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RESEARCH ARTICLE

Application of Zeolite Nanofiltration for Removal of Heavy Metals from Urban Wastewater

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Abstract

In this study, the adsorption and the filtration processes were coupled by a zeolite nanoparticle impregnated polysulfone (PSf) membrane which was used to remove the lead and the nickel cations from synthetically prepared solutions. The results obtained from X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) analysis indicated that the synthesized zeolite nanoparticles, using the conventional hydrothermal method, produced a pure NaX with ultrafine and uniform particles. The performance of the hybrid membrane was determined under dynamic conditions. The results also revealed that the sorption capacity, as well as the water hydraulic permeability of the membranes, could both be improved by simply tuning the membrane fabricating conditions such as evaporation period of the casting film and NaX loading. The maximum sorption capacity of the hybrid membrane for the lead and nickel ions was measured as 682 and 122 mg/g respectively at the end of 60 min of filtration, under 1 bar of transmembrane pressure. The coupling process suggested that membrane architecture could be efficiently used for treating metal solutions with low concentrations and transmembrane pressures.

Keywords: Adsorption, metal removal, Ultrafiltration, Zeolite nanoparticles

1. Introduction

The preservation of quality and adequate water resources to sustain the needs of modern society has become a major problem today, due to excessive increases in volumetric production of industrial effluents, as well as inadequate conventional wastewater treatments that do not meet the discharge limits proposed by the environmental and health organizations.

The conventional processes of removing heavy metals generally include chemical precipitation, ion-exchange and electrochemical deposition which have many disadvantages, such as high energy requirements especially when the contaminant concentrations range from 10 to 100 mg/L, excessive toxic sludge production which is required for further treatment and a lack of quality of the treated water within acceptable limits [1-5].

On the other hand, adsorption is considered to be a simple and effective method used in wastewater treatment especially when with low cost sorbents. Zeolites have also been extensively used in the application of separation and purification processes because of their well-defined porous structures and offering mobility of alkali and alkaline earth metals, in order to compensate net negative charge between Si^{4+} and Al^{3+} in the framework. Meanwhile, nanoparticles known as high efficient adsorbents are replaced with micrometer-sized counterparts due to their high specific surface area and interfacial activity [6-10]. However, instability, difficulty in regeneration and agglomeration of the nano-adsorbents during adsorption process is still a challenging issue. In addition, separation of the nano-adsorbents from treated water is limited its practical application. Membrane water treatments are successfully used in wastewater treatment and up to 98% rejection of cadmium ions through asymmetric PSf membrane has been reported. However, rejected metals cannot be recovered through these treatments: in concentrated solution they need further treatment [11-15]. As a result, more sophisticated membrane architectures are required to achieve desired objectives. A new class of membrane has recently been

designed by combining polymeric materials with nano-particles for the specific water treatments. The so-called hybrid membranes could provide desired outputs by simply tuning their hydrophilicity, their pore size, porosity, charge density and mechanical stability. Moreover, they introduce unique functionalities such as photocatalytic, antibacterial or adsorptive capabilities. For example, water flux and rejection values of the PSf membrane were simultaneously improved by simply adding a zeolite 4A to the membrane's selective layer [15-19].

In the following study, the adsorption and the filtration processes were coupled using a zeolite nanoparticle impregnated PSf membrane, which was used to remove the Ni^{2+} and the Pb^{2+} cations from synthetically prepared solution. In literature, homogeneous nano-composite membranes have been extensively studied in gas phase applications by utilizing the adsorption capabilities of the nanomaterials which alters the selectivity of the gas mixtures. However, limited studies concerning about the filtration performance and the removal capacity of the hybrid membrane against heavy metals under dynamic conditions have been reported in literature [20-24]. The objective of this study is to test the feasibility of the prepared membrane architecture for the removal of the metal ions. It is thought that, the combined approach can be used to improve water hydraulic permeability as well as metal sorption capacity of the membrane, while providing a continuous separation with low energy consumption and a complete treatment in a single step. For this purpose, zeolite nanoparticles were fabricated via conventional and microwave heating methods and then incorporated into a polysulfone. The physical and chemical structures of the prepared membranes were characterized by XRD, SEM-EDX, FTIR-ATR, TGA and water contact angle analyses. The effect of membrane fabricating conditions, including casting compositions, evaporating periods and the nanoparticles loading on the hydraulic permeability and on the metal sorption capacity of the membrane were examined [25-28].

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2. Materials and Methods

2.1 Materials

Polysulfone beads ($M_n=22,000$ g/mol) and N-methyl-2-pyrrolidone (NMP) for the preparation of ultrafiltration membranes were supplied by Sigma-Aldrich. During production of zeolite nanoparticles, fumed silica having $0.007\ \mu\text{m}$ particle size and sodium aluminate from Sigma-Aldrich were used. Sodium hydroxide pellets was purchased from Merck and nickel (II) chloride (NiCl_2) and lead (II) nitrate ($\text{Pb}(\text{NO}_3)_2$) solutions as atomic spectroscopic standards were supplied from Fluka. Necessary dilutions were performed with Milli-Q water having resistivity higher than $18\ \text{M}\Omega\cdot\text{cm}$. The wastewater was sampled through Water and Wastewater Organization of Kuala Lumpur.

2.2. Methods

2.2.1 Synthesis of zeolite nanoparticles

During synthesizing zeolite nanoparticles, hydrothermal procedure with organic free template was selected. It offers mild process condition, tunable crystal size, high purity and homogeneity of the final product in a single step. Two methods; classical hydrothermal and microwave heating methods were used. Accordingly, aluminosilicate gel was prepared by mixing aluminate and silica solutions in the molar ratio of $5.5\ \text{Na}_2\text{O}:1.0\ \text{Al}_2\text{O}_3:4.0\ \text{SiO}_2:190\ \text{H}_2\text{O}$. It was achieved by mixing $5.34\ \text{g NaOH}$, $2.42\ \text{g NaAlO}_2$, $3.43\ \text{g SiO}_2$ and $50.0\ \text{g H}_2\text{O}$. Solution was stirred continuously at room conditions during 24 hours (30-36). Then, crystallization process was initiated at 60°C and allowed for 4 days for the conventional hydrothermal method (TK 120 nũve test cabinet) and 90°C and 100°C for 4 hours for the microwave heating method (Cem MARS 6). At the end of the crystallization, the solid particles were separated from the aliquots by centrifugation and then washed repeatedly with water until the pH reached below 9. For further characterizations, it was dried in a vacuum oven at 100°C for 5 hours (37-39).

2.2.2. Membrane preparation

Asymmetric PSf membranes were prepared by nonsolvent-induced phase separation technique. PSf beads (15% w/w) were dissolved in NMP over night by constant stirring at a rate of 500 rpm. Homogeneous solution was poured onto a clean glass plate spread with the aid of an automatic film applicator (Sheen Automatic Film Applicator, 1132) at a speed of $200\ \text{mm/s}$. The thickness of the solution was adjusted by an applicator to $300\ \mu\text{m}$. The nascent membrane was evaporated at 25°C and 50% relative humidity for different time (0-300s). Then, it was immediately immersed into coagulation bath at 4°C for 1 day. The membrane was then peeled off, subsequently rinsed and stored in water at 4°C .

2.2.3. Hybrid membrane characterization

The crystal structure of zeolite nanoparticles was confirmed with the powder's X-ray diffraction (XRD) patterns which were recorded on a PAN analytical instrument Empyrean model with a scanning rate of $0.005^\circ\ 2\ \text{min}^{-1}$ in between 6° to 45° intervals. The morphologies of the zeolite nanoparticles and porous membranes were characterized by scanning electron microscopy (Quanta 250 FEG) (40-44).

To analyze cross section of the membranes, samples were fractured cryogenically in liquid nitrogen and then subsequently coated with gold using a Magnetron Sputter Coating Instrument for 90 s. EDX was used to evaluate the elemental compositions of the nanoparticles and to determine Si/Al ratio.

In order to determine hydrophobic and hydrophilic characteristics of the membranes Attention Theta optical tensiometer was used. Five mL of water droplets on the surface of the membranes were analyzed with drop-fitting profile using Young-Laplace equation. The reported contact angle value represents an average of 60 image analyzes/min for each droplet and 4 different droplets for each membrane. Contact angle change with dropping time was recorded during 5 min. The variation occurred in the bulk and on the surface of the membrane with the addition of zeolite nanoparticles, Agilent FT-IR system (Carry 660) with ATR module (Pike) was used. Single diamond ATR crystal with 45° reflection incidence was used to obtain FTIR spectrums of vacuum dried membranes between $4000\text{-}400\ \text{cm}^{-1}$ with a resolution of $4\ \text{cm}^{-1}$. In order to increase signal to noise ratio, number of scans was set to 8 for all runs.

The amount of zeolite in the composite membranes were determined by TGA analyzes. For this reason, PSf membranes with different zeolite content were sliced into $1\times 1\ \text{cm}^2$ area and heated from room temperature to 800°C with a heating rate of 10°C/min under nitrogen atmosphere.

2.2.4. Filtration

Performances of the membranes were characterized under dynamic conditions using dead-end stirred cell filtration system (Model 8050, Millipore Corp, Bedford, MA) with a total internal volume of 50 mL and an active surface area of $13.4\ \text{cm}^2$. The detailed in filtration protocol has been given in literature [19]. Filtration data was used to calculate water fluxes, $J_v\ (\text{L/m}^2\cdot\text{h})$ by dividing the slope of the volumetric flowrate, $V_p\ (\text{L/h})$ to the effective membrane area $A\ (\text{m}^2)$. The hydraulic permeability, $L_p\ (\text{L/m}^2\cdot\text{h}\cdot\text{bar})$, through the membrane was determined from the slope of the plot of the solution flux as a function of transmembrane pressure. Filtration of the metal solutions were carried out at a fixed concentration and transmembrane pressure for 60 min. At certain times, samples were withdrawn from the filtrate. Necessary dilutions were performed with the supernatants and their concentrations were determined by atomic absorption spectroscopy (Perkin Elmer Analyst 800 with air-acetylene oxidizing flame).

2.2.5 Sapling and Sample preparation

To ensure that sampling is consistent, and of good quality and traceability, samples need to be representative of the body from which they were taken. If the sample integrity is altered, the information gained from analysis could be misleading and ultimately result in mismanagement of water resources and/or polluting of the resource. The main processes that have the potential to affect the integrity of a sample are listed below. These processes are interlinked and a change in one thing may have a flow-on effect that will influence another, eg a change in temperature can cause chemical changes.

The regulations specify minimum sampling requirements for wastewater treatment systems based on system classification. As well, sampling requirements for wastewater treatment systems may also be stipulated in a Certificate of Approval (COA) issued under Section 16 of the Environmental Protection Act. The following minimum sampling requirements apply to a Class I wastewater treatment facility:

- Carbonaceous biochemical oxygen demand (CBOD5), total suspended solids (TSS), and faecal coliform on a quarterly basis
- Ammonia (NH_3), total phosphorous (TP) and total nitrogen (TN) on an annual basis. The following minimum sampling requirements apply to a Class II, Class III or Class IV wastewater treatment facility:
- Carbonaceous biochemical oxygen demand (CBOD5), Total suspended solids, and faecal coliform on a monthly basis
- Ammonia (NH_3), total phosphorous (TP) and total nitrogen (TN) on an annual basis

The regulations also require that the utility report summary statistics on effluent quality to their customers at least once a year.

2.2.6 Prefiltration process

Multimedia filtration (also called prefiltration, sand filtration or multilayered filtration) is mainly aimed at removing sediments and suspended matter. Suspended contaminants are trapped in small crevices and, as a result, water turbidity is improved. A number of medias are distinctly layered with the coarsest on top so the suspended matter is collected throughout the depth of the filter according to size. The filter beds need to be backwashed periodically as the backpressure increases; however, backwashing removes the filter from use. To avoid downtime, often a dual filter bed system is installed. During construction, the filtration unit should be installed before all the walls are erected so it can be kept upright, in which case the vendor before shipping can charge the filters. This would reduce chances of damage to the internals during loading. The unit, of course, should be inspected thoroughly upon receiving. Before shipping, the vendor will often disconnect controls to minimize potential damage. Sufficient time should be allowed to reconnect all of these. Finally, to avoid bacteria building up, start-up should be delayed until a constant water flow is assured.

3. Results and Discussion

3.1 Zeolite Characterization

The powder XRD patterns of the zeolites which were prepared by hydrothermal and microwave heating techniques at different crystallization temperatures, are presented in Figure 1. The starred peaks reflect the crystals of pure zeolite A [18]. From Figure 1, it was observed that increasing the temperature enhanced the intensity and sharpness of the diffraction peaks in the case of the microwave method. Moreover, a higher temperature caused a decrease in the ratio of zeolite X and allowed furthermore the zeolite A crystal to grow rapidly. On the other hand, the XRD pattern observed at the end of the conventional hydrothermal method exactly matched with those faujasite (FAU) NaX zeolite reported in the literature [20,21], which indicates that the synthesized crystal is pure FAU-NaX.

Figure 1. XRD patterns of zeolite nanoparticles produced by hydrothermal and microwave methods

The SEM pictures of the zeolite nanoparticles synthesized with hydrothermal and microwave methods at their corresponding temperatures are shown in Figure 2. Ultrafine and almost uniformly distributed particles around 170 nm were obtained at the end of the hydrothermal crystallization process, while particle size inhomogeneity as well as larger particles were obtained as a final product using microwave heating methods. Formation of building units, nucleation and crystal growth all occurred sequentially during the zeolite crystal formation. The key factors controlling the particle size and the zeolite phases are the nucleation process and the crystallization temperature. The ratio of the nucleation rate to the growth rate of the crystal determines the crystal size and zeolitic phase. Relatively low synthesis temperature and strong stirring rate synergistically accelerate nucleation, while keeping the crystal growth rates low, hence leading to ultrafine zeolitic crystals [17]. On the other hand, increasing crystallization temperature as in the case of microwave heating method increases the number of formations of zeolitic nuclei inside the solution, which therefore leads to crystal formation and resolution of zeolite crystal simultaneously progressed, hence creates a larger zeolite particle. The unit cells of the synthesized zeolites were calculated based on the EDX analysis obtained from different parts of the sample and their average values were estimated as $\text{Na}_{104}[\text{Si}_{119}\text{Al}_{96}\text{O}_{526}]$ for the hydrothermal method, $\text{Na}_{88}[\text{Si}_{112}\text{Al}_{93}\text{O}_{494}]$ and $\text{Na}_{92}[\text{Si}_{103}\text{Al}_{96}\text{O}_{483}]$ for the microwave methods at 90°C and 100°C respectively. The unit cell compositions were then used to calculate the Si/Al ratio of the nanozeolites.

They were determined as 1.24, 1.21 and 1.07, respectively. Because of yielding higher exchangeable cations, uniform and ultrafine zeolite particles with high purity, NaX nanoparticles produced by conventional hydrothermal method was used for further experiments.

Figure 2. SEM images of nano-zeolites synthesized by (a) hydrothermal method at 60°C and microwave heating method at (b) 90°C and (c) 100°C.

3.2. Membrane Characterization

Two important parameters mainly affect the filtration performance of the membranes which are the pore size formed during the evaporation stage at the specified conditions (temperature and humidity of the environment) and the amount of additive (NaX nanoparticles) were studied. The effect of the NaX addition in between 0-10w%, using 30 sec evaporation time on the cross section of the PSf membranes are presented. All the membranes exhibit a typical asymmetric structure, with a dense thin top layer and a porous sub-layer, which is filled up by the closed cells within polymer matrix and finger like microvoids. The NaX nanoparticles are well dispersed through the thickness of the membrane and the membrane could reach a saturation level where the maximum NaX loading was attained. Increasing the amount of NaX in the membrane caused a gradual decrease in the thickness of its top dense layer, while greater and enlarged finger like microvoids were formed across the membrane's thickness. These findings could be explained by the difference in solvent and the nonsolvent exchange rates. It is known that the slow separation leads to formation of a denser structure [3,22]. Magnified images of the top and bottom sides of the membrane's cross sections are also illustrated, respectively from left to right, where pore enlargements by the addition of NaX nanoparticles could be more evident.

The effect of the evaporation time on the membrane's morphologies is illustrated in Figure 4. Finger like microvoids were suppressed and completely turned into cell like pores when the evaporation time was prolonged from 0 to 300 seconds. The PSf10-300 membrane exhibited a gradient cell size distribution with relatively larger cells localized near the upper surface and quasi uniform cell size along the remaining membrane thickness. The mechanism of the structural changes which has been discussed by Bouyer et al [23] is mainly caused by the difference in the exchange rate of the solvent and the nonsolvent. The thickness of the fabricated membranes increased from 138 to 196 μm with the increase in evaporation time. This could be explained by the difference in the occurrence of empty space filling during separation process. SEM microphotographs of the top and bottom surfaces of the PSf0-30 and PSf10-30 membranes. The bottom surface of the unmodified membrane is almost nonporous, while, some small voids around 200 nm are visible on its top surface. On the other hand, new voids larger in sizes (650 nm) were developed by adding NaX.

Owing to the fact that nano particles have high surface energy and affinity to water molecules, NaX are inclined to agglomerate during phase separation and formation of the aggregates can release from the polymer solution into coagulation bath leaving voids larger in sizes on the surface of the membrane. Fast separation and aggregate formation would produce larger pores [23]. In order to calculate membrane's porosity, a small piece of the membrane was saturated in water at room conditions for 24 hours and dried in a vacuum oven at 50°C under vacuum overnight. Membrane porosity, and calculated by gravimetric method using the expression given below [24]. Porosity was reduced from 82 to 76% by increasing the amount of NaX in the membrane. Pore radius of the membranes was calculated, and their variations with respect to transmembrane pressures are illustrated. As expected, pore radius of the membranes was increased by the addition of NaX due to the instantaneous precipitation occurred during phase separation. On the other hand, the applied pressure has negligible effect on the pore sizes of the membrane, indicates that the hybrid membrane can preserve its main structure even at higher pressures. The surface functional groups of the pure and NaX added PSf membranes were determined by FTIR-ATR spectrometer and the spectrums in the range of 4000-400 cm^{-1} are illustrated. The bands visualized in the spectrum at 2970, 1450-1600, 1295-1360, 1160-1120 and 1000-1250 cm^{-1} correspond to saturated and unsaturated -CH, aromatic benzene rings, asymmetric and symmetric stretching vibrations of -S=O functional groups and Ether-O- groups available in PSf membrane. A broad band at 3500 cm^{-1} was assigned to -OH

stretching and the peak intensities increased with the number of nanoparticles inside the membrane. This could be attributed to the hydrophilic nature of the zeolite which can adsorb water molecules through hydrogen bonding, hence increasing the hydrophilic characters of the membrane. The presence of NaX-nanoparticles on the membrane surface is reflected at about 970-1000 cm^{-1} which is assigned to Si-O-Al species and the intensity is increased with the increase in the loading number of NaX-nanoparticles. The results of TGA for the pure and NaX added PSf membranes under nitrogen atmosphere are investigated. Weight losses occurred mainly in two stages. The first up to 200°C corresponded to desorption of water molecules previously adsorbed by the NaX-nanoparticles, and the second starting from 470°C and lasting at 590°C was ascribed to decomposition of PSf. The weight loss data represents 1 cm^2 of membrane area, so one can calculate the number of NaX-nanoparticles present in a unit surface area under the assumptions if there is no reaction between PSf and nanoparticles and the zeolite can preserve its main structure within the temperature intervals. The percentage weight loss data of the native PSf membrane was used as a reference and calculation were based on the dry weight of each sample. Then, the number of nanoparticles in a unit surface area of each membrane based on the percentage weight loss data between 200°C and 800°C were estimated as 0.30, 0.58 and 1.08 mg/cm^2 for the PSf1-30, PSf5-30 and PSf10-30 membranes respectively. The difference in estimated and loading values (1:5:10) of NaX in the membranes comes from the fact that some portion of nanoparticles might be released into coagulation bath during phase separation, since NaX nanoparticles have high surface free energy and a high affinity to water molecules. The former is related to NaX agglomeration and the latter is about the mobility of the nanoparticles.

The effect of adding NaX on the membrane's surface properties (hydrophilicity/ hydrophobicity) were examined by means of water contact angle measurements. The results are shown, the contact angle of the pure PSf membrane was started to decrease from 69° to 65° within a 5 min time interval. These values were slightly enhanced from 68° to 63° and from 67° to 61° for the PSf1-30 and PSf5-30 membranes respectively. An improvement of the difference between the initial and final values of the contact angles indicates that wettability is slightly increased with respect to NaX loading. On the other hand, the highest contact angle which reflects the highest hydrophobic surface was obtained for the PSf10-30. It could be the result in the voids formed on the surface of the membrane during phase inversion process which causes to lower the surface free energy, hence increase the contact angle. However, the rate of decrease of contact angle (0.053°/s) observed was much higher than those obtained on the other membranes, implying that water molecules penetrated into the membrane. The flow of water molecules can be accelerated through porous membrane via hydrogen bonding that occurred between sulfonic groups of PSf and -OH groups of zeolites that improve hydrophilicity and hence reduce the flow hindrance [15].

3.3. Membrane Filtration

The performance of the fabricated composite membranes was measured under dynamic condition. The change in water flux with respect to time collected at different transmembrane pressures for the PSf0-30 membrane. During filtration period, water fluxes at each pressure remained constant which indicates obtaining a stable membrane structure.

Water hydraulic permeability, Figure 3 represents the hydraulic permeability of water through unmodified and NaX added PSf membranes. Addition of NaX had no effect on L_p up to 5%. However, a sudden increase in L_p was obtained when the amount of NaX reached maxima. This could be attributed to the formation of new pores in larger sizes and an increased in hydrophilicity during the passage of the water molecules through PSf10-30 membrane. The increase in L_p with the addition of NaX was also supported by the results obtained from SEM, FTIR-ATR, TGA and contact angle analyzes. In addition, the effect of evaporation time during fabrication of the composite membrane on the filtration performance was also studied.

In Figure 3, extending (PSf10-300) or neglecting (PSf10-0) the evaporation stage ensured the lowest and the highest hydraulic permeabilities respectively due to the delayed and instantaneous precipitation which could have altered the membrane structure significantly.

The ion-exchange performances of the membranes under dynamic conditions were performed by following the reduction of metal

concentrations in permeate and hence, by calculating the exchanged metal ions as a function of NaX loading. Filtrations of 500 mg/L metal solutions under 1 bar transmembrane pressure were carried out through PSf0-30, PSf1-30, PSf5-30 and PSf10-30 membranes for 60 min. The results illustrated in Figure 12 show the adsorbed metal ions against filtration time. Lead ions were retained by the pure PSf membrane and adsorption proceeded almost linearly with the increase in NaX content. However, no rejection was observed during the filtration of nickel ions through the same membrane. It is known that the ionic radius of the lead (1.19 nm) is nearly two times larger than the radius of the nickel ion (0.69 nm) and absolute electronegativity's of the lead and nickel ions are reported as 2.33 and 1.99 respectively [25]. The former can be related to a sieving effect of the membrane through which the lead ions are sterically hindered and the latter may explain the higher adsorbed amount of lead which is not only exchanged by the sodium atoms in the NaX framework but also has a stronger interaction with the lone pairs of electrons on oxygen. The maximum amount of lead and nickel ions on the solid phase were achieved at maximum NaX loading.

In order to satisfy the maximum throughput, the highest water permeable PSf10-0 membrane was tested under the same filtration conditions used for the membranes above.

Figure 3. Water hydraulic permeabilities through native and NaX added PSf membranes.

The sorption capacities of the PSf10-0 membrane during filtration of lead and nickel solutions as a function of time are illustrated in Figure 13. At the lowest Pb^{2+} concentration, the rate of adsorption increased linearly during filtration period, which indicated that there were enough adsorption sites for Pb^{2+} to be accommodated. When the initial feed concentrations were increased, the active sites of NaX were occupied quickly up to 20 min and then the rate of adsorptions were decreased. This may result in the shorten residence time of the lead ions to contact with the remaining active sites of the NaX. According to Figure 13, increasing the feed concentrations also increased the adsorption capacity of Pb^{2+} in the hybrid membrane. On the other hand, equilibrium was almost attained even at lower nickel concentrations. When the number of nanoparticles is known in a unit surface area, one can calculate the maximum specific adsorption capacity of the PSf10-0 membrane that is attained at the end of the filtration period as 682 and 122 mg/g for the lead and nickel ions respectively. The values measured in this study are much higher than the values reported in literature [7, 26].

The sorption and filtration coupling process allows the use of all active sites of the adsorbent, by taking the advantage of the convective flow compared to slow diffusion mechanisms in the batch adsorption systems. In addition, sieving, drag retardation and concentration polarization may sterically accelerate the removal of metal ions from the feed solution. Two or more mechanisms influence the rate of metal adsorption by the hybrid membrane. The first one is the convective flow of the metal ions from the bulk solution to the nearby membrane interface. The second one is the diffusional flow of the metal ions through the membrane and inside the pores of the NaX and the third one is the ion exchange reaction occurred between the Na^+ cations in the NaX framework with the metal ions. If the reaction is slower mechanism than the others, then the filtration process is said to be reaction controlled. Filtrate concentrations for both of the metal solutions increased as time prolonged. On the other hand, the increase in filtrate concentration was more pronounced when the feed concentration was increased. The definite adsorption capacity of

membrane absorbers limits their application for treating solutions with higher lead or nickel loading. The removal efficiency of the PSf10-0 membrane attained at the end of 60 min of filtration was defined as the percentage recovery of metals by the expression given below, where, C_0 and C_f represent initial and filtrate concentrations of the metal solutions respectively.

The percentage of recoveries, as a function of initial metal solution, suggests that the hybrid membrane could be effectively used for treating the lead solution that has 100 ppm of initial concentration under 1 bar of transmembrane pressure.

4. Conclusions

In the present study, NaX nanoparticles incorporated PSf composite membranes have been fabricated for the removal of Pb^{2+} and Ni^{2+} ions from aqueous solutions. The characterization of the nanoparticles revealed that the conventional hydrothermal method produced pure NaX with uniform and ultrafine particles. Asymmetric membranes in desired structures were produced by simply tuning the membrane's fabricating conditions. Elimination of the evaporating stage and the addition of NaX simultaneously improved the adsorption and the filtration performances of the hybrid membrane.

During coupling process, the rate of reaction was smaller than the mass transfer rate, especially when the initial metal concentration was high, showing that the definite adsorption capacity of membrane adsorber limits their application when treating solutions with higher lead or nickel loading. To conclude, the results of this study suggest that the PSf10-0 membrane can be effectively used for dynamic removal of lead and nickel ions from water, especially when their concentrations and the operating pressure are low. However, further testing is needed to evaluate reusability, selectivity and antifouling characteristics of the membrane.

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