

ORIGINAL RESEARCH PAPER

Multiwalled Carbon Nanotubes/Polyethersulfone Mixed Matrix Nanofiltration Membrane for the removal of cobalt ion

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ABSTRACT

In the present research work, the mixed matrix membranes (MMMs) containing various amount of polyethersulfone (PES) and functionalized multi-walled carbon nanotubes (fMWCNTs) were fabricated and used to investigate the removal of cobalt ions from wastewater by nanofiltration process. Pristine MWCNTs and fMWCNTs were characterized by Fourier transformed infrared spectroscopy and thermogravimetric analysis. FESEM analysis revealed that the mixed matrix membranes have fewer surface defects and better membrane performance compared with neat polymeric in the removal of cobalt ions. Permeation test results showed that the MMM containing 22 wt. % PES and 0.6 wt. % fMWCNTs (with an outer diameter of 10-20 nm) has the optimum performance from the permeability and cobalt removal point of view. In continuation, the effect of pressure, feed flow rate, cobalt concentration, permeation test time and feed solution pH on the removal of cobalt by selected the MMM was investigated. The obtained results indicated that only pressure has a considerable effect on permeation flux. However, all parameters showed different influence on rejection percent of cobalt ions.

Keywords: Cobalt; Multi-Walled Carbon Nanotubes; Nanofiltration; Polymeric Mixed Matrix Membranes; Removal

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INTRODUCTION

Nowadays, because of the excessive operation of some diverse industries, the amount of released heavy metals in the environment is on the increase. Cobalt is one of the heavy metals existed in the form of various salts in the environment. As a result of the widespread activities of various industries such as machines, paints, varnishes, metallurgical, electroplating and mining, a lot of waste stream rich in cobalt ions was produced [1]. Therefore, the accumulation of these contaminations in tissues of living organisms and their non-biodegradable properties can be a serious threat to a living being.

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The presence of cobalt at trace level in human beings has vital importance for metabolic processes while its higher concentrations can result in some disease for example; low blood pressure, lung irritations, paralysis, diarrhea, and bone defects, and may also cause mutations in living cells [2]. On the other hand, Cobalt-60 as one of the most important of cobalt radionuclides can produce and realize in the environment as a result of the operation of nuclear power plants. This radioisotope is usually generated in two ways; I) as a by-product of uranium fission and II) neutron activation of nonradioactive cobalt element present in the corrosion product of



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stainless steel equipment used in a nuclear power reactor establishment. Cobalt-60 is used in a large number of industries especially in medicine for radiotherapy [3]. Because of its gamma emission with high energy (2.5 MeV), beta emission and relatively long half-life ($t_{1/2}=5.26$ years), Cobalt-60 is a major concern in the field of water pollution [4]. Therefore, considering the threat of the excess amount of cobalt ion and its radionuclide (^{60}Co) in the environment to human and all other living beings, introducing a facile and effective method to reduce cobalt ion concentrations below the permissible level is vital.

Different treatment techniques such as precipitation [5], adsorption and biosorption [6], ion-exchange [7], solvent extraction [8], liquid membrane [9], nanofiltration [10] and combination of these methods [11] have been reported to eliminate cobalt ions from aqueous solution. Among them, nanofiltration (NF) which has been defined as a process intermediate between reverse osmosis (RO) and ultrafiltration processes is the most effective method. And that is due to its cost-effective, simplicity, higher flux compared to RO and suitable operation conditions for radioactive wastewater treatment. In addition, NF method presents high recovery rate and selective separation of multivalent ions from monovalent ions by various mechanisms such as size exclusion as well as Donnan and dielectric effects. These properties have considered NF as a promising process for the treatment and removal of heavy metals and hazardous radionuclides from nuclear and various industrial wastewater [12]. The most important materials used for fabricating membranes in NF process are polymers such as polyamide, acetate cellulose, polysulfone and polyethersulfone (PES). However, PES has been extensively used in NF membrane because of good mechanical, thermal, and chemical stability, usage in wide pH range, environmental endurance and a broader range of pore sizes. Nevertheless, the main problem in the application of PES is its relative hydrophobic character and consequently, membrane fouling as a result of adsorption of nonpolar solutes, hydrophobic particles or bacteria [13]. Hence, different approaches have been studied to improve the antifouling properties of PES membranes. One of the most effective manners is the addition of hydrophilic additives to the membrane for the preparation of the mixed matrix membranes (MMMs) [14].

In this regard, functionalized carbon nanotubes were mostly used to improve the membrane properties such as the increase in hydrophilicity and surface charge of membrane layer [15]. Because of particular properties of carbon nanotubes such as low mass density, compatibility with polymer membrane, permeability and high flexibility, it is well considered for the fabrication of the MMMs [16].

A survey of the literature shows that few studies have been performed on the MMMs membrane for the removal of cobalt from aqueous solution. However, no work has been yet reported on the fabrication and application of NF membrane including PES and functionalized MWCNTs for the removal of cobalt ions. Therefore, the aim of this study was to fabricate PES/fMWCNTs Mixed Matrix Nanofiltration Membrane for the removal of cobalt(II) ions from wastewater by nanofiltration process.

EXPERIMENTAL

Materials

Polyethersulfone (PES) used in this work was purchased from BASF SE, Germany. MWCNTs (purity=95%, outer diameter =10-20 nm, length = 5-15 μm) was supplied by Chengdu Organic Chemical Co. Ltd., China. Other chemicals and reagents used were of the analytical grade obtained from E. Merck or Fluka companies. A stock solution of cobalt (1000 mg.L^{-1}) was prepared by dissolving a specific amount of cobalt nitrate in demineralized water (DMW). To prepare the solutions with desired concentrations, this stock solution was further diluted with demineralized water. Meanwhile, to adjust the solution pH, nitric acid and sodium hydroxide solutions with the concentration of 0.01 mol.L^{-1} was used.

Purification and functionalization of MWCNTs

As purchased MWCNTs have some impurities such as amorphous carbon, carbon block, graphite sheet and nanoparticles on the internal and external surface of MWCNTs, it is necessary to be removed. Hence, the pristine MWCNTs were immersed in 3M nitric acid solution and shaken in an ultrasonic (Daihan, Korea) for 24 h in ambient temperature. After that, the mixture was filtered through a polytetrafluoroethylene (PTFE) filter membrane ($0.45 \mu\text{m}$ pore size), washed by DMW for several times, and dried for 24 h in an oven at 50°C .

On the other hand, to introduce the functional

groups on the surface of purified MWCNTs and to modify their surface, a specified amount of purified MWCNTs were mixed with concentrated nitric acid (65%) and refluxed for 3 h at 140°C. In the next step, the functionalized MWCNTs (fMWCNTs) was filtered and washed by DMW to achieve a pH value of 6.5. In the end, fMWCNTs were dried in an oven for 24 h at 85°C [17].

Membrane Fabrication

The flat sheet nanofiltration membranes including pure PES and PES/fMWCNTs were fabricated by a wet phase inversion method. For this purpose, the specific amount of pure PES was added to N-methyl pyrrolidone (NMP). For particle uniform dispersion in a solvent, the suspension was sonicated for 30 minutes and stirred for 24 h. To prepare the MMMs, at first, the specific amount of fMWCNTs (0.05, 0.1, 0.3 0.6 and 1 %wt) was added to NMP and after the dispersion of fMWCNTs in NMP by ultrasonic bath (for 30 min), PES was then added to the mixture and sonicated for 30 minutes and stirred for 24 h to be distributed entirely in the solvent. For omitting the air bubbles (degassing) in both mixtures, the polymeric solutions were sonicated again for 30 min and were allowed to settle overnight. The mixtures were casted on a glass plate by a casting knife with a thickness of 150µm and they were immersed immediately in DMW bath. To complete phase separation and removal of the remaining solvent from the membrane, the obtained polymeric film was kept in distilled water for 24 h. Finally, the prepared flat sheet membranes were dried at ambient temperature [18].

Equipment

MWCNTs (before and after functionalization) were characterized by Fourier transformed infrared spectroscopy (FTIR) (Bruker, Vector

22, Germany) and thermogravimetric analyses (TGA; Rheometric Scientific, STA1500, England). Morphology of fabricated membranes was characterized by using field emission scanning electron microscopy (FESEM) model S-4160, Hitachi, Japan. Cobalt ions concentrations in feed and permeate solutions were analyzed by a UV-visible spectrometer (GBC, Cintra 6, Australia). In this method, the color intensity of the formed complex during the reaction of cobalt ions with thiocyanate was measured by reading the intensity of the absorbance at a 620nm wavelength [19]. The static contact angle was measured by the sessile drop method using a contact angle measurement instrument (OCA15EC, Dataphysics, Germany).

The performance of the pure PES and the mixed matrix membranes for cobalt removal was evaluated by permeation tests (permeate flux and rejection percentage). The experiments were carried out by a cross-flow stainless steel nanofiltration (NF) setup shown schematically in Fig. 1. As shown in Fig. 1, the NF setup is outfitted with a membrane cell with an effective area of 33 cm². This cell lay between two pressure gauges (Wika, Korea) for monitoring the operating pressure on both sides of the cell. In addition, the feed solution is pumped into the membrane cell using a high-pressure dosing pump (Jesco, Germany). Two flow-meter on permeate and retentate streams, one pressure control valve and one pressure safety valve are the other main constituents of the NF setup. After membrane cell, retentate solution is recycled to the feed container and permeate solution flows to the permeate container.

The permeate flux (J_v) in L.m⁻².h⁻¹ and the cobalt rejection percentage of membranes were calculated by equations 1 and 2, respectively:

$$J_v = \frac{Q}{A} \quad (1)$$

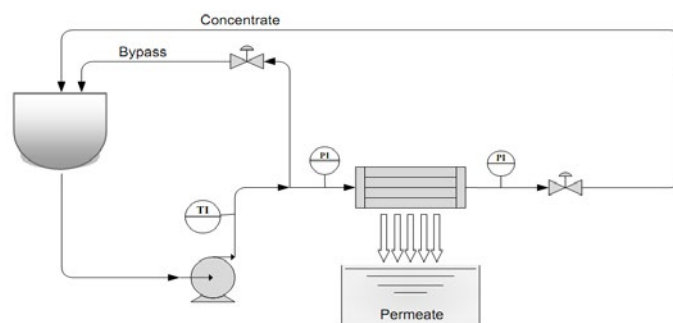


Fig. 1. Schematic depiction of nanofiltration setup

$$R (\%) = \left(1 - \frac{C_p}{C_f}\right) \times 100 \quad (2)$$

where Q is volumetric flow rate of permeate ($L \cdot h^{-1}$), A is the effective membrane area (m^2), C_p and C_f are cobalt concentration in permeate and feed solution, respectively.

RESULTS AND DISCUSSION

MWCNTs and membrane characterization

Fig. 2a and 2b Show FTIR spectra of Purified MWCNTs and fMWCNTs. In both spectra, two peaks at about 2930 and 2895 cm^{-1} can be assigned to the asymmetric and symmetric stretching vibrations of $\nu_{as}(CH_2)$ and $\nu_s(CH_2)$. The presence of the stretching vibration of $C=C$ in carbon

skeleton of graphite structure was confirmed by the peak at 1640 cm^{-1} . the stretching vibration properties of carboxylic groups are observed at 1540 and 1730 cm^{-1} [15]. The stretching vibration of OH band from carboxylic groups (COOH and COH) and adsorbed water molecules on the surface of MWCNTs and fMWCNTs can be seen by the asymmetric broad and strong bond between 3200 and 3700 cm^{-1} with a maximum at 3425 cm^{-1} . Moreover, the absorption bands at 2350 and 1130 cm^{-1} can also be assigned to O-H stretching vibration mode of strong H-bonded-COOH [21]. All of the mentioned bands became sharper after oxidation of MWCNTs by concentrated nitric acid.

TGA diagrams of the MWCNTs and fMWCNTs are shown in Fig. 3. As shown in TGA diagram of pristine MWCNTs (dashed line), a slight weight loss

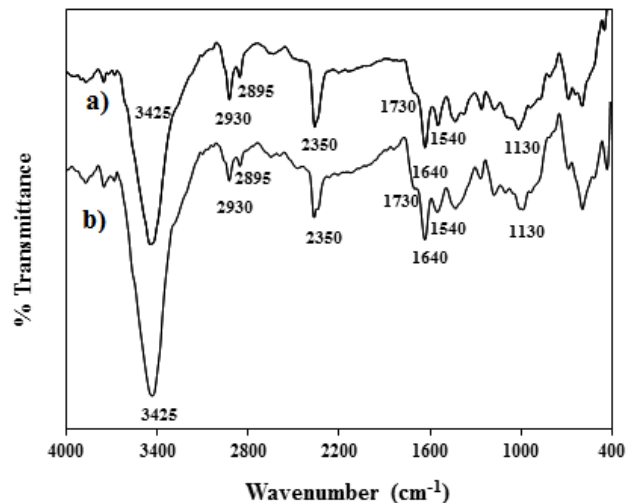


Fig. 2. FTIR spectra of MWCNTs (a) before and (b) after functionalization

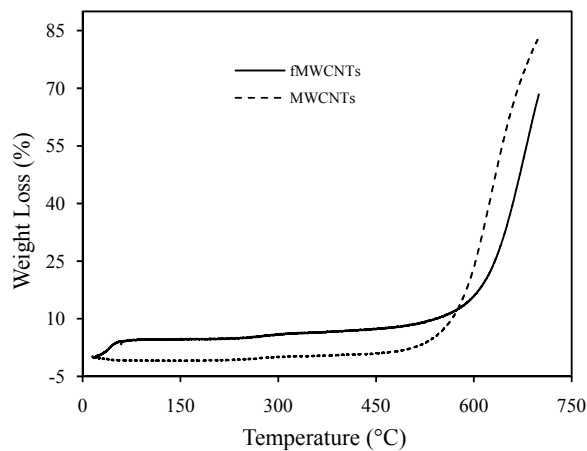


Fig. 3. TGA plots of pristine and functionalized MWCNTs

(about 2%) occurred below 250 °C can be attributed to the removal of physically adsorbed moisture and gases from the surface of MWCNTs. A drastic weight loss near 540 °C indicates the beginning of MWCNTs decomposition [22]. In comparison with the thermogram of fMWCNTs, some differences between these two thermograms were observed which can be attributed to the presence of phenolic, carbonyl and carboxyl groups on the surface of the fMWCNTs. Introducing functional groups to MWCNTs increases the polarity and hydrophilicity of fMWCNTs surface which consequently led to increasing of the amount of adsorbed moisture on the sample. Therefore, the relatively greater weight loss (about 6 wt. %) up to 250 was observed in the thermogram of fMWCNTs. In continuation of the thermogram, about 2 wt. % weight loss up to 540 °C is seen which is because of the decomposition of the attached functional groups. This weight loss

confirms the presence of phenolic, carbonyl and carboxyl groups on the surface of fMWCNTs [23]. Finally, considerable weight loss of around 540 °C is related to the fMWCNTs decomposition.

The membrane structure of PES before and after addition of fMWCNTs was studied by FESEM. Figs. 4(a, b) and 4(c, d) show the FESEM images of cross-sectional of pure PES and mixed matrix membranes (PES containing 0.6 wt% fMWCNTs), respectively. As can be seen, both membranes have an asymmetric cross-sectional structure in which sponge-like porous substrates support the dense active layer. The comparison between these figures shows that the finger-like macrovoids are shorter in the MMM compared with pure PES and these finger-like defects don't continue to the surface of the membrane. It means that the MMM probably has fewer surface defects than neat one and likely it exhibits better rejection properties

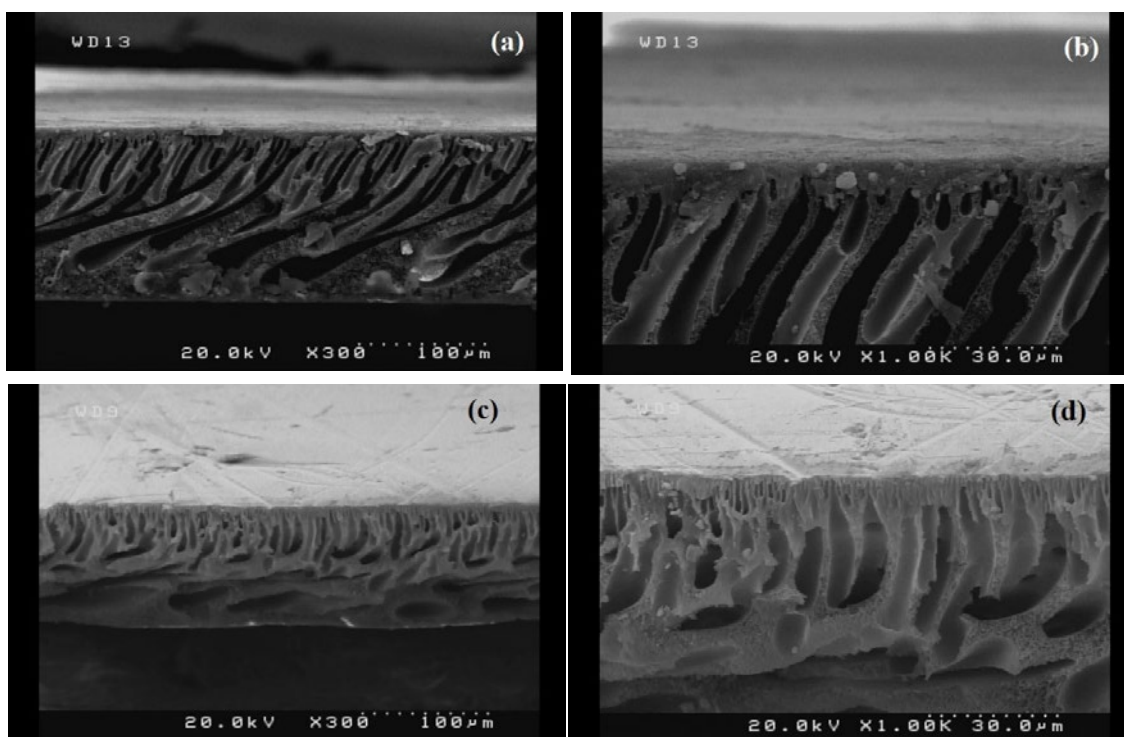


Fig. 4. Cross sectional FESEM micrographs of the neat membrane containing 22 wt. % PES (a and b) and the mixed matrix membrane containing 22 wt. % PES and 0.6 wt.% fMWCNTs (c and d)

Table 1. Water contact angels of neat membrane containing 22 wt. % PES and the MMM containing 22 wt. % PES and 0.6 wt.% fMWCNTs.

Sample	Contact angle
PES (22% wt.)	77.9 °
MMM (PES, 22%wt. / fMWCNTs, 0.6% wt.)	60.75 °

[24]. These effects can be attributed to the viscosity of polymeric solution which increases by the addition of fMWCNTs. This agent can delay phase inversion and limit nonsolvent attraction during phase inversion process [25]. Consequently, it would encourage the formation of macrovoids and contribute to larger flux [26].

The static contact angle was measured to evaluate the membrane surface hydrophilicity by the sessile drop method. Table 1 shows the obtained contact angles results of neat membrane containing 22 wt. % PES and the mixed matrix membrane containing 22 wt. % PES and 0.6 wt. % fMWCNTs. As shown, the contact angles of MMM is lower than that of neat PES membrane. This can be due to the presence of multiwall carbon nanotubes containing hydrophilic functional groups on the external surface of the membrane.

Permeation test results

In order to investigate the effect of polymer concentration on the behavior and performance of the membrane, four solutions containing 20, 22, 24 and 26 wt. % PES were prepared and fabricated by a wet phase inversion method. Fig. 5 shows the results of the permeability and cobalt ion rejection percentage. As can be seen, the membrane permeability decreased with an increase in polymer concentration. The rise in polymer content causes the increase of the viscosity and more adhesion of the polymer chains which lead to the rise in the thickness of polymer active layer and consequently the decrease in the size of porosity

[16]. This phenomena influence the amount of solvent passing and thus, reduce the amount of flux or permeability. On the other hand, the decline in the size of the membrane pores results in the rise in sieving property of the membrane and consequently increases the cobalt rejection.

By comparison the results and considering the amount of cobalt ion rejection percentage (60.15%) and flux (6.03), the membrane containing 22 wt. % PES was selected in the continuation of our work.

To investigate the effect of MWCNTs content on the removal of cobalt by the MMM, membranes containing 0.05, 0.1, 0.3, 0.6 and 1 wt. % (solid base) fMWCNTs in PES matrix (containing 22 wt. % PES) were fabricated. Fig. 6 shows the permeate results of the prepared membrane samples. As shown, the membrane permeates flux of the MMMs increases considerably as fMWCNTs increases by 0.05 wt. % of fMWCNTs and then it decreases by increasing the number of fMWCNTs. The initial increase of flux (from 6.03 to 9.95 L/m².h) can be explained by hydrophilic property of fMWCNTs in polymeric solution which consequently causes to increase the membrane porosity. Indeed, the addition of fMWCNTs containing functional groups and hydrogen bonds increases the water affinity of the MMM and causes fast exchange of solvent and non-solvent during phase inversion. Therefore, this exchange creates more pores in the membrane which results in more permeate flux. With the more increase of fMWCNTs, the viscosity increasing compensates the hydrophilic effect of fMWCNTs, which induce instantaneous

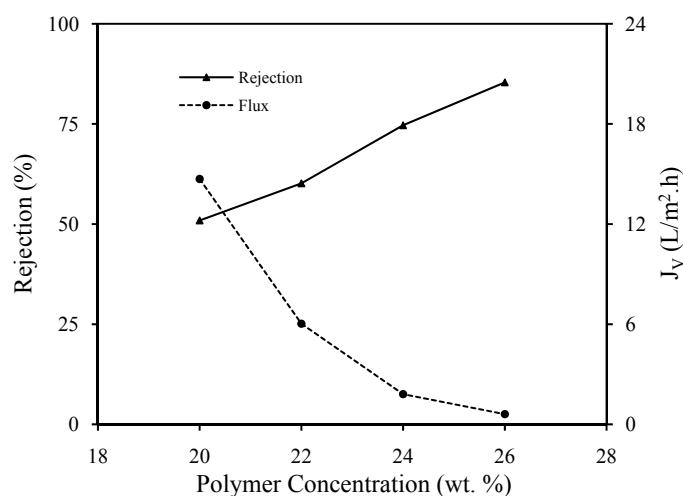


Fig. 5. Permeate flux and cobalt ion rejection percentage by the pure PES membranes versus the polymer concentration (wt.%) (20 bar, 40 L/h, 20 ppm Co(NO₃)₂, pH=5.5 ± 0.1, 90 min)

phase inversion. Hence, the membrane porosities decrease which lead to the permeate flux reducing in spite of membrane hydrophilicity increasing.

On the other hand, as can be seen in Fig. 6, with increasing of fMWCNTs in the mixed matrix membranes, the rise in cobalt ion rejection is observed.

It seems that restructuring of the membrane by adding the fMWCNTs and increment in hydrophilicity of the membrane gives rise to the increase in the water permeability without considerable permeation enhancement of cobalt. This phenomenon can be attributed to the created electrical charge on the membrane surface, due to the presence of fMWCNTs, which causes the

electrostatic attraction of the positive cobalt ions by negatively functional groups of fMWCNTs in the MMM [27]. In spite of the fact that the removal of cobalt in 1% fMWCNTs membrane is higher than other concentration of fMWCNTs, the fMWCNTs weight percentage of membrane in the next experiments was selected to be 0.6, base on the relatively good permeation flux (3.02 L/m².h) and good cobalt ion rejection percentage (83.51%).

The effect of pressure on permeate flux and rejection percentage of cobalt ions was studied at three different operating pressures (15, 20 and 25 bar). The diagram depicted in Fig. 7 shows the result of this study. Whereas the driving force in the membrane processes is the difference of the

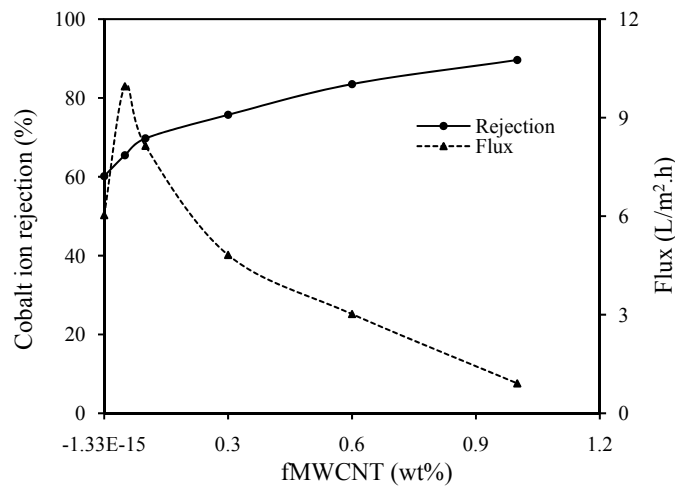


Fig. 6. Permeate flux and cobalt ion rejection percentage by the MMM (containing 22 wt. % PES) versus the different amount of fMWCNTs (20 bar, 40 L/h, 20 ppm Co(NO₃)₂, pH=5.5 ± 0.1, 90 min)

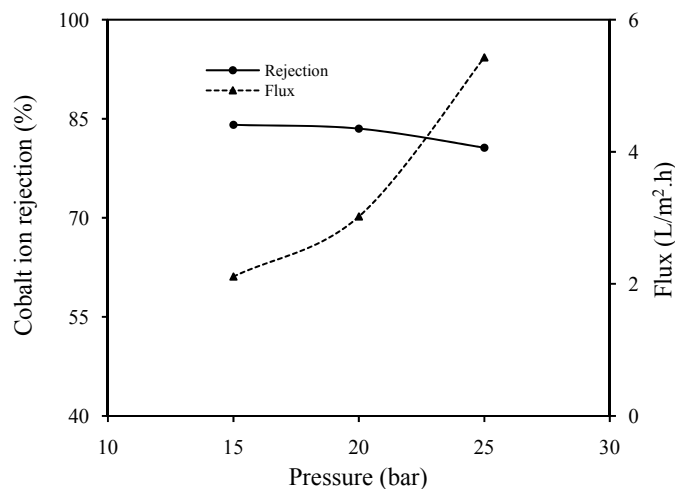


Fig. 7. Permeate flux and cobalt ions rejection percentage by the MMM containing 22 wt. % PES and 0.6 wt. % fMWCNTs versus operating pressure (40 L/h, 20 ppm Co(NO₃)₂, pH=5.5±0.1, 90 min)

pressure, it is evident that the increase in operating pressure leads to the rise in the permeate flux (Fig. 7). However, to obtain the high flux by increasing the operating pressure does not sound desirable from the commercial applications point of view (due to the need for greater investment in equipment and more operating costs). Furthermore, using higher operating pressures results in rapid fouling of the membrane which is another disadvantage of higher operating pressures [28]. Therefore, the operating pressure of 20 bar with higher cobalt ion rejection (83.51%) and permeation flux (3.02 L/m².h) was selected for the next parameter study.

On the other hand, Fig. 7 shows that cobalt ion removal remains almost constant by raising the

pressure. This phenomenon could be attributed to an intrinsic property of the fabricated membrane which has not been influenced by the pressure in the range of 15 to 25bar.

The feed flow rate was investigated as another important factor that could affect the performance of the membrane. For this purpose, the permeation test was performed on a PES/0.6 wt.% fMWCNTs at three different flow rates (10, 25 and 40 liters per hour). Fig. 8 shows the result of this study. As shown, the increase in the feed flow rate leads to a slight increase in the permeate flux. It can be attributed to the mass transfer mechanism affected by feed velocity [29]. In addition, an increase in feed flow rate causes a slight increase in cobalt ions rejection. Since

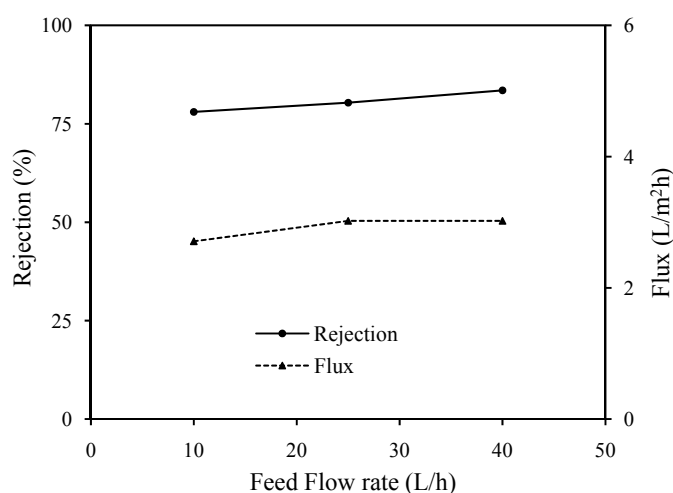


Fig. 8. Permeate flux and rejection percent of cobalt ions by the MMM containing 22 wt. % PES, 0.6 wt. % fMWCNTs versus Feed Flow rate (20 bar, 20 ppm Co(NO₃)₂, pH=5.5±0.1, 90 min)

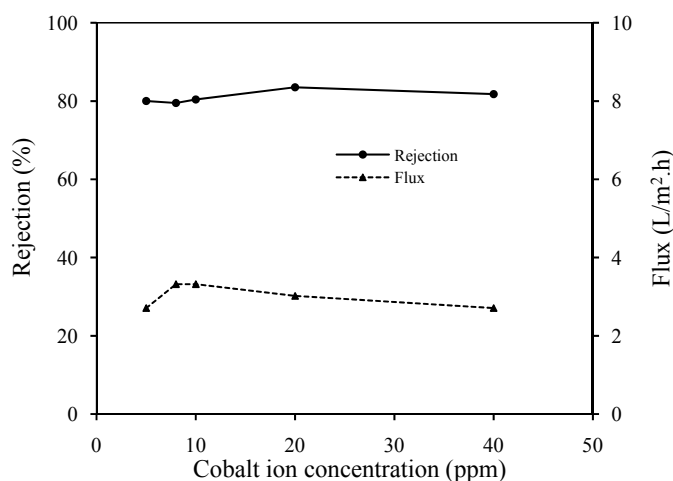


Fig. 9. Permeate flux and cobalt ions rejection by the MMM containing 22 wt. % PES, 0.6 wt. % fMWCNTs versus cobalt ion concentration in feed solution (20 bar, 40 L/h, pH=5.5±0.1, 90 min)

feed flow rate cannot affect separation performance of the membrane intrinsically, it can probably be due to the decrease in the thickness of the concentration polarization layer as a result of increasing the feed flow rate. This fact decreases the driven force and leads to the increasing rejection percent of cobalt ion. Contrary to this, some reports ascribed this phenomenon to the surface forces of the membrane which get stronger than forces within the membrane matrix as feed flow rate increases [30].

To evaluate the effect of cobalt ion concentration in feed solution on the separation performance of the MMM, solutions containing 5, 8, 10, 20, and 40 ppm of cobalt ions were prepared and used in permeation tests. The obtained results have been shown in Fig. 9. As can be seen, the permeate flux increases with a rise in cobalt ion concentration from 5 to 8 ppm and then decreases slightly by increasing the cobalt ions concentration. The increase of the permeate flux in the region of 5 to 8 ppm can be related to concentration polarization effect which increases when cobalt ions concentration increases in aqueous feed solution [28].

According to Fig. 9, the increase in the concentration of cobalt ions in the studied region has an insignificant effect on cobalt ions rejection by the MMM. It can be due to the formation of a complex between cobalt ions and carboxylic, ketone and phenolic functional groups of fMWCNTs in the MMM. In other words, with a rise in cobalt ion concentration, the interaction of Co^{2+} with these free groups to form a positively charged complex is increased. Therefore, the negative

charge of the membrane is reduced and may even be slightly positive. Consequently, the selectivity of the membrane could only be done by the space prevention induced by the size of solutes [31].

Fig. 10 shows the effect of permeation test time on rejection and permeate flux of the membrane at three different times of 30, 90 and 180 min. As can be seen, by increasing the time of the experiment, a slight decrease in permeate flux of the MMM (22 wt. % PES/ 0.6 wt.% fMWCNTs) is shown. This effect can be attributed to the concentration polarization effect which causes more mass transfer resistance and results in a decrease in permeate flux. In addition, Fig. 10 shows a downward trend in cobalt ions rejection from 84.63% (in 30 min) to 79.52% (in 180 min). It can be attributed to the salt concentration on the membrane surface which causes anions to be rejected by the negatively charged membrane surface. In other words, nitrate and cobalt concentration gradually increase in the locality of the membrane surface and consequently the fixed negative charge of the membrane is reduced. Therefore, it leads to a reduction of cobalt ions rejection [24].

The effect of feed solution pH on the rejection of cobalt ions and permeate flux was investigated. Fig. 11 shows the effect of the solution pH on the rejection of cobalt ions and permeate flux. According to the solubility product of $\text{Co}(\text{OH})_2$ ($\text{pK}_{\text{sp}} = 14.8$), it is clear that the most dominant species of cobalt at pH values above 6 was found to be as $\text{Co}(\text{OH})_2$, and other species such as Co^{2+} and $\text{Co}(\text{OH})^+$ is negligible. Therefore, at above pH, the fouling of the membrane is another challenge to investigate the scrutiny of

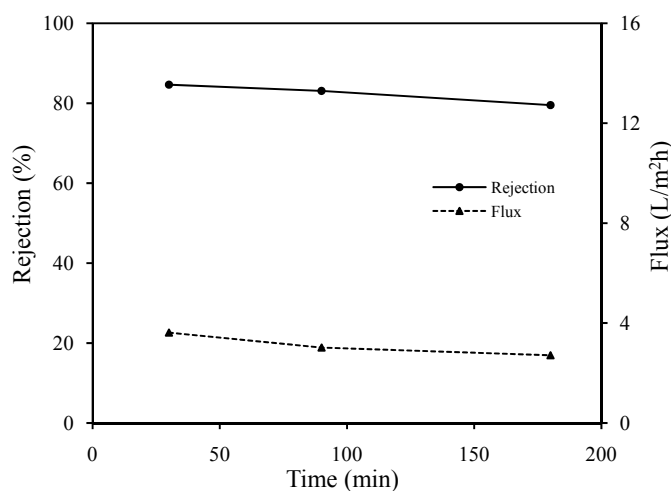


Fig. 10. Permeate flux and rejection percent of cobalt ions by the MMM containing 22 wt. % PES, 0.6 wt.% fMWCNTs versus time (PES-0.6 fMWCNTs, 20 bar, 40 L/h, 20 ppm $\text{Co}(\text{NO}_3)_2$, $\text{pH} = 5.5 \pm 0.1$)

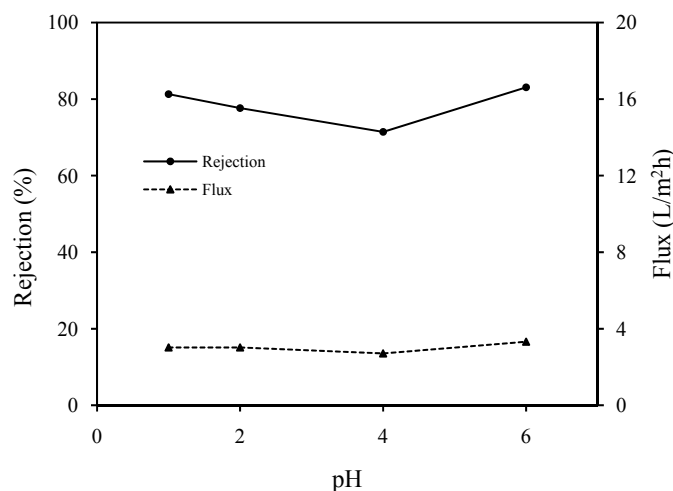


Fig. 11. Permeate flux and rejection percent of cobalt ions by the MMM containing 22 wt. % PES, 0.6 wt.% fMWCNTs versus the pH of the feed solution (20 bar, 40 L/h, 20 ppm $\text{Co}(\text{NO}_3)_2$, 90 min)

cobalt ion rejection by the MMM.

As shown in Fig 11, the change in the solution pH had a negligible effect on the permeate flux. However, there is a fall in cobalt ions rejection percent by increasing in the pH value up to 4. This can be explained by the change in the membrane surface charge while the solution pH increases. The membrane used in this research (PES) has neutral charge near pH=4 [32], which will be resulted in minimum removal of cobalt. It means that in this pH, the sieving mechanism is an only effective factor for the membrane selectivity because of steric hindrance of ions size.

As can be seen in Fig. 11, cobalt ion rejection increases in acidic pH below 4. When the solution pH decrease, the positive charge of the membrane increases and consequently rejects more Co^{2+} ions. Hence, the electrical charge in comparison with steric hindrance gives rise to more increase in cobalt ions rejection. On the other hand, the increase in pH solution (higher than 4) brings about an increase in the negative charge of the membrane. Consequently, nitrate ions are refused by the membrane and resulted in an increase in cobalt ion rejection because the cation and anion cannot act independently. In other words, Co^{2+} is rejected to keep the neutral electrical condition of the solution [33].

CONCLUSIONS

In this paper, multi-walled carbon nanotubes (MWCNTs) were purified and functionalized by nitric acid and characterized by FTIR and TGA experiments. In addition, the flat sheet membranes

containing different amounts of functionalized MWCNTs and PES were fabricated by wet phase inversion (immersion precipitation) technique and characterized by FESEM. The performance of the prepared pure PES and MMMs was investigated by Permeation tests for the removal of cobalt ions from wastewater. The results showed that the MMM containing 22 wt. % PES and 0.6 wt. % fMWCNTs has the best performance on the removal of cobalt ions. Moreover, the effect of operating conditions on the membrane performance for cobalt ions removal was studied in details. Permeation test results exhibit that the increase in operating pressure results in the increase in permeate flux while it does not have a considerable effect on cobalt rejection percentage. The increasing of feed flow rate indicated that both parameters, permeate flux and cobalt rejection, have increased slightly. It was found that by increasing cobalt ion concentration in the feed solution, the membrane flux first increased and then decreased while cobalt rejection remained almost constant. In addition, prolonging the test time affected on the MMM performance by a partial decrease in permeate flux and decrease in cobalt rejection. Also, the obtained results from the effect of feed solution pH on the membrane performance showed that feed pH does not have a significant effect on the permeate flux while the cobalt rejection decreased and then increased. The obtained results show that the prepared membrane can be a promising candidate for the removal of cobalt ions and other multivalent cationic from wastewater.

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CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

REFERENCES

- Chen J.P. 2012 Decontamination of Heavy Metals: Processes, Mechanisms, and Applications. Taylor and Francis Group, CRC Press.
- Alguacil FJ, Garcia-Diaz I, Lopez F, Sastre AM. Cobalt(II) membrane-extraction by DP-8R/Exxsol D100 using pseudo-emulsion based hollow fiber strip dispersion (PEHFSD) processing. *Separation and Purification Technology*. 2011;80(3):467-72.
- Omar H, Arida H, Daifullah A. Adsorption of ⁶⁰Co radionuclides from aqueous solution by raw and modified bentonite. *Applied Clay Science*. 2009;44(1-2):21-6.
- Jia F, Yin Y, Wang J. Removal of cobalt ions from simulated radioactive wastewater by vacuum membrane distillation. *Progress in Nuclear Energy*. 2018;103:20-7.
- Gokhale AS, Venkateswaran G, Moorthy PN. Waste treatment by ion-exchange and precipitation methods after lomi decontamination. *Waste Management*. 1994;14(8):703-8.
- Zhu Y, Hu J, Wang J. Removal of Co²⁺ from radioactive wastewater by polyvinyl alcohol (PVA)/chitosan magnetic composite. *Progress in Nuclear Energy*. 2014;71:172-8.
- Rengaraj S, Moon S-H. Kinetics of adsorption of Co(II) removal from water and wastewater by ion exchange resins. *Water Research*. 2002;36(7):1783-93.
- Swain B, Jeong J, Lee J-c, Lee G-H. Extraction of Co(II) by supported liquid membrane and solvent extraction using Cyanex 272 as an extractant: A comparison study. *Journal of Membrane Science*. 2007;288(1-2):139-48.
- León G, Guzmán MA. Facilitated transport of cobalt through bulk liquid membranes containing D2EHPA as carrier. Kinetic study of the influence of some operational variables. *Desalination and Water Treatment*. 2010;13(1-3):267-73.
- Gherasim C-V, Hancková K, Palarčík J, Mikulášek P. Investigation of cobalt(II) retention from aqueous solutions by a polyamide nanofiltration membrane. *Journal of Membrane Science*. 2015;490:46-56.
- Kryvoruchko AP, Atamanenko ID, Yurlova LY. Concentration/purification of Co(II) ions by reverse osmosis and ultrafiltration combined with sorption on clay mineral montmorillonite and cation-exchange resin KU-2-8n. *Journal of Membrane Science*. 2004;228(1):77-81.
- Al-Rashdi BAM, Johnson DJ, Hilal N. Removal of heavy metal ions by nanofiltration. *Desalination*. 2013;315:2-17.
- Van der Bruggen B. Chemical modification of polyethersulfone nanofiltration membranes: A review. *Journal of Applied Polymer Science*. 2009;114(1):630-42.
- Hosseini SM, Koranian P, Gholami A, Madaeni SS, Moghadassi AR, Sakinejad P, et al. Fabrication of mixed matrix heterogeneous ion exchange membrane by multiwalled carbon nanotubes: Electrochemical characterization and transport properties of mono and bivalent cations. *Desalination*. 2013;329:62-7.
- Mansourpanah Y, Madaeni SS, Rahimpour A, Adeli M, Hashemi MY, Moradian MR. Fabrication new PES-based mixed matrix nanocomposite membranes using polycaprolactone modified carbon nanotubes as the additive: Property changes and morphological studies. *Desalination*. 2011;277(1-3):171-7.
- Ismail AF, Goh PS, Sanip SM, Aziz M. Transport and separation properties of carbon nanotube-mixed matrix membrane. *Separation and Purification Technology*. 2009;70(1):12-26.
- Yavari R, Davarkhah R. Application of modified multiwall carbon nanotubes as a sorbent for zirconium (IV) adsorption from aqueous solution. *Journal of Radioanalytical and Nuclear Chemistry*. 2013;298(2):835-45.
- Vatanpour V, Esmaeili M, Farahani MHDA. Fouling reduction and retention increment of polyethersulfone nanofiltration membranes embedded by amine-functionalized multi-walled carbon nanotubes. *Journal of Membrane Science*. 2014;466:70-81.
- [19] Marczenko Z. & Balcerzak M. 2000 *Separation, Preconcentration and Spectrophotometry in Inorganic Analysis*, Volume 10 (Analytical Spectroscopy Library), Naokowskiego 3, 00-664 Warsaw, Poland.
- Asadollahi N, Yavari R, Ghanadzadeh H. Preparation, characterization and analytical application of stannic molybdophosphate immobilized on multiwalled carbon nanotubes as a new adsorbent for the removal of strontium from wastewater. *Journal of Radioanalytical and Nuclear Chemistry*. 2014.
- Vuković GD, Marinković AD, Čolić M, Ristić MD, Aleksić R, Perić-Grujić AA, et al. Removal of cadmium from aqueous solutions by oxidized and ethylenediamine-functionalized multi-walled carbon nanotubes. *Chemical Engineering Journal*. 2010;157(1):238-48.
- Xu J, Yao P, Li X, He F. Synthesis and characterization of water-soluble and conducting sulfonated polyaniline/para-phenylenediamine-functionalized multi-walled carbon nanotubes nano-composite. *Materials Science and Engineering: B*. 2008;151(3):210-9.
- Bustero I, Ainara G, Isabel O, Roberto M, Inés R, Amaya A. Control of the Properties of Carbon Nanotubes Synthesized by CVD for Application in Electrochemical Biosensors. *Microchimica Acta*. 2005;152(3-4):239-47.
- Daraei P, Madaeni SS, Ghaemi N, Ahmadi Monfared H, Khadivi MA. Fabrication of PES nanofiltration membrane by simultaneous use of multi-walled carbon nanotube and surface graft polymerization method: Comparison of MWCNT and PAA modified MWCNT. *Separation and Purification Technology*. 2013;104:32-44.
- Taniguchi M, Kilduff JE, Belfort G. Low fouling synthetic membranes by UV-assisted graft polymerization: monomer selection to mitigate fouling by natural organic matter. *Journal of Membrane Science*. 2003;222(1-2):59-70.
- Barth G, Gonçalves MC, Pires ATN, Roeder J, Wolf BA. Asymmetric polysulfone and polyethersulfone membranes: effects of thermodynamic conditions during formation on their performance. *Journal of Membrane Science*. 2000;169(2):287-99.
- Vatanpour V, Madaeni SS, Moradian R, Zinadini S, Astinchap B. Fabrication and characterization of novel antifouling

- ing nanofiltration membrane prepared from oxidized multiwalled carbon nanotube/polyethersulfone nanocomposite. *Journal of Membrane Science*. 2011;375(1-2):284-94.
28. Qin J, Dai X, Zhou Y, Zhang L, Chen H, Gao C. Desalting and recovering naphthalenesulfonic acid from wastewater with concentrated bivalent salt by nanofiltration process. *Journal of Membrane Science*. 2014;468:242-9.
- [29] Winston Ho W.S. & Sirkar M.M. 1992 *Membrane Handbook*, Springer.
30. Frarès NB, Taha S, Dorange G. Influence of the operating conditions on the elimination of zinc ions by nanofiltration. *Desalination*. 2005;185(1-3):245-53.
31. Paugam L, Taha S, Dorange G, Jaouen P, Quéméneur F. Mechanism of nitrate ions transfer in nanofiltration depending on pressure, pH, concentration and medium composition. *Journal of Membrane Science*. 2004;231(1-2):37-46.
32. Boussu K, Van der Bruggen B, Volodin A, Van Haesendonck C, Delcour JA, Van der Meeren P, et al. Characterization of commercial nanofiltration membranes and comparison with self-made polyethersulfone membranes. *Desalination*. 2006;191(1-3):245-53.
33. Ismail AF, Hassan AR. Formation and characterization of asymmetric nanofiltration membrane: Effect of shear rate and polymer concentration. *Journal of Membrane Science*. 2006;270(1-2):57-72.