



Research Article

Performance Evaluation of Polyethersulfone Membranes for Competitive Removal of Cd^{2+} , Co^{2+} , and Pb^{2+} Ions from Simulated Groundwater

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This paper presents studying the performance of three types of polyethersulfone (PES) membrane for the simultaneous removal of Co^{2+} ions, Cd^{2+} ions, and Pb^{2+} ions from binary and ternary aqueous solutions. Co^{2+} ions, Cd^{2+} ions, and Pb^{2+} ions with two different initial concentrations (e.g., 10 and 50 ppm) were selected as examples of heavy metals that contaminate the groundwater as a result of geological and human activities. This study investigated the effect of types of PES membrane and metal ions concentration on the separation process. For the binary aqueous solutions, the permeation flux of the PES2 membranes was higher for the separation process of solutions containing 50 ppm of Cd^{2+} ions and 10 ppm of Co^{2+} ions ($24.7 \text{ L/m}^2 \cdot \text{h}$) and Pb^{2+} ions ($23.7 \text{ L/m}^2 \cdot \text{h}$). All the metals in the binary solutions had high rejection when their initial concentration was lower than the initial concentration of the other metal present in the same solution. Using PES2, the maximum rejection of Cd^{2+} ions was 61.3% when the initial concentrations were 50 ppm Pb^{2+} ions: 10 ppm Cd^{2+} ions and 55.4% for Pb^{2+} ions when the initial concentrations were 10 ppm Pb^{2+} ions: 50 ppm Cd^{2+} ions. For the ternary aqueous solutions, the rejection and the permeation flux of the PES membranes increased with decreasing the heavy metal initial concentration. Using PES2, the maximum permeation flux was $21.6 \text{ L/m}^2 \cdot \text{h}$ when the initial concentration of the metals was 10 ppm; and the maximum rejection of the metals obtained at initial concentration of 10 ppm was 50.5% for Co^{2+} ions, 48.3% for Cd^{2+} ions, and 40% for Pb^{2+} ions. The results of the filtration process using PES2 of simulated contaminated-groundwater indicated the efficient treatment of groundwater containing Co^{2+} , Cd^{2+} , and Pb^{2+} ions.

1. Introduction

Nowadays, contamination of groundwater is one of the most important environmental issues because it contains wide

range of contaminants that influence water resources such as heavy metals [1]. The sources of groundwater pollution by heavy metals are mainly geological actions and human activities represented by industries and domestic activities

[2]. A potential source of groundwater pollution by heavy metals is contaminant seepage from the disposal sites as well as they are normally present in high concentrations in the landfill leachate [3]. Heavy metals such as cadmium, copper, lead, nickel, and zinc are naturally occurring elements and are actually necessary for human health when they are present in small amounts in our environment [4]. However, various industrial activities release different concentrations of heavy metals in water such as textile industries, battery manufacturing, electroplating, automotive industries, mining, and metal finishing [5]. Discharges of different industrial activities are the main reasons of water pollution because they consist of different poisonous heavy metal ions that accumulate in microorganisms and aquatic fauna and flora which may enter inside the human body through a food chain causing health problems [6].

Also, the discharges of the nuclear fuel cycle and the production and applications of radioisotopes are the main reason behind pollution by radioactive waste. Besides, the other sources of radioactive waste are the byproducts resultant of exploitation of natural resources and raw materials containing radioactive isotopes that are used for the production of agricultural and medical products [7]. The waste stream of these activities may contain radionuclides of individual elements such as cesium, molybdenum, strontium, iodine, tritium, cobalt, actinides, and lanthanides [8]. The contaminated soil and water by radioactive wastes have harmful effects on the living organisms, natural resources, and the environment; thus, they are hazardous to the health and safety of the human and other creatures [7].

Because the removal of heavy metals and radioactive wastes that exist in the form of cations has become an urgent issue, different treatment technologies have been used and improved so far to achieve an effective reduction of the concentrations of the toxic pollutant such as chemical precipitation, evaporation, extraction, membrane filtration, adsorption, coagulation, flocculation, sedimentation, thermal treatment, and ion exchange [9–12]. The above techniques show some drawbacks such as the cost of flotation and chemical precipitation resulting from generating extra sludge; poor selectivity and high sensitivity to pH for the ion-exchange process, nonselective, and generating intractable sludge for adsorption process. However, both ion exchange and adsorption are relatively low-cost, easily handled, and effective for low metal concentrations [13–15].

Membrane filtration technologies including microfiltration (MF), nanofiltration (NF), membrane distillation (MD), and reverse osmosis (RO) are successfully able to offer a significant solution in the field of the environment such as reducing of pollutions, reusing of water, and recycling of the valuable elements from waste effluents [16–19]. Different membrane technologies were applied for the membrane bioreactor (MBR) technique to treat the oil refinery wastewater [20–22], ultrafiltration membrane for dye removal from leather tanning factory [23, 24], ultrafiltration membrane for treating refinery wastewater [25], ultrafiltration membrane for protein and dye removal [26], and ultrafiltration and nanofiltration membranes for produced water treatment [27]. Also, membrane technologies have been considered as

promising technologies for removing heavy metals and radioactive wastes because they are highly efficient (high rejection to contaminants), easy to operation, saving space, reliable, and comparatively low energy consumption [14, 28].

Nanofiltration (NF) is theoretically more efficient than ultrafiltration (UF) and gives higher permeate than reverse osmosis (RO); therefore, it has attracted much attention in the applications including food, pharmaceutical, petrochemical industries, and wastewater treatment [15]. Separation of metal ions by NF occurs via size exclusion (sieving effect) and Donnan exclusion (electrostatic repulsion) [29]. The structural features of NF membranes create this combination of effects [30]. In the size exclusion, the species are strictly retained if they have larger hydrated size than the membrane pore size; however, the membrane pores were an obstacle to the species with a similar size. In the Donnan (charge) exclusion, the ions with the same charge (coions) are repelled by a membrane with fixed charged groups while the ions with an opposite charge (counterions) are attracted [31]. NF demands lower pressure and thus lower energy than RO, and it allows high permeate rate with selectively high rejection of divalent ions but low rejection monovalent ions which make NF recommended for treating various industrial effluents and drinking water [30, 32].

Due to the intrinsically rigid nature of lead, cadmium, and cobalt ions when they are discharged into the environment, and their major toxicity with the noxious effect on organic systems, the present work is mainly focused on using the filtration process to treat a simulated groundwater. In the current work, three types of PES membranes were prepared and examined for the removal of lead, cadmium, and cobalt ions from binary and ternary aqueous solutions at various conditions including initial metal ion concentrations and ratio of metals.

2. Chemicals and Experimental Work

Polyether sulfone (PES type Radel, provided by Solvay Advanced Polymers, Belgium) was used to prepare three different PES membranes, which were symbolized by PES1, PES2, and PES3, by the dry/wet phase inversion method. The spinning parameters were air gap distance of 5 cm, extrusion pressure of 1.5 bar, and bore fluid flow rate of 2.5 mL/min. This process required internal and external coagulants; thus, pure water was used for this purpose, and more details regarding the spinning process of hollow fibers were presented elsewhere [33, 34]. PES1, PES2, and PES3 hollow fibers were examined in treating stimulated groundwater containing combination of Cd^{2+} and Co^{2+} and Pb^{2+} ions using crossflow pattern filtration module as shown in Figure 1. The membrane pore size and pore size distribution were measured using Atomic force microscopy (AFM) (SPM AA300; Angstrom Advanced Inc., Stoughton, MA, USA). Each hollow fiber was exposed to a wide surface analysis with an appropriate silicon tip. Also, the dimensions of the PES hollow fibers were measured via scanning electron microscopy (SEM) (TESCAN VEGA3 LM (Oxford Instruments), X-Man, Czech Republic). A statistical test of the pore size

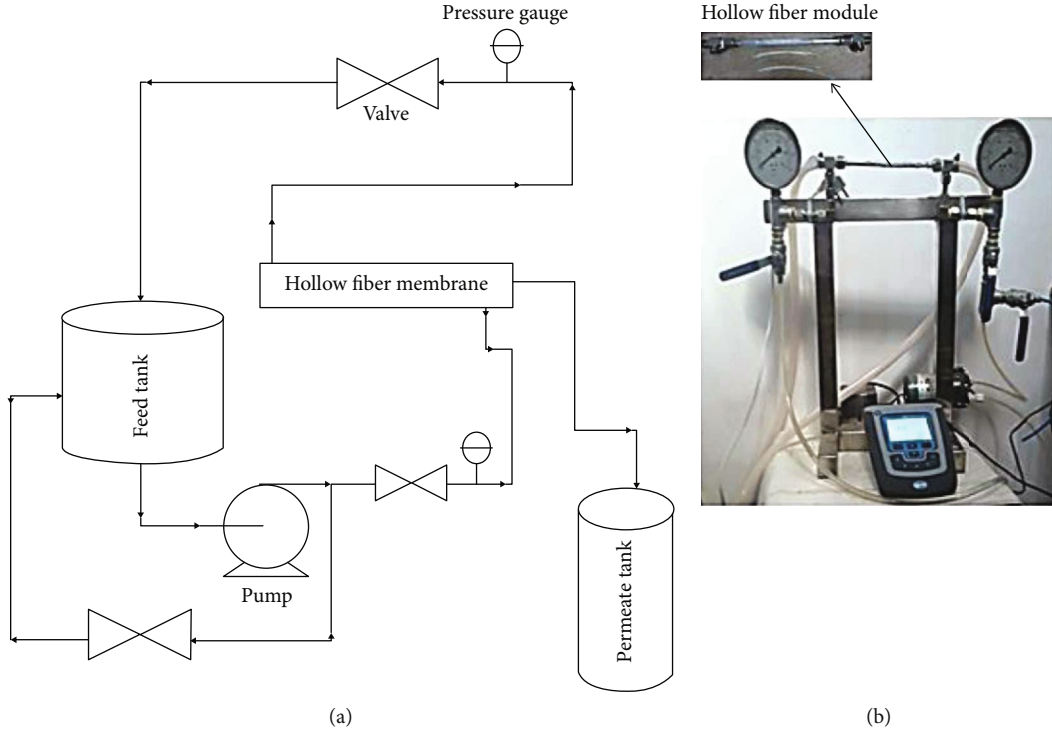


FIGURE 1: (a) A schematic diagram of the membrane filtration setup. (b) Photo of the membrane filtration setup and hollow fibers.

TABLE 1: The characteristics of the polyethersulfone (PES) membrane texture.

Membrane symbol	PES content (%)	Average pore size (nm)	Pore size distribution (nm)	Porosity (%)	Outside diameter (μm)	Inside diameter (μm)	Membrane thickness (μm)
PES1	29	52.04	25–100	52.5 ± 1.4	1012	620	196 ± 0.8
PES2	27	58.11	35–130	67.6 ± 0.9	958.4	576	191.2 ± 1.7
PES3	27	47.75	20–115	58.1 ± 1.1	1005	603.6	200.7 ± 2.1

was made for all PES hollow fiber surface via IMAGER 4.3.1 software [33].

The porosity (void fraction) of the hollow fiber ε (%) was estimated by measuring the density of the hollow fiber (e.g., weight of the sample divided by its volume). Then, the porosity of the hollow fibers was calculated by Equation (1) as follows:

$$\varepsilon = 1 - \frac{\rho_m}{\rho_p}, \quad (1)$$

where ρ_p is the density of the PES (g cm^{-3}) which was 1.370 g cm^{-3} , and ρ_m is the hollow fiber density (g cm^{-3}).

The characteristic of the surface morphology and the other specifications of the prepared PES membranes are displayed in Table 1. The simulated wastewater was prepared from dissolving nitrate salts of Cd^{2+} ions ($\text{Cd}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), Co^{2+} ions ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), and Pb^{2+} ions ($\text{Pb}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) ions in distilled water and stored in a polyethylene container at room temperature. The concentrations of metal ions in the solutions were prepared in the range of 10–250 ppm. The pH value of the stimulated wastewater was adjusted using 1 M HCl and 1 M NaOH

to be in the range of 5.5–6.5 [5], and the temperature of the solutions were maintained $25^\circ\text{C} \pm 3^\circ\text{C}$. The PES process was chosen to run at 1 bar during the removal process due to the low concentration of the metal ions.

Each hollow fiber was pressurized for 60 minutes at 3 bar to compact the fibers before measuring the permeation flux in a crossflow filtration mode. Equation (1) was used to calculate the permeate flux ($J_v, \text{L/m}^2 \text{ h}$).

$$J_v = \frac{V}{t \cdot A}, \quad (2)$$

where V (L) is the volume of permeate, t (h) is time to collect permeate, and A (m^2) is the surface area of the membrane. Each hollow fiber module has 7 hollow fibers with an effective area of 4.9×10^{-3} , 5.5×10^{-3} , and $5.8 \times 10^{-3} \text{ m}^2$, for PES1, PES2, and PES3, respectively. The feed flow rate was set on 0.6 (l/min) with a feed temperature of $25 \pm 3^\circ\text{C}$. Moreover, Equation (2) was used to calculate the rejection percentage ($R\%$) of metal ions.

$$R\% = \frac{C_b - C_p}{C_b} \times 100, \quad (3)$$

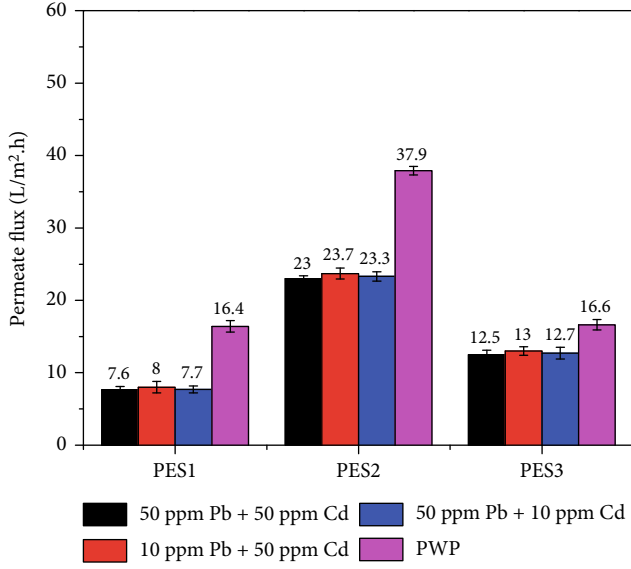


FIGURE 2: Effect of initial feed concentration of binary aqueous solutions containing Pb^{2+} ions and Cd^{2+} ions on permeate flux for three types of PES hollow fiber membrane ($pH 6 \pm 0.2$ and time 30 min, feed temperature of $25^\circ C \pm 3^\circ C$, and transmembrane pressure of 1 bar).

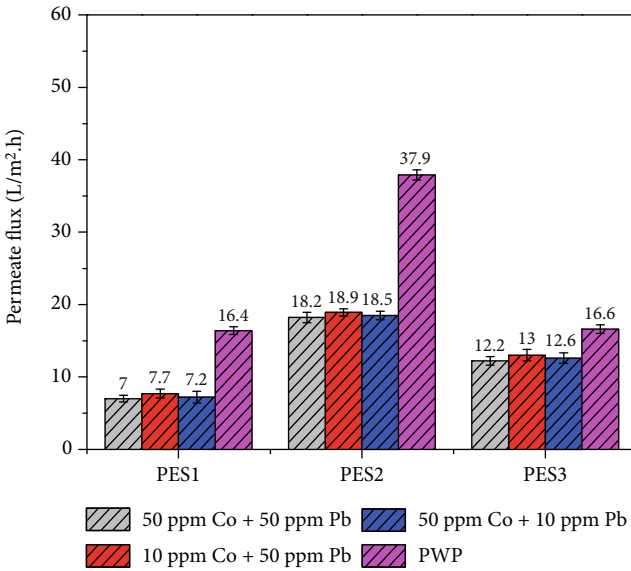


FIGURE 3: Effect of initial feed concentration of binary aqueous solutions containing Co^{2+} ions and Pb^{2+} ions on permeate flux for three types of PES hollow fiber membrane ($pH 6 \pm 0.2$ and time 30 min, feed temperature of $25^\circ C \pm 3^\circ C$, and transmembrane pressure of 1 bar).

where C_p is the concentration (ppm) of metal ions in permeate, and C_b (ppm) is an average of bulk concentration of metal ions in the feed (C_f , ppm) and concentrate/retentate (C_r , ppm) and is calculated using Equation (3).

$$C_p = \frac{C_f + C_r}{2}. \quad (4)$$

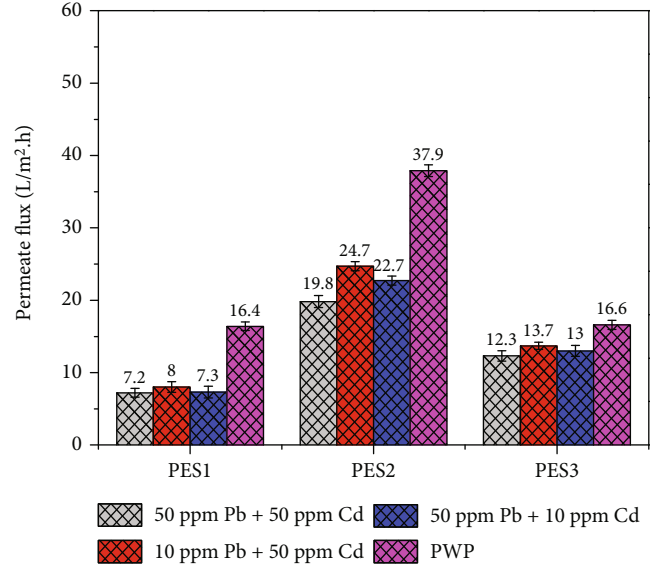


FIGURE 4: Effect of initial feed concentration of binary aqueous solutions containing Co^{2+} ions and Cd^{2+} ions on permeate flux for three types of PES hollow fiber membrane ($pH 6 \pm 0.2$ and time 30 min, feed temperature of $25^\circ C \pm 3^\circ C$, and transmembrane pressure of 1 bar).

To clean the setup, distilled water was used to rinse it for 60 min at 4 bar pressure after each set of experiments. Permeate of pure water then was measured to make sure that the initial flux of the membrane is restored.

The concentrations of metal ions in the samples were measured by an AAS-6200 atomic absorption flame emission spectrophotometer (Shimadzu Company, Japan). This equipment was frequently calibrated before start measuring each set of samples.

3. Results and Discussion

3.1. The Separation Performance of PES Fibers for Binary Solutions. The performance of separation Co^{2+} , Cd^{2+} , and Pb^{2+} ions from binary solutions using PES hollow fiber membranes was studied by measuring the permeate flux (shown in Figures 2–4) and metals rejection (Figures 5–7). Comparing to the permeate flux of pure distilled water (PWP), the results presented in Figures 2–4 show that all types of PES fibers gave permeation flux lower than for pure water permeate. PES2 had significantly higher flux among the other types when they were used for simulated wastewater. These results can be illustrated as that the efficacy of hollow fiber highly depends on the texture properties of membrane such as the wall thickness of the fiber, porosity, pore size, and pore size distribution at the fiber surface shown in Table 1. The characterization of PES2, PES1, and PES3 discussed previously in [35] showed that PES2 had the lower thickness, wider pore size distribution, larger pore size, and porosity; thus, it gave the higher permeation flux.

Figure 2 displays the effect of initial Pb^{2+} ion and Cd^{2+} ion concentration on the permeate flux for three types of PES membrane used for the separation of binary aqueous

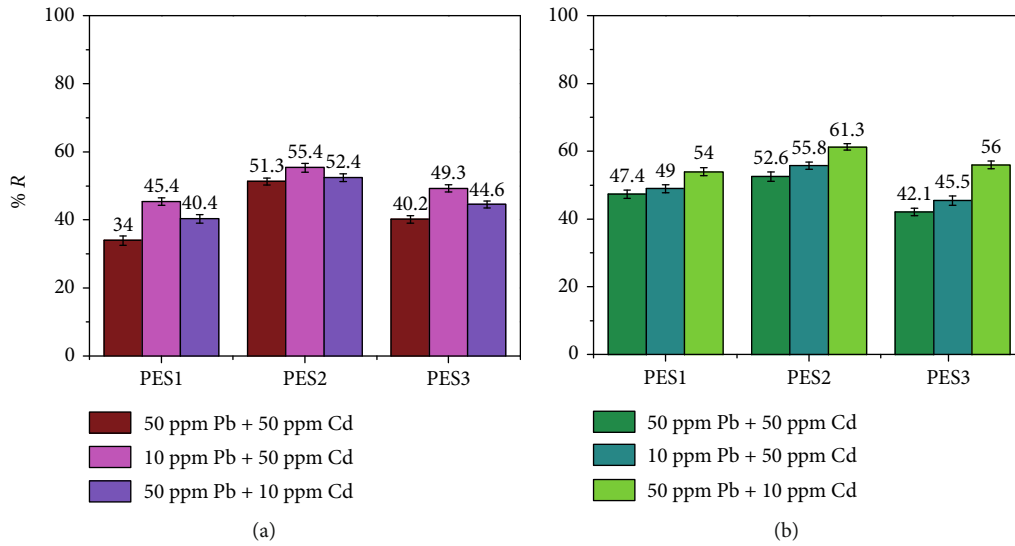


FIGURE 5: Effect of initial feed concentration of binary aqueous solutions containing Pb²⁺ ions and Cd²⁺ ions on rejection for three types of PES hollow fiber membrane (pH 6 ± 0.2 and time 30 min, feed temperature of 25°C ± 3°C, and transmembrane pressure of 1 bar). (a) Pb²⁺ ions. (b) Cd²⁺ ions.

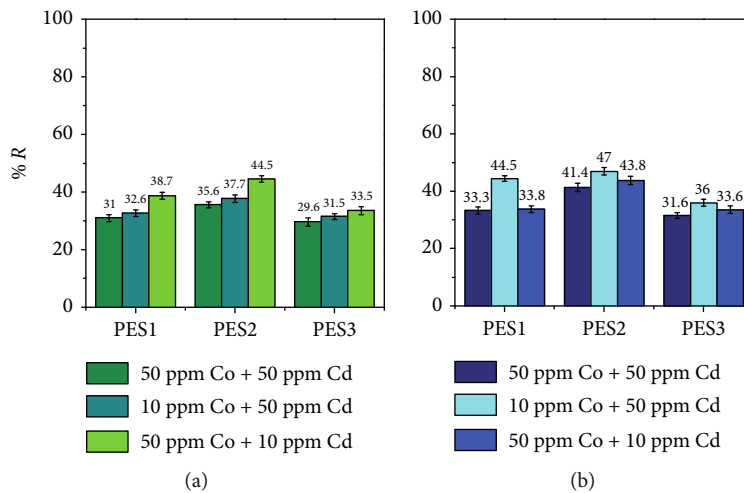


FIGURE 6: Effect of initial feed concentration of binary aqueous solutions containing Cd²⁺ ions and Co²⁺ ions on rejection for three types of PES hollow fiber membrane (pH 6 ± 0.2 and time 30 min, feed temperature of 25°C ± 3°C, and transmembrane pressure of 1 bar). (a) Cd²⁺ ions. (b) Co²⁺ ions.

solution at pH 6 ± 0.2 for a time of 30 min. For three types of fibers, changing the concentration ratio of Pb²⁺ ions to Cd²⁺ ions did not make change in the permeate flux in spite of reducing the concentration of Pb²⁺ ions to 10 ppm in the feed solution that slightly rose the flux. The maximum permeate flux obtained in this case was 23.7 L/m²·h.

Figure 3 displays the effect of initial Co²⁺ ion and Pb²⁺ ion concentration on the permeate flux for three types of PES membrane used for the separation of binary aqueous solution at pH 6 ± 0.2 for a time of 30 min. A comparison based on the permeation flux, same results were obtained for the three types of fibers when the concentration ratio of Pb²⁺ ions to Co²⁺ ions was changed in the feed solution. Also, reducing the concentration of Pb²⁺ ions to 10 ppm in the feed solution

caused slight increased the permeate flux to reach the maximum permeate flux of 18.9 L/m²·h.

The same results were obtained from Figure 4 that presents the effect of initial Cd²⁺ ion and Co²⁺ ion concentration on the permeate flux of PES1 and PES3 membrane used for the separation of binary aqueous solution at pH 6 ± 0.2 for a time of 30 min. The permeate flux obtained by PES2 was obviously changed when the Pb²⁺ ion concentration to Co²⁺ ion concentration changed in the feed solution, whereas the maximum permeation flux obtained was 24.7 L/m²·h when the concentration of Pb²⁺ ions in the feed solution was 10 ppm.

Figure 5 shows the rejection of Pb²⁺ ions and Cd²⁺ ions from binary aqueous solutions using three types of PES

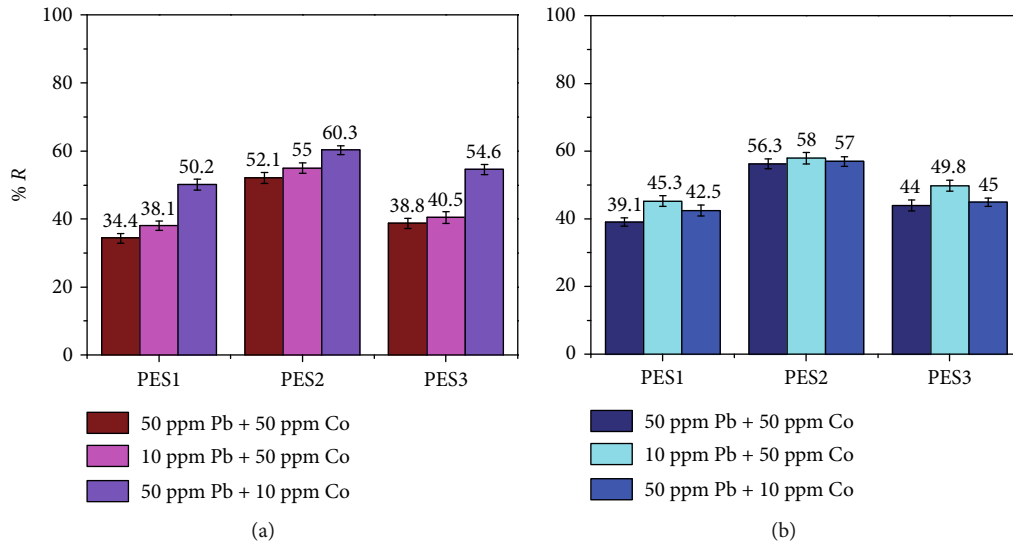


FIGURE 7: Effect of initial feed concentration of binary aqueous solutions containing Pb²⁺ ions and Co²⁺ ions on rejection for three types of PES hollow fiber membrane (pH 6 ± 0.2 and time 30 min, feed temperature of $25^\circ\text{C} \pm 3^\circ\text{C}$, and transmembrane pressure of 1 bar). (a) Pb²⁺ ions. (b) Co²⁺ ions.

hollow fiber membrane. In general, the rejection of Cd²⁺ ions was higher than of Pb²⁺ ions for different concentrations using all three types of membranes. The rejection of Cd²⁺ ions was higher when the initial concentration of Cd²⁺ ions was lower than the initial concentration of Pb²⁺ ions (i.e., 50 ppm Pb²⁺ ions: 10 ppm Cd²⁺ ions). Also, the rejection of Pb²⁺ ions increased when the initial concentrations were in the following sequence: 10 ppm Pb²⁺ ions : 50 ppm Cd²⁺ ions > 50 ppm Pb²⁺ ions : 10 ppm Cd²⁺ ions > 50 ppm Pb²⁺ ions : 50 ppm Cd²⁺ ions. Therefore, the higher rejection of Cd²⁺ ions (61.3%) was obtained using PES2 when the initial concentrations were 50 ppm of Pb²⁺ ions and 10 ppm of Cd²⁺ ions; however, it was 55.4% for Pb²⁺ ions when the initial concentrations were 10 ppm of Pb²⁺ ions and 50 ppm of Cd²⁺ ions using PES2.

Figure 6 shows the rejection of Co²⁺ ions and Cd²⁺ ions from binary aqueous solutions using three types of PES hollow fiber membrane. The results show that the rejection of Co²⁺ ions was higher than of Cd²⁺ ions for different concentrations using all three types of membranes, except when the initial feed contained 50 ppm Co²⁺ ions: 10 ppm Cd²⁺ ions, the rejection of both metals were convergent. The rejection of Cd²⁺ ions kept the same behavior obtained above as it was higher when the initial concentration of Cd²⁺ ions were in the following sequence: 50 ppm Co²⁺ ions : 10 ppm Cd²⁺ ions > 10 ppm Co²⁺ ions : 50 ppm Cd²⁺ ions > 50 ppm Pb²⁺ ions : 50 ppm Cd²⁺ ions. The rejection of Co²⁺ ions rose when the initial concentrations were in the following sequence: 10 ppm Co²⁺ ions : 50 ppm Cd²⁺ ions > 10 ppm Co²⁺ ions : 50 ppm Cd²⁺ ions > 50 ppm Pb²⁺ ions : 50 ppm Cd²⁺ ions. According to this, the higher rejection of Cd²⁺ ions (44.5%) was obtained using PES2 when the initial concentrations were 50 ppm Co²⁺ ions: 10 ppm of Cd²⁺ ions; but it was 47% for Co²⁺ ions when the initial concentrations were 10 ppm Co²⁺ ions and 50 ppm of Cd²⁺ ions using PES2.

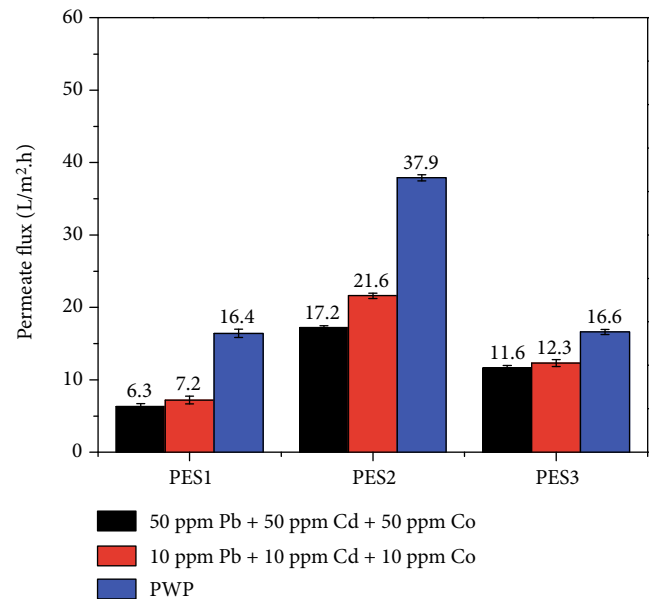


FIGURE 8: Effect of initial feed concentration of ternary aqueous solutions on permeate flux for three types of PES hollow fiber membrane (pH 6 ± 0.2 and time 30 min, feed temperature of $25^\circ\text{C} \pm 3^\circ\text{C}$, and transmembrane pressure of 1 bar).

The results of present rejection of Pb²⁺ ions and Co²⁺ ions from a binary solution containing using for three types of PES hollow fibers membrane are shown in Figure 7. Both the metal ions had the same behavior as before when they were incorporated with Cd²⁺ ions in binary solutions. The maximum rejection of Pb²⁺ ions (60.3%) was achieved using PES2 when the initial concentrations were 10 ppm Pb²⁺ ions: 50 ppm Co²⁺ ions, while the maximum rejection of Co²⁺ ions (58%) was achieved using PES2 when the initial concentrations were 10 ppm Pb²⁺ ions: 50 ppm Co²⁺ ions.

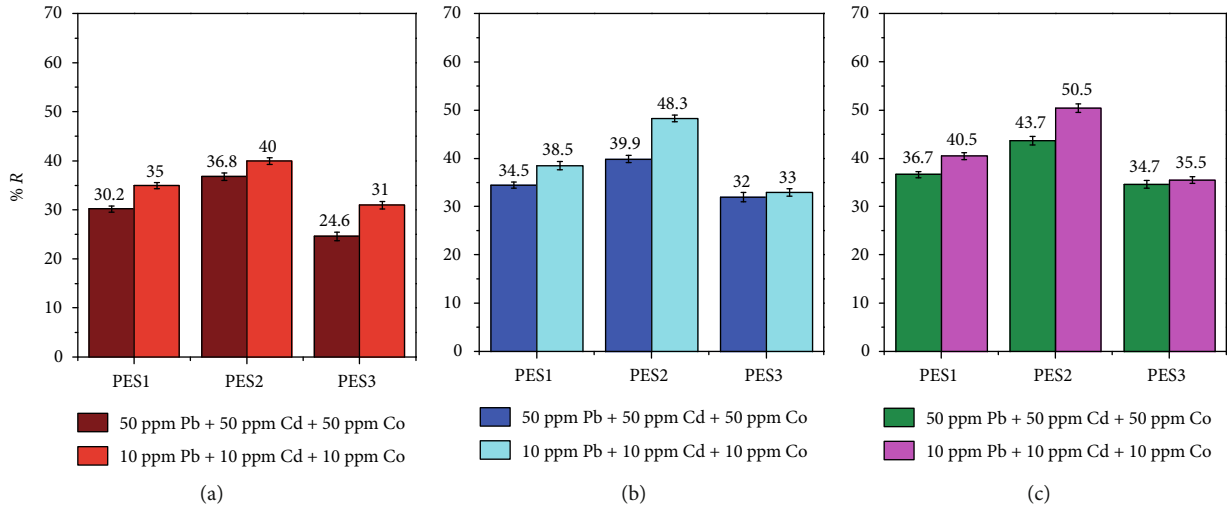


FIGURE 9: Effect of initial feed concentration of ternary aqueous solutions on the rejection for three types of PES hollow fiber membrane (pH 6 ± 0.2 and time 30 min, feed temperature of $25^\circ\text{C} \pm 3^\circ\text{C}$, and transmembrane pressure of 1 bar). (a) Pb^{2+} ions, (b) Cd^{2+} ions, and (c) Co^{2+} ions.

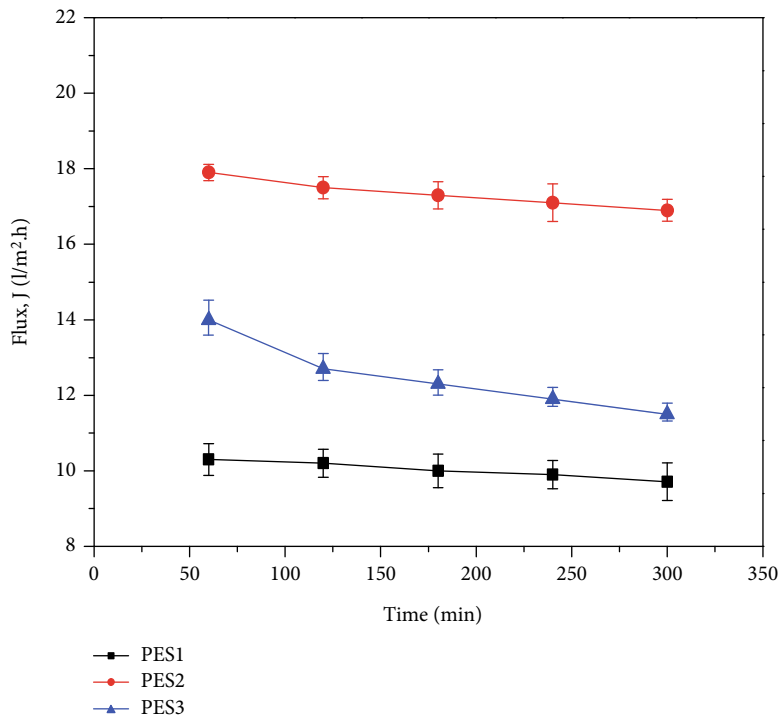


FIGURE 10: Effect of operating times for ternary aqueous solutions on permeate flux for three types of PES hollow fiber membrane (pH 6 ± 0.2 and time 300 min, feed temperature of $25^\circ\text{C} \pm 3^\circ\text{C}$, and transmembrane pressure of 1 bar) and concentration of metal ions 100 ppm.

In short words, for a separation of binary system using PES fibers, the higher rejection of metal can be obtained when its initial concentration was reduced to be less than the initial concentration of the other metal presenting in the same solution. Far from the effect of ionic radius of the studied metals on the removal process based on the sieving property of the membrane texture, this result can be related to the metal solubility in the aqueous solutions. Since the sol-

ubility of metal salts depends on the metal ion concentration and the pH of the solution, it is likely that the pH of a single metal solution changed when another metal ions is added which alters the solubility of metal ions in the solution [36, 37]. Increasing the solubility of metal ions due to the pH change leads to increase the tendency of metals to attach to water molecules and pass through the membrane pores within the permeate. Therefore, the rejection of the single

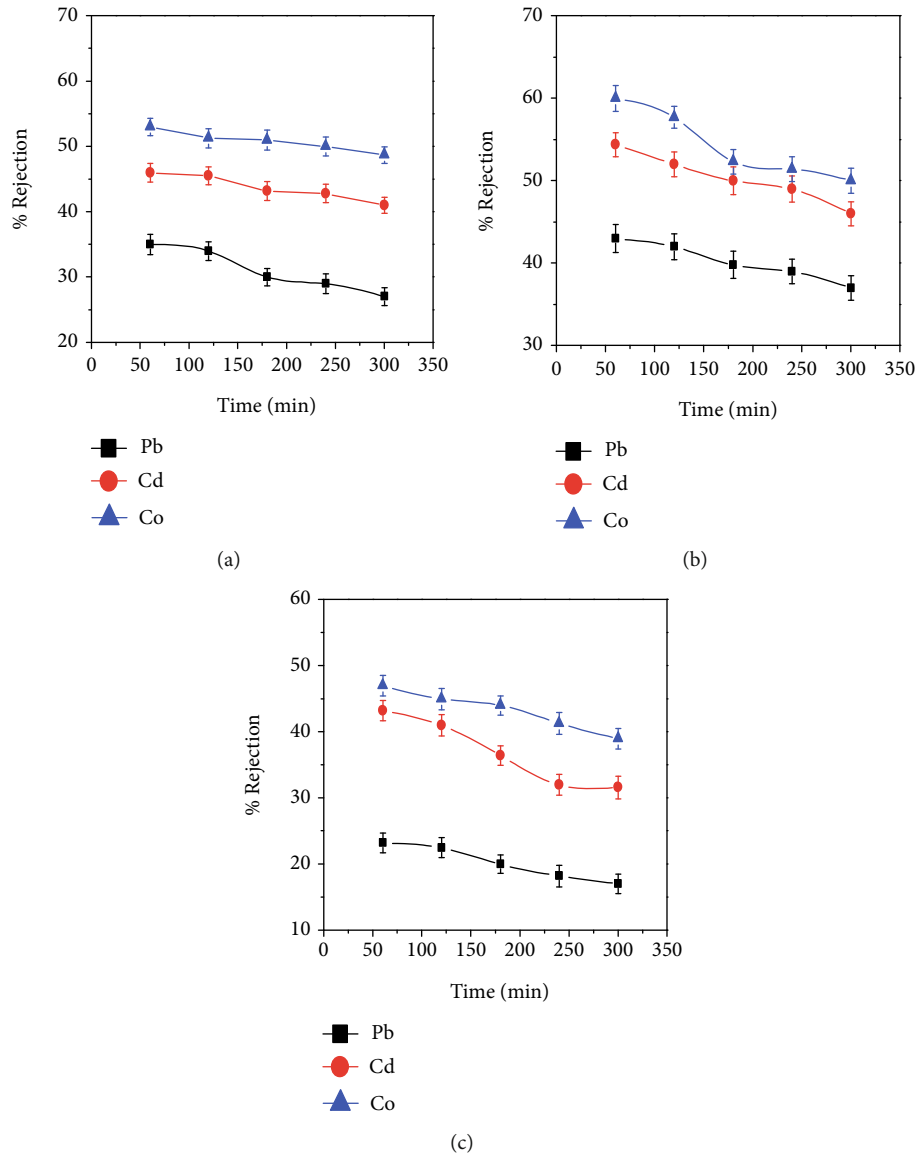


FIGURE 11: Effect of operating times for ternary aqueous solutions on rejection for three types of PES hollow fiber membrane ($\text{pH } 6 \pm 0.2$ and time 300 min, feed temperature of $25^\circ\text{C} \pm 3^\circ\text{C}$, and transmembrane pressure of 1 bar) and concentration of metal ions 100 ppm. (a) PES1, (b) PES2, and (c) PES3.

metals using the prepared PES fibers was significantly higher the rejection of them when they were incorporated in binary solutions in the current study [35].

3.2. The Separation Performance of PES Fibers for Ternary Solutions. Figure 8 shows the performance of the three prepared PES membranes during the separation process of the metal ions from ternary solution of two different initial metal concentrations (10 and 50 ppm). PES2 gave higher permeate flux than other membranes followed by PES3 and PES1, which can be attributed to the distinguished texture properties of PES2. The permeation flux of PES2 was $21.6 \text{ (L/m}^2\cdot\text{h)}$ when the initial metal concentrations was 10 ppm; however, it obviously dropped to $17.2 \text{ (L/m}^2\cdot\text{h)}$ when the initial metal concentrations increased to 50 ppm. The permeate

flux given by both PES1 and PES3 did not significantly vary when the initial metal concentrations changed from 10 to 50 ppm.

Figure 9 shows the rejection of the studied heavy metals from a ternary solution by three types of PES membranes in the separation process at a feed temperature of 25°C , $\text{pH} = 6 \pm 0.2$, and transmembrane pressure of 1 bar. According to the increasing of the rejection of the metals ions, the membranes were in the following order: $\text{PES2} > \text{PES1} > \text{PES3}$. Despite the ionic radius of these metals (Co^{2+} ions of 79 pm, Cd^{2+} ions of 97 pm, Pb^{2+} ions of 133 pm) [38], the tendency of each membrane towards the selected metals ions was as follows: Co^{2+} ions $>$ Cd^{2+} ions $>$ Pb^{2+} ions. This result can be attributed to that presence of Cd^{2+} ions and Co^{2+} ions in the solution containing Pb^{2+} ions led to change

TABLE 2: Comparison results of the present work and other membranes found in the literature that used for rejection of metal ions by considering the different parameters.

Membrane	Process	Heavy metals	Pressure (bar)	Heavy metal concentration	pH value	Rejection (%)	PWF (L/m ² h)	Ref.
PES (dead-end mode)	Complexation and UF-filtration with poly(itaconic acid)	Pb ²⁺	-	20 (ppm)	7	83.8	46.1	[39]
		Sn ²⁺				63.9		
		Zn ²⁺				57.1		
		Cu ²⁺				61.4		
		Cd ²⁺				36.5		
PVDF/APTES functionalized halloysite-magnetic graphene oxide/metformin	NF	Cu ²⁺	5	5 (ppm)	5.5	47.9	14.2	[40]
		Cd ²⁺				44.2		
		Cr ²⁺				52.3		
Dual layer polybenzimidazole/PES	NF	Cr ²⁺	-	200 (ppm)	12	98	8.3	[41]
		Pb ²⁺			93			
		Cd ²⁺			70			
DL provided by SEPA CF GE Osmonics, Florida, USA	NF (crossflow mode)	Cd ²⁺	3	0.001 Mol/l	6.83	48	20	[42]
		Zn ²⁺				60		
		Cu				65		
Polyamide flat sheet, spiral wound	Flat-sheet, spiral wound NF	Pb ²⁺ + Ni ²⁺	6	1	3-4	86 93	-	[43]
NF270 commercial membrane	Flat-sheet NF	Pb ²⁺	5	2000 (ppm)	1.5-5	74	12-33.8	[44]
		Cd ²⁺				99		
		Mn						
		As						
PES membrane	Hollow fiber UF	Ternary	1	10-50 (ppm)	6	40	16.4	This study
		Pb ²⁺				48.3	37.9	
		Cd ²⁺				50.5	16.6	
		Co ²⁺						
PES membrane	Hollow fiber UF	Binary	1	10-50 (ppm)	6	60.3		This study
		Pb ²⁺				58		
		Co ²⁺				44.5		
		Cd ²⁺						

the pH of the solution and increase the solubility of Pb²⁺ ions in the solution. Also, increasing the initial metal concentration reduced the rejection of all metals using three types of PES membranes. This behavior is obvious for PES2 membranes for Co²⁺ ions and Cd²⁺ ions; however, it was obvious for PES3 for Pb²⁺ ions.

Figure 10 shows the permeate flux for the three types of PES fibers with time of separation ternary aqueous solutions. The figure shows a slightly reduction in the permeate flux of the three types of PES fibers with operation time which can be due to the metal ion deposition on the fiber surface.

Figure 11 shows the rejection of Co²⁺ ions, Cd²⁺ ions, and Pb²⁺ ions from a ternary solution containing 100 ppm of each metal and pH of 6 ± 0.2 using three different PES membranes with operating time. The rejection of Cd²⁺ ions and Co²⁺ ions reduced sharply by both PES2 and PES3; however, the rejection of Pb²⁺ ions reduced similarly for the three membrane types. The maximum rejection obtained by PES2 was 60% for Co²⁺ ions, 54.4% for Cd²⁺ ions, and 43% for Pb²⁺ ions after 50 min. The minimum rejection

obtained by PES2 was 50% for Co²⁺ ions, 46% for Cd²⁺ ions, and 37% for Pb²⁺ ions after 300 min.

From the results of the current work, it can be observed that the rejection of the Co²⁺ ions was higher than Pb²⁺ ions. Both Co²⁺ and Pb²⁺ are co-ions; however, Pb²⁺ has a larger ability than Co²⁺ to move through the membrane under the effect of electrical potential gradient, and thus low rejection of Pb²⁺ ions was obtained. This can be because of the higher diffusivity that Pb²⁺ ions have (e.g., DPb²⁺, ∞ = 9.45 × 10⁻¹⁰ m²/s and DCo²⁺, ∞ = 7.32 × 10⁻¹⁰ m²/s). Also, the rejection of Co²⁺ ions was higher than that of the Cd²⁺ ions due to the slower movement of Co²⁺ within the membrane than Cd²⁺ under the effect of electrical potential gradient; therefore, lower cadmium rejected was obtained. This trend can be because of the higher diffusivity that Cd²⁺ ions have (e.g., DCd²⁺, ∞ = 14.4 × 10⁻¹⁰ m²/s and DCo²⁺, ∞ = 7.32 × 10⁻¹⁰ m²/s). Regarding the rejection mechanism of Pb²⁺/Cd²⁺ aqueous solution, it can be noticed that lower rejection of Pb²⁺ than Cd²⁺ because of the lower hydration energy of Pb²⁺ ions (e.g., -1755 kJ/mol of Cd²⁺ > -1425 kJ/mol of

Pb²⁺). The competitive removal of heavy metals for each membrane was reduced with increasing of the initial metal ion concentration due to the Donnan effect. When the pH value is higher than the isoelectric point (e.g., pH>5.5), the membrane surface has negative charge, whereas the metal ions are positively charged which increase the attraction between them. Also, increasing the metal ion initial concentrations leads to increasing the accumulation of ions on the surface of the membrane which causes clogging of pores, formation of cake layer, increasing the concentration polarization, and thus low ions rejection.

3.3. Comparative Study. Table 2 shows comparison results between the present work and other membranes found in the literature that are used for metal ion removal with considering different parameters. Also, this table presents the most important operating parameters such as feed solution pH, initial concentration of the heavy metals ions, and transmembrane pressure. The performance factor of the three PES membranes used in the present work simultaneously has reasonable values of the metal ion (Pb²⁺, Cd²⁺, and Co²⁺) rejection in comparison with that of different membrane separation processes selected from the literature. Moreover, it can be observed that the rejection of most of the heavy metals present simultaneously in a solution reduced in the same way of their rejection from solutions in which they individually present.

4. Conclusions

The current work studied the removal of Co²⁺ ions, Cd²⁺ ions, and Pb²⁺ ions from binary and ternary solutions using three types of PES membranes. PES2 proved its performance in the separation process for the binary and ternary solutions at different initial concentrations. The performance of the selected metal ions during the separation process changed when they were incorporated in binary or ternary aqueous solutions. For binary solutions, all the metals had high rejection when their initial concentration was lower than the initial concentration of the other metal present in the same solution. However, for ternary solution, the tendency of the three types of fibers tended to remove the metal ions according to this sequence: Co²⁺ ions > Cd²⁺ ions > Pb²⁺ ions. Also, the rejection of metals ions was higher when their initial concentrations reduced from 50 ppm to 10 ppm. Finally, the groundwater containing Co²⁺ ions, Cd²⁺ ions, and Pb²⁺ ions can be efficiently treated by the filtration process using PES hollow fibers.

Data Availability

The underlying data used to support the findings of the current work are included within the text of the manuscript.

Conflicts of Interest

The authors declare no conflict of interest.

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