

Porous Chitosan-silica-polyethylene Glycol Membrane for Dynamic Adsorption of Binary Mixtures Cu(II) and Zn(II) Ions

F. Widhi Mahatmanti, Nuryono, and Narsito

Abstract—The adsorption of binary mixtures of Cu(II) and Zn(II) ions was studied using dynamic methods employing chitosan-silica-polyethylene glycol (Ch/Si/P) as adsorptive membrane. Ch/Si/P membrane was synthesized by blending rice hull ash (RHA) silica and polyethylene glycol into chitosan. Silica and polyethylene glycol blended into the Ch to improve the mechanical properties and the membrane porous. The membrane was characterized using mechanical properties test, scanning electron microscopy (SEM) and swelling test. Dynamic adsorption experiments suggested that the adsorption capacity depended on adsorbent morphology and differences concentration between the source phase and the stripping phase. Ch/Si/P membrane presented more affinity for Cu(II) than for Zn(II). The decrease of the amount of metal adsorbed onto Ch/Si/P membrane in binary system showed that the competition effects between two metal ions. The desorption was also investigated, Cu(II) and Zn(II) ions could be selectivity permeated using a process by water, HCl, and Na₂EDTA solution as the stripping phase.

Index Terms—Chitosan, membrane, dynamic adsorption, Cu(II) and Zn(II).

I. INTRODUCTION

Heavy metal contamination exists in aqueous waste streams of many industries, such as metal plating, mining operations, electroplating and pharmaceutical industry. The soil surrounding these sites is also polluted and can contaminate groundwater and surface water. Heavy metals are not biodegradable and tend to accumulate in living organisms, causing various diseases and disorders [1]-[3]. Copper and zinc pollution are of particular concern. Copper plays an essential role in animal metabolism. It is toxic at high concentrations, with effect including vomiting, cramps, convulsions and even death [1]. Zinc is most often found in plating and galvanizing operations. In plating shops the zinc is often complexed with cyanide and the cyanide must be treated to free the zinc before precipitation can occur. Traditional cyanide destruct systems use sodium hypochlorite to oxidize the cyanide [4].

The conventional treatments used to remove heavy metals from wastewaters are precipitation, coagulation, reduction, solvent extraction, electrochemical separation through membranes, ion exchange and adsorption [1], [2], [5], [6]. These methods usually concentrate the metal ions into a

smaller volume followed by recovery or secure disposal. Recently, membrane adsorption has appeared as a powerful technique for removal of heavy metal ions from effluents [6], [7]. Compared to the conventional methods e.g. chemical precipitation, ion exchange and adsorption columns, adsorptive membranes offer several advantages for separation of heavy metals such as excellent removal efficiency, high flow rate, low pressure drop, faster kinetic, reusability, smaller footprint and easy of scale up [1]-[3].

Chitosan, (1, 4)-[2-amino-2-deoxy-D-glucose] was a natural biopolymer derivative obtained from the partial deacetylation of chitin. Therefore, chitosan has amine side functional groups which are responsible for the poly-cationic character and the formation of well-known intermolecular complexes with carboxylic and polycarboxylic acids. In addition, it is a desirable polymer in chemical and biomedical fields due to its biodegradable performance [3], [7], [8]. The membrane prepared by chitosan plays an important role in the separation and recovery of heavy metal ions, because of its inexpensive, simple and biodegradable nature which could be used for the majority of heavy metal ion forms. However, the scope of preparing pure chitosan membrane has been largely limited due to the poor mechanical strength and chemical stability of chitosan [8]. To improve the mechanical strength, blending chitosan with silica and PEG has been found to be an effective way to overcome the problem, because blending, especially at the microscopic level through chemical interactions, could provide chitosan with the desired mechanical strength and chemical stability [8], [9].

The aim of this study was to compare the adsorption and desorption behavior of binary mixture Cu(II) and Zn(II) ions onto Ch/Si/P membrane. Desorption experiments were performed in one step, using water, HCl, and Na₂EDTA solution, with the objective of permeating selectivity these species.

II. EXPERIMENTAL SECTION

A. Materials and Methods

1) Materials

Chitosan was purchased from CV Ocean Fresh Bandung with a molecular weight, determined through viscometer method, of 8.78 kDa. All other chemicals (acetic acid, sodium hydroxide, hydrochloric acid, PEG, copper nitrate, zinc nitrate) were of analytical grade used without further purification. The solution was prepared using deionized water.

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Sodium silicate (25% SiO_2) was obtained from extraction rice hull ash.

2) Instruments

The membrane cell consists of cylindrical chamber that is separated into two halves by membrane Ch/Si/P (Fig. 1) [10], the effective volume of each chamber was 50 mL and the effective diameter of membrane was 2.5 cm. Atomic absorption spectroscopy/AAS (Perkin- Elmer AA200) was applied for determination of metal ions concentration in the sample solution.

- Feed solution phase
- Magnetic stirrer
- Stripping solution phase
- Membrane Ch/Si/P

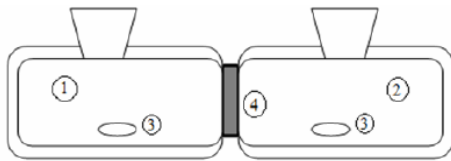


Fig. 1. Experimental set-up.

B. Preparation of Chitosan-silica-PEG Membrane (Ch/Si/P)

A silica and PEG blended chitosan membrane (Ch/Si/P) was prepared by mixing 1.0 g chitosan solution containing in 100 mL of 2 vol% acetic acid solution, mixing 0.8 g of rice hull ash sodium silicate solution and 0.5 g PEG were mixed with the chitosan solution. The mixture was thoroughly stirred until there was no air bubble in the solution. Membrane was obtained by casting the mixture on a glass plate and was allowed to evaporate the solvent under an ambient temperature for 3 days. Membrane was neutralized with a 5% (w/v) NaOH solution after drying. Afterward, the membrane was washed with water to remove the remaining NaOH. Finally, the membrane was characterized using mechanical properties test, SEM and swelling test.

C. Dynamic Adsorption Experiments

Binary component adsorption. The aqueous feed solution was prepared by dissolving metal ions in deionized water at concentration 25 mg/L, pH = 6.0. The deionized water, HCl 10^{-5} M, and Na_2EDTA 0.08 mM solution were used as the stripping phase. Transport process was done by placing of metal ion solution (25 mg/L) into the source phase chamber and 50 mL deionized water into the stripping phase chamber, and stirred (150 rpm) at room temperature, the transport test for 24 hours. Afterward deionized water was replaced by HCl 10^{-5} M and Na_2EDTA 0.08 mM solution. The concentration of metal ion present in the source and stripping phases were analyzed using Atomic absorption spectroscopy (Perkin- Elmer AA200).

III. RESULTS AND DISCUSSION

A. Characteristics Membrane

Effect of the PEG addition on the tensile strength,

elongation percentage and Modulus young of the chitosan-silica membrane is expressed in Table I, showing that blending with PEG changes the properties of the membrane. The tensile strength tends to decline with addition of PEG 0.5 g and more than that mass shows constant in the tensile strength. It may be attributed to the strong inner-stress existing in the membrane [9]. Mass ratio of chitosan/silica/PEG 1:0.8:0.5 have maximum percent Elongation and minimum Young's modulus, it is indicated that membrane strong and flexible.

TABLE I: TENSILE STRENGTH, PERCENT ELONGATION AND MODULUS YOUNG OF CH/SI/P MEMBRANE

Membrane Composition (chitosan:silica:PEG, in g)	Tensile Strength (MPa)	% Elongation	Modulus Young
1 : 0	24.1 ± 1.1	19.7 ± 0.1	122.3
1 : 0.8	24.4 ± 1.0	19.0 ± 0.2	128.4
1 : 0.8:0.5	16.5 ± 0.9	20.5 ± 0.4	80.5

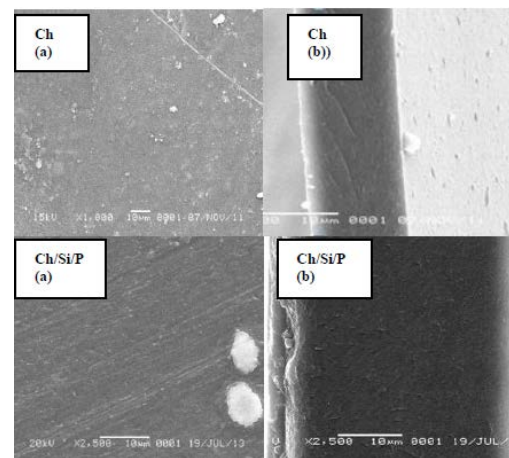


Fig. 2. SEM images of the Ch and Ch/Si/P membranes: (a) Surface, (b) Cross section.

Fig. 2(a) and Fig. 2(b) surface and cross section image Ch membrane showed that dense membrane. The addition of silica and PEG into chitosan membrane (Ch) resulted in the pores increases. The calculation of the value of the pore size distribution using SEM photograph with a computer program *Image J* as performed by [11], [12]. Ch/Si/P membrane has an average value of pore size $1.9 \mu\text{m}$.

Fig. 3 presents the swelling capability represented by swelling index (%) of the membranes. The sensitivity of the membrane toward pH is from the nature of chitosan. Hydrophilicity of the membrane increases with the addition of PEG and decreases with the addition of silica. In general, the modifying with silica and PEG influenced the physical properties and water adsorption [9].

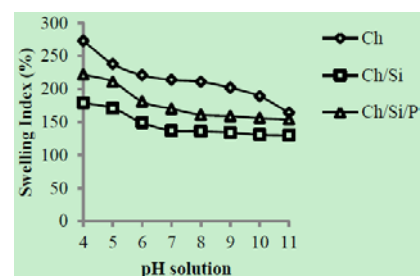


Fig. 3. Plot of swelling index (%) for Ch, Ch/Si, and Ch/Si/P membranes in a buffer solution with various pHs.

B. Binary Component Adsorption Result

Fig. 4(a) and Fig. 4(b) show the adsorption and desorption (permeated) of binary copper and zinc ions onto Ch/Si/P membranes in various phase stripping solution. In the water, HCl and Na₂EDTA as phase stripping solution, adsorption Cu(II) > Zn(II). The ions Cu(II) and Zn(II) are an intermediate acid according to the HSAB concept, so the two ions have the same tendency to bind with -NH₂ [13]. The amount of ions were adsorbed on the medium to follow the order of water > HCl > Na₂EDTA, and vice versa permeated ions in Na₂EDTA > HCl > water. It indicates that the stability of the complex compounds formed between ions with -NH₂ greater in Na₂EDTA medium compared with water and HCl. The Na₂EDTA is a chelating agent that is strong compared with HCl and water. These results can be explained that the formation of complex compounds with metal ions -NH₂ largely through the formation of complex compounds with Na₂EDTA relatively stable so difficult to be released again. In HCl medium, the formation of complex compounds made possible through the mechanism of the formation of hydrogen bonds are less stable so that the metal ion be easily detached [14]. The amount of Cu(II) adsorbed greater than Zn(II), this can be explained by the ionic radii of metal ions. This fact can be correlated with the ionic radii: Cu(II) < Zn(II). This resulted in the environment around the Zn(II) is more crowded than Cu(II), so that the Cu(II) more easily bind to the active groups on the membrane. Thus the complex compounds of Cu(II)-NH₂ in the membrane more stable than Zn(II)-NH₂. These data are supported by the value of the equilibrium constant of the first formation of metal complexes with ligands NH₃ (K₁) 4.04 and 2.21 for Cu(II) and Zn(II), respectively [15]. The larger the value of K₁, the more stable complex compounds formed.

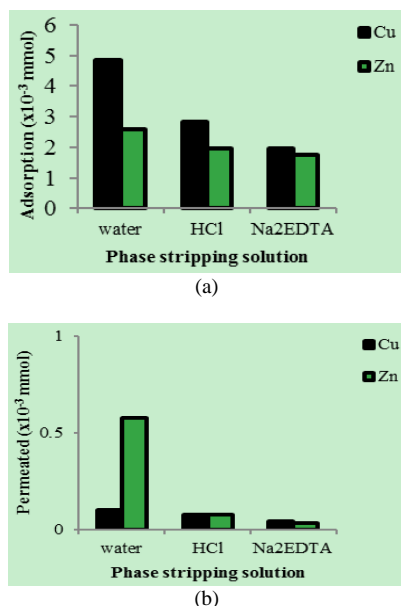


Fig. 4. (a) Adsorption and (b) Permeated mixtures Cu(II) and Zn(II) ions onto Ch/Si/P membrane in various phase stripping solution.

IV. CONCLUSIONS

Chitosan-silica-PEG membrane (Ch/Si/P) has been successfully synthesized. Blending chitosan with

polyethylene glycol and silica enhances adsorption behaviour probable due to pore size and water affinity of membrane. Cu(II) is the best ion to form complex with the Ch/Si/P membrane compared to Zn(II). The competition in binary mixture revealed a complex phenomenon. The presence of zinc ion in the mixture has a more significant impact on the copper adsorption. Desorption results showed that it was possible to separate copper from zinc using water, HCl, and Na₂EDTA solution for Cu and Zn recovery. Ch/Si/P membrane can mainly find application in the field of separation sciences.

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