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Membrane Technology in Treatment of Coal Chemical Industry Saline Wastewater

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For the wastewater recovery in coal chemical industry, the reverse osmosis + dish-tube reverse osmosis membrane separation technology was taken to concentrate the saline wastewater (the concentration of sodium sulfate was 2.5 %) after biological treatment. The experimental result showed that the concentration of sodium sulfate can reached 23 and 94.4 % of sodium sulfate was recovered. The recovery rate of primary reverse osmosis system and secondary dish-tube reverse osmosis system were 50 and 80 %, respectively, meanwhile, the sodium sulfate concentration of reverse osmosis and dish-tube reverse osmosis permeated water were 0.116 and 0.611 g/L severally. The chemical oxygen demand index were 4.5 and 23.96 mg/L as well. The study verified the application of membrane technology in the treatment of saline wastewater and it illustrated that the dish-tube reverse osmosisprocess can be used as further concentration process of saline wastewater.

Keywords: Membrane technology, Saline Wastewater, Concentration, Sodium sulfate.

INTRODUCTION

In recent years, high oil prices in the world market have promoted faster development of China's coal chemical industry (especially in 2007)[1]. However, the discharge of wastewater has been restricting the sustainable development of coal chemical industry in a long time. The wastewater mostly discharged from coal conversion processes (coking, gasification and liquefaction process) and refining process of coal byproducts can also discharge wastewater, which usually has a characteristic of dark black colour and nauseating odor[2,3]. Recently, it can be generally divided into COD organic wastewater and saline wastewater in China[4]. The former contains components such as phenols, polycyclic aromatic hydrocarbons and humic substances, which leads to chemical oxygen demand (COD)[5,6], while the latter contains various inorganic salts. Most companies treat the COD organic wastewater by the method of physical and chemical pretreatment + biological treatment and for the saline wastewater, it will be discharged as drained water in most cases. With the increasing of industrial wastewater discharge standards, especially in some environmentally sensitive areas, the "zero discharge" environmental standard should be implemented strictly so as to reuse wastewater in maximum extent. In such situation, the treatment of saline wastewater is gradually getting people's attention.

Currently, membrane separation technology and thermal enrichment process are widely used to concentrate salt. Using traditional membrane separation techniques of reverse osmosis (RO) and nanofiltration (NF) to concentrate wastewater has the advantages of low cost, large scale and mature technology[7], in consideration of huge amount of industrial water is used as circulating cooling water[8], the permeated water can be used for the supplement of the cooling system. On the other hand, the process requires a high quality of feed water, additionally, the membrane easily fouled is also a key restricting factor to promote this process, furthermore, the inorganic salt cannot be concentrated to a high level through this method, it will increase the cost of subsequent evaporation process undoubtedly. The energy consumption of thermal concentration process is high and this process occupies large area, applying thermal enrichment process to treat biochemical wastewater needs a huge investment, which is not wise indeed.

EXPERIMENTAL

The experiment was conducted in a certain coal chemical enterprise in Shandong province, China, the feed water was taken from the biochemical pool, its quality parameters (average) are shown in Table-1.

Reagents: 2 g/L Alizarin Red S indicator, dehydrated ethanol, 0.1 mol/L hydrochloric acid solution, 0.1 mol/L of

TABLE-1
QUALITY PARAMETERS OF FEED WATER

Item	Feed water
Colour	Colourless
Temperature (ºC)	47
pH	2.7
Hardness (mmol L^{-1}, Ca^{2+})	18
COD (mg L^{-1})	210
Sodium sulfate (w. %)	2.5

barium chloride titration solution; EDTA standard solution; Ammonia-ammonium chloride buffer solution; Chromium black T solution.

Equipment: Chemical oxygen demand analyzer: Lanzhou Lianhua Environmental Protection Technology Co., 5B-1 type.

pH meter: Suzhou Jiangdong Precision Instrument Co., pHS-25 type.

Conductivity meter: Shanghai Pengshun Scientific Instruments Co., DDS-11A type.

Resin: Offered by Beijing Xin Bai Li Technology Co., weak acid cationic type.

Reverse osmosis membrane component: Offered by Beijing Xin Bai Li Technology Co., NBL-01 type.

Dish-tube reverse osmosis membrane component: Offered by Beijing Xin Bai Li Technology Co., NBL-S01 type.

In this study, we applied the resin softening + membrane separation technology to treat coal chemical industry saline wastewater. Softening system was filled with weak acid cationic resin and a three square meters polyamide composite membrane was used in reverse osmosis system, its highest operating pressure could measure up to 4.14 MPa. The dish-tube reverse osmosis system worked with a four square meters aromatic polyamide composite membrane and its highest operating pressure could measure up to 14 MPa.

General procedure: In this paper, we repeated experiments to test the membrane separation ablitity. After resin softening system, the pretreated wastewater would be sent to membrane separation system for concentration, the process route is shown in Fig. 1.

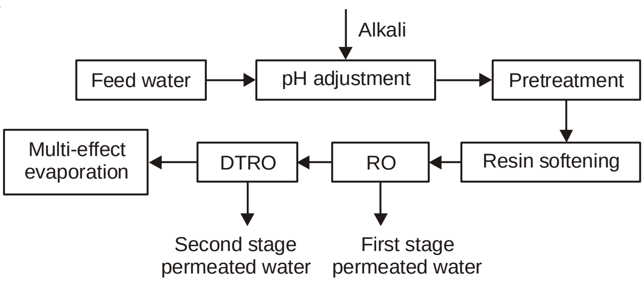

Fig 1. Process route

Detection method: Hardness: EDTA titration; COD: Dichromate titration; SO_4^{2-}: EDTA complexicretric titration method;

Technical characteristics: The study mainly discussed whether the inorganic salt content could be concentrated to a higher level applying dish-tube reverse osmosis membrane module, thus the capacity of subsequent evaporation crystallization process will be reduced. The concentrated water obtained from the above process could be evaporated and crystallized to harvest sodium sulfate by-product, it could achieve economic income to offset wastewater treatment costs partially. Pressure, flow and conductivity could be observed online directly, while COD and sodium sulfate content should be measured off-line, all parameters should be determined according to the Chinese NEPA Standard Methods[9].

The dish-tube reverse osmosis (DTRO) technology applied in this study is one of rising membrane separation technology in recent years, which has achieved a great success in leachate treatment[10]. Compared to other membrane technology, the unique flow channel and hydraulic disc design constitutes its core advantage, as shown in Fig. 2. This structure is mainly designed for separation and concentration of water which COD or salt content is high, the flow channel design based on special hydraulic, fluid continuously turn 180° and the concentration polarization is fully destroyed. Meanwhile the hydraulic disc be stride with convex points in favor of feed water to form turbulent flow, the rate of permeation and self-cleaning are also increased[11], thus will greatly reduce the phenomenon of membrane fouling and scaling.

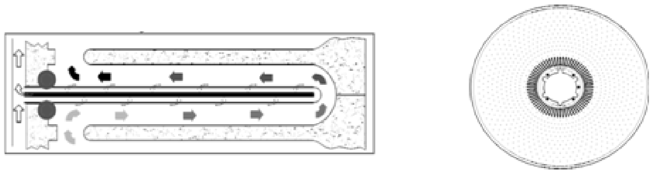

Fig. 2. Schematic of flow channel and hydraulic disc

Compared with the spiral-wound reverse osmosis, the cost of dish-tube reverse osmosis is relatively high and the loading density is low, but its advantages such as strong anti-pollution ability and high operating pressure still make it act as an important position in the industry of water treatment. In dealing with some high osmotic pressure solutions, dish-tube reverse osmosis can still work effectively[12]. The pretreatment of dish-tube reverse osmosis technology is generally simple and the requirement of feed water is not as strict as reverse osmosis. The dish-tube reverse osmosis equipment used in this study (Fig. 3).

RESULTS AND DISCUSSION

Removal of hardness: If the hardness of feed water is not removed, the reverse osmosis and dish-tube reverse osmosis system will start fouling and blocking when concentration ratio is high. Calcium sulfate is one of chemical dirt and hardly to clean for the membrane, its destruction process is irreversible. Domestic and foreign researches show that the membrane scaling can be inhibited by adding sterilizing agent and taking online ultrasonic oscillation[13], but it will reduce the life of membrane, which is not a long-term solution. There are many methods available to remove metal ions from wastewater. Among all the available methods, ion exchange is considered to be the most simple and efficient one[14]. Ion exchange resin is a kind of functional polymer material which contains ion-exchange groups in crosslinked polymer structure[15], for the advantage of deep purification, high efficiency and comprehensive recovery occupy an important position in the field of water treatment. The problem of calcium sulfate enriching in membrane surface can be solved by hardness removal through

Fig. 3. Dish-tube reverse osmosis testing equipment

resin adsorption, in this way the recovery rate can increase and the water can be reused in maximum extent. Weak acid cationic exchange resin was used to remove hardness in this article, the weak acid cationic exchange resin has its limitation compared with strong acid cationic exchange resin in exchange ability, but the former's exchange capacity is much higher than the latter, in addition, the weak resin can easily be regenerated. Specific results are shown in Table-2.

TABLE-2
EFFECT CONTRAST OF DIFFERENT RESIN

Type	Hardness		Capacity	COD	
	Before	After	(Per liter resin)	Before	After
	(mmol L^{-1})		(L)	(mg L^{-1})	
A	18.2	11.3	-	-	-
B	18.2	0	149L	195.1	158.2

A for weak acid cationic type and B for sodium type transformed from weak acid cationic type

From Table-2, it is known that the sodium type resin transformed from weak acid cationic type can remove hardness completely and 20 % of COD have been removed. The pH of feed water should be adjusted to 6-8, with 3 % hydrochloric acid and 4 % sodium hydroxide solution the saturated resin can be regenerated effectively. By the way there will be a less precipition in the process of adjusting pH, so an appropriate pretreatment measure should be taken to remove SS and coarse impurities[16], it can reduce pollution of resin and protect the next membrane system.

Reverse osmosis system: It is necessary to take a pretreatment measure for reverse osmosis system, because it has a vital impact on the overall performance of the system. Moreover, proper pretreatment can extend the service time and decrease the cost of the equipment[17]. Now sand filter or cartridge filter is widely used to remove the colloid and suspended solid. In this study, the wastewater would be cleaned through 5 μm security filter before entering reverse osmosis system to ensure the safety of next system.

After resin treatment the COD was only partially removed, for ordinary spiral-wound reverse osmosis membrane the COD cannot exceed 60 mg/L and for seawater membrane it is required less than 100 mg/L, the system can run normal at beginning but flux will decrease soon and require frequent cleaning to maintain the membrane life if COD exceed the limitation, thus will cause the equipment frequently in down-time. Over the past few decades, remarkable advances have been made in the preparation of reverse osmosis membranes from different materials[18]. It may be possible for reverse osmosis membrane to operate normally in some harsh process conditions. Therefore, according to the feed water quality, a new reverse osmosis membrane was applied in this study, the operating pressure limit can reach 4.14 MPa, even its anti-pollution ability was strong, the recovery rate was controlled to 50 %, the permeated water could be reused directly and the concentrated water would be sent into the dish-tube reverse osmosis system for further concentration. The changing trend of operating pressure was observed under the condition of maintaining certain flux (Fig. 4).

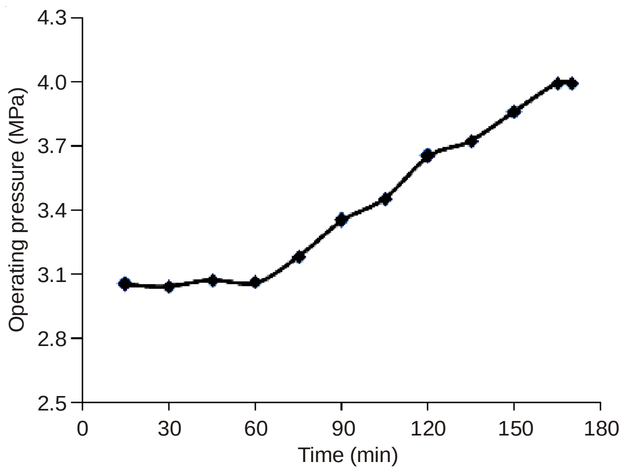

Fig. 4. Changing curve of reverse osmosis operating pressure

Fig. 4 showed that with time comsumed, the concentration of sodium sulfate continued to rise, so did the osmotic pressure, the operating pressure should be constantly increased if the flux needs to maintain. In this study, reverse osmosis system was used for initial concentration of saline wastewater, the specific results are shown in Table-3.

The feed water was concentrated 2 times by reverse osmosis (in volume), the recovery rate of sodium sulfate reached 97.3 % if the titration error was ignored, the quality of permeated water was excellent and could be reused for recycling cooling water directly (Table-3). During the whole experiment the flux was stable, trans-membrane pressure was maintained at 0.06 MPa and no significant fouling appeared. The analysis of permeated water showed that concentration of sodium sulfate was 0.116 g/L and COD was 4.5 mg/L, it conformed to the circulating cooling water reuse water quality standards.

Dish-tube reverse osmosis system: According to van't Hoff[19] osmotic pressure formula, osmotic pressure of 20 % sodium sulfate solution can reach 10.64 MPa at 30 °C, therefore

TABLE-3
INITIAL CONCENTRATION OF REVERSE OSMOSIS

Time (min)	Sodium sulfate ($g L^{-1}$) Concentrated	permeated	Flux ($L m^{-2} h^{-1}$)	Pressure (MPa)
0	24.4	0.083	24	3.06
15	25.5	0.085	24	3.05
30	26.7	0.080	24	3.04
45	28.1	0.090	24	3.07
60	29.7	0.095	24	3.06
75	31.4	0.102	23	3.18
90	33.2	0.105	24	3.35
105	35.2	0.107	23	3.45
120	37.7	0.109	24	3.65
135	40.3	0.114	24	3.72
150	43.1	0.119	23	3.86
165	46.1	0.125	23	3.99
170	47.5	0.129	22	3.99

During the experiment temperature elevated slightly

a 14 MPa high-pressure dish-tube reverse osmosis system was applied for further concentration of saline wastewater in this study, the final concentration of sodium sulfate was designed in 20 %. Taking into account of factors such as equipment safety and osmotic pressure, the maximum operating pressure was set at 12 MPa. The working state of dish-tube reverse osmosis system could be divided into two parts: maintaining flux on 33 L m^{-2} h^{-1} to concentrate at beginning, then the operating pressure was set invariable when it raised to 12 MPa, the saline wastewater was further concentrated until the concentration of sodium sulfate met the design requirements, during this process the changing flux trend was observed (Figs. 5 and 6).

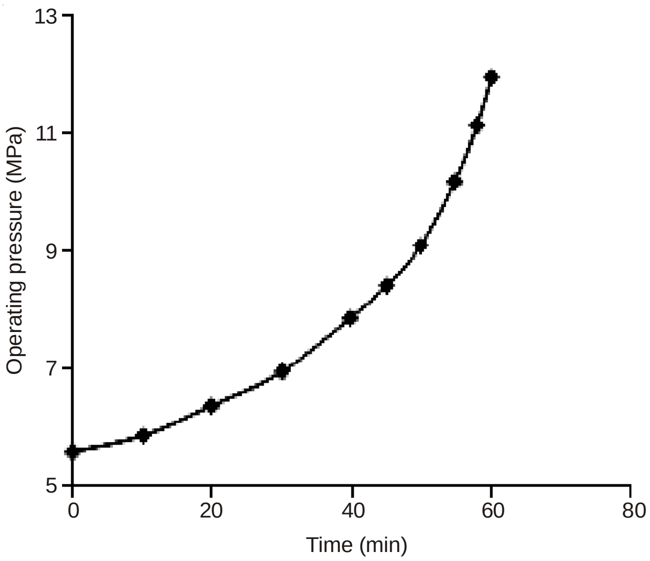

Fig. 5. Changing curve of dish-tube reverse osmosis operating pressure

Figs. 5 and 6 conclude that the concentration of sodium sulfate in trough constantly increased with the experiment proceeded, so did the osmotic pressure, operating pressure should be constantly raised to maintain the flux. When operating pressure was maintained at 12 MPa, with the concentration of sodium sulfate on membrane surface further increased, osmotic pressure raised and the effective pressure reduced,

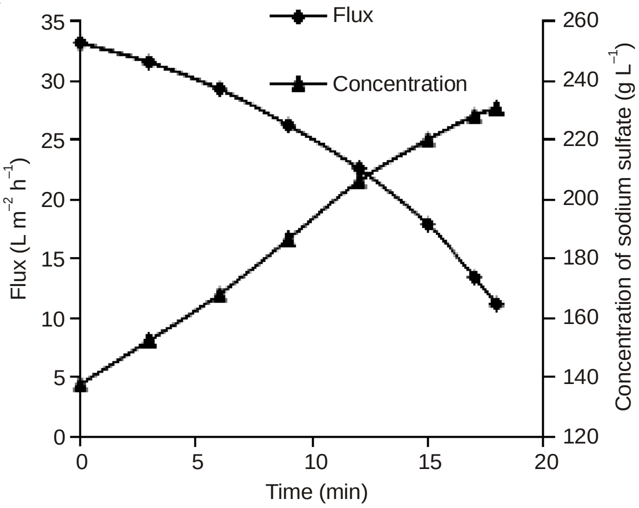

Fig. 6. Changing curve of dish-tube reverse osmosis flux and sodium sulfate concentration

the flux also dropped. Furthermore, the sodium sulfate concentration of permeated water also changed with time (Fig. 7).

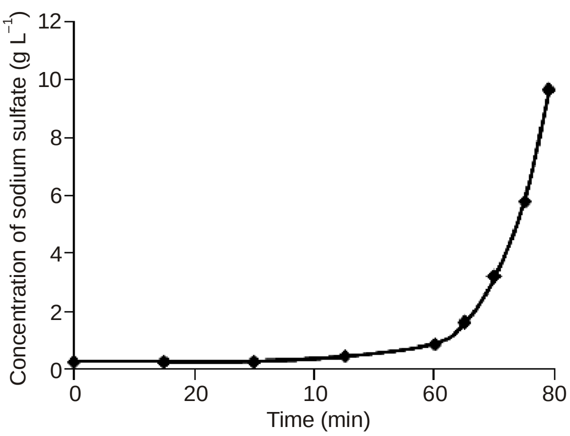

Fig. 7. Changing curve of permeated water sodium sulfate concentration

Fig. 5-7 showed that the concentration of sodium sulfate could be increased from 47.5 to 230.3 g/L by applying dish-tube reverse osmosis technology and the index of permeated water increased from 0.284 to 9.656 g/L, meanwhile the recovery rate of sodium sulfate reached 97 %. The sodium sulfate concentration of permeated water increased dramatically in final stage, especially in the process of sodium sulfate concentrated from 18 to 23 %, at the same time the flux rapidly decreased from 26 L m^{-2} h^{-1} to 11.25 L m^{-2} h^{-1}, thus the final concentration of sodium sulfate was designed at 18-20 % was desirable (Table-4).

The analysis of dish-tube reverse osmosis permeated water showed that the concentration of sodium sulfate was 0.611 g/L and COD was 23.96 mg/L. The permeated water can be discharged directly, or be reused for circulating cooling water through ordinary reverse osmosis.

Conclusion

The combined process of resin softening and membrane separation can treat coal industry saline wastewater effectively. This method can basically achieve the goal of "zero discharge".

TABLE-4
FURTHER CONCENTRATION RESULTS OF DTRO

Time (min)	Sodium sulfate (g L^{-1})		Flux (L m^{-2} h^{-1})	Pressure (MPa)
	Concentrated	permeated		
0	47.5	0.284	33	5.58
30	70.1	0.301	33	6.94
50	104.2	0.397	33	9.11
55	118.5	0.568	33	10.21
60	138.2	0.892	33	11.98
63	152.5	1.358	31.5	12.01
66	168.3	1.847	29.3	12.00
69	186.5	2.974	26.3	11.98
72	206.1	4.325	22.5	11.99
75	220.1	5.832	18	12.00
77	228.1	7.746	13.5	12.01
78	230.3	9.656	11.25	12.00

Temperature should maintained below 35 °C to ensure stable membrane performance

The pH of feed water should be adjusted to 6-8 and the weak acid cationic resin should be transformed to sodium type simultaneously, thus the hardness can be removed completely. The concentration of sodium sulfate can reach 23 % by applying membrane separation technology to concentrate saline wastewater and the water can be reused in maximum extent. However, the final sodium sulfate concentration should be controlled in 18-20 % in consideration of factors such as flux and equipment safety. Finally, this experimental study illustrate the application of membrane technology in treatment of coal chemical industry saline wastewater.

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