Implementation of hierarchically porous zeolite-polymer membrane for Chromium ions removal

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Abstract. This work deals with the preparation of a zeolite/polymer flat sheet membrane with hierarchical porosity and ion-exchange properties. The performance of the prepared membrane was examined by the removal of chromium ions from simulated wastewater. A NaY zeolite (crystal size of 745.8 nm) was prepared by conventional hydrothermal treatment and fabricated with polyethersulfone (15% PES) in dimethylformamide (DMF) to obtain an ion-exchange ultrafiltration membrane. The permeate flux was enhanced by increasing the zeolite content within the membrane texture indicating increasing the hydrophilicity of the prepared membranes and constructing a hierarchically porous system. A membrane containing 0.8% zeolite gave the higher Rejection of chromium ions (about 83.2%) for an initial chromium ion concentration of 150 ppm and trans-membrane pressure of 1 bar.

Keywords: Ion-exchange membrane, Zeolite/polymer membrane, Chromium ions, Wastewater treatment, Hierarchical porosity.

1. Introduction

The pollution problems by heavy metals have become concerning because of their severe harms to the environment and human health besides the difficulties of eliminating these metals from industrial wastewater [1]. Heavy metals are released with the effluents of different industries such as battery manufacturing, chemical manufacturing, metallurgical industry and electroplating industry [2]. Chromium is the most recognized heavy metal released as a result of industrial activities including electroplating industry crafts, leather industries, corrosion control application and manufacturing of catalysts, glass, ceramics, fungicides, pigments, and photography [3]. Leather tanning uses trivalent chromium for an effective tanning process, thus it releases wastewater containing trivalent chromium ion that is at high temperatures, alkaline medium, and aerobic conditions, oxidizes to hexavalent chromium ion which is the most harmful ion because it commonly causes cytotoxic and carcinogenic effects [4][5][6]. Therefore, to avoid oxidation of trivalent chromium to its hexavalent form in the last stages of industrial wastewater treatment, it is necessary to reduce the level of Cr³⁺ residue [4]. Different ways have been studied for heavy metals removal as cited in [7][8][9] such as solvent extraction, electrochemical treatment, reduction, reverse osmosis, membrane technology, precipitation, adsorption and ion exchange. The World Health Organization (WHO) limits the maximum allowable concentration for chromium in drinking water as 0.05 mg/L as cited in [10][11]. While, the actual environmental legislation defines 0.5–2.5 mg/L of total chromium, 0.1 mg/L of hexavalent chromium ion in industrial effluents, and 0.01 mg/L of total chromium in drinking water as cited in [12]. Ion-exchange emerged as one of the most appropriate methods for treating wastewater polluted with metal ions [13]. Different adsorbents and ion-exchangers have been used and enhanced to achieve efficient metals removal from wastewater, Hani et al., [14] mentioned different adsorbents and ion-exchangers including zeolites. Ion-
exchange by zeolites has been broadly applied for harmful ions removal from contaminated industrial water [15].

In comparison with the other known metal ions, chromium (III) ion has the largest hydrated radius (0.461 nm [12]), thus the chosen ion-exchanger for removing it has to be with an appropriate pore opening [16]. Therefore, Faujasite-type zeolites represent the most favorable ion-exchangers that allow the successful removal of large trivalent chromium ions from aqueous solutions due to their large pore size of 0.74 nm with three dimensions open network structure [12], [16]. Zeolites are microporous crystalline aluminosilicates, consists of connected [SiO₄]⁴⁺ and [AlO₄]⁴⁻ tetrahedra using sharing oxygen atoms from their bends to form an open framework with a three-dimensional network of channels, cavities and pores at molecular levels [17]. The channels of zeolites can be engaged by zeolitic water, as well as, the cavities and pores are occupied by organic and non-organic cations which balance the negative charge of the zeolite structure resulting from Al substitution in the structure [18]. The properties and the potential of zeolites are determined depending on the framework ratio (Si/Al) of the zeolite. Since it gives an indication about the maximum ion-exchange capacity of a zeolite while the actual capacity can be lower when the ion-exchange sites are hard to reach due to the zeolite's microporosity [14][17]. The problems of diffusion and large resistance to mass transfer can be overcome by preparing hierarchically porous materials that have more than one type of porosity and thus enhance the species diffusion and the separation operations [20]. Preparation of hierarchically porous materials allows spreading zeolite crystals over another porous substrate using coupling agents [21], [22], or during hydrothermal treatment [21][22][23].

Recently, introducing zeolites within a polymeric texture either fibers or membranes has attracted the attention in producing hierarchically porous zeolite composites. Zeolites can be typically dispersed as an inorganic filler in the polymeric texture to enhance the properties of ion-exchange or adsorption and molecular diffusivity through modifying the structure to improve the chemical stability and compaction resistance of the membrane [26]. Wang et al., [27] prepared a flexible zeolite membrane concept by growing a layer of zeolite within the polymer-supported by a hydrothermal method. Wang et al., [28] prepared a zeolite membrane by growing zeolite within pores of a polyethersulfone (PES) polymer or at the top of polymer support based on the level of nano zeolite seeds. In the context of fabricating zeolites and polymers to obtain hybrid-porous composites, Rad et al., [29] used the electrospinning process to obtain NaX/polymethyl alcohol nano-fibers composite and examined it for Ni and Cd ions adsorption from aqueous solutions. Anis et al., [30] fabricated nano-fibers of the Y zeolite/Polynvinylpyrrolidone composite with a hierarchical porosity using the potential of electrospinning for achieving highly efficient hydrocracking capability of Y zeolite. Liu and Cen [31] prepared a hydrophilic FAU and a hydrophobic MFI membrane obtained by direct growth method as reverse osmosis (RO) membranes for seawater desalination with about 100% Rejection of salt ions.

Membranes containing zeolites provide a unique kind of nanostructured interface having favorable interactions with individual molecules and are easily cleaned and possess catalytic activity due to their desirable merits [32]. In this study, a Y zeolite has been chosen to fabricate an ion-exchange zeolite/polymer membrane with a hierarchical porosity to be used for chromium (III) ions removal. A Y zeolite has a Faujasite framework and Si/Al > 1.5 ratio which provides an abundant number of the compensating cations for ion-exchange purposes with chromium ion as a model heavy metal [1]. Such kinds of composites provide a dual function of ion-exchange and membrane filtration for effective removal of pollutants such as heavy metals. The effects of zeolite percentage in the membrane, initial chromium concentration and pH on the removal effectiveness have been investigated.

2. Experimental work

2.1 Chemicals
LUDOX AS-40 (supplied by Hanghzous Sartort Biopharma Co. LTD.) was used as silica sources while, anhydrous sodium aluminate (55-56%wt. Al₂O₃, supplied by Riedel-deHan) was utilized as an alumina source, and sodium hydroxide (97% wt. supplied by HIMedia Laboratories Pvt. Ltd.) was used
as a cation source to prepare zeolite NaY. Polyethersulfone (PES (C_{12}H_{22}O_7S))_n, supplied by Solvay specialty polymers MW = 58,000 g/mol.) and Dimethylformamide (DMF HCON(CH_3); MW = 73.09, supplied by Romil) were utilized to prepare the flat sheet membrane. Chromium nitrate (Nonahydrate Cr(NO_3)_3.9H_2O, supplied by Alpha Chemika) and hydrochloric acid (36%) were used for the treatment process.

2.2 Synthesis of NaY zeolite
A NaY zeolite was prepared by a hydrothermal treatment following the procedures applied in the previous work[33]. The chemical formula of the gel used to produce NaY zeolite was chosen according to [33] to be: 5.25Na_2O: 1Al_2O_3: 10.5SiO_2: 185H_2O. 7.832 g of anhydrous sodium aluminate was added to an alkali solution which was prepared from dissolving 13.939 g of NaOH in 100 ml of H_2O. After the solution became clear, 68.17 g of LUDOX AS-40 was added and left to mix for 2 h to form a creamy thick gel. After that, the gel was poured into a stainless-steel autoclave lined with a Teflon bar to be aged statically at room temperature for 24 h. Then, the gel was crystallized for 18 h at 100 °C. At the end of crystallization time, the product was collected, filtered, washed, dried and characterized using several important instruments before being used for membrane preparation.

2.3 Preparation of hierarchically porous zeolite membrane
Five samples of the zeolite membrane were prepared with a NaY zeolite content percentage of 0%, 0.4%, 0.6%, 0.8%, 1% and 1.5%. The percentage of PES was kept constant for all samples at 15%. The membrane preparation method was conducted according to the previous work [34] with some modifications. According to the selected zeolite percentage in a membrane, a certain weight of the NaY zeolite was dispersed in DMF under continuous mixing at 50°C. Then, PES was added dropwise to the NaY-DMF mixture and mixed until completely dissolved. The resultant mixture was kept at a warm atmosphere no more than 50 °C overnight inside a dryer. After that, a small quantity of the zeolite-polymer mixture was kept at the top of a clean flat glass board and spread over it with a thickness of 200 µm by a clean cylindrical rod. After that and immediately, the board covered by the zeolite-polymer mixture was put in a water bath at room temperature to solidify the mixture and remove the solvent. For each membrane type, four sheets of identical membranes were made to obtain enough pieces of membranes for studying the membrane characteristics and conducting the UF process. During UF tests, the mean value of the flux and solute remaining concentrations were measured.

2.4 Removal of chromium ions experiments
Removal of chromium ions from simulated wastewater was conducted using a polymeric cell made of clear acrylic. The process was conducted under a fixed pressure (1 bar), initial chromium concentration (250, 200, 150, 100 & 50 ppm), and initial pH of chromium solution (2, 4, 5 & 6). Besides, chromium removal was studied for different zeolite percentages used to prepare the membrane. The treatment process was a continuous process and the samples were taken at each quarter of an hour for the first hour and every half hour for the second hour. The samples were analyzed for the remaining concentration of chromium ions using an atomic absorption model (Perkin Elmer 5000 Atomic Absorption Spectrometry). Also, the permeate flux was measured for the same intervals. The permeate flux is the sum of permeate flux volumes passing through a membrane surface unit area at a certain time in the existence of a used pressure. The flux value relies on the membrane structure, for instance, pore size distribution, pore shape, porosity; and it determines the efficiency of the membrane separation process [35]. The permeate flux can be obtained using Equation (1) [36].

\[ J = \frac{V}{At} \]

Where: J is the = Flux (L/m²·hour)
V is the = Volume of permeate (L)
A is the = Membrane surface area (m²) and
t is the = Time (h)
The Rejection % of chromium ions was determined using Equation (2)[37]
\[
\%\text{Rejection} = \left(1 - \frac{C_p}{C_f}\right) \times 100
\]

Where: \(C_p\) is the concentration of chromium ions remaining in permeate and \(C_f\) is the initial chromium ions concentration.

The pH of metal ions solutions was adjusted over a range of pH (2, 4, 5, and 6) using 1M sodium hydroxide solution and 1M hydrochloric acid solution to study the effect of pH on the separation process performance of Cr (III) solution of 150 ppm and trans-membrane pressure of 1 bar. Also, one batch experiment was conducted to compare the results with those obtained using the membranes. This experiment was conducted by mixing 0.2 g of the NaY zeolite with 100 ml of 150 ppm chromium solution and a solution pH of 4.

3. Characterization
The phase of zeolite was identified using an X-ray diffractometer, type Shimadzu Japan XRD 6000. The morphology of samples was obtained through Scanning Electron Microscopy (SEM type Zeiss Germany) to perform the SEM imaging, the samples were coated with gold by a sputter coater. The composition of the constituent elements of the samples was provided by Energy Dispersive Analysis by X-ray (EDAX). The crystal size of the sample was gained using ImageJ software count on the SEM images according to procedures mentioned in [17]. The surface area was measured using Brunauer-Emmett-Teller (BET) method based on the N\(_2\)-adsorption/desorption isotherms, Micromeritics TriStar II Plus Version 2.03 at \(-196.8\) °C. A contact angle measuring system was used as an optical instrument (CAM110, Taiwan)

4. Results and Discussion

4.1 Characterization of the prepared Y zeolite
Figure 1 presents the X-ray diffraction for the prepared NaY zeolite were a pure phase crystallized with sharp peaks and flat background. The successful preparation of the target zeolite was justified by appearing of the identifying peaks at 6.31° (1 1 1), 15.92° (3 3 1), 20.71° (4 4 0), 24.06° (5 3 3), 27.52° (6 4 2), 31.95° (5 5 5). The SEM image of zeolite Y shown in Figure 2 reveals obtaining a full crystallized product with a homogeneous morphology and uniform crystal size of 745.8 nm.

![Figure 1: X-ray diffraction spectrum for the prepared NaY zeolite. (Hydrothermally crystallized at 100°C for 18 h)](image_url)

![Figure 2: SEM images of the prepared Y zeolite. (Hydrothermally crystallized at 100°C for 18 h)](image_url)
Table 1: Compositional and structural analysis of the synthesized Y zeolite.

| Na  (Wt.%) | Al  (Wt.%) | Si  (Wt.%) | O  (Wt.%) | Si/Al (Unitless) | Surface area (m²/g) | Crystal size (nm) |
|-----------|-----------|-----------|---------|-----------------|---------------------|------------------|
| 9.22      | 16.74     | 30.44     | 48.22   | 1.82            | 663.6207            | 745.8            |

The surface area of the prepared NaY was determined by liquid nitrogen adsorption/desorption via BET (Brunauer, Emmett, and Teller) method and found equal to 663.6207 m²/g.

4.2 Performance of zeolite membrane in the removal of chromium ions

4.2.1 Effect of zeolite percentage on the flux and %Rejection of chromium ions: Figure 3(a) presents the results of the performance of the prepared membranes as a function of the zeolite content in the membrane texture and the results were presented in the form of permeate flux against operation time. The figure shows that as the zeolite content increased, the flux of the membranes increased at the same pressure. 1.5% zeolite/PES membrane gave the highest flux of 310 L/m².h after 120 min., whereas a membrane neat (PES) gave 6.1 L/m².h. This can be explained as the hydrophilicity of the membranes increased due to including Y zeolite which has an intermediate Si/Al ratio of 1.82 providing polar Si-Al bonds and sufficient ion-exchange sites. The high hydrophilic membranes display a relatively high flux [38]. The water contact angles of the membranes containing Y zeolite were smaller than that of the neat PES membrane. The water contact angle decreased with the increase in zeolite loading. This decrease in contact angle proves that Y zeolite imparts hydrophilicity to the membrane surface. The contact angle of the neat PES was 75.4 and 59.7, 49.4, 39.9, 37.9 and 30 for 0.4 zeolite/PES, 0.6 zeolite/PES, 0.8 zeolite/PES, 1 zeolite/PES and 1.5 zeolite/PES, respectively.

Figure 3. Effect of zeolite percentage on (a) Permeate flux (b) %Rejection value of chromium ions (Feed concentration: 150ppm; pH: 4; applied pressure: 1 bar)

Figure 3(b) shows the average %Rejection of chromium ions by the prepared membranes against the zeolite content in the membranes in the form of a histogram. A PES membrane rejects about 52% of chromium ions during the experiment time. Whereas the %Rejection increased with increasing the zeolite content in the PES membranes until it reached the maximum Rejection (to about 83.2%) for 0.8% zeolite/PES membrane, then it reduced for 1% zeolite/PES membrane (to about 74%) and 1.5% zeolite/PES membrane (to about 73%). The significant improvement in the %Rejection of chromium ions by the zeolite/PES membrane is attributed to the abundance of the ion-exchange sites within membrane texture provided by the used NaY zeolite. However, the opposite results obtained when
increasing the zeolite content can be attributed to aggregating zeolite masses within the polymer matrix [39]. Šupová et al. [40] stated that increasing the fraction of inorganic particles within the polymer matrix led to a more brittle material with a lower final tensile strength. The highest %Rejection was given by 0.8% zeolite/PES membrane; therefore, this membrane was selected to conduct the other studies. Also, it is worth mentioning that zeolite/PES membrane gathered dual functions: Rejection of cations due to the electrostatic interaction between the surface charge and cations [41][40][42] and capturing the cations crossing the membranes layer by zeolite pores. The efficiency of the fabricated NaY zeolite membrane on chromium removal was compared with other studies reported in the literature [10], [38], and it was found that the highest removal of chromium was achieved in this work. Also, the results of the 0.8% zeolite/PES membrane were compared with the results obtained from the batch experiment that gave 89.1% Rejection of chromium ions. The results were close enough based on the %Rejection, but the separation by the membrane was the most cost-effective when the comparison is based on the zeolite mass used during the same time.

4.2.2 Effect of initial chromium concentrations on the flux and Rejection value: Figure 5(a) presents the results of the performance of the Y zeolite-PES membranes as a function of initial chromium ions concentration and the results were presented in the form of permeate flux against operation time. The figure shows that the membrane flux of 0.8% zeolite/PES membrane decreased with increasing the concentration of chromium ions. The flux value was high about 244.4 L/m²·h for 50 ppm concentration and then started to decline with increasing the concentration of chromium ions until reaching 170.3 L/m²·h for 250 ppm. Also, the chromium permeate flux significantly decreased with increasing operation time. The longer the operation time, the more particles the membrane holds in the form of particle aggregation (layer-cake). This layer causes a shrinkage of the pore size that leads to low permeate flux [34][35]. At conditions of higher concentrations of chromium, incomplete plugging of the membrane pores represents a barrier layer to the ions transfer through the PES membrane pores that contain zeolite microcrystals (i.e. chromium ion fouling [44]). It is worth mentioning that even at high chromium ion concentration (250 ppm) and after 120 min, the permeate flux is still significantly higher (28 times higher) than the flux obtained using PES membrane at 150 ppm and 120 min. These important results support the claim that embedding the PES membranes with zeolite will highly enhance the performance of ultrafiltration membranes. Also, the creation of hierarchically porous systems (zeolite micropores and PES macropores (as shown by SEM image in Figure 4) save the cost resulting of both using large amounts of pure zeolite and less efficacy due to powder form ion-exchanger.

Figure 4 shows that the forms of the pores in neat PES and 0.8 zeolite/PES membranes are different. The pores in neat PES were not well-ordered, and the addition of zeolite created a more finger-like structure and well-ordered.

Figure 4: SEM images for (a) PES (b) 0.8 zeolite/PES membrane.
Figure 5: effect of initial feed concentration of chromium ions on (a) Permeate flux. (b) Rejection value (pH: 4; 0.8%Zeolite/PES membrane; applied pressure: 1 bar)

Figure 5(b) presents the %Rejection of chromium ions by the prepared membranes against the operation time. This figure shows positive results represented by increasing the %Rejection with increasing the initial chromium ion concentration to reach 87.4% for 250 ppm which indicates the feasibility of using this membrane for relatively high contaminant concentration. This is mainly due to different factors, such as osmotic pressure, concentration polarization, and fouling of the membrane around the surface of the membrane [10]. This can be due to the concentration polarization phenomena during the operation time. Fouling that takes place on the surface and inside the membrane also increases, and makes more and more cake generating on the membrane surface. The cake acts as an additional filter for contaminant separation from the water before it comes into contact with the membrane surface therefore the rate of Rejection increases [45]. Whilst, the Rejection was 60% for 50 ppm concentration which can be attributed to dilution of the chromium solution.

4.2.3 Effect of pH on the chromium ions Rejection: The pH of the solution is an important factor that controls the removal of Cr (III) by the zeolite and has a major effect on the ability of zeolite in the removal of metal ions because of the rivalry of hydrogen (H⁺) ions with the metal cations for active sites [46]. Also, the surface charge of the membrane depends on the pH of the solution containing contaminant metals [47]. Therefore, the effect of pH on the chromium ions removal by the zeolite/PES membrane was studied and the results were shown in Error! Reference source not found.(b) as a function of solution pH. Apart from separation by membrane separation, based on laboratory observations, raising the pH of the chromium ions solution above 6 leads to precipitate the metal hydroxide. The results showed that at the low pH of the solution, the %Rejection of Cr (III) declined due to the competition between metal cations and hydrogen ions to occupy the same exchange sites [48][49]. When the pH raised from 4 to 6, the magnitude of the membrane charge (negative) also increased, and consequently, the higher (negative) surface charge increases the intensity of the electrostatic attraction between the positive ions (Cr³⁺), in the solution and the membrane surface. Therefore, the Rejection was higher at higher pH. The effect of pH on the permeate flux of the membrane prepared from 0.8 %zeolite/PES is shown in Error! Reference source not found.(a) it can be observed that pH has no applicable effect on the permeation flux [48].
Figure 6 Effect of pH on (a) Permeate flux and (b) Rejection value. (Feed concentration: 150 ppm; 0.8%Zeolite/PES membrane; applied pressure: 1 bar)

5. Conclusions
NaY zeolite/PES membranes were successfully synthesized by the phase inversion method. The hydrophilicity increased with increasing content of NaY which led to enhanced flux and %Rejection. Also, creating a hierarchically porous filter consisting of microporous zeolite and microporous PES membrane highly improved the performance of the separation process. The PES membrane containing 0.8% zeolite gave the highest % Rejection of 83% and permeate flux of 253.8 L/m². h. The solution pH had significantly influenced the separation process of Cr(III) and the highest removal was 87% at a pH of 6.

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