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Preparation of high concentration polyaluminum chloride by chemical synthesis-membrane distillation method with self-made hollow fiber membrane

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Abstract
A method of direct contact membrane distillation (DCMD) with a self-made hollow polyvinylidene fluoride membrane was applied to prepare high concentration polyaluminum chloride (PACl) with high Al\textsubscript{b} content based on chemical synthesis. The permeate flux and Al species distribution were investigated. The experimental results showed that the permeate flux decreased from 14 to 6 kg/(m\textsuperscript{2}·hr) at the end of the DCMD process, which can be mainly attributed to the formation of NaCl deposits on the membrane surface. The Al\textsubscript{b} content decreased slightly, only from 86.3% to 84.4%, when the DCMD experiment finished, correspondingly the Al\textsubscript{c} content increased slightly from 7.2% to 8.5%, and the Al\textsubscript{a} content remained at 7% during the whole DCMD process. A PACl with Al\textsubscript{b} content of 84% at total aluminum concentration 2.2 mol/L was successfully prepared by the chemical synthesis-DCMD method.

Key words: polyaluminum chloride; membrane distillation; high concentration; high Al\textsubscript{b} content; PVDF hollow fiber membrane
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Introduction
Polyaluminum chloride (PACl) has been widely used as a coagulant and is the subject of extensive research in water and wastewater treatment processes (Duan and Gregory, 2003; Gao et al., 2005; Hu et al., 2006; Liu et al., 2009; Shafran and Perry, 2005; Wang et al., 2002; Yan et al., 2008). PACl is usually divided into three fractions, Al\textsubscript{a}, Al\textsubscript{b} and Al\textsubscript{c}, according to differences in the reaction rate (Bi et al., 2004; Casey et al., 2005; He et al., 2003; Ye et al., 2009; Zhou et al., 2006). It has been generally demonstrated that Al\textsubscript{b} (mainly including Al\textsubscript{13}) is regarded as the active species of PACl for coagulation (Casey, 2006; Qu and Liu, 2004; Rowsell and Nazar, 2000). Previous reports on PACl including 80% Al\textsubscript{b} were mainly focused on low concentrations (< 0.2 mol/L) (Chen et al., 2006; Huang et al., 2006; Zhang et al., 2008). Little information was available regarding preparation of high concentration PACl (>2 mol/L) with high Al\textsubscript{b} content (> 80%) (Guo et al., 2009; Jia et al., 2009). Therefore, the production of high concentration PACl with high Al\textsubscript{b} content has become the primary goal for the PACl research and production industry.

Membrane distillation (MD) is a membrane separation process with less dependence on the initial salinity of the feed as well as a higher salt rejection ratio (Hanemaaier et al., 2006; Lawson and Lloyd, 1997). Direct contact membrane distillation (DCMD) is a kind of thermally driven membrane separation process, in which two solutions at different temperatures are separated by a microporous hydrophobic membrane. The driving force of DCMD is the formation of a vapor pressure difference across the membrane resulting from the temperature gradient in the boundary layers adjacent to the membrane surface. DCMD has been applied in water desalination (Qu et al., 2009; Hsu et al., 2002; El-Bourawi et al., 2006; Yun et al., 2006), wastewater reuse (Gryta et al., 2006; Ding et al., 2006; Wang et al., 2008) and other concentration processing (Ding et al., 2008; Petrotos and Lazarides, 2001). In our previous work, the DCMD method was successfully applied to prepare high concentration PACl with high Al\textsubscript{b} content with a commercial flat Millipore PVDF membrane (Guo et al., 2009; Jia et al., 2009).

As a further continuation of the work, a self-made hollow PVDF fiber membrane was used to prepare high concentration PACl based on previous work using the DCMD method. The aim of this work was to investigate the effect of membrane and operating mode of the DCMD process on Al species.

1 Materials and methods

1.1 Materials
AlCl\textsubscript{3} and NaOH were purchased from Beijing Chemical Company (China). All reagents were of analytical grade.
and were used without any pretreatment. Ferron reagent was self-prepared; the detailed preparation process has been described in a previous study (Chen et al., 2006).

1.2 Membrane and membrane module

The hydrophobic polyvinylidene fluoride (PVDF) hollow fiber membranes used in the experiments were self-prepared by the dry/wet phase inversion preparation method (Hou et al., 2009). The membrane characteristics are shown in Table 1.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean pore diameter (μm)</td>
<td>0.20</td>
</tr>
<tr>
<td>Outer diameter/inner diameter (mm/mm)</td>
<td>1.10/0.80</td>
</tr>
<tr>
<td>Wall thickness (mm)</td>
<td>0.15</td>
</tr>
<tr>
<td>Porosity</td>
<td>75.0%</td>
</tr>
<tr>
<td>Liquid entry pressure of water (kPa)</td>
<td>150</td>
</tr>
</tbody>
</table>

The dry PVDF hollow fibers were assembled into a polyester tube (diameter (mm) \(d_{in}/d_{out} = 15/20\)) with two UPVC T-tubes and the two ends of the bundle of fibers were sealed with solidified epoxy resin to form a membrane module. The module had a total length of 240 mm and an effective length of 100 mm. The packing fraction of hollow fibers in the module was about 32%. The total effective area of the module was about 0.014 m\(^2\) based on the inner surface.

1.3 Membrane distillation tests

The DCMD experimental setup is shown in Fig. 1. It consisted of two thermostatic cycles, the feed cycle and the distillate cycle, which were connected to the membrane module. The temperature of the cold distillate water was controlled by pumping the water through a spiral glass heat exchanger located in the constant temperature bath of a cooler (SDC-6, Nanjing Xinchen Biotechnology, China). Both the feed and distillate were pumped from the bottom to the upper part of the module. The feed flowed inside and through the intertubular space in the experiment. The conductivity of the cold distillate was measured using an electrical conductivity monitor (CM-230A, Shijiazhuang Create Instrumentation Technology, China).

1.4 Preparation of high concentration PACl with high Al\(_b\) content

First, a total Al concentration (Al\(_T\)) = 0.2 mol/L PACl containing 86% Al\(_b\) was prepared by a 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, and a certain amount of 0.6 mol/L NaOH solution was pumped into the reactor with a peristaltic pump under rapid stirring until the hydrolysis ratio reached a prearranged value. After the addition of NaOH solution was finished, the reactants were continuously stirred and heated at 65°C. Next, the DCMD method was used to concentrate the 0.2 mol/L PACl. In the experiment, the distillate temperature was controlled at 20°C. The 0.2 mol/L PACl solution containing 86% Al\(_b\) in the stirred tank was pumped into the feed side of the membrane module, and returned to the stirred tank for circulation. Pure water was pumped into the distillate side of the membrane module to provide heat exchange.

The permeate flux was measured by the increase of pure water mass on the permeate side. The value of the permeate flux (\(N\)) was calculated by the following equation:

\[
N = \frac{m_2 - m_1}{A \times t}
\]

where, \(m_1\) is the mass of water in the permeate side pure water tank of the DCMD system at the start of the DCMD process, and \(m_2\) is the mass of water in the permeate side pure water tank through \(t\) time during the DCMD process. \(A\) is the effective membrane area in the DCMD module, and \(t\) is the time of the pure water collection in the DCMD process.

1.5 Al species analytical methods

The Al species were measured by Ferron assay with a timed colorimetric reaction with Ferron reagent to provide speciation based on chemical reactivity, using a UV-Vis spectrophotometer (DR/4000U, HACH, USA). Based on the difference of the dissociation and complex reaction kinetic rate between Ferron reagent and Al species, the Al species could be divided into three types: monomeric species (Al\(_m\)) (reacting with Ferron within 1 min), planar oligomeric and medium polymeric species (Al\(_b\)) (reacting with Ferron from 1 min to 120 min), and three dimensional species or sol-gels (Al\(_g\)) (reacting with Ferron after 120 min or non-reacting with Ferron). Al\(_g\) was measured based on a titrimetric method (Chen et al., 2006; Guo et al., 2007).

1.6 Scanning electron microscope (SEM) of the hollow fiber membrane

The morphology of the fresh and used membrane was observed by scanning electron microscope (SEM). For SEM observation, the hollow fiber membrane was quenched in liquid nitrogen, cut with a single-edged razor blade, attached to the sample supports, coated with a gold layer and examined with a Hitachi S-3000 (Japan). Elemental analysis of the scaled membranes was accomplished using an energy dispersive X-ray spectroscopy (EDS) analysis system coupled to the SEM.
2 Results and discussion

2.1 Effect of feed temperature on water flux

To investigate the water vapor permeability of the membrane, a set of experiments were carried out using pure water as the feed side. During the run, the feed temperature varied from 30 to 80°C while the distillate temperature was maintained at 20°C and distillate rate of 0.15 m/sec. The effect of feed temperature on permeate flux is shown in Fig. 2.

From Fig. 2 we can see that the feed temperature had a remarkable influence on the permeate flux. The permeate flux increased from 3.2 to 42 kg/(m²-hr) when the feed temperature changed from 30 to 80°C with the feed flow rate at 0.52 m/sec. At the same feed flow rate, increasing the feed temperature enhanced the permeate flux. This trend may be explained by the Antoine equation which predicts an exponential relationship between the driving force (vapor pressure difference) and temperature (Hou et al., 2010). The permeate flux increased with the feed flow rate at the same feed temperature, but the effect of the feed rate on the membrane permeability was small.

2.2 Permeate flux during DCMD process

To investigate the flux change during preparation of high concentration PACI with high Al\textsubscript{b} content, PACI with 86% Al\textsubscript{b} at Al\textsubscript{T} 0.2 mol/L obtained in our lab was used as the initial feed to concentrate by the DCMD process. In the experiment, the feed temperature and the distillate temperature were controlled at 60 and 20°C respectively with the feed flow rate at 0.3 m/sec. The resulting gradual concentration of PACI is shown in Fig. 3. From Fig. 3 we can see that the concentration factor (defined as permeate concentration divided by initial feed concentration) had a significant influence on the DCMD performance. With increasing concentration factor from 1 to 11, the permeate flux decreased from 14 to 6 kg/(m²-hr), and the permeate conductivity increased from 8 to 18 μS/cm. Flux decline meant membrane fouling occurred, and pollutants were mainly due to the formation of deposits during the concentration process, which formed on the membrane surface and clogged and wetted a fraction of the membrane pores.

Figure 4 shows the membrane morphology taken before and after concentrating the PACI solution. It can be seen that the quantities of micro-pores visually decreased after the experiments finished (Fig. 4a2). A large amount of pores decreased in size and some even closed. As shown in the membrane cross-section in Fig. 4b, the bottoms of the finger-like pores were smooth before the experiments, while the bottoms of the finger-like pores were fragmented adjacent to the inner skin after the experiments. The changes were directly found at the bottom of the finger-like pores. During the frequent mass transfer processes, water vapor transferred from finger-like pores to sponge pores, like transferring from a wide channel to much smaller pores. Thus at the bottom of the finger-like pores, the transfer resistance became larger, which resulted in the permeate flux decrease.

The SEM-EDS analysis (Fig. 5) revealed that this deposit (pollutant) was mainly composed of NaCl and small amounts of Al and O along with fresh membrane including C and F. Furthermore, the decline of the permeate flux shown in Fig. 3 was also associated with pore clogging by scale deposits formed on the membrane surface and the concentration polarization phenomenon caused by the increase of the concentration factor.

2.3 Al species distribution during DCMD process

To investigate Al species distribution during the preparation of high concentration PACI with high Al\textsubscript{b} content, the Al species content was measured by Ferron assay at different Al\textsubscript{T}, and the corresponding results are shown in Fig. 6.

It can be seen that with the Al\textsubscript{T} increase during the DCMD process, the Al\textsubscript{b} content is almost stable, and decreased slightly, only from 86.3% to 84.4%, when the MD experiment finished. Correspondingly the Al\textsubscript{c} content increased slightly from 7.2% to 8.5%, and the Al\textsubscript{c} content remained 7% during the whole DCMD process. This indicates that the DCMD process is feasible for the preparation of high concentration PACI with high Al\textsubscript{b} content.
3 Conclusions

In this study, a self-made hollow PVDF membrane was used to prepare high concentration PACl with high Al_b content by a chemical synthesis-DCMD method. It was found that the permeate flux was enhanced with increases in the feed temperature or flow rate. The permeate flux decreased from 14 to 6 kg/(m²·hr) during concentration of the PACl solution, which can be mainly attributed to the formation of NaCl deposits on the membrane surface, fouling the membrane surface. The Al_b content decreased only slightly, from 86.3% to 84.4%, when the MD experiment finished. Correspondingly the Al_c content increased slightly from 7.2% to 8.5%, and the Al_a content remained at 7% during the whole DCMD process. A PACl with Al_b content of 84% at Al_T 2.2 mol/L was successfully prepared.
prepared by the chemical synthesis-DCMD process. The results indicated that the DCMD concentration method with a hollow fiber membrane was feasible to prepare high concentration PACI with high Al\textsubscript{b} content.

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