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REMOVAL OF CD^{2+} AND PB^{2+} HEAVY METALS IN WATER BY USING ADSORPTION-ULTRAFILTRATION HYBRID PROCESS

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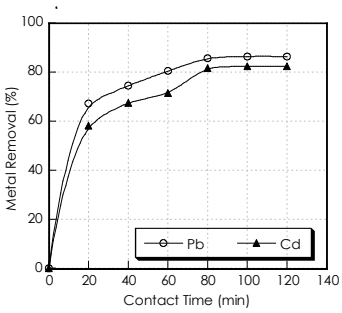
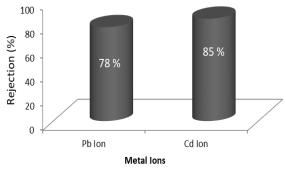
Graphical abstract





Abstract

Pollution caused by heavy metals is a serious problem for the environment. Cadmium and Lead are heavy metals that are highly toxic to living beings. These metals are non-biodegradable and remain in the environment for a long period of time. The removal process of these heavy metals with adsorption using Aceh natural zeolite followed by the membrane filtration has been conducted. Operating parameters such as contact time, sample pH and adsorbent dose found to affect the removal efficiency in the adsorption process. PES membrane which prepared by phase inversion technique was used to eliminate the residual heavy metals remained in the effluent of adsorption process. The final concentration after removal with both processess was 0.21 mg/L and 0.242 mg/L for Cd^{2+} and Pb^{2+}, respectively. Although the concentration are still above the permitted threshold, which is no more than 0.005 mg/L for Cd^{2+} and 0.01 mg/L at maximum for Pb^{2+}, this combination can however still be an alternative that can be employed to remove heavy metals in water.

Keywords: Cadmium, Lead, zeolite, adsorption, ultrafiltration

1.0 INTRODUCTION

The presence of heavy metals in water and wastewater is an important concern to public health because most of these heavy metals are non-biodegradable[1]. The toxicity of heavy metals is increasing with the accumulation in body tissues of living organisms. The particularly dangerous heavy metals that can pollute the environment include mercury (Hg), lead (Pb), arsenic (As), cadmium (Cd), chromium (Cr), and nickel (Ni). Cadmium metal (Cd) is the most toxic heavy metal element after mercury (Hg). Therefore, special attention is needed to find an effective and efficient method of removing it from ground water. According to the Ministry of Population and Environment Decree No.20/MENKLH/II/1990, the specified maximum levels of Cd^{2+} and Pb^{2+} in drinking water are 0.005 and 0.05 mg/L, respectively.

A number of technologies such as adsorption[2-5], coagulation [3], bioflocculant [6], synthetic polymers [7], flotation [8], ion exchange, algae [9] has been performed to reduce the content of Cd^{2+} and Pb^{2+} in water and wastewater. However, adsorption is by far the most widely used process because it is easy, simple and environmentally friendly [10]. Commonly used adsorbents include zeolites, clay, activated carbon, biomass and polymeric materials. Even so, these adsorbent have a low adsorption capacity.

Membrane separation process, especially the ultrafiltration (UF), becomes an alternative process for reducing cadmium metal in water. This is because this process has several advantages including low energy consumption, does not require additional chemicals, easy to scale up, and easily combined with other processes [11]. The use of membrane process to remove cadmium metal has been done by several researchers such as emulsion liquid membrane [12], nanofiltration [13]. Partially, separation by adsorption and filtration method has been done by a number of researchers, however, optimum results were hardly obtained. The hybrid of 'adsorption-ultrafiltration' process is one of the options that can be used to remove metal Cd^{2+} and Pb^{2+} contained in water. This combination of processes is expected to provide better process efficiency [3].

The adsorption process was carried out using Aceh's natural zeolite adsorbent. Process parameters such as contact time, adsorbent dose, and sample pH were evaluated on the adsorption process. Effluent resulting from adsorption process was then used as a feed for ultrafiltration process. The supporting PES membrane was made by phase inversion method by using polyethersulfone polymer as the main material of membrane constituents. This polymer is the most widely used as a material for polymeric membranes because it is resistant to high temperature, wide pH tolerance, has excellent mechanical and chemical strength and is easy to manufacture [14]. N-Methyl Pyrrolidone (NMP) was used as a solvent. Pure water flux test, morphological test, Molecular Weight Cut-off (MWCO) were performed to characterize the membrane. Flux and rejection of metals Pb^{2+} and Cd^{2+} were carried out to evaluate the membrane performance.

2.0 METHODOLOGY

2.1 Adsorption Process

Zeolite which acquired from Ujung Pancu Aceh was used as an adsorbent. The zeolite was shrunk to a size of 100 mesh. The preparation and composition analysis of Aceh natural zeolite have been described in the previous paper [15]. A total of 1000 mg/L stock solution of Cd^{2+} and Pb^{2+} metals was prepared separately by dissolving $Cd(NO_3)_2$ and $Pb(NO_3)_2$ in distilled water. The stock solution was then diluted again with distilled water to make solution with desired concentration, the pH is adjusted by adding 1M solution of HCl or NaOH.

The batch adsorption process was carried out by placing 100 ml of sample solution into a 250 ml beaker glass and 1 g of adsorbent. Following that, the mixture was stirred using a stirrer with speed of 100 rpm. Contact time interval was set in a range of 20; 40; 60; 80; 100 and 120 minutes. Various operating conditions such as pH of sample solution (3, 4, 5, 6, 7, 8, and 9), adsorbent dose (0.1, 0.3, 0.5, 0.7, 0.9; 1 g) were also determined in this research. Concentrations before and after the adsorption process were examined using Atomic Absorption Spectroscopy (AAS).

2.2 Preparation of PES Membrane

The fabrication of asymmetric PES membrane was done via phase inversion technique by immersion precipitation method. The casting solution was prepared by mixing PES powder with NMP solvent with a composition ratio of 17.5: 82.5%. The mixture was stirred until homogeneous. The transparent homogeneous solution is called dope. The dope solution was stored in the refrigerator for more than 24 hours to remove air bubbles. Prior to casting, the dope was allowed in the room condition for some time until it reaches room temperature. Following that, the dope was poured onto a glass plate and flattened onto the entire glass surface using the Casting Knife. The formed thin layer was left at room temperature for 15s (evaporation of the solvent). Afterward, the casted glass was dipped in a coagulation bath containing precipitant media in the form of technical isopropanol that serves as a non-solvent (precipitation process). This process was allowed until the membrane layer was detached from the glass plate. During precipitation process, the temperature of the coagulation bath was kept constant at room temperature of 27°C. The manufactured membrane was then through annealing process by heating slowly to a temperature of 70°C. The temperature was maintained for 10 minutes. After that the membrane was stored in distilled water until further use.

2.3 Membrane Characterization

The morphology, pure water flux and cadmium metal removal of the fabricated membrane were characterized with procedures as described below.

2.3.1 Membrane Morphological Analysis

The morphology of the membrane was analyzed by means of Scanning Electron Microscopy (SEM). The membrane was cut to a small size and then dried by using a freeze dryer for 24 hours to remove the water content. After that, the membrane was coated by using platinum to provide electrical conductivity to the membrane. The surface structure, cross sectional

and macrovoid structures of the membrane were observed.

2.3.2 Pure Water Permeation

The ultrafiltration experiment was carried out using the apparatus as shown in Figure 1. Pure water flux testing was conducted in batch system. A plate-shaped membrane module made of stainless steel was used in this experiment. The effective area of the membrane was 0.0152 m^2. The experiment was performed on several variations of operating pressure namely 1; 1.25; 1.5; 1.75 and 2 bar. The procedure was done by passing pure water through the membrane. Furthermore, the permeate was accommodated and measured. The pure water flux was calculated using equation (1).

$$J = \frac{\Delta V}{\Delta t} xA \qquad (1)$$

Where J represents the flux (Lm^{-2} $hour^{-1}$); ΔV is the volume of permeate (L), Δt is time (h) and A is the membrane surface area (m^2).

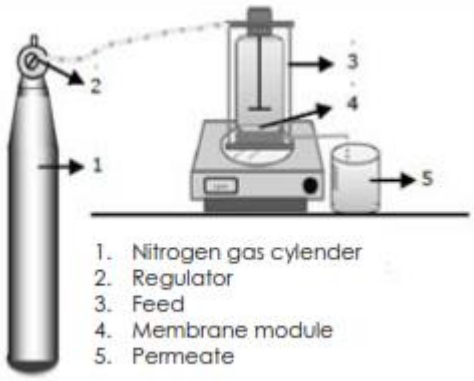


Figure 1 Ultrafitration equipment process

2.3.3 Molecular Weight Cut-Off (MWCO) Test

Polyethylene glycol (PEG) with molecular weights of 2000, 6000 and 20,000 da were used to determine the MWCO of the PES membrane. The dextran solution of various molecular weights was prepared with a concentration of 50 mg/L. The PEG solution was passed through the membrane with a trans membrane pressure (TMP) of 1.25 bar and then the resulting permeate was accommodated and measured over a period of time and its concentration was analyzed using a UV-Visible Spectrophotometer at a wavelength of 273 nm.

2.3.4 Cd^{2+} and Pb^{2+} Removal Evaluation

The dead end membrane process was performed to continue the removal process of Cd^{2+} and Pb^{2+} metals. Membrane performance was determined by the flux and rejection of Cd^{2+} and Pb^{2+}.The feed used was the effluent from adsorption process. The feed was flowed to the membrane unit using compressive gas as a driving force with variations of operating pressure of 1, 1.25, 1.5, 1.75 and 2 bar. Permeate was collected over a period of time to evaluate the flux. The permeate was then analyzed using AAS. The rejection percentage can be calculated using equation (2).

$$R(\%) = \left(1 - \frac{Cp}{Cf}\right) x100 \qquad (2)$$

Where Cp is the permeate concentration and Cf is the concentration of the feed solution.

3.0 RESULTS AND DISCUSSION

3.1 Adsorption Process

3.1.1 Influence of Contact Time on the Removal of Cd^{2+} and Pb^{2+}

The effect of contact time on Cd^{2+} and Pb^{2+} metals adsorption was studied by adding 1 g of adsorbent to 100 ml of a metal-containing solution into each beaker glass. Beaker glass was then stirred at a certain time interval range (20-120 minutes) with a stirring speed of 100 rpm. The temperature condition was set at room temperature (30 °C).

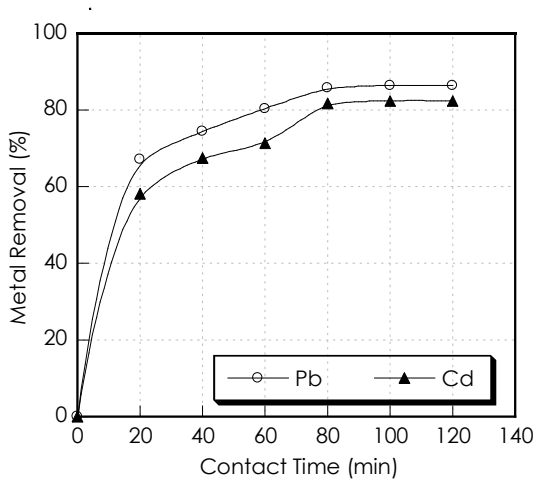


Figure 2 Effect of contact time on percentage of Cd^{2+} and Pb^{2+} metals absorption under operating conditions: metal concentration of 20 mg/L; Stirring speed of 100 rpm; Dose of adsorbent 1 g; Temperature of 30°C

Figure 2 displays the effect of contact time on Cd^{2+} and Pb^{2+} adsorption percentage. The results showed that the adsorption rate was rapid in the first 20 minutes time range, then increased and reached constant in the 80 minutes contact time. This is due to the decreasing of the active side or the contact surface of the adsorbent. In addition, the rate of absorption depends on the metal ion transported from the bulk liquid phase to the active side of the adsorbent [3]. From the results it can be concluded that Aceh natural zeolite can be used to absorb heavy metals Cd^{2+} and Pb^{2+}. Absorption of metal Pb^{2+} is higher than that of metal Cd^{2+}.

3.1.2 Influence of pH on the Removal of Cd^{2+} and Pb^{2+}

One of the factors that influence the adsorption process is the pH of the sample solution. The pH of the solution may affect the charge on the surface of the adsorbent [16]. The pH value also affects the chemical equilibrium, either on the adsorbate or on the adsorbent. The effect of the pH of the solution was studied in the range of 2-9 as shown in Figure 3. The removal percentage of the two heavy metals is strongly influenced by this parameter. The absorption percentage is obtained rather low under acid solution condition (low pH). This is due to competition between metal ions and H_3O^+ .The amount of heavy metal adsorbed increases with increasing pH of the solution. Maximum adsorption occurs at pH 7.

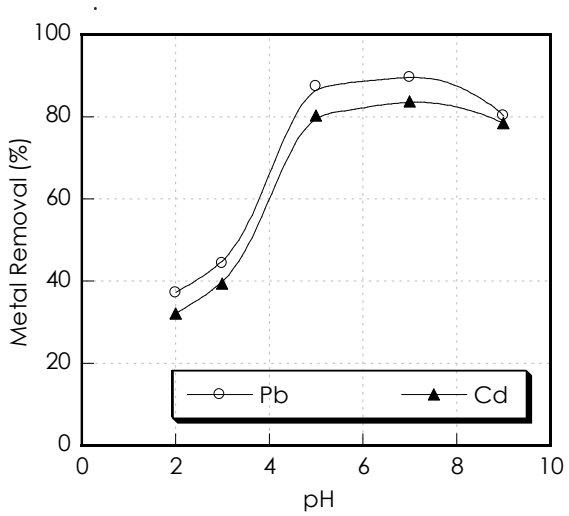


Figure 3 Effect of pH of sample solution on the percentage of Cd^{2+} and Pb^{2+} metals absorption under operating conditions: metal concentration of 20 mg/L; Stirring speed of 100 rpm; Dose of adsorbent 1 g; Temperature of 30°C

3.1.3 Influence of adsorbent dosage on the removal of Cd^{2+} and Pb^{2+}

The dose of adsorbent has an effect on adsorption process. The effect of adsorbent dose on the percentage of Cd^{2+} and Pb^{2+} metals removal as shown in Figure 3. The percentage of absorption of both metals increases with increasing dose of adsorbent. This is due to the increasing surface area and active site of the adsorbent [17]. In addition, increased doses of the adsorbent also increase the surface functional groups, hence more active surface sides can be interchanged with heavy metals to form complexes with metal ions [18]. Maximum absorption for Cd^{2+} and Pb^{2+} are 86 and 89%, respectively.

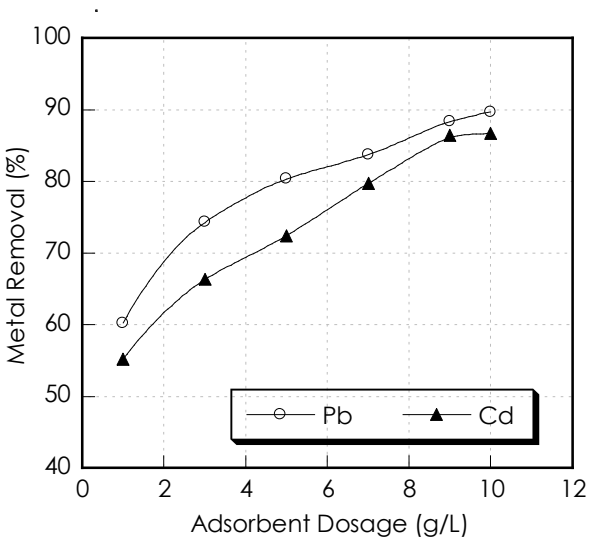


Figure 3 Effect of pH solution on percentage of Cd^{2+} and Pb^{2+} metals absorption at operating condition: metal concentration 20 mg / L; Stirring speed 100 rpm; Dose of adsorbent 1 g; Temperature of 30°C

3.2 Membrane Filtration Process

The resulting Cd^{2+} and Pb^{2+} containing solution from adsorption process was passed through the ultrafiltration membrane. The membrane was fabricated by phase inversion techniques through immersion precipitation. Prior to use, the membrane undergone several characterization such as the following:

3.2.1 Membrane Morphological Test

The surface and cross sectional structures of PES/NMP membrane were analyzed using Scanning Electron Microscopy (SEM), the result is presented in Figure 4. From the figure, it can be confirmed that the obtained membrane has an asymmetric structure. The membrane surface has a dense structure, meanwhile the bottom side has a porous structure and nonwoven support.

The forming process of the upper surface of the pores is influenced by the thermodynamic properties of the dope solution and the kinetics during the formation of the membrane. In the formation stage, the membrane was allowed to evaporate solvent for 15 seconds, this was where the active top layer was formed. The second stage during the immersion of PES membrane (which is rich in polymer) can be considered stable, where solvent and nonsolvent diffuses in the coagulation bath [14]. The diffusion rate between the solvent and the non-solvent in the coagulation bath affecting the process of sublayer formation. In the PES membrane fabricated in this study, finger-like porous sublayer was obtained.

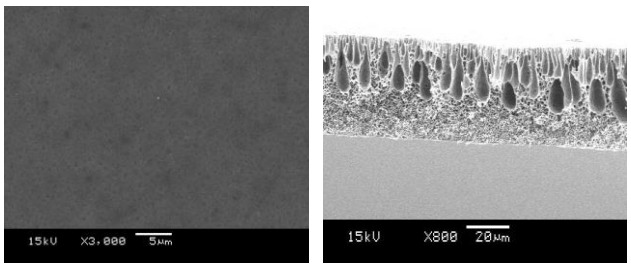


Figure 4 SEM image of PES/NMP membrane. Left: Surface Section, Right: Cross Section

3.2.2 Pure Water Permeation

Pure water flux is an important parameter used for industrial processes. Pure water flux has a direct relationship with the number and size of pores on the membrane surface [19].The relationship between pure water flux with Trans Membrane Pressure (TMP) is shown in Figure 5, where the increase in TMP is directly proportional to the resulting flux. The highest flux was obtained at 32.25 L/m^2.h at 2 bar TMP condition.

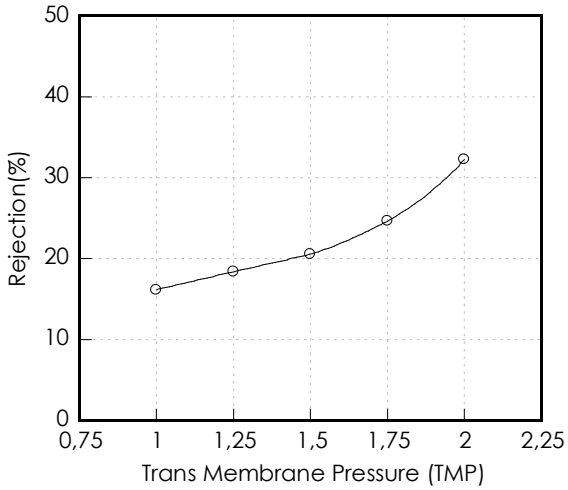


Figure 5 Pure Water Flux of PES Membrane

3.2.3 Molecular Weight Cut-Off (MWCO)

MWCO is a characteristic of membrane pores associated with rejection of a solution with variation in molecular weights [14]. The percentage of rejection is in the range of 100 to 0%, where 100% shows a complex rejection whereas 0% means no solutes are retained on the membrane. Generally, 80% of the molecular weight retained by the membrane is decided as a criterion for the determination of MWCO [20]. The polyethylene glycol (PEG) and MWCO rejection of the prepared membrane can be seen in Figure 6. The results show that the rejection of PEG with molecular weight of 16000 Da reaches 80%. Therefore, it can be concluded that the MWCO of the PES membrane is 16000 Da

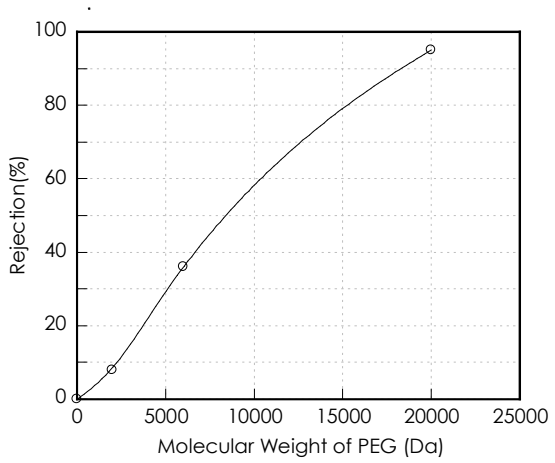


Figure 3 Molecular Weight Cut-Off (MWCO) of PES Membrane

3.2.4 Metal Ion Separation

The maximum removal rate of Cd^{2+} and Pb^{2+} with adsorption process using Aceh natural zeolite were 86% and 89%, respectively. The concentration of Cd^{2+} after the adsorption process was 1.4 mg/L, meanwhile the remaining Pb^{2+} metal after the adsorption process was 1.1 mg/L. The concentrations of these two metals are still above the threshold of drinking water quality standard. The maximum content of Cd^{2+} allowed in drinking water is 0.005 mg/L, whereas for Pb^{2+} it is 0.01 mg/L. Therefore, further processing is required in order to reduce the content of metals contained in water for it to comply to the permitted standards. In this case, the effluent from the adsorption process is then fed to the ultrafiltration process. To evaluate the performance of the ultrafiltration process, the respective metal feed concentrations were 1.4 mg/L and 1.1 mg/L for Cd^{2+} and Pb^{2+} metals. Figure 6 shows the performance of the two metals removal using the membrane filtration process. Rejection for metal Pb^{2+} was higher than that of Cd^{2+}. The final concentration of Cd^{2+} was 0.21 mg/L and 0.242 mg/L for Pb^{2+}.

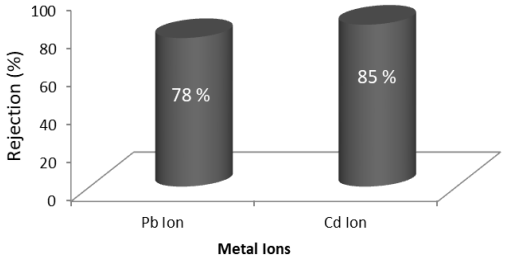


Figure 6 The Rejection of Metal Ions on Membrane Ultrafiltration Process

From the obtained results, it is certain that the adsorption followed by the ultrafiltration process can

improve the removal of Cd^{2+} heavy metals existing in the sample solution. This process can be one of the alternative approaches that can be used to diminish heavy metals in water

4.0 CONCLUSION

The separation of Cd2+ and Pb2+ heavy metals in water using natural zeolite has been studied. Operating parameters such as contact time, sample pH and adsorbent dose were studied on the percentage of Cd2+ and Pb2+ removal. It has been confirmed that these variables did influence the removal performance of Cd2+ and Pb2+. After the adsorption process, the concentrations of Cd2+ and Pb2+ were still considerably high and require further treatment. Therefore, the effluent of the adsorption stage was handled further by ultrafiltration technique. The final concentration of Cd2+ was 0.21 mg/L, and 0.242 mg/L for Pb2+. Even though the final concentrations were still slightly above the permissible threshold, it can still be concluded that the combination of these process can be employed as a potential alternative process to reduce metal Cd2+ and Pb2+ in water.

Acknowledgement

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