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Effect of pretreatment on membrane fouling and VMD performance in the treatment of RO-concentrated wastewater

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ABSTRACT

The polyvinylidene fluoride hollow fiber hydrophobic membrane was applied in vacuum membrane distillation (VMD) process for the treatment of reverse osmosis-concentrated wastewater from a steel plant. The effects of pretreatment methods on the COD_{cr} removal, the performance and membrane fouling of VMD process were studied. The morphology and composition of the fouling layer were studied by scanning electron microscope and energy dispersive spectroscopy, respectively. The reason for the flux declination in VMD process was discussed. The results showed that the COD_{cr} removal reached 40%, and the flux of VMD process was increased after the pretreatment of coagulation and ultrafiltration, when the concentration factor reached eight, the flux of VMD process using properly pretreated solution was 30% higher than that using un-pretreated solution as the feed. The membrane surface morphology and elemental analysis testified that the fouling of membrane surface was obviously alleviated by pretreatment.

Keywords: Vacuum membrane distillation; RO-concentrated wastewater; Coagulation; Pretreatment; Membrane fouling

1. Introduction

Currently, reverse osmosis (RO) technology has been widely applied in industrial wastewater treatment, desalination, food and beverage processing [1–5]. The water recovery of RO is in the range of 50–75% [6], and the direct discharge of concentrated wastewater may cause environmental pollution and other problems. It is necessary and urgent to develop efficient treating and reclamation method for the high-concentration wastewater, which has got worldwide attention.

Membrane distillation (MD) is a combination of membrane separation process and conventional evaporation. The separation mechanism of the MD process is based on the vapor/liquid equilibrium of liquid mixtures. The advantages of MD process in comparison with conventional separation processes rely on the lower operating temperature and pressure, high retention rate for nonvolatile substance such as inorganic salt, macromolecules, and the ability for the treatment of solutions at high concentration, and so on [7–10]. It has been looked on as an effective replenish for RO [11].

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Along with the development of MD technology, the problem of membrane fouling is more and more concerned by researchers. It has been revealed that membrane fouling is the main reason for serious flux declination, even the destroying of the hydrophobic character of the membrane [12–18]. Direct Contact Membrane Distillation (DCMD) tests carried out by Srisurichan et al. [19,20] demonstrated that the charged humic acid (HA) molecules and divalent ions such as Ca^{2+} is easy to form coordination compound and deposit on the membrane surface, resulting in membrane flux reduction. Chen's work [21] revealed that the existence of organic component in the feed solution accelerates membrane fouling greatly. DCMD tests carried out by Khayet et al. [22] using polytetrafluoroethylene and polyvinylidene fluoride (PVDF) membranes, demonstrated a preferential absorption of HA at the surface of membranes exhibiting higher hydrophobic character, with a consequent more pronounced deterioration of the trans-membrane flux.

Many researchers have developed hardness removal and other methods to remove the sparingly soluble inorganic salts from wastewater, the feed of MD process, so as to reduce membrane fouling in MD process. But seldom work has been reported on organic contamination removal and the effects on MD process. In this study, a pretreatment method was designed to remove organic matter in RO-concentrated wastewater from a steel plant. The effects of pretreatment method, the type and dosage of coagulation agents on the COD_{cr} removal, vacuum membrane distillation (VMD) performance and membrane fouling were studied.

2. Materials and methods

2.1. Feed water

RO-concentrated wastewater from a steel plant in Tianjin of China was used in this study. The water quality parameters are shown in Table 1.

Table 1
The quality parameters of RO concentrated wastewater

Constituent	Value
Sodium /$mg\,L^{-1}$	2,416.0
Chloride/$mg\,L^{-1}$	3,625.5
Calcium /$mg\,L^{-1}$	237.6
Magnesium/$mg\,L^{-1}$	232.8
Total hardness/$mg\,L^{-1}$	877.2
Conductance/$\mu S\,cm^{-1}$	10,800
Turbidity/NTU	1.64
pH	6.93
SS/$mg\,L^{-1}$	1.60
COD_{cr}/$mg\,L^{-1}$	63

2.2. Membrane and membrane module

PVDF hollow fiber hydrophobic membranes for MD processes and hydrophilic membranes for ultrafiltration (UF) processes were prepared by non-solvent induced phase separation method in this group. The parameters of hydrophobic membranes and membrane modules are shown in Table 2. An external pressure U-type membrane module was used in UF processes. The inner and external diameter of the UF hydrophilic membrane was 0.70 and 1.2 mm, respectively.

Table 2
The parameters of PVDF hydrophobic hollow fiber membrane and module

Parameters	Value
Inner diameter of the hollow fibers/mm	0.80
External diameter of the hollow fibers/mm	1.10
Wall thickness/mm	0.15
Nominal pore diameter/μm	0.16
Porosity (%)	82–85
Number of hollow fibers	50
Effective membrane area/m^2	0.025
Filling density/%	5.42

2.3. Pretreatment experiments

2.3.1. Coagulation experiments

Standard jar tests were carried out for coagulation experiments at room temperature. Ferric chloride ($FeCl_3$), polymeric aluminum chloride (PAC) and polypropylene acid ammonium (PAM) (all of the coagulations are analytical grade pure) were selected as coagulations. Coagulations with destined dosages were added in raw RO-concentrated wastewater and agitated for 31 min (rapid mixing of 1 min at 120 rpm, gentle mixing of 30 min at 50 rpm. These conditions had been experimentally determined to be optimum). The coagulated water was then settled for 30 min. The optimal dosages of coagulations were determined by measuring the COD_{cr} in the supernatant which was collected from 2 cm below the water surface after sedimentation in the coagulation test.

2.3.2. UF of the coagulated feed solution

After the coagulation with optimized dosage of coagulations, the feed solution was further treated with UF membrane by dead end filtration model. The COD_{cr} of the product water from UF process was measured, and the effect of UF on the composition of the feed was discussed.

2.4. VMD experiments

The VMD experimental setup is shown in Fig. 1. The hydrophobic membrane module was immersed in the feed solution. The feed solution flowed through the lumen side of the hollow fiber membranes and the vacuum system was connected to the shell of the module. The experiments were carried out with the feed temperature of 70℃, the feed velocity of 1.0 m/s and the vacuum of 0.085 (±0.002) MPa.

The weight, conductivity, and pH of the product water were measured each 30 min, and the quality of concentrated solution such as Baume degrees, conductivity, turbidity etc. was measured each 90 min also. The value of the VMD flux was calculated by the equation.

$$J = W/(A \times t) \tag{1}$$

where J is the values of the VMD flux, kg/(m^{2}h), W is the weight of the product water, kg, A is the effective membrane area of hollow fiber membranes in the VMD module, m^2, and t is the time of the pure water collection in the VMD process.

Normalized flux (J_t/J_0) calculated by dividing the flux (J_t) along the operation time by the initial flux (J_0) was plotted against operation time.

2.5. Analytical methods

The COD_{cr} value of the feed, product and concentrated solution was measured by potassium dichromate oxidation method. The turbidity of the samples collected was measured by a Hach turbidimeter (2100 N, Hach, USA), the conductivity was measured by a conductivity meter (DDS-11A, Leici, China), the pH was measured by a pH meter (PHS-3C, Leici, China). The morphology and composition of the fouling layer were studied by scanning electron microscope (SEM) (FESEM, HITACHI S-4800) and energy dispersive spectroscopy (EDS) (K-Alpha, Thermo Fisher Scientific Inc), respectively.

3. Results and discussion

3.1. Effect of pretreatment on COD_{cr} removal

3.1.1. Effect of coagulation dosage on COD_{cr} removal

Coagulation method was adopted for the removal of organic contaminant from the feed solution, which was designed to be concentrated by VMD process. The effects of the type and dosage of coagulants on the COD_{cr} removal are demonstrated in Fig. 2.

It can be seen that the variation trend of the COD_{cr} removal with the increase in coagulant dosage is similar. All of the three curves increase firstly with the increase in coagulation dosage and then decline after getting a top value. But the effects of the type and dosage of the coagulants on the COD_{cr} removal are obvious. When $FeCl_3$ was used as coagulant, the COD_{cr} removal reached maximum, 32%, as the dosage was 15 mg/L. As for PAC, the maximum removal 32% appeared when the dosage was 8 mg/L. When

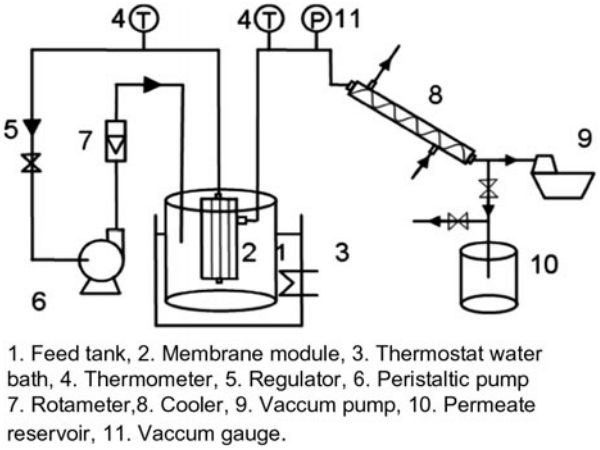

Fig. 1. Schematic diagram of the experimental apparatus used for the VMD experiment.

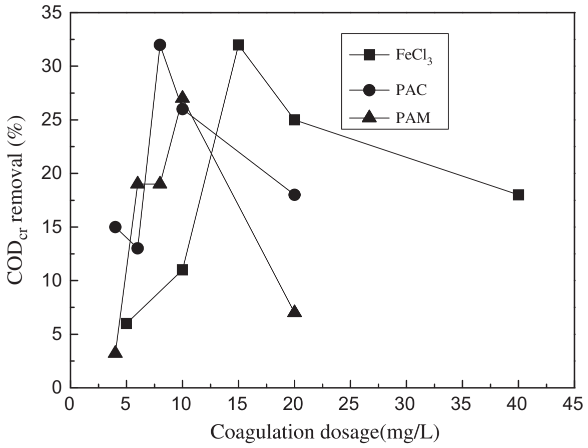

Fig. 2. Effect of the type and dosage of coagulant on the COD_{cr} removal.

PAM was adopted, the maximum COD_{cr} removal was just 27%, which appeared as the dosage got 10 mg/L.

Compared with other two reagents, PAC may be better for the treatment of this wastewater. When PAC was used, relatively higher COD_{cr} removal was obtained with less dosage.

Overall, it is not very effective for the removal of COD_{cr} by coagulation method. This can be explained as follows: Coagulation mechanisms are more effective for suspended substance, colloid and macromolecule organic matter than dissolved material and small molecular organic matter which were main organic components of the feed solution used in the study [23]. Therefore, it is not ideal method that coagulation was individually carried out to remove COD_{cr} from RO-concentrated wastewater.

3.1.2. Effect of UF in conjunction with coagulation on COD_{cr} removal

To improve the COD_{cr} removal, UF was adopted and set behind the coagulation process. The results are shown in Fig. 3.

The results show that UF improved the COD_{cr} removal on the basis of coagulation treatment. Nonetheless, the improvements of the three coagulation and UF processes were quite different. The COD_{cr} removal of $FeCl_3$ + UF process was 35%, about 3% higher than that of one step $FeCl_3$ coagulation process. As for PAM + UF, the COD_{cr} removal was 34%, approximately 6% higher than one-step coagulation by PAM. The COD_{cr} removal of PAC + UF reached 40%, approaching 8% improvement was obtained. Both of the improvement obtained by UF and the total COD_{cr} removal of PAC + UF conjunction process were higher than other two processes. So it was chosen as the wastewater pretreatment method for VMD process.

Table 3
The quality parameters of the feeds after pretreatments

Constituent	PAC	PAC + UF
Sodium/mg L^{-1}	2,400.0	2,398.5
Chloride/mg L^{-1}	3,685.0	3,635.5
Calcium/mg L^{-1}	240.1	235.9
Magnesium/mg L^{-1}	232.5	228.9
Total hardness/mg L^{-1}	885.5	876.0
Conductance/μS cm^{-1}	11,000	10,900
Turbidity/NTU	2.32	0.58
pH	7.00	6.95
SS/mg L^{-1}	1.65	1.45
COD_{cr}/mg L^{-1}	43	38

3.2. Effect of pretreatment on VMD performance and membrane fouling

The un-pretreated RO-concentrated wastewater, the wastewater pretreated by coagulation of PAC and the one pretreated by PAC + UF method were used as the feed solution of VMD process, respectively. The composition of the pretreated feed solution is shown in Table 3. The variations of the membrane flux, the Baume degree, COD_{cr}, and turbidity of the feed solution were studied. The results are illustrated below.

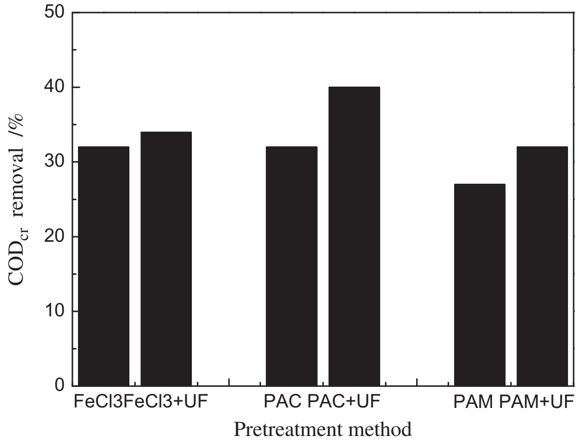

Fig. 3. Effect of pretreatment method on the COD_{cr} removal.

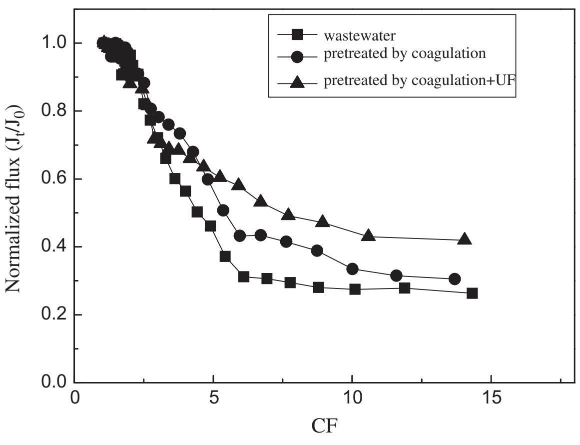

Fig. 4. Variation of the normalized flux during VMD process.

3.2.1. Effect of pretreatment on the flux of VMD process

Fig. 4 illustrates the variation of normalized flux during VMD concentration experiments.

From the figure, one can see that the declination of normalized flux for VMD process using three different feed solutions illustrated the same trend, and all declined from 1.0 to 0.8 when the concentration factor (CF) was below three. Then, as the CF further increased, different variation trends were observed. When un-pretreated wastewater was used as the feed solution, the normalized flux declined fastest, got 0.3 when the CF was 6. When the solution pretreated by coagulation + UF method was used as the feed, the declination of the normalized flux was much slower. The normalized flux was 0.6 when the CF got 6, twice of the flux using un-pretreated solution as the feed. As the CF exceeded 11, the normalized flux became stable and kept at about 0.4, also about twice of the flux using un-pretreated solution. As for the experiments using the solution pretreated by coagulation method as the feed, the declination speed was in the middle of the upper two systems.

The results show that the pretreatments on the RO-concentrated wastewater could decrease the flux declination of VMD process obviously. The reason is analyzed by the characterization of the variation of the feed solution and membrane surface morphology during VMD process. The results are illustrated below.

As the VMD process was carried out over a long period of time, an increase in fouled layer thickness on the membrane surface takes place. The deposits formed on membrane surfaces mainly caused the reduction in the driving force and then result in the permeate flux decrease. The faster permeate flux decrease for the un-pretreated RO-concentrated wastewater may be due to the higher content of natural organic matter (NOM) in the feed solution. The NOM, especially the macromolecular humic substances that contain negatively charged carboxyl groups can form coagulate form with positively charged inorganic ions such as Ca^{2+}, Mg^{2+}. The coagulate form is also more favorably adsorbed onto hydrophobic membranes due to the sorption between humic macromolecules and hydrophobic membrane [24,25]. The NOM contenting in RO-concentrated wastewater was reduced by UF in conjunction with coagulation processes, and the negatively charged carboxyl groups of humic acid were reduced also. At finally, the probability of organic compounds and inorganic cations (such as Ca^{2+}) form coagulate was reduced, thus reducing membrane fouling.

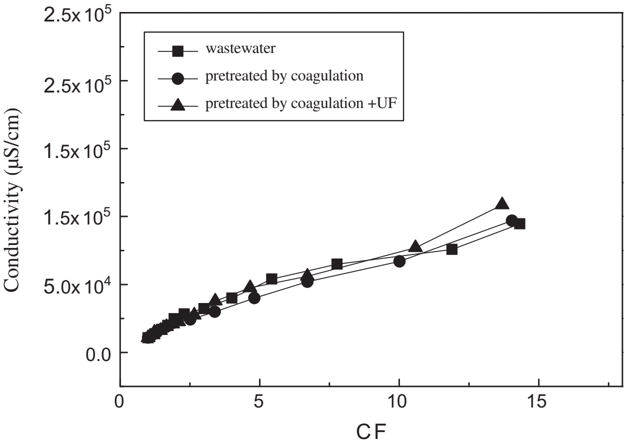

Fig. 5. Variation of the conductivity of the feed solution during VMD process.

3.2.2. Variation of the feed solution during VMD processes

Figs. 5–7 show the variation of the conductivity, Baume degree and turbidity of the feed solutions during VMD processes.

From Figs. 5 and 6, one can see that the conductivity and Baume degree of the three feed solutions were in the same level and show the same variation trend during VMD process. Both the conductivity and Baume degree of the feed solutions increased as the CF enhanced. And the conductivity, Baume degree of the feed solutions with pretreatment were higher than that with un-pretreated at CF above eight. It can be explained that trace PAC dissolved in RO-concentrated water, effectively inhibited or slowed inorganic salt deposition, and played a role of antiscalant.

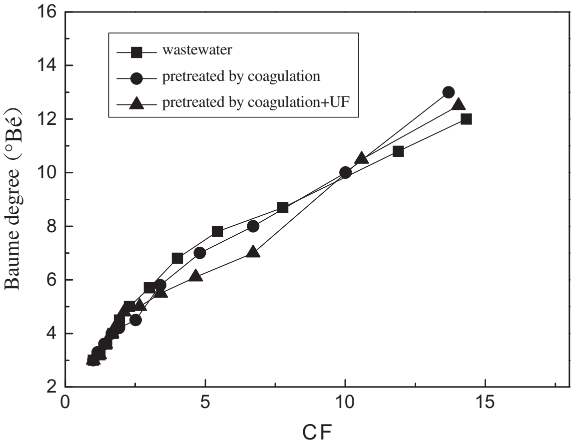

Fig. 6. Variation of the Baume degree of the feed solution during VMD process.

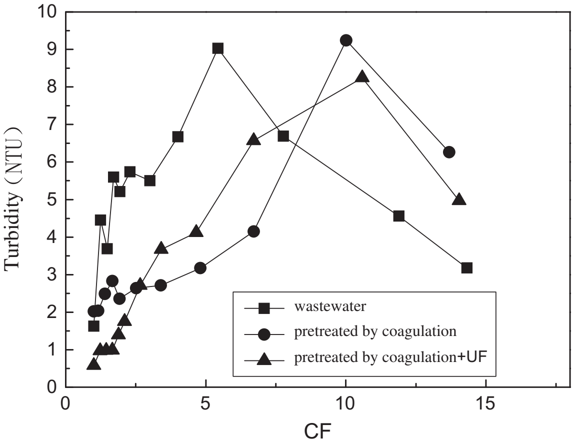

Fig. 7. Variation of the turbidity of the feed solution during VMD process.

While the results in Fig. 7 show that the turbidity of the three feed solutions was quite different. The initial turbidity of the feed solution pretreated by coagulation and UF method was 0.5 NTU, much lower than the other one (1.6~2.0 NTU). The turbidity of the un-pretreated feed solution increased obviously at the beginning of VMD process and got its maximum, 9 NTU, as the CF reached 6. Then, it declined as the VMD process continued and CF further enhanced. As for the other two pretreated feed solutions, the turbidity increased much slower than that of the un-pretreated one and got their maximum, 8 and 9 NTU as the CF exceeded 10. Then, turbidity declination was also observed as the CF further enhanced.

The enhancement of turbidity may be because of the increasing of feed concentration and the formation of aggregations by organic and inorganic solutes. The declination of turbidity after it reached the maximum may be because of the crystallization and coagulation of the aggregations. The pretreatment of the feed solution could stave off the coagulation of the feed solution and alleviate membrane fouling and flux declination.

By comparison with three pretreatments, the turbidity of the feed solution with un-pretreated reached the maximum value firstly. It shows crystals in RO-concentrated water with un-pretreated generated earlier than other pretreatment methods, and it demonstrates that coagulation could extend the induction period of inorganic salts [26]. The inorganic salts have some inhibition effect, thereby slowing inorganic salt scaling.

The distillate electrical conductivity for the three series is stable and is in the range of 1–3 μS/cm. These results indicate that serious membrane hydrophilization do not occur in the whole VMD processes.

3.2.3. Membrane morphology and fouling study

As the CF got 14, the inner surface morphology of the hollow fiber membranes used in the VMD concentration processes for the three solutions were characterized by SEM, the composition of the fouling on membrane surface was analyzed by EDS. The results are shown in Fig. 8 and Table 4.

From the SEM photos, one can see that the crystals on Fig. 8(b) and (c) are much bigger and fluffy than those on the surface of Fig. 8(a).

From the EDS data presents in Table 3, one can see that when the un-pretreated wastewater was used as the feed, the contaminant on membrane surface mainly contained NaCl, $CaSO_4$, $CaCO_3$, and trace organic matter. When the feed solution was pretreated by coagulation and UF, the contaminant mainly composed of $CaSO_4$.

The reason for different crystal sizes is the difference in the induction period for the three feed solutions. The induction period for a solution refers to the metastability of a supersaturated solution during which precipitation does not occur. As the NOM appearance in the feed solution, the induction period can be shortened [19], and as a result, the crystal did not have enough time and free space to grow up (Fig. 8(a)). When NOM was removed by pretreatment method (Fig. 8(b) and (c)), the induction period was relative longer, so the scale mainly deposited in the form of bigger crystals and resulted in a relatively porous contaminant layer, which was more permeable for water than the contaminant layer formed in Fig. 8 (a).

The analysis of chemical composition and morphology of the deposit on membrane surface shows that UF in conjunction with coagulation pretreatment for RO-concentrated wastewater is an effective measure to alleviate membrane fouling. Since UF in conjunction with coagulation pretreatment remove 40% COD_{cr} from the raw solution, and two negatively charged carboxyl functional groups containing in NOM act like a binding agent of inorganic ions, and the crystal deposition firmly attached to the hydrophobic membrane surface [18]. Organic matter in the feed solution could accelerate inorganic salt nucleation on membrane surface [21].

A comprehensive analysis of all data above and the pretreatment of UF in conjunction with coagulation can effectively alleviate the membrane flux decrease and control membrane fouling by reducing the content of organic matter in the feed water.

The variation of the normalized flux with CF (as Fig. 4) for the feed solution with pretreated by coagulation and UF can be divided into three states: substeady, presteady, and steady. In the substeady state (CF is in the range of 1–2), the flux dropped slightly versus CF. After reaching presteady state (CF is in the range of 2–8), the flux sharply decreased to the initial flux of about 50% until it reached the steady state. In the steady state (CF is in the range of 8–14), the flux slowly decreased to the initial flux of about 40%.

For further study on the variation of membrane surface morphology and chemical composition in different stages during VMD process with UF in conjunction with coagulation pretreatment, membrane samples which were collected from the MD module in different stages for the examination was analyzed by SEM and EDS method. The results show in Fig. 9 and Table 5.

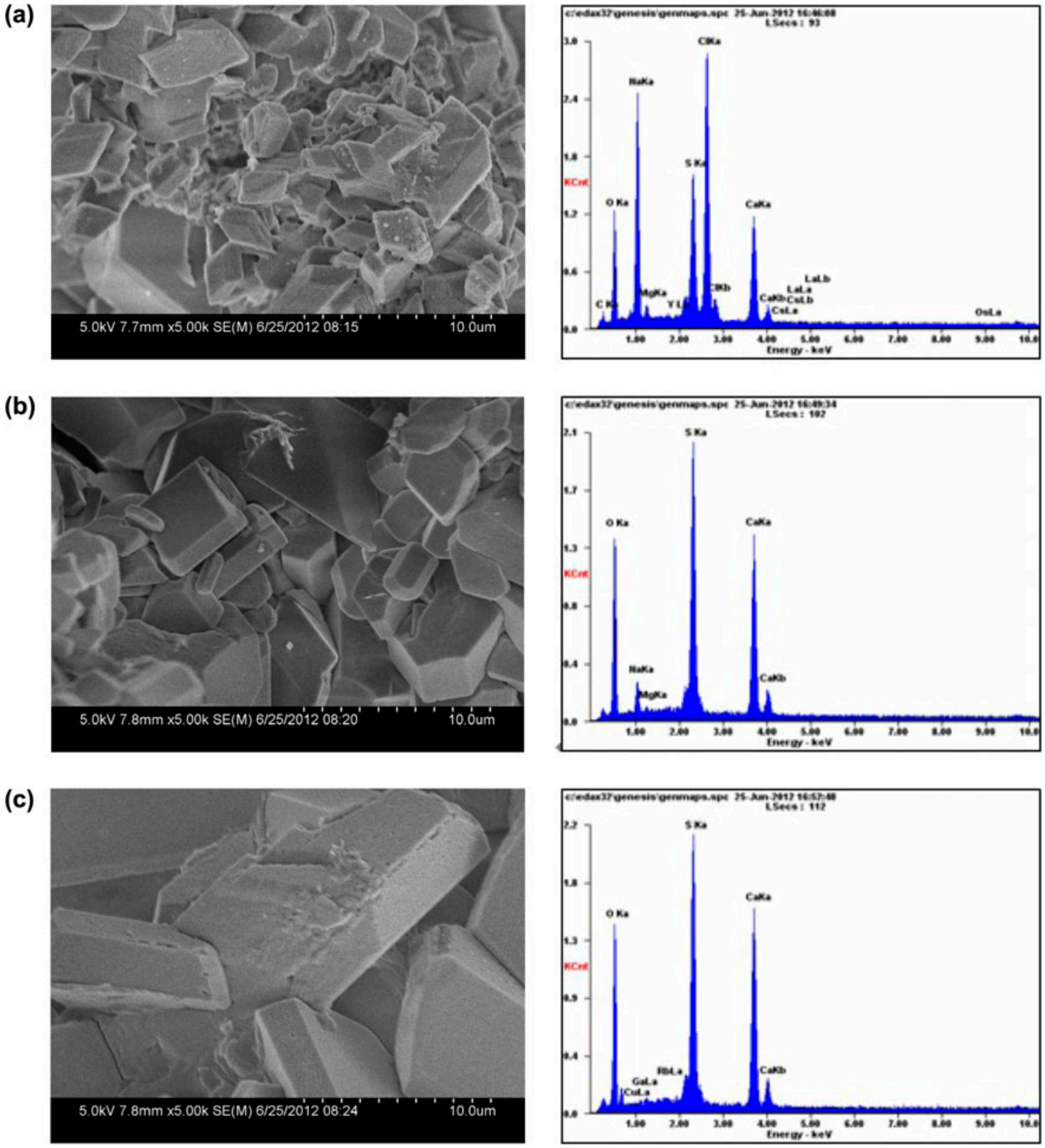

Fig. 8. Surface SEM micrographs (at magnification 5,000×) and EDS charts of the membrane used in VMD concentration process. The feed solutions are: (a) wastewater, (b) pretreated by coagulation and (c) pretreated by coagulation + UF.

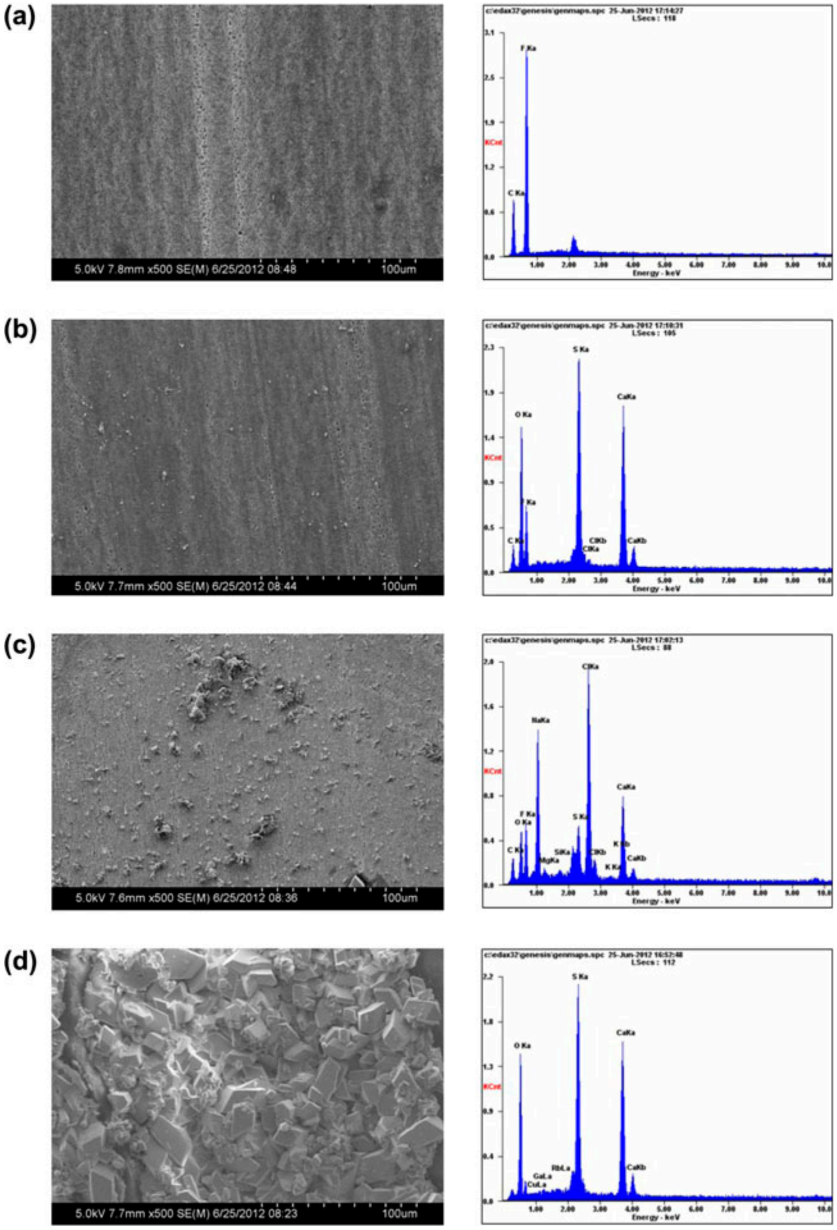

Fig. 9. SEM micrographs of the inner surfaces (500×) and the result of SEM–EDS analysis of deposit formed on the inner surface during VMD process. (a) virgin PVDF membrane; (b) PVDF membrane at solution CF of two; (c) PVDF membrane at solution CF of 8; and (d) PVDF membrane at solution CF of 14.

From the SEM photos (Fig. 9), one can see that the surface of virgin membrane was clean, and there was only few particles could be seen on the membrane surface, when the CF was two. When the CF reached eight, obvious contaminants could be observed on the membrane surface. The membrane surface was densely covered with crystals, when the CF got 14.

The results in Table 5 show that the contaminant on the membrane surface mainly contained $CaSO_4$, $CaCO_3$, and trace organic matter in the substeady state. Reaching presteady state, the contaminants on the membrane surface mainly contained NaCl, $CaSO_4$, $CaCO_3$, and trace organic matter. And the surface elemental analysis of the fouled membrane confirmed the contaminant mainly composed of $CaSO_4$ when the CF reached 14.

As shown in Fig. 9 and Table 5, the surface morphology of the membrane and the composition of the deposition on the membrane surface during VMD process at different stages. The deposition had not

Table 4
Composition of the membrane surface layer after VMD concentration of different solutions

Elemental (Wt%)	O	C	Na	Cl	Ca	S
a	27.54	7.36	21.45	20.63	10.96	9.05
b	53.76	–	4.91	–	21	19.84
c	56.02	–	–	–	23.13	19.81

(a) wastewater. (b) pretreated by coagulation. (c) pretreated by coagulation + UF.

Table 5
Composition of the membrane surface layer before and after VMD process

Elemental (Wt%)	O	C	Na	Cl	Ca	S	F
a	–	35.56	–	–	–	–	64.44
b	38.67	10.18	–	0.53	17.11	14.70	18.81
c	16.26	16.72	19.00	18.26	10.07	3.95	13.82
d	56.02	–	–	–	23.13	19.81	–

(a) virgin PVDF membrane. (b) PVDF membrane at solution CF of 2. (c) PVDF membrane at solution CF of 8. (d) PVDF membrane at solution CF of 14.

been formed on the membrane surface when the CF was in the range of 1–2 (Fig. 9(b)). The reasons are as follows: When the concentration of inorganic salt was far from saturation, almost no crystal form, and the content of suspended matters in the liquid was extremely low. Fig. 9(c) shows that a much more fine and dense layer deposition formed on the membrane surface in this stage. The concentration of the solution near membrane surface had reached saturation. Therefore, the feed solution concentration of the boundary layer differed greatly from the bulk solution such that the concentration polarization resistance and membrane fouling resistance increased sharply [8]. From Table 4, one can see that, when the CF got eight, the contaminant on the membrane surface mainly contained NaCl, $CaCO_3$, and trace organic matter. The organic matter with lower electronegativity adsorbed preferentially onto hydrophobic PVDF membrane surface and formed organic contaminant layer, and the organic matter played a role of crystal nucleus, accelerating the growth of inorganic salt crystal on hydrophobic membrane surface [21]. During this stage, crystallization of the initial crystal was lesser can enter into the membrane pores, blocking membrane pores, which resulted in the membrane flux sharp decline [23]. In Fig. 9(d), the membrane surface was densely covered with inorganic crystals. The presence of NaCl in the feed solution, increasing the solubility of $CaSO_4$ [27], and $CaSO_4$ crystals could precipitate and grow up gradually on the membrane surface as the CF was in the range 8–14. At last, the membrane surface was fully covered by $CaSO_4$ crystals.

4. Conclusions

Coagulation and UF are effective methods to remove COD_{cr} from RO-concentrated wastewater, and PAC is the best coagulation agents compared with PAM and $FeCl_3$. COD_{cr} removal reached 32% when 8.0 mg/L PAC was added in the wastewater. It could be enhanced to 40% when UF was applied after the coagulation method. The results of VMD experiments showed that proper pretreatment could alleviate membrane fouling and membrane flux declination obviously. When the CF was six, the normalized flux of the VMD process using solution pretreated by PAC + UF method was 0.60, while that using un-pretreated solution was just about 0.30. The membrane fouling analysis illustrated that the fouling process during VMD concentration could be divided into three steps, proper design of pretreatment method and VMD termination control would effectively alleviate membrane fouling and improve process performance.

Acknowledgment

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