



## Chitosan/zeolite composite membranes for the elimination of trace metal ions in the evacuation permeability process

TRANG THI CAM TRUONG<sup>1</sup>, KOBAYASHI TAKAOMI<sup>2</sup> and HA MANH BUI<sup>3,4\*</sup>

<sup>1</sup>Faculty of Environmental Sciences, University of Science, Vietnam National University, 227 Nguyen Van Cu St., District 5, Ho Chi Minh City 700000, Vietnam, <sup>2</sup>Department of Material Science and Technology, Nagaoka University of Technology, 1603-1 Kamitomioka, Nagaoka, Niigata 940-2188, Japan, <sup>3</sup>Department of Environmental Sciences, Saigon University, 273 An Duong Vuong St., District 5, Ho Chi Minh City 700000, Vietnam and <sup>4</sup>NTT Institute of High Technology, Nguyen Tat Thanh University, 300A Nguyen Tat Thanh St., District 4, Ho Chi Minh City 700000, Vietnam

(Received 6 June; revised 26 September, accepted 11 October 2018)

**Abstract:** Chitosan was combined with zeolites into composite membranes reinforced with glutaraldehyde crosslinking. The zeolite loading in the composite membranes was varied in the range 10–50 %, and the resulting membrane loading was varied at around 50 wt. %. The zeolite-loaded membranes showed better mechanical properties. The elimination of trace metal cations, Cr, As, Cd and Pb, by the chitosan–zeolite composite membranes was examined through the evacuation permeation process (EPP). In the permeability at each applied pressure, the selectivity of the composite membranes to the Cr ion was shown in the order of Cr > As > Cd > Pb at pH 5.5. It was noticed that the composite membrane with 20 wt. % zeolite loading showed the highest performance in the adsorption selectivity to the Cr cations. These results reveal the potential ability of the composite membrane to purify wastewater by removal of trace metal ions.

**Keywords:** evacuation; chitosan membrane; zeolite; trace metals.

### INTRODUCTION

There has been rapid growth of the trace metal industries, including within the metallurgical and mechanical industries, and electroplating has significantly contributed to the economy as it developed year by year. However, serious soil and water pollution are caused by the discharge of toxic trace metal ions into the environment through industrial wastewater.<sup>1,2</sup> Mercury, lead, cadmium, and chromium are common metal ions discharged in industrial wastewater and they are toxic, causing serious damage to the human body.<sup>3</sup> Therefore, wastewater containing these metal ions causes numerous problems for living organisms, inc-

\* Corresponding author E-mail: manhhakg@yahoo.com.vn  
<https://doi.org/10.2298/JSC180606085T>

luding reduced growth and development, cancer, organ damage, nervous system damage, and death.<sup>4–7</sup> Thus, it is very important to establish removal technologies for industrial wastewater and then for it to be treated sensibly and completely by an advanced technology, such as ion exchange, precipitation, ultrafiltration, reverse osmosis, electro-dialysis, and membrane technology.<sup>8–10</sup> Among these options, biomass membranes are interesting materials for sustainable sources. Biomass is a biological material derived from living, or recently living, organisms.<sup>11</sup> A useful biomass polymer is chitosan, a cationic linear polysaccharide usually synthesized from the deacetylation of crustacean chitin extracted from crab or shrimp shells, that has been used for wastewater treatment.<sup>12</sup> Known to be a good candidate for the remove of metal ions, chitosan, comprised principally of a linear chain of  $\beta$ -(1→4)-2-acetoamido-2-deoxy-D-glucose, has both reactive amino and hydroxyl groups. These reactive can participate in chemical reactions *via* chelating formation through the nitrogen atom and electrostatic forces between the heavy metal ions and the protonated hydroxyl group.<sup>13</sup> Moreover, the hydrophilicity of these groups within chitosan is considered to play an important role in preferential water sorption and diffusion through the membrane. Furthermore, it was reported that chitosan was used in pervaporation separation based on its good film-forming characteristics and excellent chemical-resistant properties.<sup>14</sup> However, there were few reports on the pervaporation processes in the separation of trace metal ions.

On the other hand, it is also known that trace metal ions are adsorbed well by zeolites, which are crystallized, microporous, and hydrated aluminum–silicates of alkaline or alkaline earth metals with a three-dimensional framework structure. Thus, a zeolite composed of  $[\text{SiO}_4]^{4-}$  and  $[\text{AlO}_4]^{5-}$  tetrahedral segments, having a corner-share to form different open structures,<sup>15</sup> has a cage space of approximately 0.3–1 nm.<sup>16</sup> Due to the isomorphous replacement of  $\text{Si}^{4+}$  by  $\text{Al}^{3+}$  inside the tetrahedral structures, there is a negative charge in the lattice of the cage space, which can include metal ions through ion exchange within the pore space.<sup>17</sup> These cation sites are exchangeable sites useful for mercury, lead, cadmium, or chromium uptake, and natural zeolites have been used frequently to eliminate these undesirable trace metal ions in industrial wastewater.<sup>18,19</sup> Already there have been several research studies on this aspect of zeolite functionality in the decontamination of trace metal ions using composite zeolite materials.<sup>20,21</sup> In addition, biomaterials combined in a composite with zeolites were reported to eliminate successfully trace metal ions from wastewater.<sup>22</sup>

In the present study, chitosan was used in a composite with zeolite to fabricate biomass–inorganic composite membranes that were then applied to trace metal ions in pervaporation treatment. The preparation of the chitosan/zeolite composite membranes is described from the viewpoint of trace metal adsorbents. Composite membranes were successfully fabricated by crosslinking chitosan and

zeolites with glutaraldehyde. In these composite membranes, the adsorbency of the biomass composite membranes were characterized and validated for their adsorption capacity for trace metal ions. Due to the potential abilities of zeolite absorbents in composition with chitosan, this paper includes a proposal based on the obtained original results for a new wastewater treatment membrane in trace metal separation.

## EXPERIMENTAL

### Materials

Chitosan (480,000 Daltons), with an 80 % degree of deacetylation, was purchased from Spectrum Chemicals & Laboratory Products Co., Ltd. (China). Synthesized zeolites (Linde Type A framework with a particle size of  $<75\text{ }\mu\text{m}$ ) were supplied by WAKO (Japan). Glutaraldehyde, purchased from Merck (Germany), was used without purification. All reagents used were of analytical-reagent grade, and distilled water was used throughout this study. The synthetic stock solutions of arsenic, chromium, cadmium, and lead were prepared using their nitrate salts in deionized water adjusted to the desired concentrations.

### *Preparation of zeolite/chitosan (CS/ZE) composite membranes*

The CS/Ze composite membranes were prepared as depicted in the procedure in Fig. 1. First, an aqueous 2 wt. % chitosan solution was prepared with 10 g of chitosan dissolved in 500 mL of 2 vol. % aqueous solution of acetic acid at room temperature.

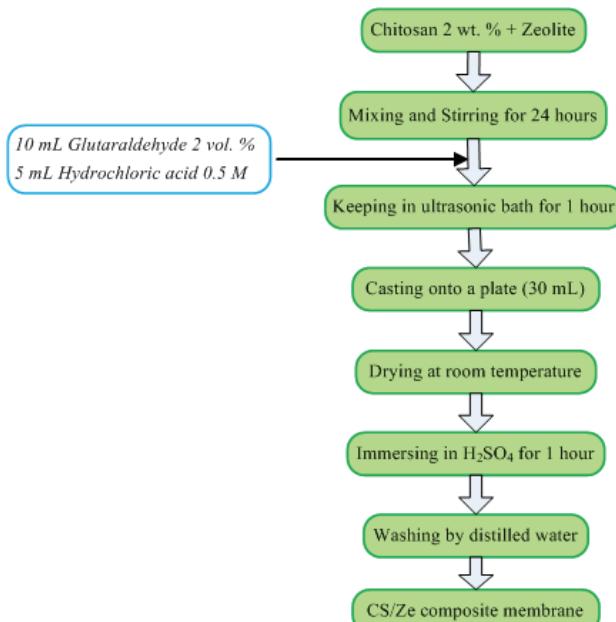


Fig. 1. Procedure for the preparation of CS/Ze composite membranes.

The aqueous chitosan solution was stirred for 24 h to become a completely clear homogeneous solution, and then filtered to eliminate impurities and undissolved particles. The

resulting homogeneous solution was mixed with zeolite powders under vigorous stirring at 250 rpm, and the mixture was kept at room temperature for 24 h. Then, the cross-linking reagent glutaraldehyde (10 mL) was mixed in 0.5 M hydrochloric acid (5 mL) added to the chitosan/zeolite suspension in a 2 vol. % concentration. After this addition, the mixed solution was kept under ultrasonic conditions for 1 h. Here, the ultrasonic treatment was important to avoid aggregation of the zeolite powder and to increase the dispersion of the zeolite in the aqueous suspension. The suspension solution was then degassed by evacuation with an aspirator, and the bubble-free chitosan–zeolite suspension solution (30 mL) was cast onto a clean glass plate using a casting knife with an approximate thickness of 3 mm. The casted solution was dried at room temperature for 2–3 days to obtain the membrane composites. The dried membranes were peeled off the plate and put into 20 mL of a 0.5 M H<sub>2</sub>SO<sub>4</sub> solution. After 1 h of immersion, the membranes were washed in deionized water for 2–3 h, followed by vacuum drying for 3 h to remove the remaining traces of aqueous solvent. The zeolite contents were varied at 10, 20, 30, 40, and 50 wt. %, and the resulting CS/Ze membranes were designated as CS/Ze-9/1, CS/Ze-8/2, CS/Ze-7/3, CS/Ze-6/4, and CS/Ze-5/5, respectively. As a reference membrane, the composite membrane was also prepared without zeolite (CS/Ze-10/0).

#### *Characterization of the CS/Ze composite membranes*

For the morphology characteristics of the CS/Ze membranes, scanning electron microscopy (SEM) (JSM-5300LV; JEOL Ltd., Japan) was used at 15 keV to observe the surface and cross-section of the resultant membranes. First, the membrane specimens were dried under a vacuum at room temperature for 24 h and were then fractured in liquid nitrogen to avoid spoiling the polymer structures before the measurements. The fractured sections of the CS/Ze membranes were coated with a sputtered conductive gold layer. A Fourier transform infrared (FT-IR) spectrometer, the Shimadzu FT-IR spectrometer Model 4000, was used in transmission mode to analyze and identify the resultant membrane samples with an approximately 3 mm thick sample for each aqueous suspension solution. The tensile strength of the membranes was measured at room temperature using a LTS-500N-S20 instrument with an operating head load of 5 kN at a constant testing rate of 12.5 mm min<sup>-1</sup>. The cross-sectional area of the samples of known width (10 mm) and thickness (0.1 mm) was calculated in mm<sup>-2</sup>. The values of tensile strength (in N mm<sup>-2</sup>) were calculated using the equation:

$$\text{Tensile strength} = \frac{\text{Maximum load}}{\text{Cross-section area}}$$

Water swelling of the CS/Ze membranes was measured as follows. The dried membranes of known weight were immersed in water at room temperature. After a specified time of soaking in water, *i.e.*, 1, 2, 3, 6, 9, 12, or 24 h, the membrane samples were carefully taken out of the aqueous solution, wiped with filter papers to remove surface liquid, and then measured for their length and weight as quickly as possible. The swelling degree (*SD*) of the CS/Ze composite membranes was determined as the change in the size of the membranes in length before and after immersion in water. The swelling degree is expressed as:

$$SD = \frac{D_a}{D_b}$$

where *D<sub>a</sub>* and *D<sub>b</sub>* designate the length of the membranes before and after adsorption in water, respectively.

The water content of the swollen membranes was determined from the difference in the weight of the membranes before and after immersion in water. The solvent content (*SC*) was calculated by the following equation:

$$SC / \% = 100 \frac{W_s - W_d}{W_d}$$

where  $W_s$  stands for the weight of the swollen membrane and  $W_d$  for the weight of the dry membrane.

#### *The membrane separation process under evacuation conditions*

The membrane separation experiment occurred under an evacuation atmosphere.<sup>23,24</sup> Here, a membrane with a diameter of 17.3 cm was placed on a porous plastic support and sealed. The effective area of the membrane placed in contact with the feed stream was  $1.73 \times 10^{-4} \text{ m}^2$ . The upper stream on the membrane contained an aqueous trace metal ion solution with a pH of 5.5 and the downstream was kept under vacuum at a determined applied pressure. The aqueous phase permeated through the membrane and was trapped in the downstream by a cold trap. The permeate solution was collected after 1 h in the trap and the aqueous amount in the cold trap were measured for the calculation of the permeate flux ( $\text{m}^3 \text{ m}^{-2} \text{ s}^{-1}$ ) of the permeation. In addition, the concentrations of trace metal ion in the upstream and downstream phases were determined by ICP-MS (Agilent 7700X). Membrane selectivity is typically expressed in terms of a separation factor, or a permeability factor,  $\alpha$ . For a mixture consisting of the components, trace ions (a) and water (w), the value of the permeability factor  $\alpha$  is defined as:

$$\alpha_{wa^{-1}} = \frac{Y_w X_a}{Y_a X_w}$$

where  $X$  and  $Y$  are the weight fractions of the components in the feed (upstream phase) and the permeate (downstream phase), respectively. The values of  $X$  and  $Y$  were measured by liquid chromatography. Here, the descriptions of metal and water were subscripted as  $a$  and  $w$ , respectively. In the case of the separation of the ions, a similar equation was used for the separation factor. The permeate flux,  $J$ , was calculated using the following equation:

$$J = \frac{Q}{AT}$$

where  $Q / \text{g}$  is the total permeate mass for  $t$  hours, and  $A / \text{m}^2$  denotes the effective area ( $17 \times 10^{-4} \text{ m}^2$ ) of the CS/Ze composite membrane.

#### *Reusability of the absorbents*

*Desorption from loaded composite membranes.* After being immersed in solutions containing the heavy metal ions at the appropriated concentrations, the loaded composite membranes were removed and dried at room temperature. Then, these adsorbents were placed in an aqueous 0.1 M HCl solution under mechanical stirring at 180 rpm. The solutions were collected after 30, 60, 90, 120, 150, and 180 min to evaluate the optimal desorption time, or when the adsorbed heavy metal ions were completely removed from the adsorbents. Then, the composite membranes were washed free of the heavy metals with excess distilled water until a neutral pH was achieved and dried at 60 °C for the following experiment.

*Adsorption on the regenerated composite membranes.* The regenerated adsorbents were transferred into 20 mL glass bottles containing 50 ppm of the heavy metal salts at the optimal

pH. These samples were stirred at 180 rpm and stored at room temperature for 180 min. After shaking at the optimal sorbed time, the composite membranes were filtrated through a filter paper. The concentrations of each heavy metal ion remaining in the solutions were determined by ICP-MS (Agilent 7700X). The test was repeated until the removal capacity of the adsorbents was below 50 %.

## RESULTS AND DISCUSSION

### *Characteristics of chitosan–zeolite membranes*

Scanning electron micrographs (SEM) of the surface and cross-sections of the chitosan/zeolite (CS/Ze) composite membranes are shown in Fig. 2. The numbers after the name CS/Ze give the weight percents of chitosan and zeolite in the composite membranes, respectively. The micrographs indicate that the chitosan and zeolite were well composited in the dense membrane in each case. It is apparent that the zeolite loaded with a CS layer was consistently distributed in the polymer scaffold for all membranes. Moreover, when the amount of zeolite powder was increased in the membrane, the cross-section of the SEM images showed that the high amounts of zeolite were highly incorporated with the chitosan layer in the composite membranes. In addition, the dense structure was observed to be void-free even in the case of high zeolite loading, and hence, the reaction process of glutaraldehyde with chitosan and zeolite proceeded successively. It could be that the membrane without zeolites CS/Ze-10/0 had a dense membrane, but that when the zeolite loading was increased, a void space was observed in the cross-section, as seen in Figs. 2d and f. In addition, the presence of zeolite particles of approximately a few  $\mu\text{m}$  in size was observed in the case of Fig. 2h for CS/Ze- 9/1. These changes in the SEM view suggested that zeolite powders were present in the membrane at different loading ratios of CS and Ze.

The fabrication of glutaraldehyde with the chitosan and zeolite was also confirmed by the FT-IR spectra, as presented in Fig. 3. As seen, the IR bands of the CHO group of glutaraldehyde, *i.e.*, CH stretching in the 2700–2800  $\text{cm}^{-1}$  region<sup>25</sup> and C=O stretching at about 1750  $\text{cm}^{-1}$ , were not visible in the composite membranes meaning that no unreacted glutaraldehyde was present. In the case of the zeolites (Fig. 3b), there were peaks at 3619 and 1015  $\text{cm}^{-1}$  with the Al–OH and the Si–O, respectively, which confirmed the chemical formation of Ze. For pure chitosan, there was a double peak at around 1650  $\text{cm}^{-1}$  indicating the presence of the NH<sub>2</sub> Amide I group and at approximately 1550  $\text{cm}^{-1}$  representing the Amide II groups. However, as seen in the IR spectra of the cross-linked chitosan (Fig. 3c, d and e), the intensity of the peak around 1650  $\text{cm}^{-1}$  was reduced and formed only one peak. This strongly suggested that there are double bonds between the C atom in the aldehyde group of glutaraldehyde and the N atom in the amino group of the chitosan structure. In addition, the peak of Amide

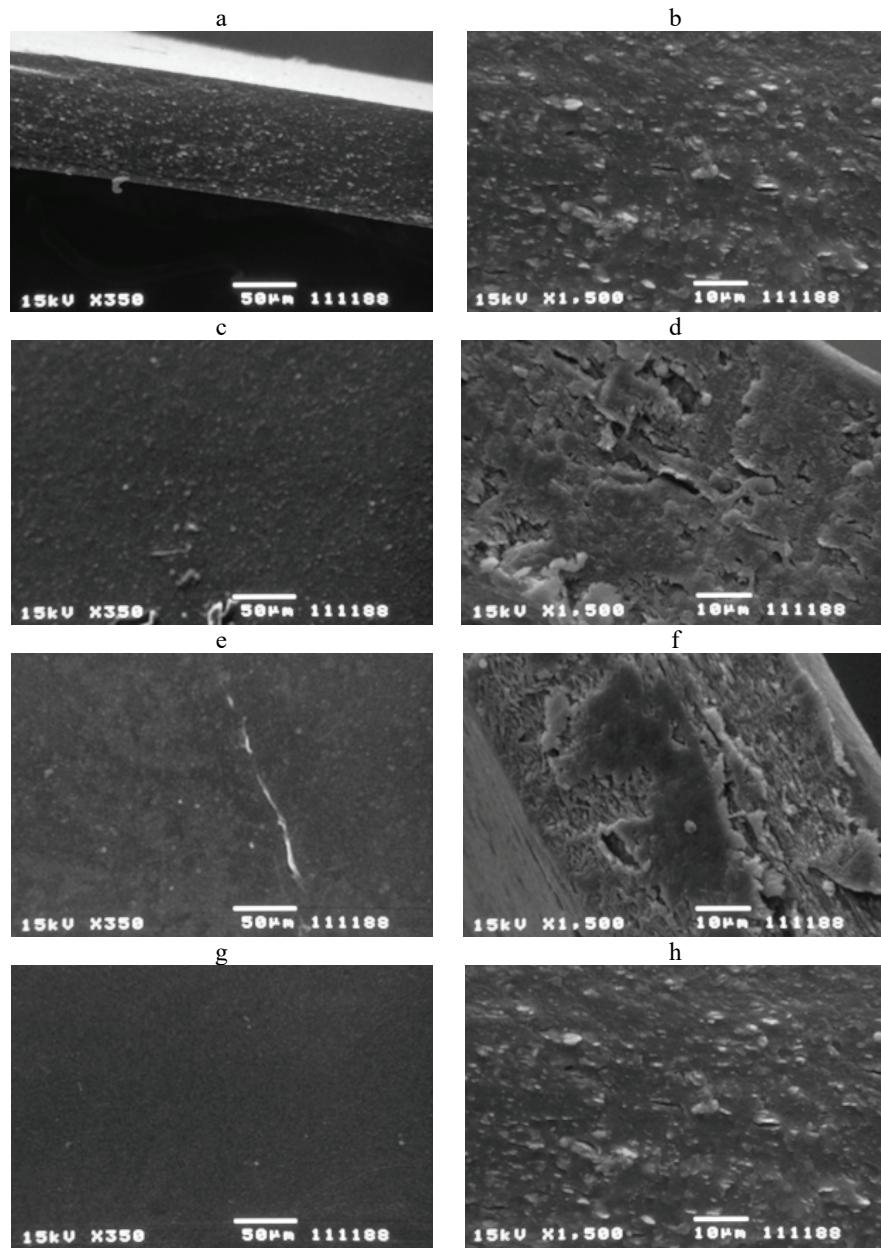


Fig. 2. SEM pictures of the surface of the membranes: a) CS/Ze-5/5, c) CS/Ze-7/3, e) CS/Ze-8/2 and g) CS/Ze-9/1 and of the cross section of: b) CS/Ze-5/5, d) CS/Ze-7/3; f) CS/Ze-8/2 and (h) CS/Ze-9/1.

In the pure chitosan was shifted to a higher wavelength, which implies an interaction between the components in the composite. Therefore, the chemical process of chitosan and zeolite was followed with the glutaraldehyde cross-link process as illustrated below in Fig. 4.

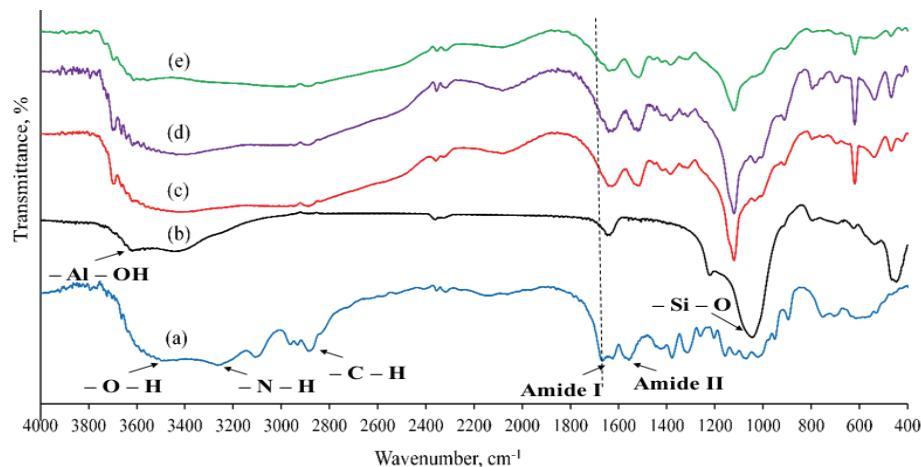


Fig. 3. FT-IR spectra of (a) pure chitosan (CS/Ze-10/0), (b) zeolite, (c) CS/Ze-7/3, (d) CS/Ze-8/2, and (e) CS/Ze-9/1 membranes.

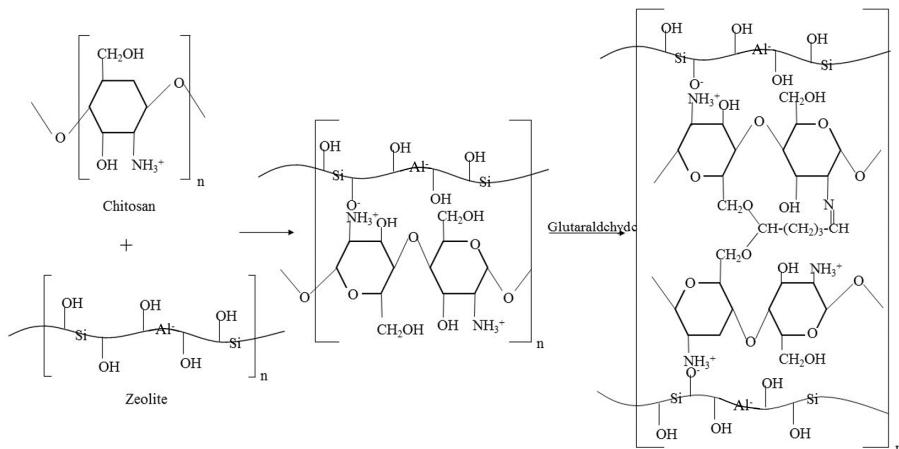


Fig. 4. The reaction scheme of chitosan and zeolite cross-linked with glutaraldehyde.

The values of the tensile strengths and contact angles of water droplets for each membrane are listed in Table I. The table depicts the thickness of the membranes, as determined by the SEM view. In addition, the values of the contact angles were measured 300 s after water had been dropped on the surface of the membrane. This parameter significantly affects the quality of the membrane

because of its effects on the size and thickness of the membrane. It was noticed that the contact angle increased with time and Ze dosage. Normally, the surface contact angle is an indicator to confirm the hydrophilicity or hydrophobicity of a sample. If the value of the contact angle is below 90°, the surface is hydrophilic. Meanwhile, the greater the hydrophobicity, the higher is the contact angle. Here, all of the hydrophilic properties of the membrane composites remained, which showed their potential for application to the separation of the heavy metal solutions. The membrane strength could also be expressed by the value of the tensile strength of the membranes. These values were calculated as 57.8, 54.4, 46.1, 38.7 and 35.6 N mm<sup>-2</sup> for CS/Ze-5/5, CS/Ze-7/3, CS/Ze-8/2, CS/Ze-9/1, and CS/Ze-10/0, respectively. As seen in Table I, with increased amounts of zeolite incorporated into the chitosan, the tensile strength values of the membranes increased.

Increasing the zeolite loading also decreased the void-free dense structure in the membrane because the zeolite powder filled the membrane pores and hence, this structural transformation restricted the water sorption ability of the membranes and, then, increased their tensile strength. The improvement in the mechanical properties of these membranes could be clarified through extensive intra- and intermolecular hydrogen bond interactions involving the -NH<sub>2</sub> and -OH groups of CS in addition to the formation of an interpenetrating polymer network upon crosslinking with glutaraldehyde.

TABLE I. Physical properties of the CS/Ze membranes

Membrane	Width, mm	Thickness, µm	Tensile strength, N mm <sup>-2</sup>	Cross section, mm <sup>2</sup>	θ / °
CS/Ze-5/5	10	0.09	57.8	0.82	82.6
CS/Ze-7/3	10	0.09	54.4	0.89	71.6
CS/Ze-8/2	10	0.09	46.1	0.91	66.5
CS/Ze-9/1	10	0.09	38.7	0.94	62.4
CS/Ze-10/0	10	0.09	35.6	1.12	60.4

The rate of sorption of water by each composite membrane is shown in Fig. 5a. The values of water sorption increased when the membrane had been immersed in water for about one hour and, then, were constant in the range of 42–50 %. It was noted that a higher loading of the zeolite had a tendency to decrease the water contents. A similar tendency was observed for the degree of swelling with immersion time. As presented in Fig. 5b, the degree of swelling was saturated within one hour for each composite membrane. This means that the membrane absorbed water through its chitosan parts that strongly interact with the constituents of water in the composite membranes. As listed in Table I, the values of the water contact angles also supported the fact that the composite membranes containing higher zeolite loadings showed water resistance. That is, the zeolites loaded in the membranes behaved so that they increased the penetration of water molecules into the membranes.

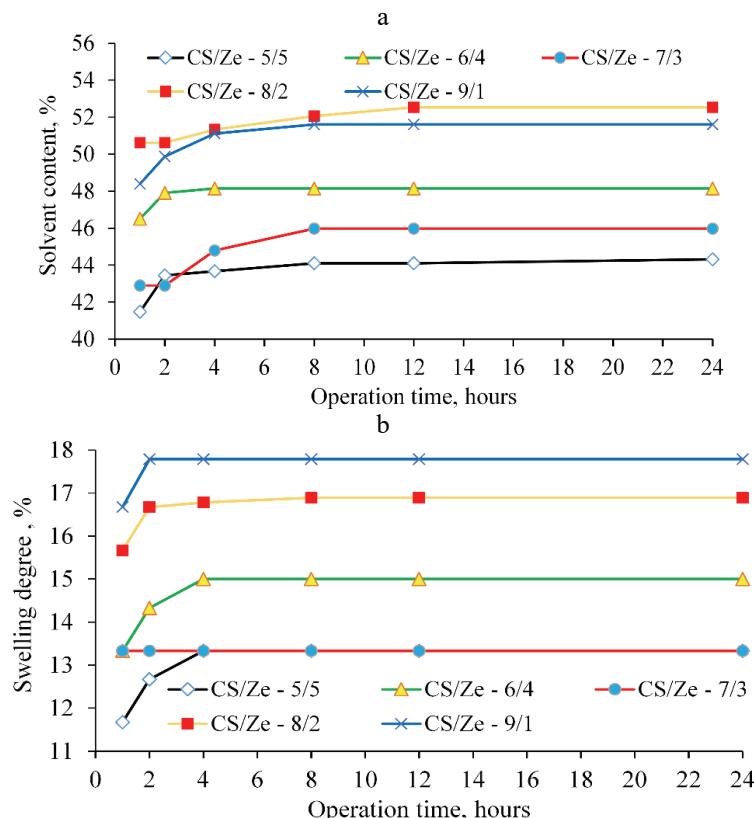


Fig. 5. Solvent content (a) and swelling degree (b) of the CS/Ze composite membranes observed at different times.

#### The permeability process by EPP for trace metal ions

Since the hydrophilic parts of the chitosan scaffold adsorbed water, the water component could permeate through the composite membranes. It is well known that in the pervaporation of organic molecules in a membrane separation process the separation becomes great enough to separate through membrane permeation.<sup>25</sup> On the other hand, in a similar process for water metal ion solutions, the elimination performance of trace metal ions has not yet been reported. Thus, the evacuation permeation process (EPP) is quite interesting for examining the CS/Ze membranes for trace metal ion separation. In the process, the feed water solution was included with Cr, As, Cd and Pb ion each with a 40 ppm concentration at a pH 5.5. Then, the total permeation flux ( $\text{m}^3 \text{ m}^{-2} \text{ s}^{-1}$ ) and separation factor were obtained, as shown in Fig. 6.

The values of the permeate flux for each of the CS/Ze composite membranes were plotted in Fig. 6a against each single metal ion solution. For each metal ion,

the permeation of the aqueous solution responded to the loading amounts of zeolite in the membrane, showing a decrease in the total permeation flux in the case of a high loading of zeolite. It was considered that the membrane composites influenced the permeation flux, for example, through the factors void size of the membrane, the ion solubility in the water medium and the hydrated radius of the ion. As seen in the SEM pictures, the void size of the composite membranes increased with increasing zeolite loading, and Fig. 6a (a) shows this tendency. In addition, the solubility of  $Pb^{2+}$  and  $Cr^{2+}$  were  $5.2 \times 10^5$  mg L<sup>-1</sup> for  $Pb(NO_3)_2$  and  $8.1 \times 10^5$  mg L<sup>-1</sup> for  $Cr(NO_3)_3$ . This might be influenced by the retardation of the chromium ion in its permeability through the membrane. Here, the hydrated radius of lead and chromium ions were 4.01 and 4.13 Å, respectively, *i.e.*, their sizes are similar. It is important to note that the retardation of the total permeate flux was greatly enhanced in the highly-loaded zeolite membranes for the case of chromium. Therefore, the comparison indicated that the permeability might be influenced by the chromium–zeolite interaction when the solubility was high in the aqueous medium.

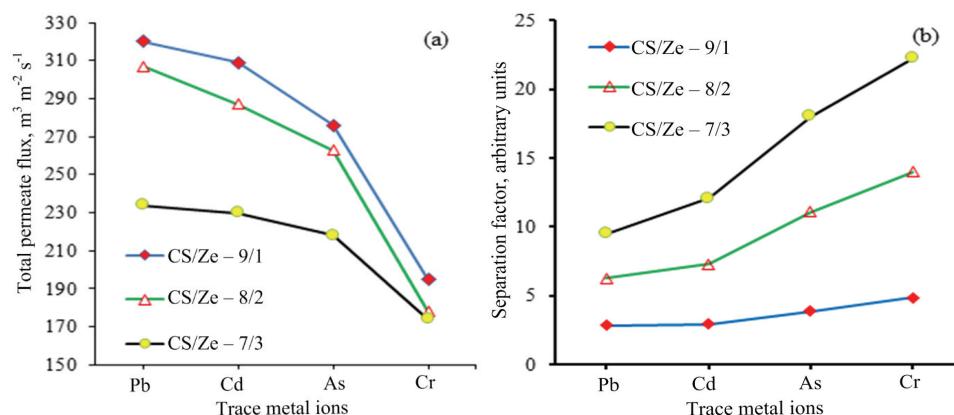


Fig. 6. The effects of CS and Ze contents in CS/Ze membranes on: a) the total permeation flux and b) permeability factor of trace metal ions.

It was noted in the permeability factor ( $\alpha$ ) that the value was increased in cases of a high loading of zeolite (Fig. 6b). With increasing zeolite loading in the composite membranes, the value of the permeability factor increased, but a lower permeation flux was also obtained. It was noted that the prepared composite membrane strongly retarded the permeability of the Cr ion when the permeate flux was lowered.

Thus, as seen in Fig. 6b, the value of the permeability factor for this membrane was approximately 18 for the As ion and even as high as 20 for the Cr ion, for negatively charged zeolites in the pH region 3–8.<sup>27</sup> There was electrostatic

interaction between the chromium and zeolites. This might be understood through the electrostatic chelating of chromium being one of the driving forces of the high adsorption by the interaction of chromium with the  $-NH_2$  group and zeolite powders in the composites (Fig. 7).

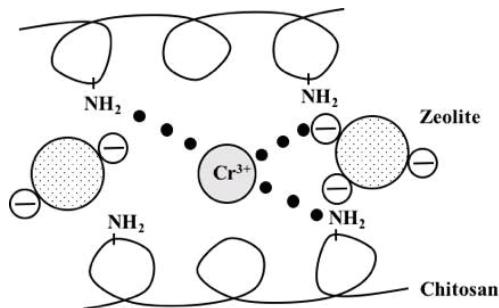


Fig. 7. Illustration of chelating incorporated with electrostatic interaction in chitosan-zeolite composites.

The removal of As, Cd, Cr, and Pb ions in water samples was performed in a separation experiment with a quaternary mixed solution and the results are shown through a column chart in Fig. 8.

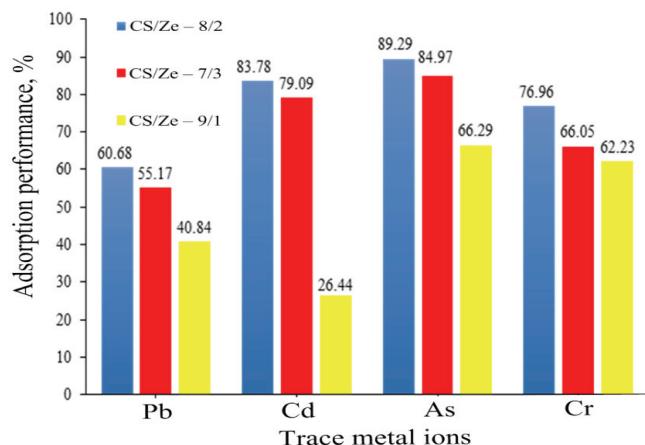


Fig. 8. The effects of CS and Ze content in CS/Ze membranes on: a) the total permeation flux and b) separation factors of the trace metal ions.

Here, the aqueous solution contained 40 ppm of each metal ion, and the same equation was used for the calculation of the separation factor used as that used for the calculation of the permeability factor for a single ion. It could be seen that the composite membranes removed the trace metal ions in the water and showed a high-performance capability for the removal of the Cr ion with a yield of over 65 %. In particular, the results obtained by the composite membrane CS/Ze-8/2 indicated that it was better than the other composite membranes, for an

80/20 separation of the Cr ion with s percentage removal of 89.3 %. In addition, the loading zeolite expressed a high removal performance for Cd and Pb ions of 83.8 and 60.7 %, respectively.

It was expected that the adsorption removal would be higher as the zeolite loading was increased. However, in the membrane of the zeolite powder (Fig. 2d and f), when the zeolite was changed in CS/Ze-8/2 and CS/Ze-9/1, the As adsorption dramatically decreased. This means that the As, chelating with the -NH<sub>2</sub> groups of chitosan, seem to be retarded in the presence of a large amount of zeolite that is negatively charged. Thus, the negatively charged arsenious acid, As(OH)<sub>3</sub>, was electrorepulsed in the CS/Ze-9/1. Therefore, the composite membranes act in an incorporative manner on Cr<sup>+3</sup> through chelation and ionic interaction with the NH<sub>2</sub> groups of CS and the negatively charged groups of zeolites, as seen in Fig. 7.

It was meaningful to determine the regeneration times of the metal-loaded adsorbents to assess their potential application in practice. Fig. 9 shows that after 6-times regeneration, the metal-retaining capacity of the adsorbents was higher than 90 %. This strongly suggests that CTS is one of the adsorbents having a high potential for the elimination of heavy metal ions in practice.

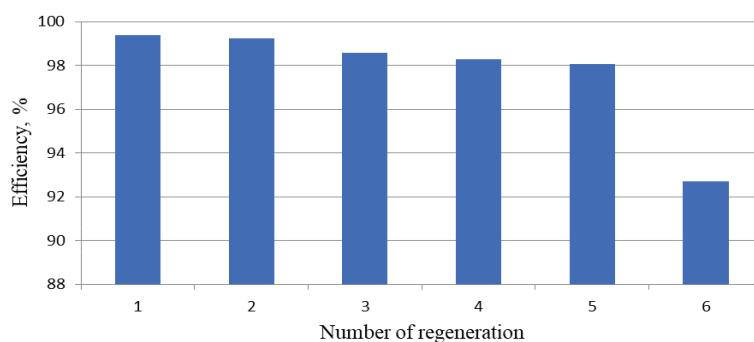


Fig. 9. The regeneration potential of the metal-loaded adsorbents.

#### CONCLUSIONS

In this study, the chitosan–zeolite composite membranes were successfully synthesized by crosslinking with glutaraldehyde. The membranes were characterized and applied in pervaporation experiments for the removal of trace metal ions widely contained in industrial wastewater, especially chromium and arsenious acid. Removing over 80 % of the trace metal ions contained in aqueous solutions, the CS/Ze-8/2 membrane, with an 80/20 ratio of chitosan and zeolites, showed great mechanical properties and separation performances for becoming a new potential wastewater treatment technology *via* the corporative effects of chitosan and zeolite.

## И З В О Д

КОМПОЗИТНЕ ХИТОЗАН/ЗЕОЛИТСКЕ МЕМБРАНЕ ЗА ЕЛИМИНАЦИЈУ ТРАГОВА  
МЕТАЛНИХ ЈОНА ЕВАКУАЦИОНОМ ПЕРМЕАБИЛНОШЋУTRANG THI CAM TRUONG<sup>1</sup>, KOBAYASHI TAKAOMI<sup>2</sup> и НА МАНН ВУІ<sup>3,4</sup>

<sup>1</sup>Faculty of Environmental Sciences, University of Science, Vietnam National University, 227 Nguyen Van Cu St., District 5, Ho Chi Minh City 7000000, Vietnam, <sup>2</sup>Department of Material Science and Technology, Nagaoka University of Technology, 1603-1 Kamitomioka, Nagaoka, Niigata 940-2188, Japan, <sup>3</sup>Department of Environmental Sciences, Saigon University, 273 An Duong Vuong St., District 5, Ho Chi Minh City 7000000, Vietnam и <sup>4</sup>NTT Institute of High Technology, Nguyen Tat Thanh University, 300A Nguyen Tat Thanh St., District 4, Ho Chi Minh City 7000000, Vietnam

Хитозан је комбинован са зеолитом да би се направиле композитне мембрane, ојачане умрежавањем глутаралдехидом. Садржај зеолита у композитима је варирани у опсегу 10–50 %, а у добијена мембрани око 50 мас. %. Зеолит је показао боље механичке особине. Елиминисање металних катиона, Cr, As, Cd и Pb, испитано је евакуационом пермеабилношћу хитозан–зеолитских композитних мембрана. Показало се да је на сваком примењеном притиску селективност на Cr јон била Cr > As > Cd > Pb при pH 5,5. Најбоље перформансне према апсорпционој селективности је показала композитна мембрана са 20 мас. % зеолита. Ови резултати откривају потенцијал композитних мембрана да пречисте отпадну воду уклањањем трагова металних јона.

(Примљено 6. јуна, ревидирано 27. септембра, прихваћено 11. октобра 2018)

## REFERENCES

1. A. J. Hargreaves, C. Constantino, G. Dotro, E. Cartmell, P. Campo, *Environ. Technol. Rev.* **7** (2018) 1 (<http://dx.doi.org/10.1080/21622515.2017.1423398>)
2. T. Uragami, K. Okazaki, H. Matsugi, T. Miyata, *Macromolecules* **35** (2002) 9156 (<http://dx.doi.org/10.1021/ma020850u>)
3. S. Deniz, N. Taşci, E. K. Yetimoğlu, M. V. Kahraman, *J. Serb. Chem. Soc.* **82** (2017) 215 (<http://dx.doi.org/10.2298/JSC160816098D>)
4. S. Khan, Q. Cao, Y. M. Zheng, Y. Z. Huang, Y. G. Zhu, *Environ. Pollut.* **152** (2008) 686 (<http://dx.doi.org/10.1016/j.envpol.2007.06.056>)
5. L. Järup, *Br. Med. Bull.* **68** (2003) 167 (<http://dx.doi.org/10.1093/bmb/lgd032>)
6. F. S. Khoo, H. B. Esmaeili, *J. Serb. Chem. Soc.* **83** (2002) 237 (<http://dx.doi.org/10.2298/JSC170704098S>)
7. S. Chakraborty, A. R. Dutta, S. Sural, D. Gupta, S. Sen, *Ann. Clin. Biochem.* **50** (2013) 492 (<http://dx.doi.org/10.1177/0004563213481207>)
8. A. A. Kittur, M. Y. Kariduragaranavar, U. S. Toti, K. Ramesh, T. M. Aminabhavi, *J. Appl. Polym. Sci.* **90** (2003) 2441 (<http://dx.doi.org/10.1002/app.12930>)
9. D. Sarkhel, D. Roy, M. Bandyopadhyay, P. Bhattacharya, *Sep. Purif. Technol.* **30** (2003) 89 ([http://dx.doi.org/10.1016/S1383-5866\(02\)00135-1](http://dx.doi.org/10.1016/S1383-5866(02)00135-1))
10. S. C. George, K. N. Ninan, S. Thomas, *J. Membr. Sci.* **176** (2000) 131 ([http://dx.doi.org/10.1016/S0376-7388\(00\)00439-7](http://dx.doi.org/10.1016/S0376-7388(00)00439-7))
11. G. Crini, *Bioresour. Technol.* **97** (2006) 1061 (<http://dx.doi.org/10.1016/j.biortech.2005.05.001>)
12. W. S. W. Ngah, A. Musa, *J. Appl. Polym. Sci.* **69** (1998) 2305 <http://dx.doi.org/10.1002/%28SICI%291097-4628%2819980919%2969%3A12<2305%3A%3AAID-APP1>3.0.CO%3B2-C>)
13. F. C. Wu, R. L. Tseng, R. S. Juang, *J. Hazard. Mater.* **81** (2001) 167 ([http://dx.doi.org/10.1016/S0304-3894\(00\)00340-X](http://dx.doi.org/10.1016/S0304-3894(00)00340-X))

14. M. N. V. R. Kumar, *React. Funct. Polym.* **46** (2000) 1 ([http://dx.doi.org/10.1016/S1381-5148\(00\)00038-9](http://dx.doi.org/10.1016/S1381-5148(00)00038-9))
15. P. Y. Chiang, T. W. Lin, J. H. Dai, B. C. Chang, K. H. Lii, *Inorg. Chem.* **46** (2007) 3619 (<http://dx.doi.org/10.1021/ic0700304>)
16. C. S. Cundy, P. A. Cox, *Chem. Rev.* **103** (2003) 663 (<http://dx.doi.org/10.1021/cr020060i>)
17. T. Motsi, N. A. Rowson, M. J. H. Simmons, *Int. J. Miner. Process.* **92** (2009) 42 (<http://dx.doi.org/10.1016/j.minpro.2009.02.005>)
18. L. Zhu, J. Ji, S. Wang, C. Xu, K. Yang, M. Xu, *Chemosphere* **206** (2018) 278 (<http://dx.doi.org/10.1016/j.chemosphere.2018.05.001>)
19. P. S. De Velasco-Maldonado, V. Hernández-Montoya, M. A. Montes-Morán, N. A.-R. Vázquez, M. A. Pérez-Cruz, *Appl. Surf. Sci.* **434** (2018) 1193 (<http://dx.doi.org/10.1016/j.apsusc.2017.11.023>)
20. K. Z. Elwakeel, A. A. El-Binary, E. Y. Kouta, E. Guibal, *Chem. Eng. J.* **332** (2018) 727 (<http://dx.doi.org/10.1016/j.cej.2017.09.091>)
21. Z. Li, L. Wang, J. Meng, X. Liu, J. Xu, F. Wang, P. Brookes, *J. Hazard. Mater.* **344** (2018) 1 (<http://dx.doi.org/10.1016/j.jhazmat.2017.09.036>)
22. M. Kragović, S. Pašalić, M. Marković, M. Petrović, B. Nedeljković, M. Momčilović, M. Stojmenović, *Minerals* **8** (2018) 1 (<http://dx.doi.org/10.3390/min8010011>)
23. T. T. C. Trang, T. Kobayashi, *J. Appl. Polym. Sci.* **121** (2011) 639 (<http://dx.doi.org/10.1002/app.33258>)
24. T. T. C. Trang, N. T. Nhun, T. Kobayashi, *Engineering* **3** (2011) 110 (<http://dx.doi.org/10.4236/eng.2011.32014>)
25. R. G. Mathys, W. Heinzelmann, B. Witholt, *Chem. Eng. J.* **67** (1997) 191 (<http://dx.doi.org/10.1002/app.1994.070530405>).