $C_{B0} = 2.0$ mol/L, $\text{TMP}_0 = 0.0085$ MPa, $u_0 = 1.06$ m/s and $T = 305$ K.

During the synthesis, small base drops homogeneously permeate into the membrane lumen, leading to the formation of $\text{Al}(\text{OH})_4^-$ at the base-Al solution interface. With the increase in B , the amount of $\text{Al}(\text{OH})_4^-$ increases due to the homogeneous distribution of OH^- in the Al solution, and most of the Al_{13} polymer is formed at a rapid rate. However, at much higher values of B ($B > 2.25$), quantities of $\text{Al}(\text{OH})_4^-$ are so large that the octahedral component is not present in sufficient amount to interact with the $\text{Al}(\text{OH})_4^-$ to form Al_{13} species (Bertsch, 1987). Instead, the colloidal and precipitated $\text{Al}(\text{OH})_3$ are formed in a larger amount. As shown in Fig. 2, there is an optimum basicity ($B = 2.25$) associated with the maximum content of Al_{13} (79%). And the Al_c species appear obvious only after $B = 1.5$, which may be the result of the delay in the formation of the critical nuclei.

The pH- B curve (Fig. 3) records approximately the hydrolysis and polymerization process for the neutralization.

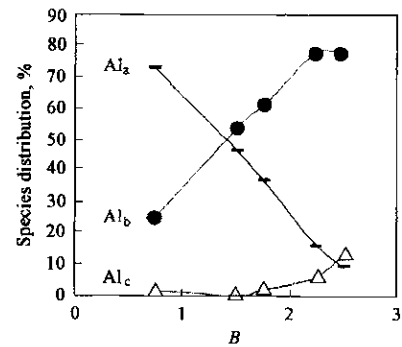


Fig. 2 Distribution of Al species as a function of B

Before $B = 0.5$, the pH values increase quickly, and then slowly until around $B = 2.25$. After $B = 2.25$, pH increase fast again. It is reported that the H^+ ions, generated from hydrolysis, is neutralized by OH^- with a rate constant of 1.4×10^{11} mol/($\text{dm}^3 \cdot \text{s}$) (Sykes, 1970). Therefore, without polymerization, due to the continuous and quick neutralization, pH values would increase linearly with the permeation of base drops. In other words, the polymerization, as well as the increase in the polymerization degree, for this synthesis, occurs mainly from $B = 0.5$ to 2.25 ($3.4 < \text{pH} < 3.7$). During this period, the OH^- ions neutralize the H^+

ions originated from the hydrolysis of Al solution, and enhance the polymerization to form Al_{13} , the partly neutralized stable polymer. As presumed by some literature, there may be a strong ligand binding of hydroxyl ions in Al_{13} polymer.

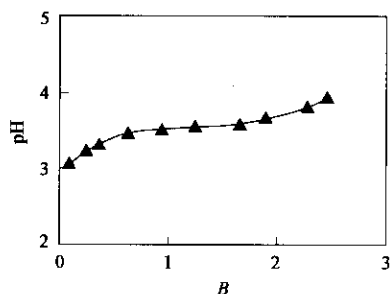


Fig.3 Changes of pH values with B

2.3 PAC synthesized with Na_2CO_3

By using the membrane reactor, PAC flocculant was also synthesized with a kind of weak base, Na_2CO_3 . The species distribution of PAC is shown in Table 2. It is found that, with the permeation of Na_2CO_3 drops, the content of Al_n decreases and Al_b increases; when pH values reaches 4.42, the content of Al_b rises to 84.6%; and the amount of Al_c only slightly increases with the proceeding of the reaction. It seems that the weak base is more favorable to form Al_b than the strong base ($NaOH$), which may be the benefits from the effects of slower addition of OH^- ions, due to the slower hydrolysis of Na_2CO_3 .

Table 2 The species distribution of PAC synthesized with $AlCl_3$ and Na_2CO_3 solution

pH	3.24	3.65	4.02	4.25	4.42
Al_T , mol/L	0.41	0.34	0.29	0.27	0.26
Al_n , %	89.9	77.1	42.7	14.9	13.2
Al_b , %	9.5	22.5	56.8	83.9	84.6
Al_c , %	0.6	0.4	0.5	1.2	2.2

2.4 The effects of hydrodynamic conditions

Because the hydrodynamic conditions have a close relationship with the micro-mixing in the membrane reactor, the effects of transmembrane pressures and flow rates on the composition of PAC products were tested. The results showed that, when the original transmembrane pressure was kept 0.0090 MPa, 0.018 MPa and 0.029 MPa, respectively, the corresponding maximum content of Al_b in PAC product was 68%, 62% and 58%. And when the flow rate of al solution was 0.53 m/s and 1.13 m/s, the maximum Al_b content in the product was respectively 77% and 72%. Thus the lower transmembrane pressure and the faster flow rate are favorable for the micromixing in the membrane reactor. In a word, with the optimized operation parameters to enhance the micro-mixing between the base drops and Al solution, the content of Al_b in PAC products is presumed to increase further. Other researches based on this idea are being conducted in detail in our lab.

2.5 Results of ^{27}Al -NMR determination

Here the ^{27}Al -NMR spectra were used to compare with the species distribution determined with Ferron methods. A typical ^{27}Al -NMR spectrum is shown in Fig. 4. Before the detection, PAC samples had been aged for 24 h. The signal near 0.3 ppm represents the monomeric aluminum (Al_{mono}) such as Al^{3+} , $Al(OH)^{2+}$, and $Al(OH)_2^+$. The signal at the 63 ppm denotes $Al_{13}O_4(OH)_{24}^+(Al_{13})$, formed by 12 aluminum atoms (six coordination) surrounding an aluminum atom (four coordination) and connected by hydroxyl. Only the symmetric four-coordination aluminum ion can produce visible signals, and the asymmetric six coordination aluminum ion cannot, so that the signal at the 63 ppm represents 1/13 of $Al_{13}O_4(OH)_{24}^+$. The results showed that Al_n are higher than Al_{mono} determined by the NMR method with differences about 5%. However, the content of species Al_b and Al_{13} are the same, indicating that contents of Al_b determined by Al-Ferron within 120 min are comparable to the contents of Al_{13} determined by ^{27}Al -NMR. This result agrees well with previous reports (Bertsch, 1986).

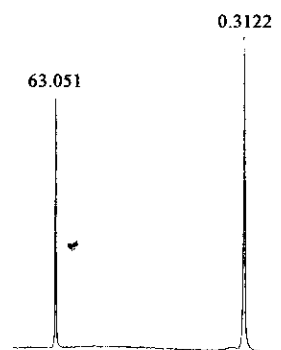


Fig.4 ^{27}Al NMR spectrum

2.6 The results of the flocculation experiments

Coagulation effects of our synthesized PAC (syn-PAC) and Dagang PAC (D-PAC) are compared in Fig. 5. Our preformed PAC has shown a wider range to flocculate the kaolin to the same residual turbidity. In other words, for the same dosed PAC, the flocculant produced in our lab has a lower residual turbidity. It is said that the D-PAC is one of the best-seller flocculant in our country, so the flocculation test proved that our preformed PAC is a competitive product, even without any addition of auxoflocculant. This result should be attributed to the high content Al_{13} in our flocculant, which is temporary refractory to hydrolysis before adsorption to particle surfaces, and has higher positive charge and strong binding ability to aggregate. Thus the adsorptive charge neutralization, and subsequent bridging enmeshment and sweep coagulation are easy to go along, leading to the great reduction in the residual turbidity.

3 Conclusions

Polyaluminum chloride (PAC) with high Al_b quantity,

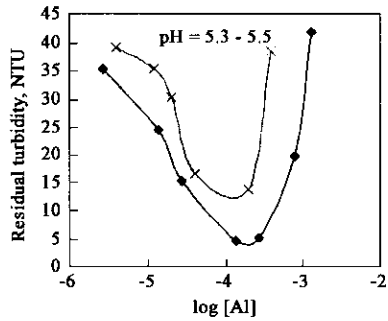


Fig.5 Residual turbidity after addition of alum at different pH
 ◆: syn-PAC; ×: D-PAC

around 80%, was synthesized with a membrane reactor.

The kind of base seems to have effects on the composition of PAC. The weak base is favorable for the increase in the content of PAC.

The hydrodynamic conditions, including the transmembrane pressure and flow rate, have a close relationship with the species distribution of the PAC products.

The results of the ^{27}Al -NMR determination revealed that for this synthesis, the content of Al_{13} is equal to that of Al_6 , determined with the Ferron method.

The flocculation experiments provide a better turbidity-removing result with our synthesized PAC than with one of the best seller PAC flocculants.

By enhancing the micro-mixing conditions, the membrane reactor shows great commercial prospect for the synthesis of PAC with high Al_6 content.

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