Recovery of Sodium Dichromate in Process of Chlorate Production

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A large amount of sludge was generated for removal sulfate radical using chemical precipitation during sodium chlorate industry. The sludge also contains sodium dichromate, Cr(VI) in it pollutes the environment when the sludge is discarded without treatment. Recently the treatment of mother liquor in sodium chlorate industry gains much interest. The use of ion exchange resin and nanofiltration membrane device integrated treatment of sodium chlorate industry crystallization mother liquor was presented. The recovery rate of sodium dichromate can reach 98 % and sodium sulfate in the crystallization mother liquor is less than 3 g/L after treatment, reaching the recycling requirement.

Keywords: Sodium sulfate, Ion exchange resin, Nanofiltration, Sodium dichromate.

INTRODUCTION

The sodium chlorate industry generates a large amount of sludge and sodium dichromate which pollutes the environment when the sludge is discarded without treatment. The production process consists of refining process, salt electrolysis, crystallization process and drying process[1,2]. In the electrolysis process, sodium dichromate is added in the saline solution before entering the electrolytic tank, for inhibiting side reaction and protecting the cathode[3]. After the treatment, the mother liquor inflow the tank of dissolving salt. Sulfate is the main impurity ions in the salt water and the steady accumulation of sulfate can increase the side effect in the electrolytic process, declining the current efficiency. In order to make the electrolytic cell have high current efficient and work steadily, it is necessary to keep the sulfate radical in low content.

At present, there are mainly 6 kinds of well-known ways of removing sulfate radical *e.g.*, method of calcium chloride, barium chloride, freezing, sodium carbonate, ion exchange and membrane separation. Presently, several methods of treating sodium dichromate are used in factory, like photochemical catalysis[4-7]. The chemical precipitation is often applied in the factory, however, the sludge produces a certain amount of Cr(VI) which is harmful to the environment[8,9]. There are only a few investigations presented for treating the mother liquor of sodium chlorate, several of which have shown that nanofiltration membrane is adequate for removing sulfate radical and ion exchange resin works well on treating Cr(VI)[10-13].

In this paper, we focused on the combination of ion exchange resin and nanofiltration membrane for treating the mother liquor in view of recycling.

EXPERIMENTAL

In this paper, the nanofiltration is 2540. The used membrane was a roll type membrane module with an effective membrane area of 2.5 square meters. Nanofiltration experiments were performed on laboratory scale. The temperature in all experiments was maintained at 22 °C. The membrane pressure and the feed flow were changed under different conditions. Before the experiment, the membrane was washed with distilled water to remove the protecting coating and soaked in distilled water for 24 h. There are two steps in the experiment. At first, the pure water flux of the membrane was measured with distilled water. Subsequently, the mother liquor from the ion exchange resin was filtered using nanofiltration membranes to remove the sulfate radical.

Experiment process and devices: Firstly, the mother liquor flows into the ion exchange resin to remove the sodium dichromate and the residue is hydroxyl ion. When the solution from the ion exchange resin is not qualified, we need to regenerate the resin with soda solution. After regeneration, sodium dichromate was recycled. Utilizing the high pressure pump, the solution was delivered to the nanofiltration device in order to remove the sulfate radical. After comprehensive treatment, the mother liquor was reused in the tank of dissol-

ving salt and the sodium dichromate was reused in the electrolysis process. The experiment device was shown in Fig. 1.
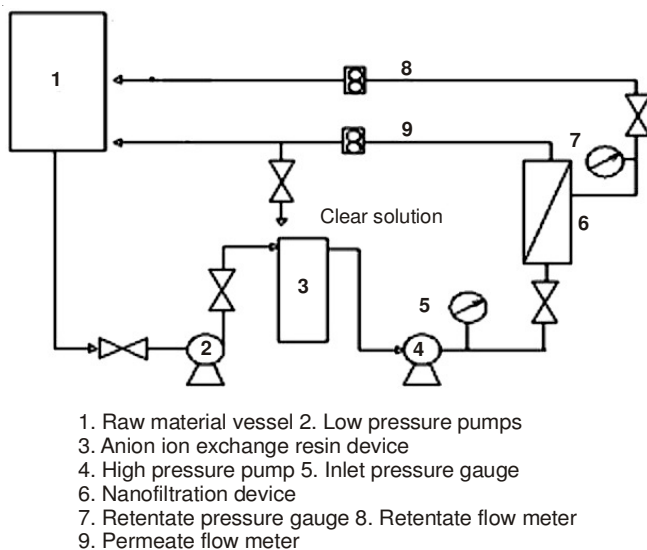

1. Raw material vessel 2. Low pressure pumps
3. Anion ion exchange resin device
4. High pressure pump 5. Inlet pressure gauge
6. Nanofiltration device
7. Retentate pressure gauge 8. Retentate flow meter
9. Permeate flow meter

Fig.1. Process flow diagram of the experiment device

Analytical methods: Concentration of retentate and permeate were measured with CIC-100 ion chromatograph which is a well-established liquid chromatography technique for the separation of small ions. The CIC-100 was made by Qingdao Shenghan Technology Company and column type is SI-52-4E. pH was measured with pH meter. The pH meter is delta 320.

RESULTS AND DISCUSSION

In the recovery of sodium dichromate, repeated experiments were carried out using IRA-400 highly alkaline quaternary ammonium referring to the environment protection bureau of Fuzhou. The exchange will stop when the content of chromium in the inlet reached 49.5 mg/L and the content in the outlet is 0.24 mg/L. The exchange efficiency can reach 99 % and the average content of sodium dichromate in the mother liquor is 24 mg/L after treatment. And then the sodium dichromate recovered was reused in the electrolysis process.

The pH range is from 2 to 5.5, because Cr(VI) exists in the form of $Cr_2O_7^{2-}$ in the acidic environment and Cr(VI) exists in the form of in a neutral or alkaline environment. The exchange efficiency is much higher in the acid environment than alkaline environment using the anion ion exchange resin. However, the acidity can't be strong because Cr(VI) will change to Cr(III)[9].

Effect of working pressure on membrane permeate flux: The concept of critical flux is important to membrane process for fouling control and energy. As we know, a high membrane flux had two contradictory effects, the first is to increase concentration polarization and thus increasing solutes transfer through membrane by diffusion and the other is permeate dilution, which decreases solutes concentration in permeate. The relation between various indexes of effluent from nanofiltration and working pressure was investigated when the working flow is 25 L/min. Fig. 2 gives the working pressure influence on membrane flux and also the relation between removal rate of sodium sulfate and working pressure.

As shown in Fig. 2, membrane flux increases continuously with working pressure build-up. Below 1.7 MPa, a strong membrane flux ascent occurred with the working pressure, furthermore, almost increases linearly with the working pressure. This can be explained by solution-diffusion model. The membrane permeate flux remains almost constant when the working pressure exceeds 1.7 MPa. When the pressure comes to a certain value, serious concentration polarization, sorption and precipitation will increase the transmission resistance, thus make the influence of pressure to flux reduced.
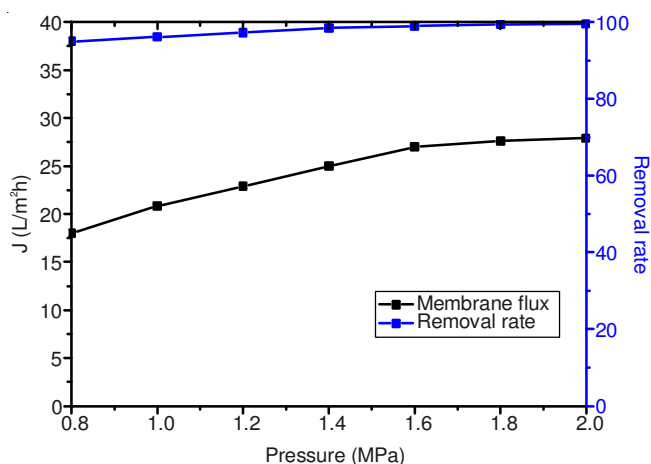

Fig. 2. Effect of working pressure on membrane flux and the removal rate of sodium sulfate

Fig. 2 showed that the removal rate of sodium sulfate increases when the working pressure become higher. The different transmission between solvent and solute is the main influence factor. The increase of working pressure will make the transmissivity of solvent ascend, which results in the accumulation of solution on the membrane surface. Furthermore, another factor is that the transmissivity of solvent is higher than the solution.

Effect of feed flow on membrane permeate flux and the removal rate of sodium sulfate: The relation between various indexes of effluent from nanofiltration and feeding flow was investigated when the working pressure 1.4 MPa. Fig. 3 gives the feeding flow influence on membrane flux and also the relation between removal rate of sodium sulfate and feeding flow.

As illustrated in Fig. 3, membrane flux increases continuously with feeding flow. This is because the increase of feeding flow will result in the ascent of velocity of flow on the membrane surface. However, much higher velocity of flow will make the pressure on the membrane surface through the system increased[8,9]. Under the low pressure, the effective pressure of the membrane surface will decline with the increase of flow capacity, consequently, it will influence the membrane flux.

Fig. 3 also gives that the removal rate of sodium sulfate remain almost constant with the change of flow capacity, which can illustrate that the nanofiltration runs stably and doesn't change with the flow capacity.

Effect of content of sodium sulfate on membrane permeate flux and the removal rate: The effect of content of sodium sulfate on membrane permeate flux and the removal
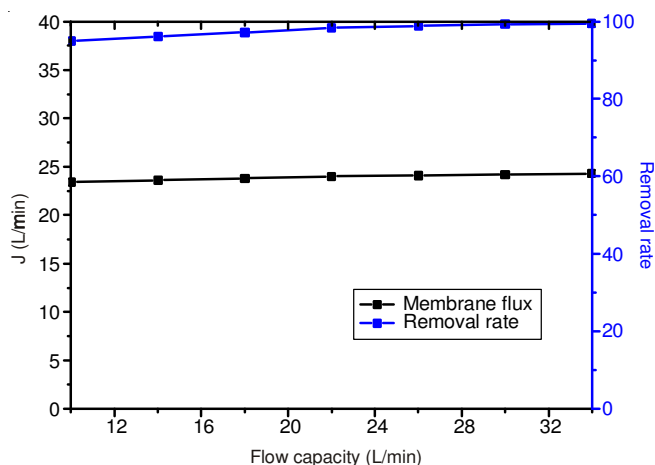
Fig. 3. Effect of flow capacity on membrane flux and the removal rate of sodium sulfate

Fig. 5. Effect of running time on membrane flux and removal rate

rate was investigated when the pressure was 1.4 MPa and the flux is 30 L/min. The content of sodium sulfate influence on membrane flux, as well as the relation between content of sodium sulfate and removal rate is shown in Fig. 4.
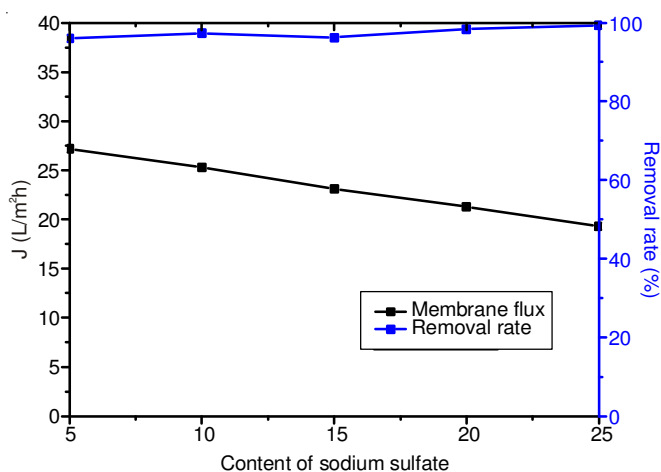

Fig. 4. Effect of the content of sodium sulfate on membrane flux and the removal rate of sodium sulfate

As is shown in Fig. 4, the content of sodium sulfate has practically no effect on the removal rate, which can be explained with the principle of nanofiltration. The rejection of sodium sulfate mainly based on the repelling action of negative charge on the membrane surface[14-16]. Consequently, the concentration of sodium sulfate will increase the osmotic pressure, which make the membrane flux decline under the same working pressure.

Effect of running time: The relation between various indexes of effluent from nanofiltration and running time was investigated when the working flow is 30 L/min and the working pressure is 1.4 MPa. From Fig. 5, the membrane flux and removal rate of sodium sulfate dropped with time. This is because the concentration of raw material becomes higher with time, which decrease the membrane flux and the removal rate.
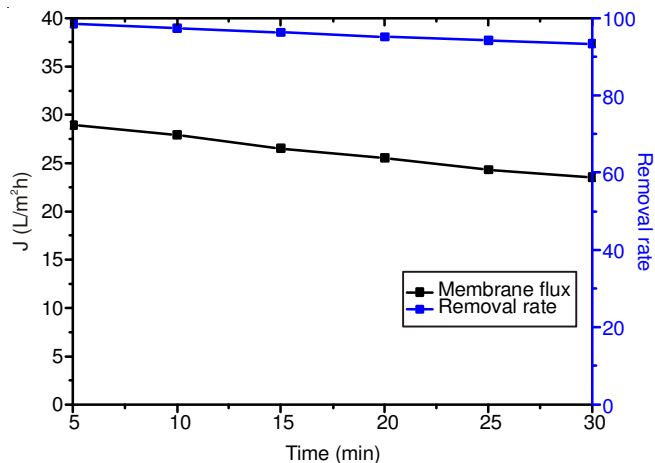
Conclusion

The result of this study showed that the combination of nanofiltration and anion exchange resin is sufficient for the mother liquor. The content of sodium sulfate is less than 3 g/L and the recovery of sodium dichromate reached 98 % after treatment, reaching the recycling requirement. In addition, there will be no sludge to produce by nanofiltration method for treating sulfate radicals, implementing the clean production process.

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