Preparation and Performance of *N,O*-Carboxymethyl Chitosan-Polyether Sulfone Composite Nanofiltration Membrane in the Separation of Nickel Ions from Aqueous Solutions

Alka G. Boricha, Z. V. P. Murthy

Department of Chemical Engineering, S.V. National Institute of Technology, Surat-395007, Gujarat, India

ABSTRACT: Nanofiltration (NF) is considered to be an intermediate process between ultrafiltration (UF) and reverse osmosis (RO). In the present work, chitosan derivative containing carboxylic acid group (—COOH), i.e. *N,O*-carboxymethyl chitosan (NOCC), is prepared. Then, the NOCC composite NF membrane having a polyether sulfone (PES) UF membrane as the substrate is prepared using a method of coating and crosslinking, in which glutaraldehyde solution is used as the crosslinking agent. The developed membranes are characterized in terms of Fourier transform infrared/attenuated total reflectance (FTIR/ATR), scanning electron microscopy/energy dispersive X-ray analysis (SEM/EDXA), elemental analysis (EA), swelling behavior, tensile strength, and thermogravimetric analysis (TGA), which confirm the formation of the target membranes. Rejection efficiency of nickel ions from aqueous solutions, of nickel sulfate and nickel chloride, is investigated. The experiments are carried out for different feed concentrations, feed flow rates and applied pressures and the corresponding permeate flux and rejections are measured. The maximum observed rejection is found to be 80 and 62% of 5 ppm, 78 and 59% of 10 ppm; and 74 and 57% of 50 ppm feed concentration of nickel sulfate-water and nickel chloride-water systems, respectively. The observed order of the separation of the nickel salts is $NiSO_4$ and $NiCl_2$. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 110: 3596–3605, 2008

Key words: chitosan; composite membrane; nanofiltration; metals; permeate; rejection

INTRODUCTION

Nanofiltration (NF) is an intermediate process between ultrafiltration (UF) and reverse osmosis (RO). The separation mechanism involves both sieving effect and electrical (Donnan) effect. This combination allows NF membranes to be effective for a range of separation of mixtures of organic molecules (neutral or charged) and salts.[1] Donnan potential is created between the charged anions in the NF membrane and the coions (i.e., anions) in the influent and because of this potential, coion in the influent are rejected. Because of the electro-neutrality requirements in the influent, the counter-ions (i.e., cations) are rejected as well.[2] Most of the NF membranes developed so far are composite in nature, with a selective layer on top of the microporous substrate.

Various membrane materials have been used for a selective layer on polymeric or inorganic microporous substrates. The choice of materials depends on both chemical and physical compatibility of selective layer with the substrate, which in turn determines the stability and performance of the resulting composite membranes. Polyacrylonitrile (PAN),[3] polysulfone (PS),[4] polytetramethylene-adipate-*co*-terephthalate,[5] polyethersulfone (PES)[6] and polytetrafloroethylene (PTFE)[7] are the versatile polymeric materials, in addition to their well established use for asymmetric ultrafiltration membranes, have been used as microporous substrate for making composite NF membranes.

Nickel (II) ion is one such heavy metal frequently encountered in raw wastewater streams from industries such as paint formulation, electroplating, nonferrous metal, mineral processing, steam-electric power plants, porcelain enameling, and copper sulfate manufacture.[8,9] The nickel (II) ion intake over the permissible levels results in different types of disease such as pulmonary fibrosis, renal edema, skin dermatitis, and gastrointestinal distress (e.g. nausea, vomiting, diarrhea).[10] The safe discharge limit for Nickel into marine coastal areas is 5.0 mg/

L.[11] The central pollution control board (CPCB) of India has set minimal national standards of 3.0 and 2.0 mg/L, for discharge of Ni(II) for the effluents of electroplating and inorganic chemical industries, respectively. So, the removal of nickel ion from the waste water is well-known issue. Chitosan is a linear polymer primarily of glucosamine. It is the second abundant biopolymer after cellulose, and this polymer is the N-deacetylated product of chitin, a natural polymer that can be extracted from outer shells of crustaceans. Chitosan molecules contain a large number of reactive hydroxyl (—OH) and amine (—NH₂) groups, therefore it can be an excellent candidate for affinity membranes.[12]

In the literature, different types of methods have been employed to prepare composite NF membranes from ultrafiltration membranes. Wang et al.[13] used heat treatment in the presence of ZnCl₂, Zhao et al.[14] used graft modification of UF membrane by Ar low temperature plasma treatment and subsequent grafting of the monomer styrene in vapor phase. Zhao et al.[15] used graft modification of membrane by Ar low temperature plasma treatment and subsequent grafting of the monomer N-vinylpyrrolidone. Among them, literature on composite NF membrane using NOCC as the active layer material was feeble. Miao et al.[16] prepared NOCC composite nanofiltration membranes having a polysulfone (PS) UF membrane as the substrate by using the method of coating and crosslinking, in which a glutaraldehyde (GA) aqueous solution was used as the crosslinking agent. They studied the effects of the composition of the casting solution of the active layer, the concentration of the crosslinking agent, and the membrane preparation techniques on the performance of the composite membrane with sodium and magnesium salts separation. But no literature was found using NOCC composite nanofiltration membranes having polyether sulfone (PES) UF membrane as the substrate to separate different metal ions from aqueous solutions.

The objective of the present study is to develop a composite NOCC NF membrane having a polyether sulfone UF membrane as the substrate; using a method of coating and crosslinking, in which glutaraldehyde aqueous solution is used as the crosslinking agent. To characterize the resulting membrane, Fourier transform infrared/attenuated total reflectance (FTIR/ATR), scanning electron microscopy/ energy dispersive X-ray analysis (SEM/EDXA), elemental analysis (EA), Swelling behavior and tensile strength are employed. Thermal stability of membrane is evaluated by thermogravimetric analysis (TGA). Then this membrane is used to investigate nickel ions removal from aqueous nickel sulfate-water and nickel chloride-water systems, at different operating conditions.

MATERIALS AND METHODS

Synthesis of NOCC

NOCC was synthesized as per the procedure described in the literature[3,16] with slight modification. Chitosan in the flakes form (85% degree of acetylation, mean molecular mass is 125,000) was obtained from M/S. Marine Chemicals (Cochin, Kerala, India). Chitosan (5 g) suspended in 50% (w/w) NaOH (30 g) was swelled for 1 h at room temperature (25°C) and kept at −10°C for alkalization for 16 h, then thawed at room temperature. The alkali-chitosan was suspended in isopropanol (150 mL) and the resulted slurry was stirred at a moderate speed. Subsequently, monochloroacetic acid (20 g) was added in five equal portions after every 5 min. The mixture was stirred for 4 h in a water bath at 50°C. Then, the resultant solution was adjusted to pH 7.0, filtered and dialyzed against deionized water. Then the resulting solution was concentrated, and precipitated by pouring into acetone. The white precipitate was thoroughly rinsed with methanol, vacuum dried at 50°C and stored in a desiccator. The reaction mechanism was followed as per the published literature.[17]

Preparation of NOCC-PES composite NF membrane

The high flux PES UF membrane (30,000 Daltons) had a pure water flux of 35 L/(m² h atm) at 25°C. Before coating the casting solution of the active layer, the PES UF membrane are immersed in water overnight, rinsed with deionized water thoroughly, and surface dried. Aqueous NOCC solution of 1.0 wt % is prepared by dissolving a certain amount of NOCC in deionized water and filtering with a sandfilter.[12] After vacuum treatment, the degassed NOCC solution is coated onto the PES UF membrane, followed by curing in an oven at 50°C for 1 h. The cured membrane is covered by the aqueous GA solution (0.25 wt %) and the excess solution is drained by holding the membrane vertically, followed by crosslinking at 60°C for 1 h. After crosslinking, the membrane was washed with deionized water extensively and immersed in deionized water for 24 h to remove the remaining unreacted glutaraldehyde. Before the permeation tests, the composite membrane was kept in water to prevent crystal formation.

Characterization of the NOCC-PES composite NF membrane

FTIR and ATR

The chemical structure of the resulting composite NF membrane was characterized by Fourier Transform Infrared (FTIR GX 2000, Perkin–Elmer) spectra
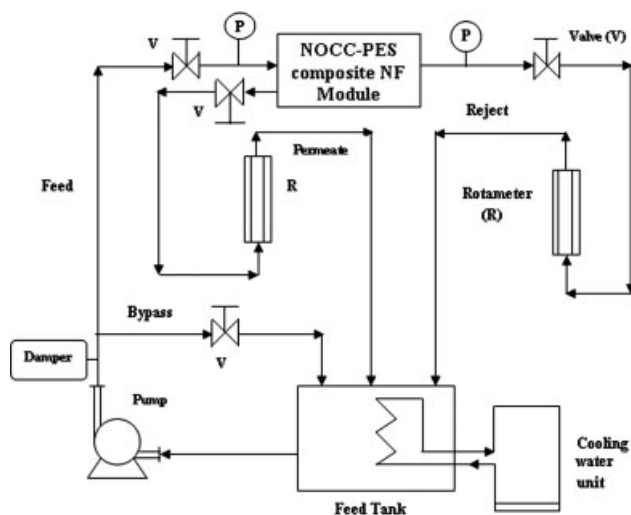
Figure 1 Perma® pilot scale membrane system.

(for chitosan and NOCC) and Attenuated Total Reflection (Spectrum GX, Perkin–Elmer) spectra (for NOCC-PES composite NF membrane).

SEM and EDXA

The top surface and cross section of the PES UF membrane and NOCC-PES composite NF membrane were analyzed using scanning electron microscopy. Energy Dispersive X-ray analysis was used to analyze the elemental composition for both the membranes with (ESTM TMP +EDXA, Philips, HOLLAND). The membranes were cut into pieces of various sizes and mopped with filter paper. These pieces were immersed in liquid nitrogen for 20–30 s and frozen. The frozen bits of the membranes were broken and kept in a desiccator. These samples were used for SEM-EDXA studies.

TGA

Thermal stability of the PES UF and composite new membrane were examined using the (TGA-7, Perkin–Elmer, Norwalk, CT). Temperature range used is 30–500°C, and heating rate employed at 10°C/min. Nitrogen gas, at the rate of 20 mL/min, was utilized for flushing purpose.

Degree of swelling

The swelling properties of the samples were studied by immersing the samples in a solution and at different periods of time at room temperature. The dried membranes are cut into small squares with some constant dimension. At predetermined time intervals, the pieces of membranes were taken out from the solutions, gently wiped with filter paper to remove the surface solution, weighed and returned to the same

container until equilibrium. The swelling ratio (SR) to these samples were calculated by using the eq. (1)

$$\text{Swelling ratio}(\%) = [(W_s - W_d)/W_d] \times 100 \quad (1)$$

where, W_d is the weight of the dry membrane and W_s is the weight of the membrane swollen in the solution.

Mechanical properties

The tensile strength and elongation (at the break) of the membranes were evaluated by the tensile testing machine (KIPL-PC2000, Pune, India) as per the procedure, outlined in ASTM D-421A test method.

Permeation experiments

The experiments were performed on a Perma® pilot scale membrane system (Permionics, Vadodara, India) using rectangular NOCC-PES composite NF membrane having filtration area of 150 cm². The experimental set-up was shown in Figure 1. The membrane-housing cell, shown in Figure 1, is made of stainless steel with two halves fastened together with high tensile bolts. The top half of cell contained the flow distribution chamber and the bottom half is used as the membrane support system. The membrane required support to prevent rupture at high hydrostatic pressures. For that type of support, following arrangement are used: A perforated 1-mm thick stainless steel plate is laid over with a stainless steel gauge of 300 mess size, which is topped by a Whatman filter paper and followed by the actual membrane with its active thin layer exposed to the high pressure fluids. This type of arrangement provides sufficient mechanical support to the test membrane at high pressures. The upper half of the test cell contains a groove for the arrangement of HDPE 'O' ring to avoid leakage at high pressure operation. Experiments are performed with a NOCC-PES composite membrane. The 1-mm thin channel passage in the membrane test cell and high cross-flow feed rates used in the experimentation help to control the concentration polarization, to some extant. Before conducting the actual experiments for the rejection of nickel ions, the NOCC-PES membrane is subjected to stabilization at 20 atm, which is the maximum pressure used in the experiments, for 2 h to avoid possible membrane compaction during the experimentation. Experiments are performed for 2 h, for each set of rejection data in batch circular mode. The permeate samples are collected from high pressure to low pressure for a particular feed concentration and feed flow rate. Both permeate and concentrates are returned to the feed vessel to keep a constant concentration. During the experiments,

with increasing the feed pressure or feed flow rate, temperature of the feed solution in the feed tank is increased. So, to maintain a constant temperature through out the process, cooling water is continuously circulated in the feed tank by using the cooling coil. Samples of permeate are collected at a given time interval, to measure the observed salt rejection (R_o) and permeate volume flux (J_V). Here, $R_o = [1 - C_{A3}/C_{A1}]$, where, C_{A1} is the feed solute concentration and C_{A3} is the permeate solute concentration. The experiments are carried out for different concentrations of $NiSO_4.6H_2O$ and $NiCl_2.7H_2O$ (5, 10, and 50 ppm), feed flow rates (4, 8, 12, and 16 L/min (LPM)), applied pressures (4, 8, 12, 16, and 20 atm) and corresponding R_o and J_v are measured. In general, the wastewaters containing nickel salts had a pH in the range of 4–6.[2,18] Hence, in the present study, all the experiments are conducted at pH 6.0. Before the solute rejection experiments, the pure water permeability (PWP) of the membrane using distilled water is measured at 25°C. A plot of PWP versus pressure will give a slope L_P, known as the PWP coefficient of the membrane. The L_P is found to be 12.56 L/(m^2 h atm). The nickel ion concentrations are measured by an Atomic Absorption Spectrophotometer (SL-173, M/S. ELICO Limited, Hyderabad, India) following standard methods.[19] After each set of experiments for a given feed concentration, the set-up is rinsed with distilled water for 30 min at 4 atm to clean the system. This procedure is followed by measurement of PWP with distilled water to ensure that the initial membrane PWP is restored.

RESULTS AND DISCUSSION

FTIR spectra of chitosan and NOCC

The FTIR spectra of chitosan is shown in Figure 2, in which the band at 3438 cm^{-1} can be attributed to
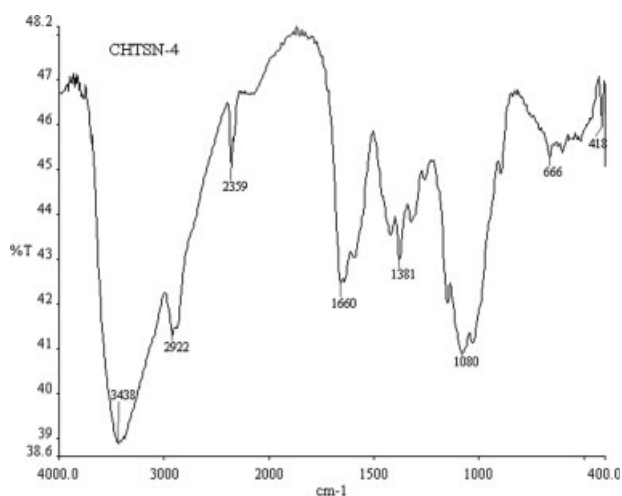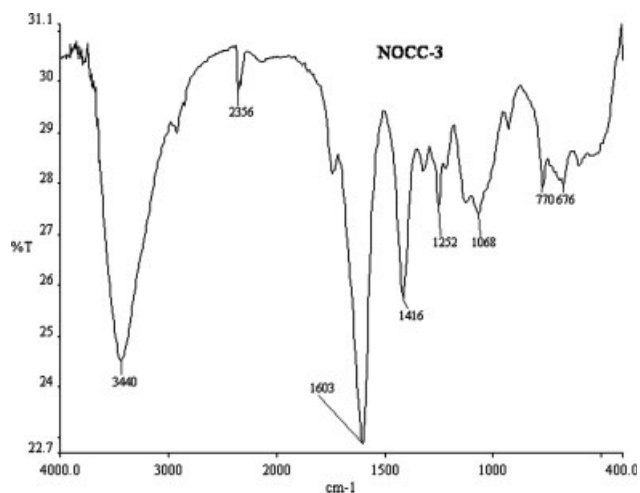
Figure 2 FT-IR spectra of Chitosan.

Figure 3 FT-IR spectra of NOCC.

the O—H and N—H stretching, the band at 2922 cm^{-1} attributed to the C—H stretching on methyl. The band at 1660 cm^{-1} is attributed to the C=O of —NH—C=O stretching and 1080 cm^{-1} attributed to C—OH stretching. The FTIR spectrum of NOCC is shown in Figure 3, in which the bands at 1603 and 1416 cm^{-1} can be attributed to the carboxylation. The formation of NOCC is also confirmed by the intensification of bands at 1068 cm^{-1} corresponding to C—O—C stretching. The band at 3440 cm^{-1} becomes wider and weaker, which suggests that carboxylation occurred on some of both the amino and primary hydroxyl sites of the glucosamine units of chitosan structure.[16,20,21]

ATR spectra of NOCC-PES composite NF membrane

The ATR spectra of the NOCC-PES composite NF membrane crosslinked by GA is shown in Figure 4. The band at 1581 cm^{-1} attributed to —C—N— stretching in —C—NHCONH$_3$. The band at 1322 cm^{-1} and 1106 cm^{-1} can be attributed to C—O—C stretching[12] and 1408 cm^{-1} for —COO stretching.[21]

SEM—EDXA of membranes

There is a close relationship between the membrane morphology and the performance. The top surface and cross-sectional views of PES-UF membrane (i.e., substrate) and composite membranes are shown in Figure 5. Figures 5(a,b) show the top surface of PES UF membrane and NOCC-PES NF membrane, respectively. It can be observed from the figures that PES UF membrane had a smooth surface but after the dense selective layer (NOCC) had been coated on the surface of the substrate membrane and because of that the selective layer, the surface of composite membrane is rougher than that of the
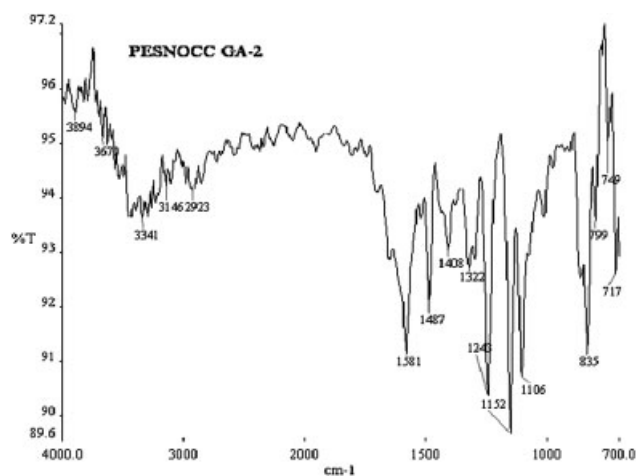
Figure 4 ATR-IR spectra of NOCC-PES Composite NF membrane.

substrate membrane. It is observed that the water flux increases as the roughness of the membrane increases.[22,23] Figure 5(c,d) show the cross-sectional views of the PES UF and NOCC-PES NF membranes, and it is clearly seen that after coating, a dense selective layer of NOCC had been formed on the substrate. Because of this dense layer of NOCC the substrate membrane becomes negatively charged which helped to increase the separation of nickel ions from the wastewater.

Figure 6(a,b) shows the EDXA line profile of C, O, and S elements in the PES UF membrane and

NOCC-PES composite NF membrane. It can be clearly seen from the figures that the composition of carbon has been increased, and it is because of a dense selective layer coating. Figure 6(a,b) confirm the earlier SEM results that NOCC had been coated on PES UF membrane.

TGA

Apart from the above membrane characteristics, membrane stability is also one of the major aspects. Temperature stability is one of them as the process may be carried out at higher temperatures. This may be because of the feed that it self is available at higher temperatures. Accordingly, testing characterization with regards to temperature stability is carried out. The Figure 7(a,b) depict thermal degradation of PES UF membrane and NOCC-PES composite membrane. Thermograms shows mass loss of a membrane subjected to the increasing temperature environment. Further, both the curves start at 100% mass and end at almost thermally decomposed form of the membrane (nearing 0%). Accordingly, it may be clearly inferred that up to around +200°C both the membranes tested are found to be thermally stable. Beyond which, there is sharp loss of mass of the membranes. Further, one may observe that decomposition temperature increase for NOCC-PES composite membrane compared to PES UF membrane.
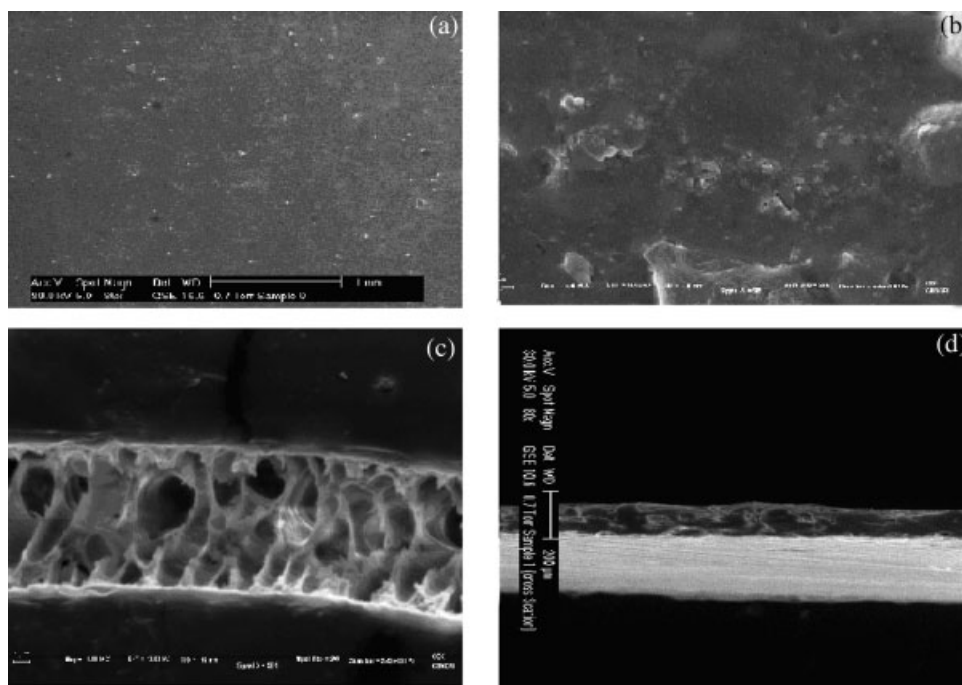

Figure 5 SEM image of (a) Top surface of PES UF membrane (b) Top surface of NOCC-PES Composite NF membrane (c) Cross section view of PES UF membrane (d) Cross section view of NOCC-PES Composite NF membrane.
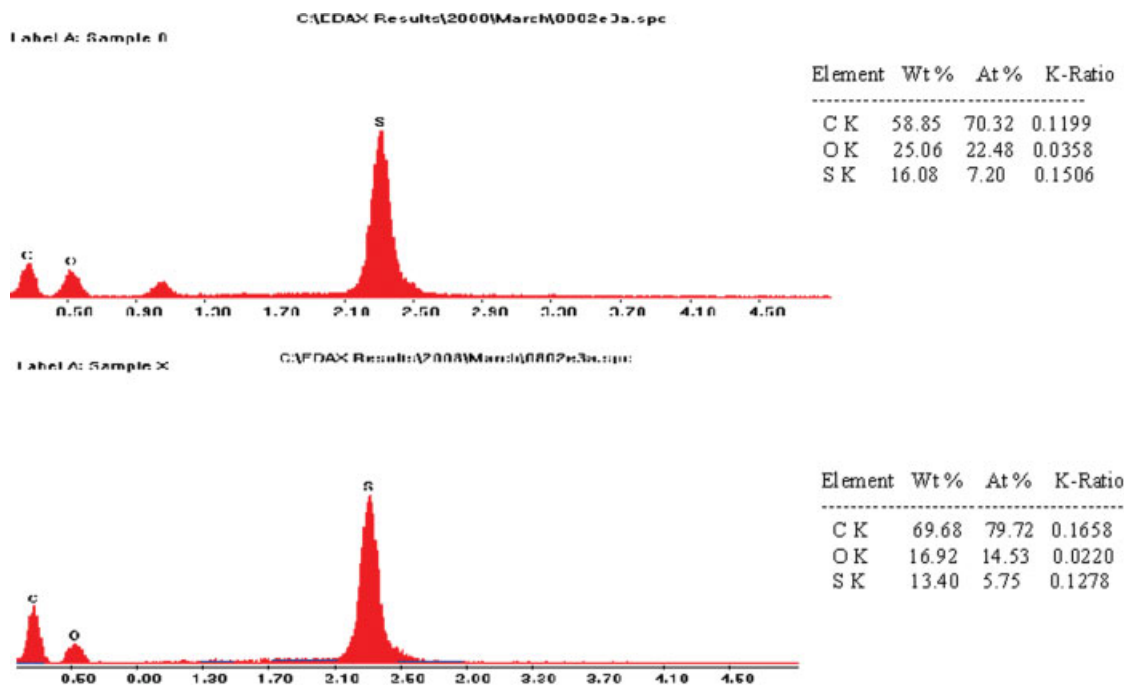
Figure 6 EDXA spectra and element composition of (a) PES UF membrane and (b) NOCC-PES composite NF membrane. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Degree of swelling

Sorption experiments are carried out for water, nickel chloride-water system and nickel sulfate-water system at room temperature and constant pH 6.0 by using NOCC-PES composite NF membrane. Figure 8 shows the plot of degree of swelling verses temperature. Initially, for all the samples, the rate of water uptake sharply increased and then begins to level off. The equilibrium swellings for all the samples are achieved after 45 min. In this study, the composite membrane showed the maximum swelling ratio (Fig. 8) with water (107), than with the nickel chloride-water system (64) and nickel sulfate-
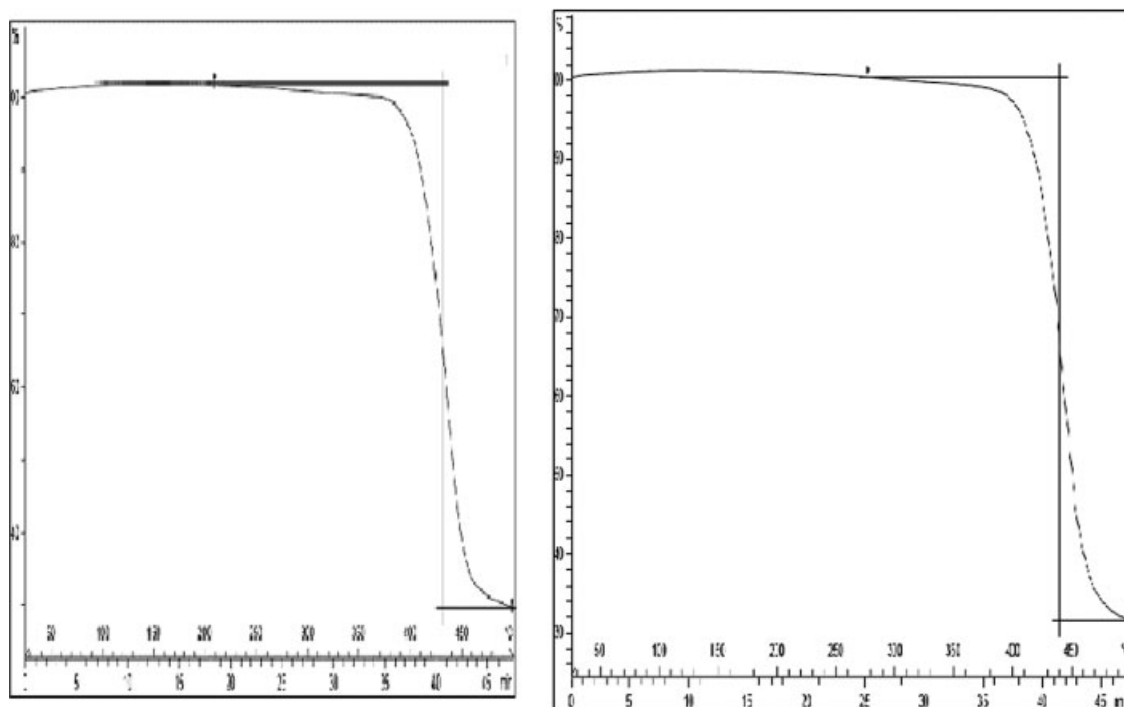

Figure 7 TGA analyses (a) of PES UF membrane (b) NOCC-PES Composite NF membrane.
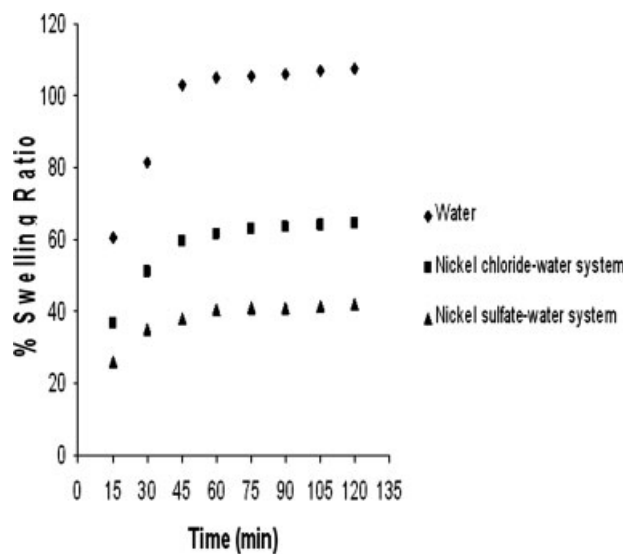
Figure 8 Temperature dependence of sorption for NOCC-PES composite NF membrane.

water system (41). This result is supported by the percent rejection data for Nickel chloride and Nickel sulfate.

Mechanical properties

For NOCC-PES composite membrane, the tensile strength is found to be 191 N/mm^2 and elongation at break is 8.32%, which are typical values of nano-filtration membranes.[24] Hence, it may be said that the new composite NF membrane has a good tensile strength and can withstand the pressures used with repeated experiments.
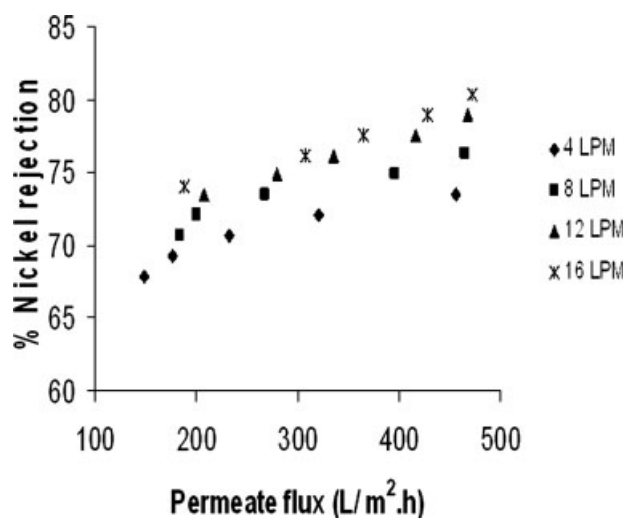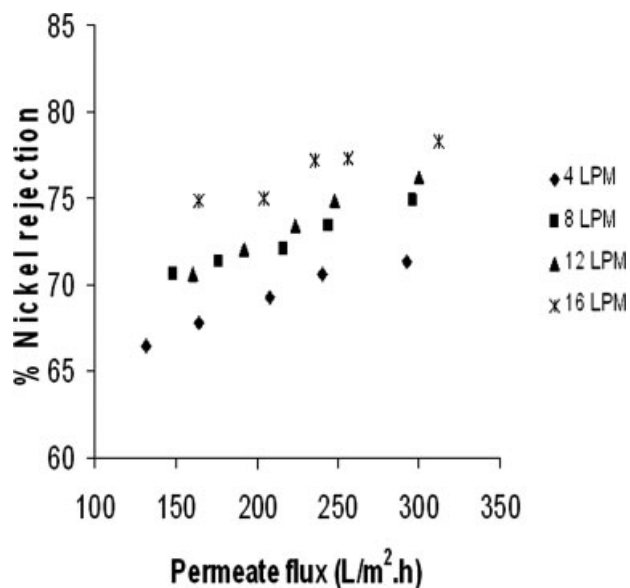

Figure 10 Relation between permeate flux versus % nickel rejection of 10 ppm NiSO$_4$ solution for different feed flow rates, different feed pressures (4–20 atm) and constant pH (6.0).

Effect of feed concentration

The effect of feed concentration on percent rejection at different concentrations; 5, 10, and 50 ppm for NiCl$_2$.7H$_2$O and NiSO$_4$.6H$_2$O; are reported through Figures 9–14. Working pressure is in the range of 4–20 atm (4, 8, 12, 16, and 20). Figures 9–11 show the effect of feed concentration of NiSO$_4$.6H$_2$O on percent rejection. It can be seen from the Figures 9–11 that the maximum rejection for nickel ion of

Figure 9 Relation between permeate flux versus % nickel rejection of 5 ppm NiSO$_4$ solution for different feed flow rates, different feed pressures (4–20 atm) and constant pH (6.0).
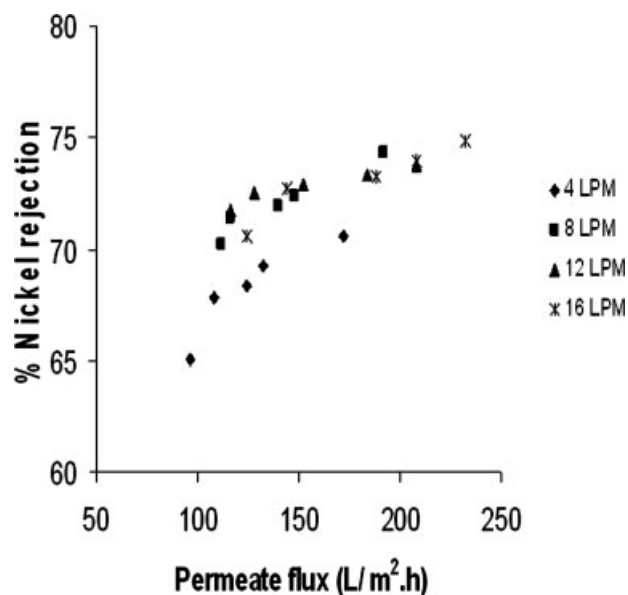

Figure 11 Relation between permeate flux versus % nickel rejection of 50 ppm NiSO$_4$ solution for different feed flow rates, different feed pressures (4–20 atm) and constant pH (6.0).
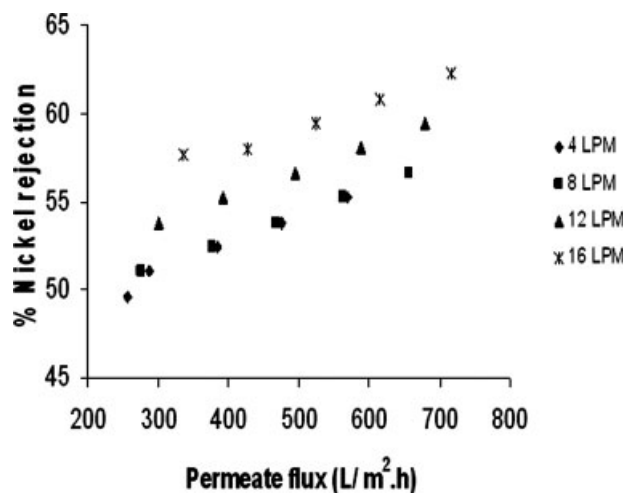
Figure 12 Relation between permeate flux versus % nickel rejection of 5 ppm $NiCl_2$ solution for different feed flow rates, different feed pressures (4–20 atm) and constant pH (6.0).

Figure 14 Relation between permeate flux versus % nickel rejection of 50 ppm $NiCl_2$ solution for different feed flow rates, different feed pressures (4–20 atm) and constant pH (6.0).
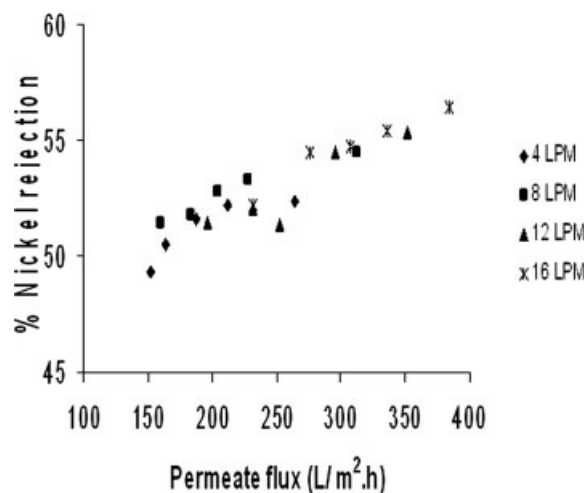
composite NOCC-PES NF membrane is found to be 80, 78, and 74 for 5, 10, and 50 ppm feed concentration of $NiSO_4.6H_2O$, respectively, with 16 LPM feed flow rate. Similarly, Figures 12–14 show the effect of feed concentration of $NiCl_2.7H_2O$ on percent rejection. The maximum rejection for nickel ions of composite NOCC-PES NF membrane is found to be 62, 59, and 57 for 5, 10, and 50 ppm feed concentration of $NiCl_2.7H_2O$, respectively, with 16 LPM feed flow rate. The active layer of NOCC-PES composite NF membrane contains carboxymethyl groups, which will have a stronger repulsion to SO_4^{2-} than Cl.[1–16]

This is a typical phenomenon of charged membranes.[25,26] Mohammad et al.[27] investigated from Ni-P electroless plating industrial wastewater that rejection decreased with the increase in salt concentration. The increase in the feed solution concentration involves a screen formation of cations adjacent to the membrane on high pressure side. This formation neutralizes the negative charges of the membrane. The total charge of the membrane decreases and the repulsion between the membrane and anion is reduced. As a result, the coion will easily pass through the membrane and due to electro neutrality,
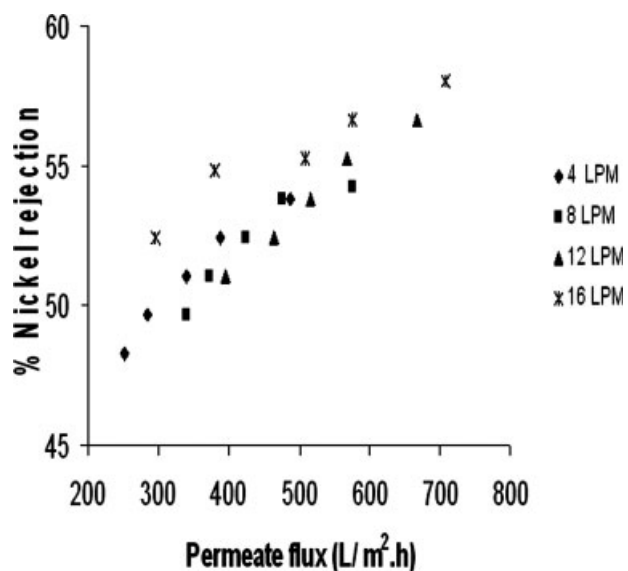

Figure 13 Relation between permeate flux versus % nickel rejection of 10 ppm $NiCl_2$ solution for different feed flow rates, different feed pressures (4–20 atm) and constant pH (6.0).
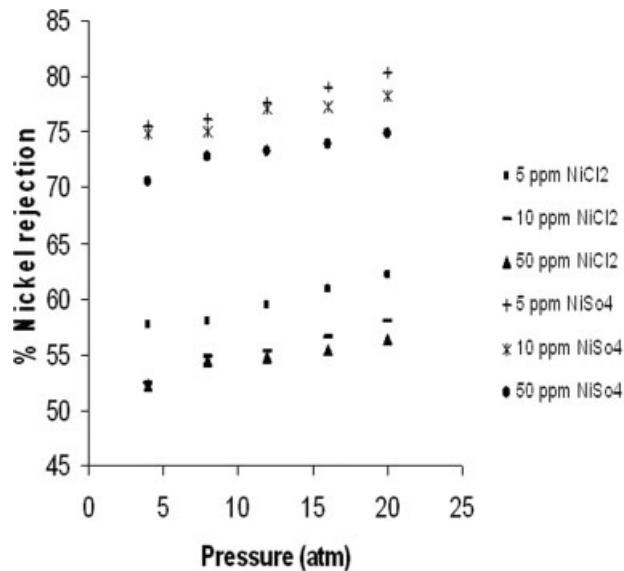

Figure 15 Influences of applied pressures on % nickel rejection of NOCC-PES composite NF membrane for different concentration of $NiCl_2$ and $NiSO_4$ solutions for 16 LPM feed flow rate and constant pH (6.0).
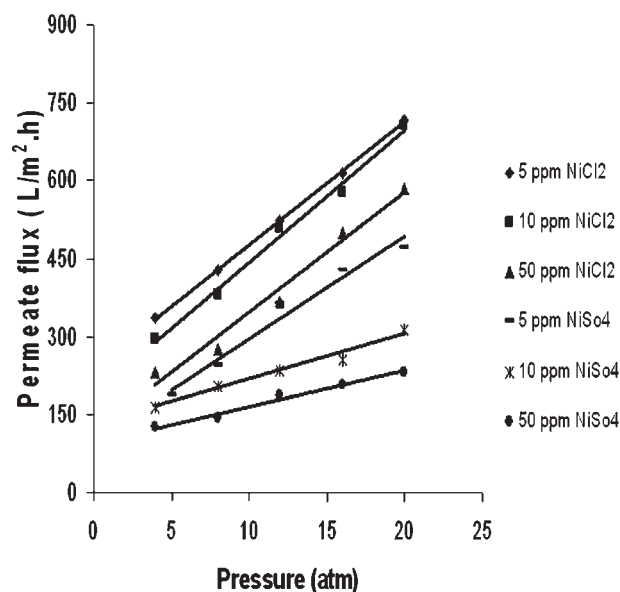
Figure 16 Influences of applied pressures on the permeate flux of NOCC-PES composite NF membrane for different concentration of $NiCl_2$ and $NiSO_4$ solutions for 16 LPM feed flow rate and constant pH (6.0).

the counter-ion will also be rejected less which is expected, in general, with RO/UF membranes.[28,29]

It can also be seen from Figures 9–14 that the rejection increases with the valency of coion, which shows that retention is enhanced when the charge valency of the associated coion is increased. These observations can be explained by the Donnan exclusion phenomena, and can be described by thermodynamic equilibrium. Thus, as the membrane is negatively charged, coions are excluded and cations are also rejected to ensure electro neutrality at both sides of the membrane. Retention is enhanced with increasing valency of the anion owing to increased electrostatic repulsion by the membrane. This is an important feature of nanofiltration. Such results can be found in the literature on nanofiltration separation membrane data obtained with different multivalent solutes. As a result, salts with SO_4^{2-} ion are rejected more than the salts with the Cl^{1-} ion.[2,27] This trend in the separation behavior holds good at all the feed concentrations used in the present studies (5, 10, 50 ppm). Mehiguene et al.[30] have reported that the retention was enhanced with increasing valency of ions owing to increased electrostatic repulsion by the membrane and Donnan et al.[31] have found that the charge effect on ion depends on the valence of the coion, and thus, there is a possibility of ion separation according to valence type.

Effect of applied pressure

Experiments are carried out to study the effect of applied pressure, ranging from 4 to 20 atm, at pH

6.0. The effect of applied pressure on nickel ions rejection is reported in Figure 15, which shows that the rejection increases with increase in pressure, because ion transport due to convection becomes significant compared to diffusion.[32] A high diffusive transport of salts through the membrane compared to convective transport may be the reason for low retention at low pressure. With increasing pressure, convective transport becomes important and retention will, therefore, also increases. Figure 16 shows the effect of applied pressure on the permeate volume flux. It can seen from Figure 16 that permeate flux for nickel salts-water systems increase linearly with increasing pressure,[33] which indicates there may be negligible concentration polarization in the membrane cell. As the feed concentration increased, the permeate flux decreases due to the increase of concentration difference across the membrane and subsequent increase in the osmotic pressure opposes the permeate flux.[2,30]

Influence of feed flow rates

Figure 17 shows the rejection percentages with change in feed concentration of nickel salts at different feed flow rates (4–16 LPM) at 20 atm applied pressure. It can be seen from Figure 17 that the increase in feed flow rate leads to an increase in the retention. Similar results are found in the case of negative surface charged membranes for the nickel ions[2] and for the zinc ions.[34] At constant feed pressure and concentration, the mass transfer coefficient increases with increase in feed flow rates which in
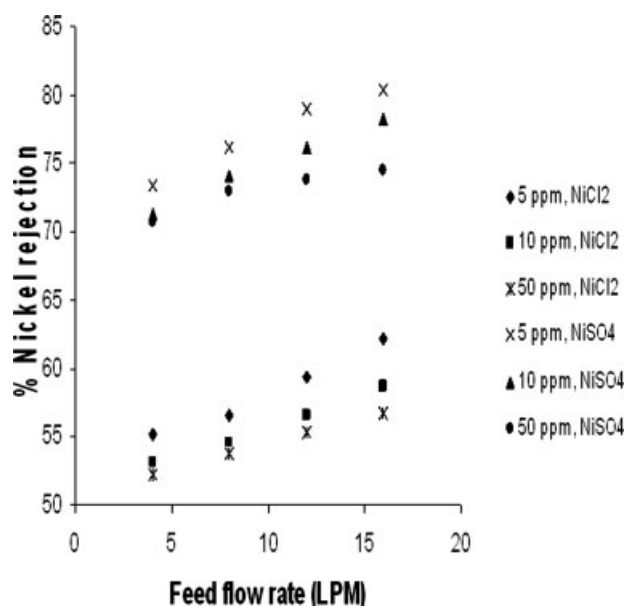

Figure 17 Effect of different feed flow rate on % nickel rejection for different concentration of $NiCl_2$ and $NiSO_4$ solutions for 20 atm pressure and constant pH (6.0).

turn reduces the concentration polarization and increase the rejection.[35]

CONCLUSIONS

In the present study, a composite NF membrane is prepared through a method of coating and crosslinking using NOCC, PES UF membrane, and glutaraldehyde as the active layer material, the base membrane, and the crosslinking agent, respectively. Fourier transform infrared, attenuated total reflection, scanning electron microscopy/energy dispersive X-ray analysis, elemental analysis, swelling behavior, tensile strength, and thermogravimetric analysis are employed to characterize the resulting membrane. Then, the performance of the NOCC-PES composite NF membrane has been studied to separate nickel ions from aqueous solutions of $NiSO_4.6H_2O$ and $NiCl_2.7H_2O$ at various operating conditions. It is observed that the rejection of nickel ions increases with increase in applied pressure and decreases with increase in feed concentration at constant feed flow rate. The rejection increases with the valency of coion. As a result, salts with SO_4^{2-} ions are rejected more than salts with the Cl^{1-} ion. It is observed that the active layer of NOCC-PES composite NF membrane contains carboxymethyl groups, which will have a stronger repulsion to SO_4^{2-} than Cl^{1-}.

References

1. Bowen, W. R.; Mohammad, A. W. Desalination 1998, 117, 257.
2. Ahn, K. H.; Song, K. G.; Cha, H. Y.; Yeom, I. T. Desalination 1999, 122, 77.
3. Musale, D. A.; Kumar, A. Sep Purif Technol 2000, 21, 27.
4. Tsai, H. A.; Chen, H. C.; Lee, K. R.; Lai, J. Y. Desalination 2006, 193, 129.
5. Yu, D. D.; Jou, C. H.; Lin, W. C.; Yang, M. C. Colloid Surface B 2007, 54, 222.
6. Zhao, Z.; Wang, Z.; Ye, N.; Wan, S. Desalination 2002, 144, 35.
7. Liu, Y. L.; Yu, C. H.; Lee, K. R.; Lai, J. Y. J Membr Sci 2007, 287, 230.
8. EPA. US Environmental Protection Agency. Treatability manual; EPA: Washington, DC, 1988, Vol. 1, pp 4.11–4.12.
9. Sittings, M. Ed., Environmental Sources and Emission Handbook; Noyes Data Corporation: Park Ridge, New Jersey, 1976.
10. Akhtar, N.; Iqbal, J.; Iqbal, M. J Hazard Mater 2004, 108, 85.
11. Central Pollution Control Board. Pollution control acts, rules and notifications issued there under, pollution control Law Series: PCLS/02/2006; Ministry of Environment and Forests, Govt. of India: New Delhi, 2006.
12. Zeng, X.; Ruckenstein, E. Ind Eng Chem Res 1996, 35, 4169.
13. Wang, J.; Yue, Z.; Ince, J. S.; Economy, J. J Membr Sci 2006, 286, 333.
14. Zhao, Z. P.; Li, J.; Chen, J.; Chen, C. X. J Membr Sci 2005, 251, 239.
15. Zhao, Z. P.; Li, J.; Wang, D.; Chen, C. X. Desalination 2005, 184, 37.
16. Miao, J.; Chen, G.; Gao, C.; Lin, C.; Wang, D.; Sun, M. J Membr Sci 2006, 280, 478.
17. Zhao, Z. P.; Wang, Z.; Wang, S. C. J Membr Sci 2003, 217, 151.
18. Sastri, V. S. Sep Sci Technol 1978, 13, 475.
19. Clesceri, L. S.; Greenberg, A. E; Eaton, A. D. Standard Methods for the Examination of Water and Wastewater, 20th ed.; American Public Health Association, American Water Work Association, and Water Environment Federation: Washington, DC, 1998.
20. Sun, S.; Wang, A. J Hazard Mater 2006, 131, 103.
21. Sun, S.; Wang, L.; Wang, A. J Hazard Mater 2006, 136, 930.
22. Lu, X.; Bian, X.; Shi, L. J Membr Sci 2002, 210, 3.
23. Gao, Y. X.; Chen, Y. H. Membr Sci Technol 1998, 18, 11.
24. Buonomenna, M. G.; Lopez, L. C.; Favia, P.; d'Agostino, R.; Gordano, A.; Drioli, E. Water Res 2007, 41, 4309.
25. Afonso, M. D. Desalination 2006, 191, 262.
26. Bowen, W. R.; Mukhtar, H. J Membr Sci 1996, 112, 263.
27. Mohammad, A. W.; Othaman, R.; Hilal, N. Desalination 2004, 168, 241.
28. Murthy, Z. V. P.; Gupta, S. K. Desalination 1997, 109, 39.
29. Murthy, Z. V. P.; Gupta, S. K. J Membr Sci 1999, 154, 89.
30. Mehiguene, K.; Garba, Y.; Taha, S.; Gondrexon, N.; Dorange, G. Sep Purif Technol 1999, 15, 181.
31. Donnan, F. G. J Membr Sci 1995, 100, 45.
32. Senthilmurugan, S.; Ahluwalia, A.; Gupta, S. K. Desalination 2005, 173, 269.
33. Huang, R.; Chen, G.; Sun, M.; Hu, Y.; Gao, C. J Membr Sci 2006, 286, 237.
34. Frares, N.; Taha, S.; Dorange, G. Desalination 2005, 185, 245.
35. Murthy, Z. V. P.; Vaidya, S. Y.; Simaria, A. V. Indian J Chem Technol 2001, 8, 335.