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The hollow fiber ultrafiltration membrane with inner skin and its application

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Abstract

The hollow fiber ultrafiltration membrane with inner skin was prepared by controlling the external coagulation condition from one or two polymer dopes with dual or triple-orifice spinneret. It was successfully used for the treatment of the wastewater from banknote printing works after characterizing the foulant and finding a suitable cleaning method, for the preparation of polyaluminum chloride (PAC) with high Alb content and the synthesis of nanosized $BaSO_4$ and $CaCO_3$ particles by a membrane reactor.

Keywords: Hollow fiber; Ultrafiltration; Wastewater from Banknote Printing Works; PAC; Nanosized particle

1. Introduction

When ultrafiltration (UF) systems are used in wastewater treatment or in biotechnology, they suffer from fouling which reduces the system capacity and restrict the UF application widely. Many scientists concern with this problem. Fouling can be reduced or solved by several ways, such as membrane material and membrane structure selection, optimization of operation conditions, suitable cleaning method, etc. The hollow fiber ultrafiltration membrane with inner skin has several advantages. (1) It is usually used for the modules with the flowing feed in lumen. The feed may be delivered into the lumens equally. (2) Since the pore sizes on the outer surface is much larger than that on the inner surface, and at the middle part of the cross-section of hollow fiber there is no sponge structure compared with the hollow fiber ultrafiltration membrane with dual skin. The substances passed

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through the inner skin could pass through the outer skin easily. (3) If the gel layer was formed when the HF membrane was used in the treatment of wastewater or in biotechnology, it was just on the inner skin and easily removed by chemical cleaning or back-wash. So the hollow fiber ultrafiltration membrane with inner skin can be used for a lot of fields. The preparation of hollow fiber ultrafiltration membrane with inner skin, the treatment of banknote printing wastewater and identification of foulant, and the synthesis of PAC and nanosized particles by a membrane reactor were studied in this paper.

2. Experiments

2.1. Materials

Polysulfone (PSf) was purchased from Dalian Plastic Plant No. 1 (Liaoning, China), with [η] 0.72; the solvents used was dimethylacetamide. The non-solvent additives include water and polyethylene glycol (PEG). Tap water was used as both the internal and the external coagulants.

2.2. Preparation of asymmetric hollow fibers

The asymmetric hollow fibers were prepared by a dry/wet-phase inversion method. The hollow fiber is to stabilize the structure and to rinse the solvent and additives.

2.3. Analytical methods

Scanning electron microscope (SEM), with a HitachiS-450 attached to an energy dispersive X-ray (EDX) unit, was used for observation of the fouled and cleaned membrane surface and determination of the components of the foulants. Inductively coupled plasma (ICP) (Apollo 9000) was used to determine total organic carbon (TOC) of two kinds of cleaning solution, i.e. HCl and NaOH cleaning solutions, respectively. The attenuated total reflection-Fourier transform infrared spectroscopy (ATR-FTIR) (460 plus, Jasco, Japan) were used to analyze the functional groups of Turkey red oil, wax, new and fouled HF membranes, and the IR peak was analyzed with Bio-Rad laboratories software.

3. Results and discussion

3.1. Preparation of the hollow fiber ultrafiltration membrane with inner skin

The preparation methods of the hollow fiber ultrafiltration membrane with inner skin can usually be divided into two sorts. One is to use a dual-orifice spinneret. Another is to use a triple-orifice spinneret.

For the first one, the spinning process is similar with that to prepare dual skin hollow fiber membrane [1]. The key difference is how to control the coagulating processes on the inner surface and on the outer surface of the hollow fiber. For the hollow fiber ultrafiltration membrane with inner skin the coagulation begins from the internal surface, but on the external surface there is no coagulation happened by controlling the external coagulation conditions. The schematic diagram of coagulation process is shown in Fig. 1.

Fig. 2 shows the SEM photograph of PAN (a) and PS (b) hollow fiber membrane with inner skin. It is obvious that the pore sizes in the outer skin are much larger than that in the inner skin.

For second one, the triple-orifice spinneret [2] was used for preparing the hollow fiber membrane with inner skin by dry/wet-phase inversion method. The spinning dope was extruded through the inner annular orifice. The internal coagulant was injected simultaneously into the tube and the external coagulant was injected simultaneously into the outer annular orifice. The hollow fiber membrane with inner skin may be formed by controlling the internal and the external coagulating rates. The schematic diagram is shown in Fig. 3.

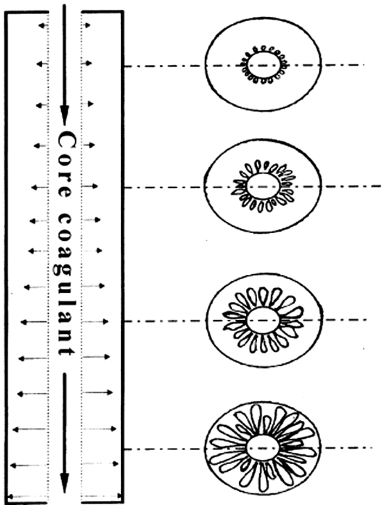
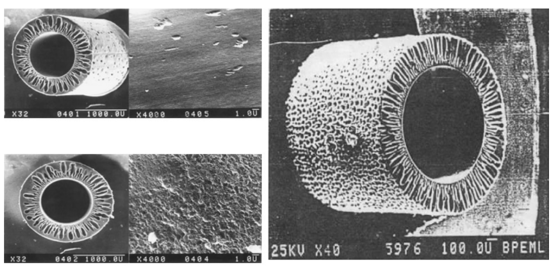


Fig. 1. Schematic diagram of coagulating process for the HF UF membrane.

The two polymer dopes may be used for the preparation of hollow fiber ultrafiltration membrane with inner skin. One dope (1) is injected into the inner orifice, whereas another dope (2) is injected into the outer orifice. The internal coagulant must be injected into the inner tube. During the spinning process, the inner dope is in contact with the internal coagulant and begins the coagulation process towards outer, while the outer dope is exposed to the environment without the coagulation happened like Fig. 1. After the hollow fiber enters into the coagulation both the porous outer skin is formed. Two dopes may



(a) (b)

Fig. 2. SEM photograph of hollow fiber membrane with inner skin: (a) PAN and (b) PS.

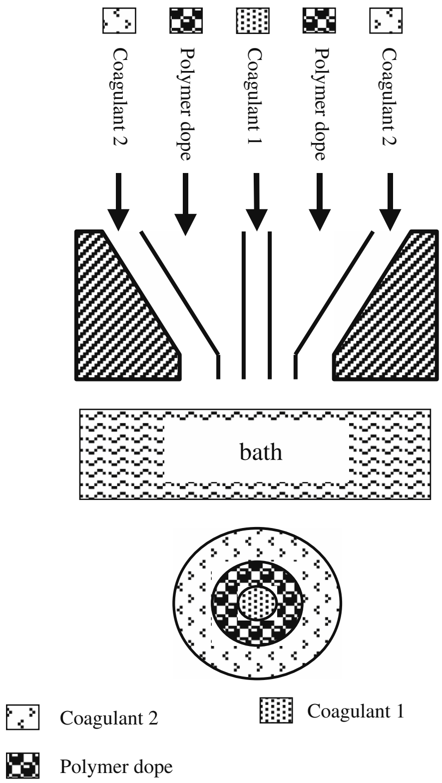


Fig. 3. Spinning process for one spinning dope.

contain same polymer but different solvent, additives and different content of them or contain different polymers but they are miscible, different solvent, additives and different content of them. It is noted that the coagulant selection and spinning conditions are very important for preparation of hollow fiber ultrafiltration membrane with inner skin. The schematic diagram of the spinning process is shown in Fig. 4.

3.2. Application

3.2.1. Ultrafiltration treatment of the wastewater from banknote printing works [3]

The hollow fiber ultrafiltration membrane with inner skin made in our laboratory has been used in the ultrafiltration treatment of the

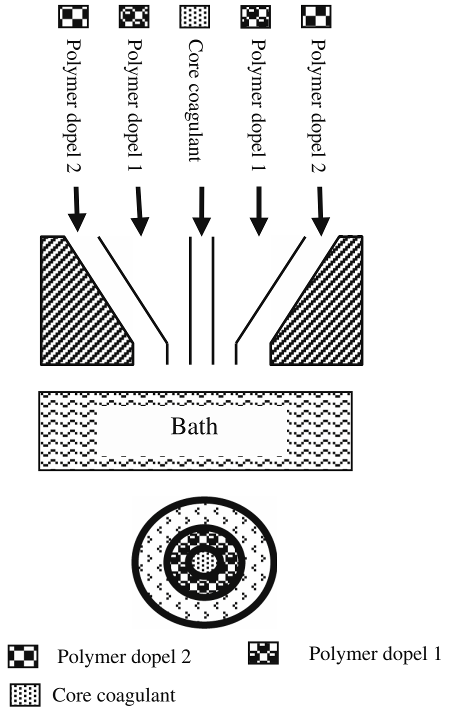


Fig. 4. Spinning process for two spinning dopes.

wastewater from banknote printing works. The schematic diagram of the ultrafiltration treatment of the wastewater from banknote printing works is shown in Fig. 5.

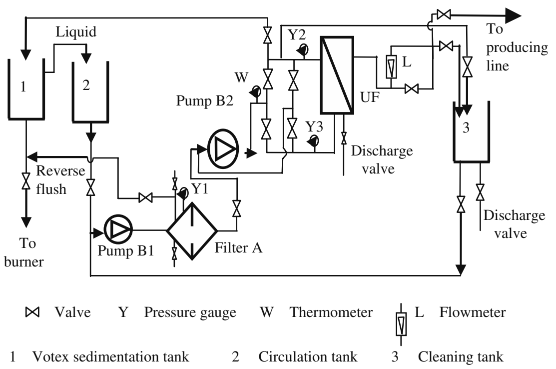


Fig. 5. Schematic diagram of the ultrafiltration treatment of the wastewater from banknote printing works.

During the running the permeate flux decreased and the HF membrane was fouled since the gel layer of foulant was formed [3]. In order to understand the reasons and to chose cleaning reagent the foulants were characterized by EDX and FTIR. The results were showed in Fig. 6. Comparing the element peaks of the virgin HF membrane with that of the fouled one (Fig. 6(a) and (b)), EDX analysis results show that the calcium is the primary fouling element. After cleaning the calcium peak becomes very small (Fig. 6(c)).

The foulants in the cleaning solutions were identified by ICP also. The results in Table 1 show the calcium content in HCl solution was very high, which means the Ca^{+} was main inorganic element.

The FTIR graph and LC-MC graph of the foulant, Turkey red oil, Wax, Resin and new membrane were listed in Figs. 7 and 8. Comparing the Figs. 7(a–e), the (a) was similar with

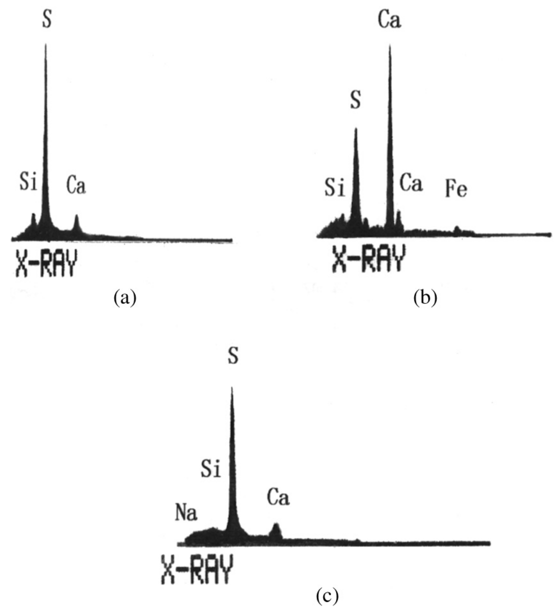
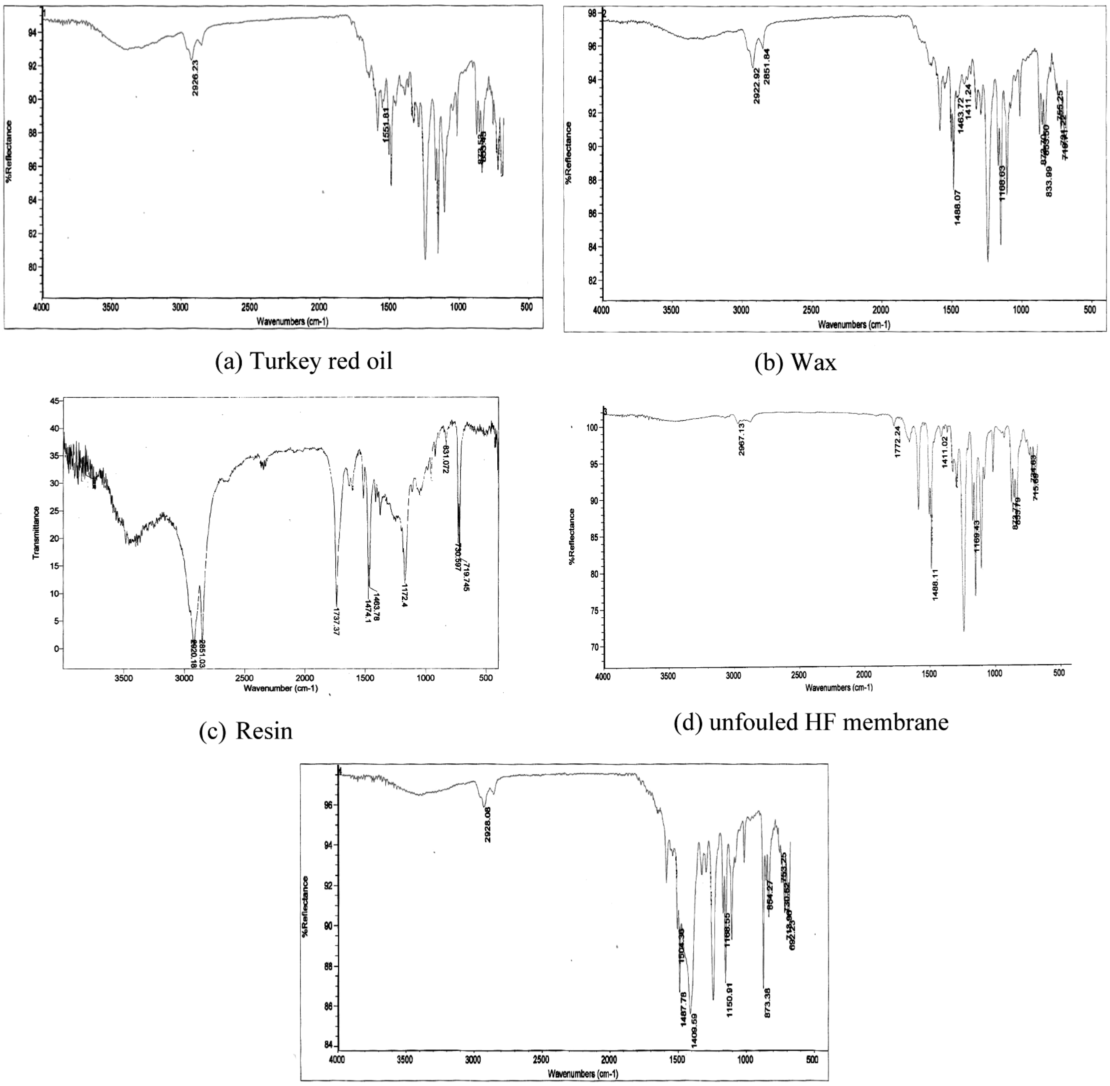


Fig. 6. (a) EDX analysis of the top surface of PS membrane before fouling; (b) EDX analysis of the top surface of PS/PDC fouled; (c) EDX analysis of the top surface of PS/PDC cleaned.

Table 1
ICP test results in the cleaning solutions

Sample element (mg/L)	Blank sample	HCl solution	NaOH solution
Ca	–	39.44	2.871
Fe	–	1.655	0.508
S	–	3.31	4.25
Ti	–	0.037	0.085

(b), and the peaks in (e) covered all the peaks in (a) and (b), but the (c) was different from others. That means the resin was not main organic foulant. In order to determine the main organic foulant the LC-MC graph of Turkey red oil and WAX were analyzed. Comparing Figs. 8(a–c), the LC-MC graph of Turkey red oil was similar with the LC-MC graph of the foulant on the HF



(a) Turkey red oil

(b) Wax

(c) Resin

(d) unfouled HF membrane

(e) Fouled HF membrane

Fig. 7. The FTIR graph.

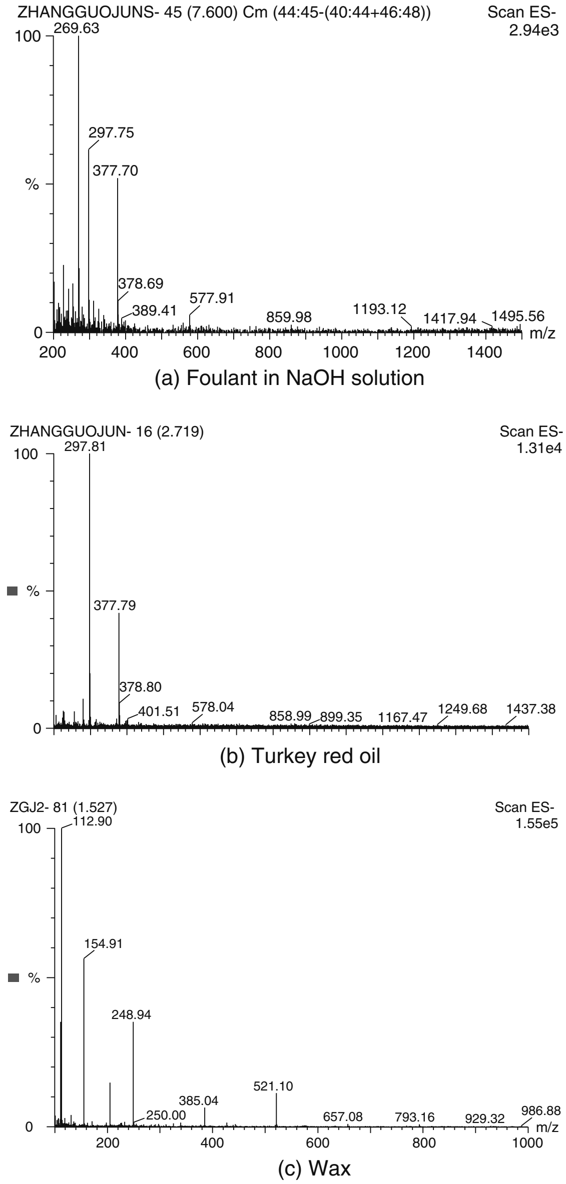


Fig. 8. The LC-MC graph.

membrane. The above results indicated the Turkey red oil was the main organic foulant.

According to the properties of foulants a four-step cleaning method was developed, that is, water–HCl solution–water–NaOH solution. The flux change of the UF equipment with membrane area 80 m^2 during 95 days running and the flux

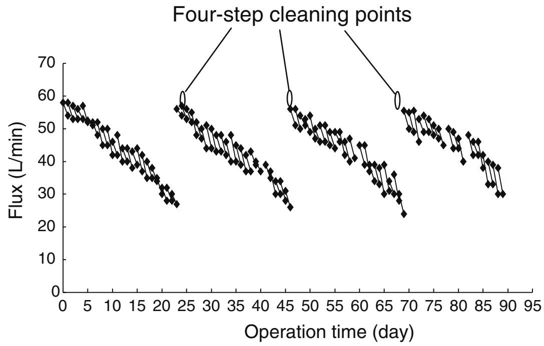


Fig. 9. The flux change during 95 days running.

change before and after cleaning are shown in Fig. 9. It shows that the cleaning method [3,9] was effective for flux recovery. But when the hollow fiber ultrafiltration membrane with dual skin was used for the treatment of the wastewater from banknote printing works, the flux decreased sharply, and it was very difficult to recover the flux by chemical cleaning since plug happened at the cross section of membrane or the back of outer surface during running.

3.2.2. Synthesis of polyaluminum chloride and nanosized particles by a membrane reactor [4–7]

Polyaluminum chloride [11] with high Alb content was prepared with a membrane reactor and the results were compared with that with other methods in Table 2. The PAC prepared with different alkali list in Table 3. The principle of membrane reactor for synthesizing PAC is similar to that for making nanosized $BaSO_4$ and $CaCO_3$ particles [5].

Experimental set-up of PAC synthesis is shown in Fig. 10.

The experimental results with different membrane MWCO and temperatures are shown in Figs. 11 and 12.

The results mentioned above indicate that the smaller MWCO and higher temperature are favorable for the formation of Alb and the

Table 2
Comparison of the results with different methods

PAC resource	Alt (M)	OH^-/Al_3^+	Ala (%)	Alb (%)	Alc (%)
Single alkali addition	0.100	2.5	15.4	55.4	29.3
Titration	0.100	2.5	12.5	82.9	4.7
Electrolysis	0.26	1.8	17.1	61.2	21.7
Electrodialysis	0.225	2.5	17.0	71.7	11.3
MR	0.14	2.4	2.4	80.1	17.5

Table 3
PAC prepared with different alkali

Al_t (M)	pH	Ala (%)	Alb (%)	Alc (%)
2 M $AlCl_3$ solution; 3.04 M Na_2CO_3 saturation solution				
0.48	4.15	19.1	79.6	1.3
0.4 M $AlCl_3$ solution; 1.6 M Na_2CO_3 solution				
0.26		13.2	84.6	2.2
2.0 M $AlCl_3$ solution; 10.0 M NaOH solution				
1.2	4.36	11.3	75.7	13.0

membrane reactor is a good method for making PAC with Alb high content.

The experimental set-up for making nano-sized $BaSO_4$ and $CaCO_3$ particles is similar to that for synthesizing PAC. The principle of

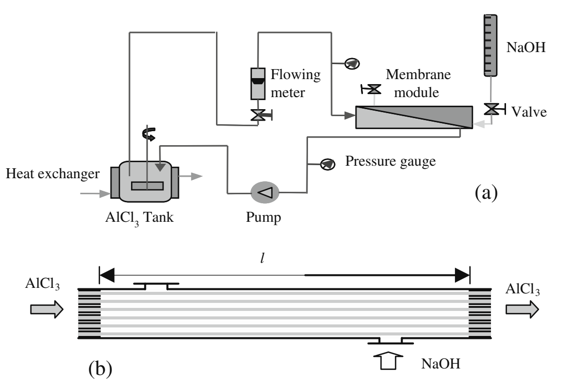


Fig. 10. Experimental set-up of PAC synthesis: (a) schematic of experimental apparatus; (b) a cross-section of the membrane module.

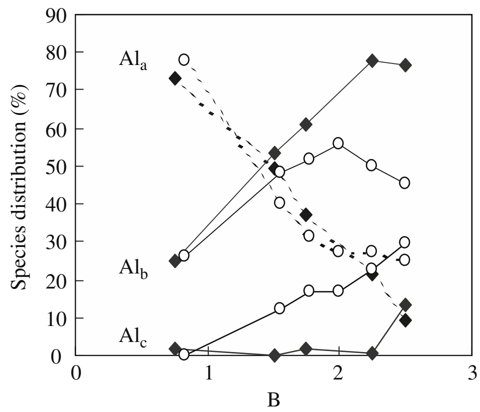


Fig. 11. Effects of membrane MWCO (◆) MWCO = 10,000 and (○) MWCO = 30,000.

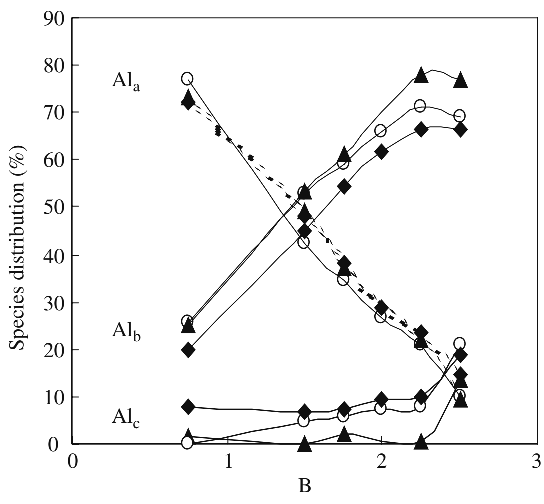


Fig. 12. Effects of temperature (◆) $t = 18°C$, (○) $t = 24°C$ and (▲) $t = 32°C$.

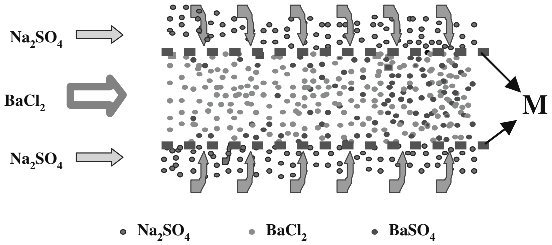


Fig. 13. Principle of membrane reactor.

membrane reactor for making nanosized $BaSO_4$ and $CaCO_3$ particle is shown in Fig.13.

The reaction is as follows:

$$Na_2SO_4 + BaCl_2 \rightarrow BaSO_4 \downarrow$$
$$Na_2CO_3 + CaCl_2 \rightarrow CaCO_3 \downarrow$$

The $BaCl_2$ solution was pumped through the lumen of HF membrane, the Na_2SO_4 solution passed through the membrane pores to enter the $BaCl_2$ solution in very small drop under a certain pressure. Since the drop size of Na_2SO_4 solution was very small and the number of the drops was very large, the reaction mentioned above can formed nanosized $BaSO_4$ particles. When we use Na_2CO_3 instead of Na_2SO_4 and use $CaCl_2$ instead of $BaCl_2$, nanosized $CaCO_3$ particles were prepared.

Nanosized $BaSO_4$ and $CaCO_3$ particles [5], about 20–30 nm in diameter, were first synthesized successfully by a membrane reactor. Under the experimental conditions, membrane with MWCO 1000 seems to be more favorable for the synthesis of nanosized particles and the high polar additives, such as ethanol, acetic acid are favorable for the dispersive nanosized particles formation (see Fig. 14).

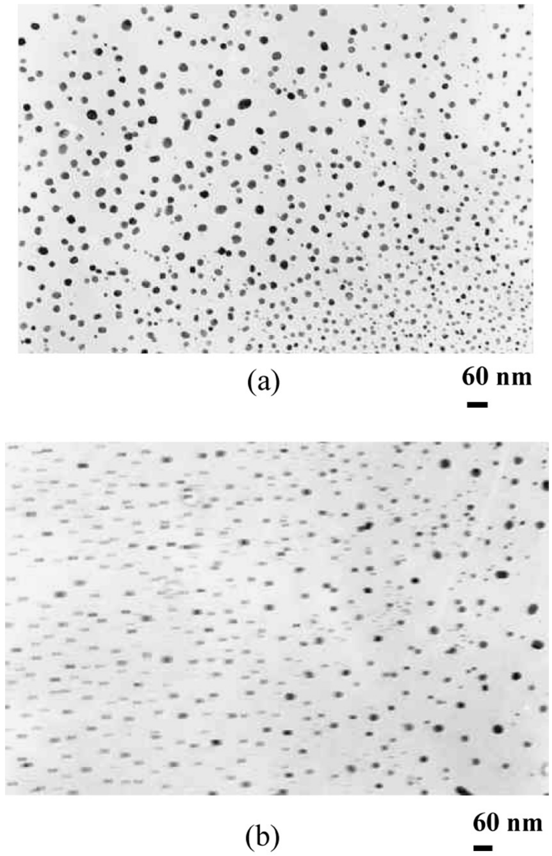


Fig. 14. Effects of additives species on the particles: (a) ethanol and (b) acetic acid.

4. Conclusion

(1) The HF UF membrane with inner skin was prepared by controlling the external coagulation condition from one or two polymer dopes with dual or triple-orifice spinneret. (2) The HF UF membrane was successfully used for the treatment of the wastewater from banknote printing works. (3) Polyaluminum chloride with high Alb content was prepared with a membrane reactor. (4) Nanosized $BaSO_4$ and $CaCO_3$ particles can be synthesized by a membrane reactor. (5) Additives play an important role in the formation of nanosized particles.

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