

Cellulose Acetate/Zeolite-A Membrane for Ni²⁺ Adsorption

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The aim of this study is to improve the performance of zeolite-A as an adsorbent material using cellulose acetate (CA) addition as a support membrane, for Ni²⁺ ions adsorption. The membrane is called as Cellulose Acetate/Zeolite-A (CA/ZA) membrane, which was prepared by a phase inversion-immersion method. The CA/ZA membrane was prepared in 12.5 wt% CA at various ZA loading of 0, 1, 2, 3, 4 wt%. The CA membrane with 3 wt% zeolite-A addition has the best performance with flux of 366.9 L.m⁻²h⁻¹ at 2 bar of pressure and has 73.46 % porosity. The best CA/ZA membrane was used for Ni²⁺ adsorption at various pH of metal ion solution. It was found that the optimum pH condition for Ni²⁺ adsorption was 10, which can adsorb Ni²⁺ ion up to 66.11% with an adsorption capacity of 0.26 mg.cm⁻². SEM-EDX characterization showed that Ni²⁺ ion was distributed in the CA/ZA membrane. FTIR spectra showed no new peak on the used membrane for adsorption, indicating the physical adsorption between Ni²⁺ ion and the membrane.

1. Introduction

The water pollution is caused by the heavy metal pollutants such as cadmium, chromium, copper, nickel and mercury (Sprynskyy et al., 2006). The heavy metal ions are usually released from wastewater from mining, electroplating and electronic industries to the environment (Elsayed-Ali et al., 2011). In the case of wastewater of electroplating industry, Vijayaraghavan (2006) reported that the waste that they studied contains Pb²⁺, Ni²⁺, and Cu²⁺ ions in a concentration of 4.5, 109.0 and 1.3 mg.L⁻¹. Martin-Lara (2014) reported an electroplating wastewater that contains 4710 mg.L⁻¹ of Ni²⁺ and 1.1 mg.L⁻¹ of Cu²⁺ with a pH about 7.6. Based on the studies, it can be seen that Ni²⁺ and Cr⁴⁺ ions were found in quite high concentration in electroplating wastewater. Ni²⁺ ion is toxic if maximum pollution loads are above 0.02 mg.L⁻¹. In drinking water, the concentration of Ni²⁺ ion that safe for human is not more than 1 mg.L⁻¹. Reducing heavy metal pollution is an important stage in wastewater treatment.

Based on the literature studies, heavy metal adsorption has been investigated using several adsorbents such as adsorption of Ni using Oil Palm Mesocarp Fiber (Syed-Hassan et al., 2014) and acetic acid and EDTA modified Cellulose which was extracted from Empty Fruit Bunches of Oil Palm (Daneshfozoun et al., 2014), Cu²⁺ ion using basic ash, Fe³⁺ ion using zeolite and Cu²⁺ and Ni²⁺ ions using zeolite-A (Ji et al., 2012), with adsorption efficiency of 98.1 %, 80 %, 20 %, 98.5 %, and 82.8 %

Zeolite is a potential adsorbent material for heavy metal adsorption. The ability of zeolites to adsorb and exchange ions is due to the cages and a negative charge of the zeolite. The cage and channel structure of zeolites are constructed by the aluminium and silicon atoms structure in three-dimensional framework of aluminosilicate tetrahedral, that are bound by the covalent bonds over common oxygen atoms in order to form interconnected cages and channel. Substitution of each aluminium ion (Al³⁺) with silicon ion (Si⁴⁺) in the zeolite framework generates a negative charge in the zeolite. The negatively charge can be exchanged with heavy metal ions on the external surface of zeolite (Widiastuti et al., 2011). However, the use of zeolite powder as an adsorbent remains challenging due to non-reusable adsorbent. An alternative method is by using support material incorporated with the zeolite.

One of materials that can be used as a supporting material is polymer material, such as cellulose acetate in the form of membrane. CA is a polymer material widely used as a membrane material. CA is an esteric polymer of hydrophilic acetic acid and cellulose. CA has several characteristics, such as high water absorption rate and heat resistance up to 60 °C. CA membrane for separating metal ions has been reported by Chen et al. (2004)

in which CA was blended with poly etherimide (PEI). The results of the study showed that the metal ion adsorption value was 7.42 mg.g^{-1} of membrane with an initial concentration of 150 mg.L^{-1} . Other studies have also reported about the use of CA as a supporting material for zeolite adsorbent formed as a membrane. This composite material was called as cellulose acetate/zeolite-A (CA/ZA) membrane. The adsorption capacity of the CA/ZA membrane was reported up to 99.5 % for Cu^{2+} metal ions.

In this study, adsorption of Ni^{2+} ions were conducted using CA/ZA membranes prepared by a phase inversion-immersion method. The aim of this research is to study the optimization of CA concentration in membranes. Furthermore, the optimum result of the membrane was added by zeolite into the membrane cast solution at a certain amount of zeolite. Membrane performance was analyzed includes membrane porosity test, water flux, metal ion solution and membrane rejection.

2. Experiments

2.1. Materials

The material used in this study was cellulose acetate (CA, MW = 52.000 Da) obtained from Fluka Analytic, N,N-dimethylacetamide (DMAC) solvents purchased from Merck, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, K_2CrO_7 and material for zeolite synthesis, such as NaOH pellets (MW 40 g.mol^{-1}) taken from Merck, NaAlO_2 and Na_2SiO_3 purchased from Sigma Aldrich, and HCl (p.a, 37 %).

2.2. Synthesis of Zeolite-A

Zeolite-A (ZA) was synthesized by a simple hydrothermal method from NaOH, NaAlO_2 and Na_2SiO_3 solutions. NaOH solution was made by dissolving NaOH pellets in deionised water. The NaOH solution was then divided into two parts and called as solution A and B. NaAlO_2 and Na_2SiO_3 were added into solution A and B, and stirred separately for 20 min. Then, the two solutions were mixed and stirred at 500 rpm for 12 h. The molar ratio of $\text{Na}_2\text{O} : \text{Al}_2\text{O}_3 : \text{SiO}_2 : \text{H}_2\text{O}$ of the mixture was 3.165: 1: 1.926: 128. The mixture was then put into a hydrothermal reactor and heated at 100°C for 15 h. The resulted precipitate was then washed with deionised water several times until the pH was reduced to 8, then, the precipitate was decanted and dried in an oven at 80°C for 12 h. The synthesized zeolite was characterised using X-ray diffraction (XRD) to find its crystal phase and crystallinity.

2.3. Preparation of CA membrane and CA/ZA membrane

CA membrane was prepared by a phase inversion-immersion method at CA = 12.5 wt% in N,N-dimethylacetamide (DMAC) solvent. CA/ZA membranes were prepared with the same method at various zeolite-A and DMAC amount as shown in Table 1.

Table 1: Composition on CA/ZA Flat Membrane Preparation

Membrane	M0	M1	M2	M3	M4
Mass percentage of DMAC	87.5	86.5	85.5	84.5	85.5
Mass percentage of ZA	0.0	1.0	2.0	3.0	4.0

2.4. Membrane characterization

Porosity of CA/ZA membrane was measured by calculation of wet and dry membrane weights of 3 pieces membrane flat sheets of 2.1 cm in diameter. The process was conducted by weighting the membrane at wet condition (W_w) and measuring the thickness and membrane surface area. Then, it was heated in the oven at 60°C for 12 h. The membrane surface was dried using a filter paper and weighted until constant. Membrane porosity was calculated using Eq(1).

$$A_k = \frac{(W_w - W_d)}{P_w \times A \times \delta} \times 100 \quad (1)$$

where, A_k is membrane porosity (%), w_1 and w_2 are weight of wet and dry membranes (g), P_w is the density of water (1 g.cm^{-3}), A is the area of membrane circle (cm^2) and δ is the membrane thickness (cm).

Flux determination was conducted by using ultrafiltration cell batch. The flux measurements were determined by measuring permeate volume per minute as shown in Eq(2).

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

J = flux ($\text{L.m}^{-2}.\text{h}^{-1}$), T = time (h), V = permeate volume (L), A = membrane surface area (m^2)

The morphology of pure and composite membrane were analyzed by Scanning Electron Microscopy (SEM). The membrane surface was coated with a thin layer of carbon. The synthesized zeolite-A was characterized

using X-Ray Diffraction (XRD) Expert PANalytical with CuK α radiation ($\lambda = 0.15406$ nm) at 40 kV and 30 mA to identify crystal phase and crystallinity.

The presence of zeolite in the membrane and the changes of functional groups before and after the adsorption process by the membrane were analyzed using Fourier Transform Infrared (FTIR). The membranes were cut in small pieces of 2 cm x 5 cm as many as 4 pieces for FTIR analyses. The IR spectra was taken from 700 to 3600 cm^{-1} .

2.5. Adsorption of Ni²⁺ ion

Analysis using Atomic Absorption Spectrophotometry (AAS) was conducted to determine the concentration of metals adsorbed by the membrane. The preparation step of the test was carried out by preparing cellulose acetate/zeolite-A membrane (2 x 5 cm^2) as many as 15 pieces. Then, the membrane was immersed in Ni solutions at pH of 2, 4, 6, 8 and 10 with the amount of CA membrane and CA/ZA membrane adsorbent of 1.5 g, volume of 50 mL, 48 h, temperature of 23°C and initial concentration of 50 mgL^{-1} .

The analysis was performed by the metal solution concentration after adsorption as can be seen in Eq(3) and Eq(4)

$$\text{Ads\%} = \frac{(C_0 - C_1)}{C_0} \times 100\% \quad (3)$$

$$q_e = \frac{(C_0 - C_e) \times V}{A} \quad (4)$$

Ads% = adsorption percentage (%), q_e = saturated adsorption capacity (mg.cm^{-2}), C_0 = initial concentration before adsorption (mg.L^{-1}), C_1 = final concentration after adsorption (mg.L^{-1}), V = volume of sample solution (L), A = membrane area (cm^2)

3. Results and discussion

3.1. Membrane morphology

Figure 1b shows that there is large number of zeolite dispersed uniformly in CA/ZA membrane as compared to the CA membrane. The dispersion of zeolite attributed by the silica and aluminium shown in Figure 1c and Figure 1d indicates that the zeolites were embedded in the cellulose acetate matrix. This is attributed to the interfacial interaction between zeolite and cellulose acetate.

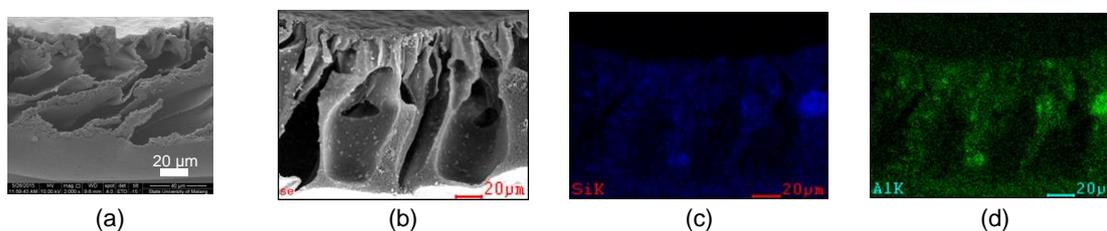


Figure 1: SEM images of (a) cross section CA membrane, (b) cross section CA/ZA membrane, (c) distribution of silica from zeolite in the membrane, (d) distribution of alumina from zeolite in the membrane.

3.2. XRD results

Figure 2 shows that the diffractogram of the synthesized zeolite is similar to JCPDS No. PDF 0038-0241 for LTA type zeolite-A [$\text{Na}_{96}(\text{AlO}_2)_{96}(\text{SiO}_2)_{96} \cdot 216\text{H}_2\text{O}$]. Furthermore, diffractogram of CA as shown in the figure, appropriates with a diffractogram reported by Fan et al. (2013), who stated that CA has distinctive angles at 2θ of 10° and 13.2°. These two typical angles were also recognized as the crystalline peaks of modified CTA II (Deus et al., 1992). In addition, Jayalakshmi et al. (2014) reported that the diffractogram of CA membrane had a typical semi crystalline angle at 2θ of 9.6° and two crystalline angles at diffraction angles of 20.1° and 26.8°. The diffractogram of CA membrane in this study were identified as a crystalline peak at 26.8°. Composite membrane also has a crystalline peak at 26.8°. Moreover, the composite membrane has also a weak peak at 10° and 13.2° indicating the typical peak of CA in different intensities. It was caused by a decreasing crystallinity form in the membrane compared to CA solids. It was reviewed that the CA/ZA membrane has a peak at an angle of 10.3, 12.6 and 16.2 indicating the presence of zeolite-A. Based on the results of the composite membrane diffractograms, it was known that zeolite-A has better dispersity in the CA porous membrane as a

filler. The same trend has been reported by Soheilmoghaddam et al. (2014), when zeolite was incorporated with cellulose in bionanocomposites.

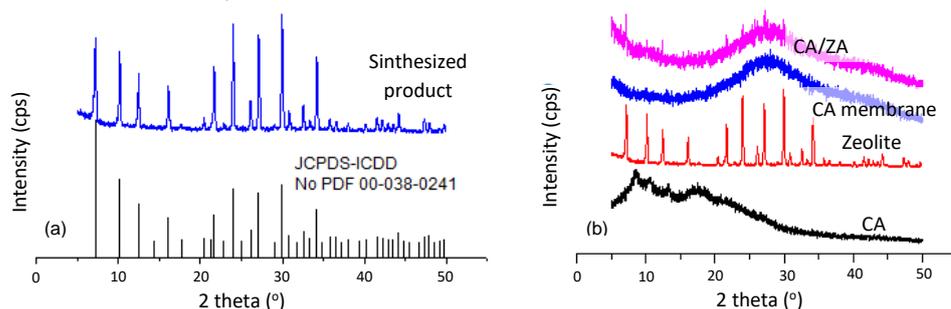


Figure 2: Comparison of X-ray Diffractograms of: (a) Zeolite-A and (b) CA, Zeolite-A, CA Membrane and CAZA Membrane

3.3. Membrane porosity and water flux of the membrane

Porosity test was conducted on CA and CAZA membrane to determine the membrane pore distribution. The greater membrane porosity, the higher membrane surface area. The pores formation on the membrane occurred during the membrane moulding process in the coagulation tub. When the dope solution was contacted with non-solvent, there was a mass exchange between solvent and non-solvent that caused the solidification of the membrane. During a mass exchange of solvent occurred, there was also a cavity in the membrane that was known as membrane pore. Figure 3a shows the effect of zeolite addition on the membrane porosity. The largest membrane porosity found on CA membrane with addition of 3 % zeolite-A. Addition of 4 % zeolite-A causes a decrease of porosity. The higher amount of zeolite added in the CA membrane caused the agglomeration of the zeolite resulting in blocking the membrane pores, thus the porosity decreased.

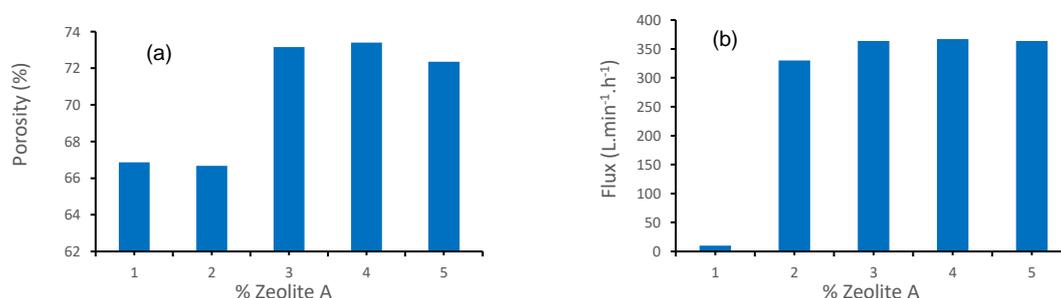


Figure 3: (a) Porosity of CA Membrane and CAZA Composite Membrane, (b) Flux of CA Membrane and CAZA Composite Membrane

Flux test on the membrane was performed to confirm the result of the porosity test. A larger pore membrane shows a high flux result, due to the diffusivity between the high membrane components. In this study, a pure water flux test was conducted to determine the optimal performance of CAZA membrane. Figure 3 (b) shows that the pure water flux highly increases with the increasing of zeolite-A content from about 10 L.m⁻².h⁻¹ of CA membrane without zeolite to 330 L.m⁻².h⁻¹ of CA membrane with zeolite addition at 1% (w/w). This is because the insertion of zeolite in the CA membrane increases the hydrophilicity of the CA membrane. Enhancing water flux could be understood on the basis of their hydrophilic nature contrived by the greater affinity of hydroxyl group for water. The best flux performance was obtained by the CA membrane at the amount of 3% (w/w) zeolite-A addition with the maximum flux of 366.9 L.m⁻².h⁻¹ at pressure of 2 bar. However, in the composition of 4 % zeolite, the membrane flux decreases to 363.85 L.m⁻².h⁻¹. As discussed before, the agglomeration of the zeolite caused blocking the membrane pore, thus the porosity and the water membrane flux decrease (Shi et al., 2012).

3.4. Adsorption of Ni²⁺ ion using CA/ZA membrane

Figure 4 shows the Ni²⁺ ion absorption in a single ion solution using a CA/ZA membrane. The maximum absorption of Ni²⁺ ion occurred at pH 10 with 66.11 % of adsorption percentage and 0.26 mg.cm⁻² of adsorption capacity. The adsorption result of Ni²⁺ ion using CA/ZA membrane from this study showed that the results were consistent with research reported by Ji et al. (2012), who states that the optimum adsorption capacity of Ni²⁺ ion in CA/ZA hollow fibre membrane occurred when the solution was in alkaline pH condition. It was due to high selectivity of the zeolite for H⁺ ions at the high H⁺ ion concentration (Hui et al., 2005). Therefore, hydrogen ions competed with Ni²⁺ ions was adsorbed at low pH solution. Increasing pH solution, decreasing hydrogen ion concentration. As a result, the competition of metal ions with hydrogen ion also decreased. Consequently, the amount of adsorbed metal ions increased.

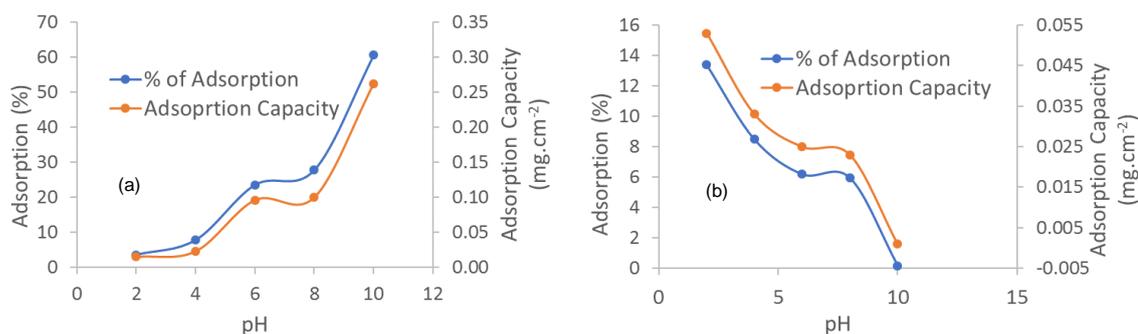


Figure 4: The relation of pH with percentage of adsorption and adsorption capacity of metal ions: (a) Ni²⁺ and (b) Cr⁴⁺. Adsorbent: 1.5 g, volume: 50 mL, time: 48 h, temperature: 23 °C and initial concentration: 50 mg.L⁻¹

Figure 5 shows the cross-sectional morphology of the CA/ZA membrane before and after metal ion adsorption. The figure shows that CA/ZA membrane has larger hollow pores before metal adsorption and the cause of reduced pores was filling of the membrane pores by Ni ions.

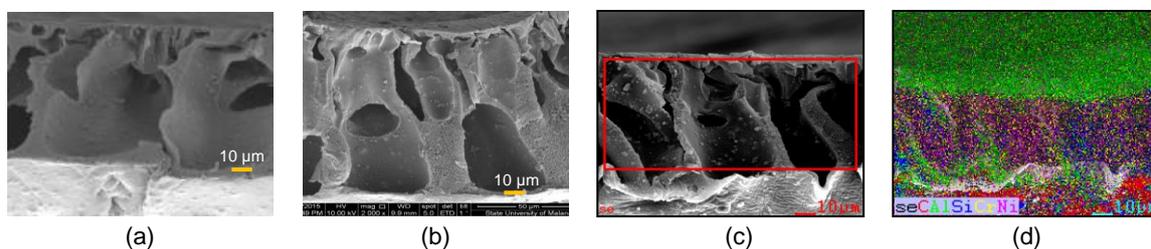


Figure 5: Morphology of CA/ZA Composite Membrane: (a) before adsorption, (b) after adsorption, (c) membrane area analyzed, and (d) dispersion of zeolite-A and Ni²⁺ ion on membrane

Figure 6 shows the FTIR spectra of membranes before and after the adsorption of metal ion. As can be seen, a peak was observed at 600-800 cm⁻¹, which is assigned to T-O-T stretching and T-O bending of zeolite (Armaroli et al., 2006).

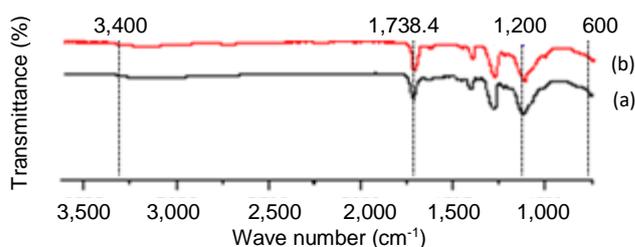


Figure 6: FTIR spectra of membrane: (a) before adsorption, (b) adsorption of metal ion of Ni (II) at pH of 10

A sharp peak in such region indicates the presence of zeolite inside the membrane. In addition, the membrane showed a peak in the region of 1,000-1,200 cm^{-1} , indicating the interaction between Si-O-Si of zeolite and CA. Some peaks were also detected at 1,735-1,738 cm^{-1} assigned to C=O stretching of CA and broad peak at about 3,400 cm^{-1} assigned to O-H stretching. Furthermore, the absence of new peaks was observed on the membrane after the adsorption process. However, the peak was slightly shifted and the peak intensity decreased. This might be due to the presence of Van der Waals force, indicating the physical adsorption between the metal ions and membrane.

4. Conclusions

The performance of zeolite-A as an adsorbent for Ni^{2+} ion has been improved significantly by using CA as a support membrane. 12.5 wt% of CA composition was used for preparing the CA/ZA membrane at various amount of ZA. Enhancement of flux and porosity were found from 11.61 $\text{L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ and 66.8 % of CA membrane to become 366.9 $\text{L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ and 73.46 % of CA/ZA membrane at 3 % (w/w) zeolite addition. From SEM images, zeolite-A was dispersed homogeneously in the CA membrane matrix and the adsorption of Ni^{2+} ion was also distributed in pore of the CA/ZA membrane. FTIR results indicated that there was physical adsorption between Ni^{2+} metal and CA membrane.

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