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Synthesis of polyaluminum chloride with a membrane reactor: Process characteristics and membrane fouling

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Abstract

Polyaluminum chloride was synthesized with a membrane reactor, in which NaOH was added into $AlCl_3$ solution through the membrane's micropores to reduce the NaOH droplets size. The content of the most efficient species increased to about 80%. The process characteristics in the reaction (i.e., flow velocity, pressure drop), and membrane fouling and cleaning were investigated. The evolution of both flow velocity and pressure drop during the reaction were related to changes in species distribution and solution viscosity. The process characteristics were well interpreted in terms of the Bernoulli equation. After reaction, the membranes were recovered by cleaning with diluted hydrochloride acid. This study is crucial for process design and scale-up of membrane reactors.

Key words: polyaluminum chloride; membrane reactor; flocculant; Al_b; Al_{13}

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Introduction

Polyaluminum chloride (PAC) is an important flocculant in water treatment (Li et al., 2010). It can be divided into three fractions (Bersillon et al., 1980; Parker and Bertsch, 1992): Al_a (mono-nuclear Al), Al_b (reactive polynuclear Al), and Al_c (larger polynuclear and solid-phase aluminum trihydroxides). Generally, Al_b is regarded as the most efficient species. Polyaluminum chloride is usually synthesized by partial neutralization of $AlCl_3$ solution with base solution (Shen and Dempsey, 1998; Zhao et al., 2009). Low adding rate and small droplet size of the base solution favor the increase in Al_b content (Bertsch, 1987; Bottero et al., 1987). Thus, various methods, such as adding base through capillary with I.D. of 0.1 mm (Vermeulen et al., 1975), electrodialysis (Lu et al., 1999), electrolysis, homogeneous hydrolysis (Vogels et al., 2005), and ultrasounds (Cheng et al., 2008) have been employed to reduce the addition rate and/or droplet size of base solutions.

In our previous work (Jia et al., 2004; He et al., 2005), a membrane reactor was employed for the synthesis of PAC, in which NaOH solution was added to $AlCl_3$ solution gradually through the micropores of hollow fiber ultrafiltration (HFUF) membranes to reduce the NaOH droplet size. The effects of membrane molecular weight cut-off (MWCO) and reactant concentration on species distribution, along with the reaction pathways, were studied. In this article, the process characteristics (i.e., flow velocity and pressure drop) in the reaction, and membrane fouling and cleaning were investigated. These studies are important, especially for the design and scale-up of membrane processes.

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1 Experimental section

All reagents, including Ferron (Sigma Chemical Co., USA), NaOH, $AlCl_3$, NaAc, and hydrochloride acid, were of analytical grade. The membrane module was fitted with 10 HFUF membranes (PS/PDC, MWCO 10000, I.D. 1.0 mm, length of 0.13 m, Zhongke Membrane R&D Center of Beijing, China).

The experimental set-up is schematically shown in Fig. 1. In the reaction, NaOH solution (2.0 mol/L) in graduated glass tubes entered the module shell-side and permeated through the membrane micropores under trans-membrane pressure (0.0090 MPa). Approximately 100.0 mL of $AlCl_3$ solution (0.40 mol/L) in the stirred tank flowed through the membrane lumens with a flow velocity of 1.09 m/sec, reacted with the permeated NaOH, and then returned to the stirred tank. When the basicity (*B*, molar ratio of NaOH to $AlCl_3$) reached 2.5, the reaction was stopped. The flow rate of the liquid was measured with a rotameter. During the reaction, the liquid in the stirred tank was sampled and species distribution was analyzed after aging for 24 hr.

In the determination of the species distribution, Ferron

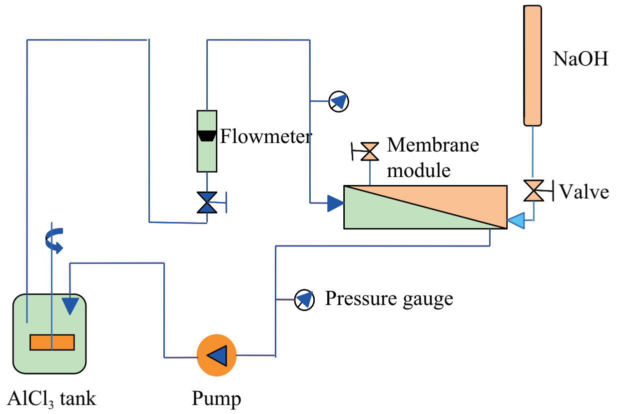

Fig. 1 Experimental set-up.

solution (0.2%), NaAc solution (20%) and dilute hydrochloride acid (V_{HCl}:V_{H_2O} = 1:9) were mixed with a volume ratio of 2.5:2:1. The as-obtained working Ferron reagent was then mixed with the PAC sample vigorously and the absorbance was immediately monitored at 370 nm with a UV-Vis spectrophotometer (UV754, Spectrum Apparatus Ltd. of Shanghai, China). The Al species that reacted before 120.0 min were assumed to be Al_a and Al_b, while those that reacted within 1.0 min were assigned to Al_a (Bersillon et al., 1980; Parker and Bertsch, 1992). We determined that Al_c was equal to the difference between total Al and the sum of Al_a and Al_b.

For the analysis of membrane fouling materials, membrane samples were washed with pure water, dried at room temperature, spurted with carbon, and then observed with SEM (S250MK3, Cambridge Instrument Company, UK).

2 Results and discussion

2.1 Process characteristics

With the addition of NaOH solution, the pH of the $AlCl_3$ solution increased. Figure 2a shows the evolution of pH values at the reaction temperature of 18, 24, and 32°C, respectively. At the same basicity, the pH decreased with increasing temperature, which was likely due to the hydrolysis of $AlCl_3$, being an endothermic reaction with high temperature shifting the hydrolysis balance to the right.

Species distribution changed with the basicity: Al_a decreased linearly; Al_b increased apparently when $0 < B < 2$–2.25, attained a maximum at B range 2–2.25 and then declined; Al_c increased slowly before $B = 2$ and then increases rapidly (Fig. 2b). With increased basicity, Al_b deprotonated and formed linear 2D or 3D structures through oxygen bridges and precipitates, and which displayed as Al_c when their reaction rates with Ferron reagent were slow enough. With increased temperature from 18 to 24, and 32°C, white precipitates appeared at B of 0.65, 1.0 and 1.4, and Al_b attained 63%, 70%, and 80% at B of 2.25 whereas Al_c reached 13%, 8% and 3%, respectively. Obviously, high temperature favored the formation of Al_b.

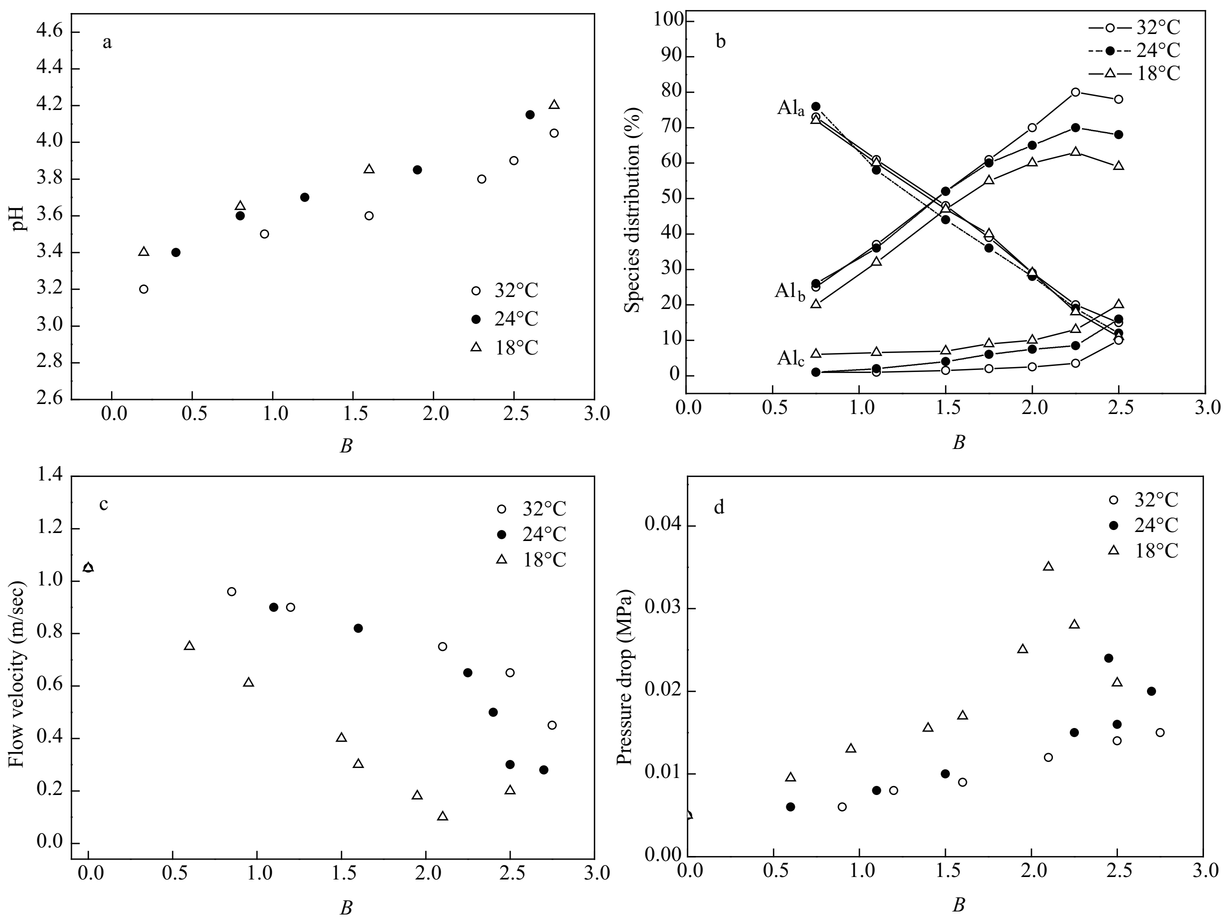

Fig. 2 Evolution of process characteristics with basicity (B, molar ratio of NaOH to $AlCl_3$) at different temperatures.

High content of Al_b led to high viscosity, which subsequently affected process characteristics. Figure 2c shows the evolution of flow velocity during the reaction. When $0 < B < 2.0–2.5$, the velocity deceased slowly, while at B of 2.0–2.5 it reached its minimum due to maximum Al_b. Velocity then showed a slight increase due to the declined Al_b content. The pressure drop in the module increased slowly when $0 < B < 1$, before rapidly increasing to a maximum at B of 2.0–2.5 (Fig. 2d). With decreasing temperature, the decrease in flow velocity and increase in pressure drop became more rapid as the colloidal particles in the PAC solution form net structures at low temperature (Stol et al., 1976).

The evolution of flow velocity and pressure drop in the reaction can be interpreted in terms of the Bernoulli equation. Assuming that the liquid surface in the stirred tank was 1-1′ and the pipe outlet of peristaltic pump was 2-2′ (Fig. 3), the Bernoulli equation can be expressed as:

$$Z_1 g + \frac{{u_1}^2}{2} + \frac{p_1}{\rho} + W_e = Z_2 g + \frac{u_2^2}{2} + \frac{p_2}{\rho} + \sum h_f \quad (1)$$

where, Z_1 and Z_2 are the heights of the liquid surface; p_1 and p_2 are the pressures; u_1 and u_2 are the flow velocities at 1-1′ and 2-2′; W_e is the energy provided by the peristaltic pump; and $\sum h_f$ is the friction resistance per kilogram fluid, including the resistance in the pipes ($\sum h_{f,2}$) and that in the membrane module ($\sum h_{f,3}$). In the membrane module, the Reynolds number (Re_3) is about 527 and the flow is laminar. Therefore, friction factor λ_3 is expressed as $64/Re_3$. As the membrane fibers can be considered as parallel pipes, the friction resistance of the module equals that of each fiber. Thus,

$$\sum h_{f,3} = \lambda_3 \frac{l_3}{d_3} \frac{u_3^2}{2} \quad (2)$$

where, d_3 is the inner diameter of the fiber, l_3 is the fiber length, and u_3 is the flow velocity in the fiber (1.09 m/sec). In the pipes, the inner diameter d_2 = 8.0 mm, u_2 = 0.166 m/sec, Re_2=1321, $\lambda_2 = 64/Re_2$. The total equivalent length of the local friction, including the valves, elbows, and entrance from tank to the pipe, is $\sum l_c$.

Then,

$$\sum h_{f,2} = \lambda_2 \frac{(l_2 + \sum l_c)}{d_2} \frac{u_2^2}{2} \quad (3)$$

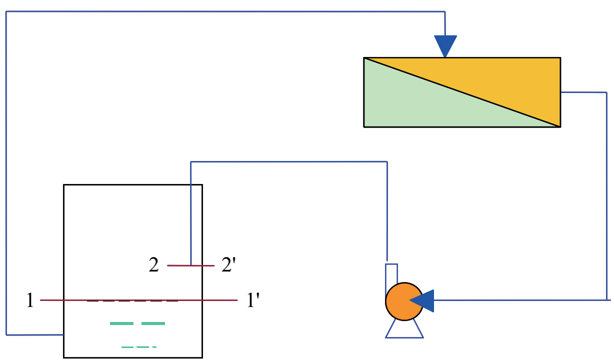

Fig. 3 Hydrodynamic analysis of the system.

$$\sum h_f = \sum h_{f,2} + \sum h_{f,3} = \frac{32 u_2 \mu}{\rho} \left(\frac{l_3 d_2^2}{n d_3^4} + \frac{(l_2 + \sum l_c)}{d_2^2} \right) \quad (4)$$

In this experiment, $Z_1 = 0$, $u_1 \approx 0$, $P_1 = P_2$, $Z_2 \approx 0$. Then, Eq. (1) can be written as:

$$W_e = \frac{u_2^2}{2} + \sum h_f \quad (5)$$

Assuming that:

$$A = \frac{l_3 d_2^2}{n d_3^4} + \frac{(l_2 + \sum l_c)}{d_2^2} \quad (6)$$

thus, Eq. (5) can be written as:

$$W_e = \frac{u_2^2}{2} + \frac{32 \mu u_2 A}{\rho} \quad (7)$$

According to Fanning equation,

$$\Delta P_f = \frac{64}{Re} \frac{l_3}{d_3} \frac{\rho u_3^2}{2} \quad (8)$$

The pressure drop in the membrane module (ΔP_f) can be written as:

$$\Delta P_f = \frac{32 \mu u_3 l_3}{d_3^2} = \frac{32 \mu d_2^2 l_3}{n d_3^4} u_2 = \left(W_e - \frac{u_2^2}{2}\right) \frac{\rho l_3 d_2^2}{A n d_3^4} \quad (9)$$

In the reaction, W_e and A are constant, whereas the viscosity of the fluids increased with basicity. From Eqs. (6) and (8), it can be seen that, with the increased viscosity, the flow velocity (u_2) declines and the pressure drop (ΔP_f) increases. These trends coincide well with the experimental results. When the pump energy and the solution viscosity are known, the flow velocity and the pressure drop can be estimated. This is important for process design and control.

2.2 Membrane fouling

In the reactions, the membranes were sampled at B 1.54 and 2.75, dried at room temperature and then spurted with carbon. The SEM images showed that at B = 1.54, the fouling of the membrane inner surface was apparent (Fig. 4a). The corresponding X-ray energy dispersion (EDX) analysis indicated that the composition of the fouling material was Cl, Na, Al, and S (Table 1). Obviously, the elements of Cl, Na, and Al were from the reactants and the products, whereas S was from the membrane material. At B = 2.75, almost all the membrane's inner surface was covered with the fouling materials (Fig. 4b), and Cl, Na, and Al content increased while S decreased significantly due to the coverage of the membrane surface.

Table 1 EDX analysis of membrane inner surface

	Cl (%)	Na (%)	Al (%)	S (%)
B = 1.54	29.18	12.13	8.10	50.60
B = 2.75	37.42	35.42	9.00	18.16

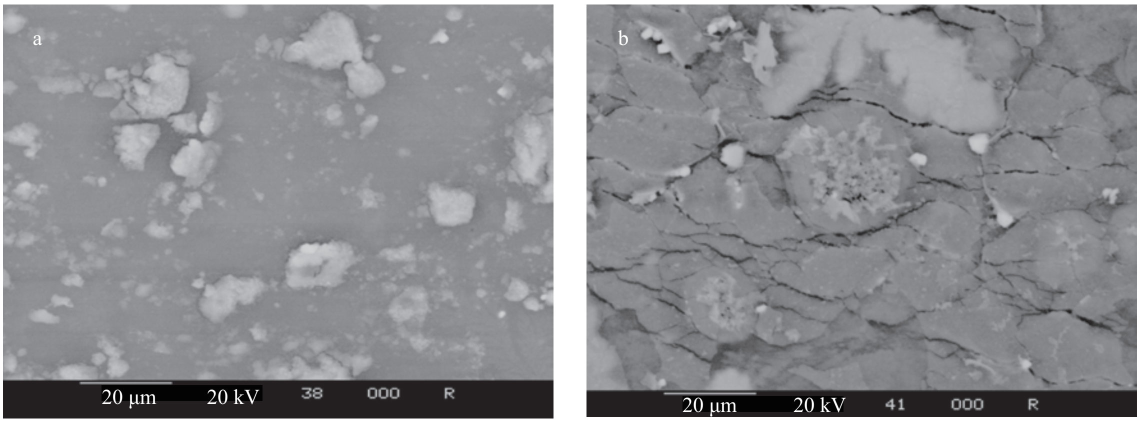

Fig. 4 SEM images of membrane inner surface. (a) B = 1.54; (b) B = 2.75.

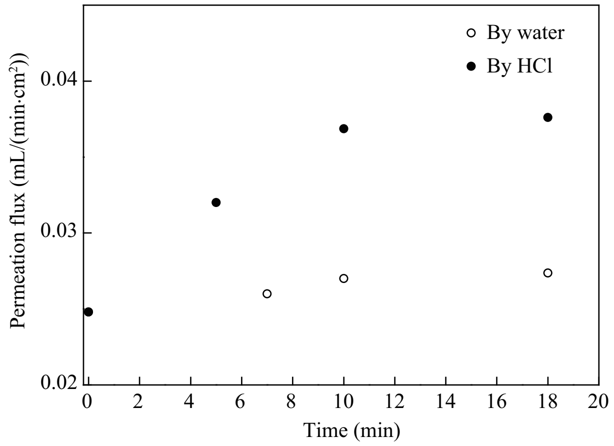

Fig. 5 Recovery of membrane permeation fluxes.

2.3 Membrane cleaning

Prior to the reaction, the water permeation flux of the membrane module was 3.8 × 10^{-2} mL/(min·cm^2) at 13°C and transmembrane pressure of 0.0185 MPa. After the reaction, water flux declined to 2.48 × 10^{-2} mL/(min·cm^2), i.e., 66% of the initial one.

In the membrane washing, 100 mL of pure water was added to the stirred tank and recirculated in the system. The permeation fluxes of pure water increased slowly and reached 72% of the initial flux after 18 min (Fig. 5). When 100 mL of hydrochloride acid (1:100, V/V) was used as the cleaning liquid, the water flux increased quickly and reached 97% of the initial flux after 10 min, indicating that hydrochloride acid was effective in dissolving the polymeric species and $Al(OH)_3$ precipitates absorbed on the membranes.

3 Conclusions

Polyaluminum chloride with Al_b content of about 80% was synthesized with a membrane reactor. Species distribution evolved with increasing basicity: Al_a content declined linearly; Al_c increased slowly; and Al_b exhibited a parabolic curve. The evolution of the flow rates and the pressure drops were ascribed to the changes in species distribution and liquid viscosity. The process characteristics were more stable at high temperature. Hydrochloride acid was effective in the membrane washing and permeation fluxes could be recovered, indicating that the membrane reactor was convenient and prospective in PAC preparation.

Acknowledgments

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