Adsorption of Ca(II), Mg(II), Zn(II), and Cd(II) on Chitosan Membrane Blended with Rice Hull Ash Silica and Polyethylene Glycol

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Received January 14, 2015; Accepted August 31, 2015

ABSTRACT

In this research, chitosan based membrane blended with rice hull ash (RHA) silica and polyethylene glycol (PEG) has been applied as adsorbent of Ca(II), Mg(II), Zn(II) and Cd(II) in an aqueous solution. Membrane was synthesized by blending RHA silica and polyethylene glycol into chitosan. Silica and polyethylene glycol blended into the chitosan to improve the mechanical properties and the membrane porous. The membrane was characterized using Fourier Transform infrared (FTIR) spectroscopy, X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), and swelling degree analyzer. Adsorption of metal ions investigated was conducted in a batch system with variation of pH, initial ion concentration and contact time. Thermodynamics and kinetics of adsorption were evaluated based on the adsorption data at initial metal ion concentration and contact time variations, respectively. Results showed that the optimum condition of adsorption was at pH 9.0 for Ca(II), 6.0 for both Mg(II) and Zn(II) and 5.5 for Cd(II), and contact time of 24 h for all ions investigated. Kinetics of all investigated metal ion adsorption followed a kinetic model of pseudo-second-order. Adsorption of Ca(II) and Mg(II) on the membrane fitted to Freundlich model with the affinity of 1.266 and 1.099, respectively; and Zn(II) and Cd(II) fitted to Langmuir one with the capacity of 182 and 106 μmol/g, respectively.

Keywords: *chitosan; silica; rice hull; polyethylene glycol; adsorption*

ABSTRAK

Dalam penelitian ini, membran kitosan-silika-polietilen glikol (Ch/Si/P) telah digunakan untuk adsorben ion Ca(II), Mg(II), Zn(II) dan Cd(II) dalam larutan. Membran dibuat dengan mencampurkan silika yang diisolasi dari abu sekam padi dan polietilen glikol ke dalam kitosan. Silika dan polietilen glikol dicampurkan ke dalam kitosan untuk meningkatkan sifat mekanik dan pori membran. Membran yang dihasilkan dikarakterisasi dengan Spektroskopi Infra-Merah, Difraksi Sinar-X, Mikroskop Elektron (SEM), dan penentuan derajat pengembangan. Membran Ch/Si/P digunakan untuk mengadsorpsi ion logam Ca(II), Mg(II), Zn(II), dan Cd(II) dalam larutan. Adsorpsi dilakukan dalam sistem batch dengan memvariasi pH, konsentrasi ion logam dan waktu kontak. Kinetika dan termodinamika adsorpsi dievaluasi berdasarkan data adsorpsi pada masing-masing variasi waktu kontak dan konsentrasi awal ion logam dalam larutan. Hasil penelitian menunjukkan bahwa adsorpsi optimum terjadi pada pH 9 untuk Ca(II), pH 6 untuk Mg(II) dan Zn(II), pH 5,5 untuk Cd(II) serta waktu kontak 24 jam untuk semua ion logam pada semua jenis membran. Adsorpsi Ca(II) dan Mg(II) pada membran Ch/Si/P mengikuti model Freundlich dengan afinitas berturut-turut sedangkan adsorpsi Zn(II) dan Cd(II) mengikuti model Langmuir. Adsorpsi semua ion logam yang dikaji mengikuti model kinetika pseudo-orde kedua. Adsorpsi Ca(II) dan Mg(II) pada membrane mengikuti model Freundlich dengan afinitas berturut-turut 1,266 dan 1,099, sedangkan Zn(II) and Cd(II) mengikuti model Langmuir dengan kapasitas adsorpsi berturut-turut 182 and 106 μmol/g.

Kata Kunci: *kitosan; silika; sekam padi; polietilen glikol; adsorpsi*

INTRODUCTION

Many techniques have been developed for heavy metals ions removal, such as chemical precipitation, filtration, electrochemical treatment, ion exchange, liquid-liquid extraction, adsorption, chemical oxidation and reduction, and evaporation recovery [1-2]. Among these methods, adsorption is one of the most effective, economical and widely used method for heavy metal ion removal in wastewater [1,3-5]. Some studies focus on adsorptive membranes to remove heavy metal ions from aqueous solutions. Heavy metal ions can be

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removed when the ions are in contact with the surface of the membrane, even when the pore sizes of the membrane are much larger than the dimensions of the metal ions [1-8].

Chitosan, N-deacetylated form of chitin, is a biopolymer with a high content of amine and hydroxyl functionalities. It has attracted great attention for preparation of affinity membranes due to high binding capacity, broad availability and excellent membrane-forming property [6-7]. However, membranes formed of pure chitosan are fragile and brittle which limits their application. Blending on chitosan is a convienient and effective way on improving its physical and mechanical properties for practical usages. Adsorptive membranes prepared by blending technique, chitosan provide the required functionalities for the metal chelation and the blended polymer supports the membrane backbone. Porogens (pore generator) are employed to generate membrane pores. In preparation of adsorptive membranes, porogens play two roles: enhancement of internal sorption (pore) capacity and dispersivity improvement [6-7,9]. Generally, the porogens for chitosan based membranes are polyethylene glycol, polyvinyl pyrrolidine (PVP), silica and salts (e.g. NaCl) [10-16]. Blending chitosan with compatible polymers such polyethylene glycol and silica results in spongy membranes also resulted in highly effective metal-affinity membranes [6,14-16].

Polyethylene glycol is a particular interest owing to its useful properties such as low toxicity, immunogenicity, biocompatible and biodegradable performance [10-12]. Sodium silicate solution from rice hull ash silica has been reported as precursor silica for preparation of silica based films [13]. The addition of sodium silicate from rice hull ash silica in the production of chitosan-silica film has been reported [14-15]. Based on the results of this study it can be concluded that the addition of silica affects the pore size of the chitosan-silica film. Particles of silica are ideal porogens for producing porous chitosan-silica film with controlled porosity and good mechanical properties [14-15].

Some researcher added silica and PEG into chitosan based membranes to improve the mechanical properties and the membrane porous. Porous membrane increasing metal ion adsorption capability and enhancement in accessibility of the ions to the adsorption sites. Dense chitosan membrane and porous chitosan-silica membrane were prepared for copper ion adsorption. Increasing the silica to chitosan ratio of the membrane leads to higher porosity and roughness, increased copper ion adsorption [2]. CPMP membrane containing combined MWCNT-NH_2 and PEG was used Salehi et al. for Cu(II) removal from water [6]. CPMP membrane provided superior adsorption performance compared to the CPMP membrane without PEG. CPMP membrane emerged as an excellent candidate for application in either static or dynamic adsorption mode to eliminate copper ions from water. Salehi and Madaeni [7] used chitosan-poly vinyl alcohol-polyethylene glycol membrane (CS/PVA/PEG) for copper ion adsorption. PEG is a potential porogen for generating macrovoids in the dense matrix on CS/PVA adsorptive membrane. Addition of PEG could enhance wettability and pore capacity of the CS/PVA membrane.

Silica and polyethylene glycol blended into the chitosan membrane to improve the mechanical properties and the membrane porous. In addition to porosity, a membrane's adsorption potential is dependent on its morphology and roughness; these parameters determine the active surface area for adsorption. The purpose of this research is to investigate the adsorption properties of Ca(II), Mg(II), Zn(II), and Cd(II) ions as individual and mixture on chitosan-silica-polyethylene glycol membrane (Ch/Si/P).

EXPERIMENTAL SECTION

Materials

Chitosan used for synthesizing Ch/Si/P membrane was supplied from CV Ocean Fresh Bandung with the deacetylation degree of 83% (determined using infrared spectroscopy method) and M_w 8.78 kDa (calculated based on Mark-Houwink equation). Additionally, sodium silicate solution from rice hull ash (25% SiO_2) and Polyethylene glycol (M_w 400), acetic acid (2% v/v), HCl (37%), and sodium hydroxide pellet were used for preparing membrane, dissolving chitosan, a catalyst in synthesis membrane, for soaking membrane, respectively. Salts of $Ca(NO_3)_2.4H_2O$, $Mg(NO_3)_2.6H_2O$, $Zn(NO_3)_2.6H_2O$, $Cd(NO_3)_24H_2O$ used to prepare solutions of Ca(II), Mg(II), Zn(II), and Cd(II), respectively were purchased from Merck in analytical grade.

Instrumentation

Instruments used for preparation of Ch/Si/P membrane and adsorption studied were pH meter (EUTECH Instrument Ecoscan), orbital Shaker (Yellow Line OS 10 basic), analytical balance (Denver Instruments). Instruments used for characterizations of membrane were FTIR spectrometer (Shimadzu Prestige-21), Scanning Electron Microscope (SEM, JSM-6360 LA), and A Shimadzu X-ray diffractometer (XRD) with Cu-Kα radiation. Atomic absorption spectroscopy, AAS (Perkin-Elmer AA 200), was applied for determination of metal ion concentration in the solution.

Procedure

Preparation of membranes

A silica and PEG bended 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. Membranes were obtained by casting the mixture on a glass plate and were allowed to evaporate the solvent under an ambient temperature for 3 days. Membranes were neutralized with a 5% (w/v) NaOH solution after drying. Afterward, the membranes were washed with water to remove the remaining NaOH. Finally, the membranes were stored in a desiccators before use. Analogue work was carried out without addition of sodium silicate solution and PEG to produce chitosan membrane (Ch) and without PEG to find chitosan-silica membrane (Ch/Si).

Characterizations of membrane

The surface morphology was identified with Scanning Electron Microscope after gold coating. The fractured cross-sections of the films were frozen in liquid nitrogen then broken and air dried. Fourier Transform-Infrared (FT-IR) spectra were obtained under dry air at a room temperature on KBr pellets in the range of 4000-500 cm^{-1}. An X-Ray diffractometer was used to record the diffractograms of the films at 25 °C. The X-Ray source was Ni-filtered Cu Kα radiation (40 kV and 30 mA). The dry films were mounted on a sample holder and the pattern was recorded in the reflection mode at an angle 2ϴ over a range of 3.0200° to 70° at a speed of 5°/min. For determination of swelling degree or swelling index (SI), a procedure reported by Chen et al. [8] was used. The following equation was used to determine SI:

$$SI\ (\%) = [(w_w - w_d) / w_d] \times 100\% \quad (1)$$

where w_w and w_d are the sample weights after swelling for 24 h and dry state, respectively. In each specimen, three samples were tested.

Adsorption experiment

The adsorption experiment was performed using a batch method at various pH from 4.0 to 12.0 for Ca(II) ion and 4.0 to 9.0 for Mg(II), Zn(II), and Cd(II) ions. The solution pH was adjusted using HCl and NH_4OH solutions. Aqueous solution of Ca(II), Mg(II), Zn(II), and Cd(II) 25 mg/L was shacked with 0.12 g membrane for 24 h at various pHs. Kinetics and thermodynamics parameters were evaluated by varying contact time (1, 2, 4, 8, 16, 24, and 26 h) and concentration (5 to 50 mg/L), respectively at optimum pH. The concentration of unabsorbed metal ion was detected with AAS.

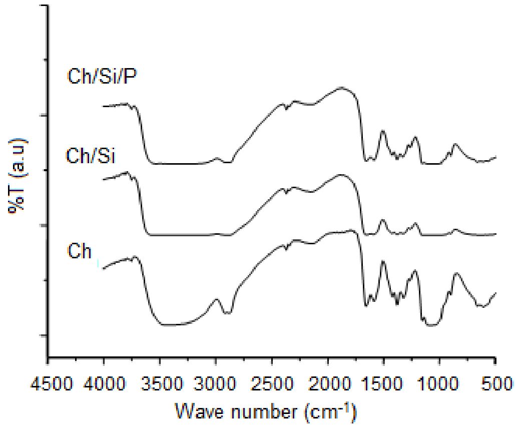

Fig 1. FTIR spectra of Ch, Ch/Si, and Ch/Si/P membranes

RESULT AND DISCUSSION

The presence of functional groups in Ch/Si/P membrane was identified based on the FTIR spectra presented in Fig. 1 and the spectra of Ch and Ch/Si as the comparison are included as well. The increase in the intensity of 1000-1100 cm^{-1} in Ch/Si membrane suggests the formation of –Si-O-C bonds [15-16], since Si-O stretching appeared at the same wave number of C-O stretching. Peaks around 1240 and 842 cm^{-1} in FTIR spectra of Ch/Si/P membrane (Fig. 1(C) indicates the presence of PEG after blending. The intermolecular interaction between chitosan and PEG should be ascribed to the hydrogen bond. Furthermore, C-O stretching vibration from C-O-H of chitosan (1151 cm^{-1}) shifts to low wavenumber. These imply the existence of an attractive intermolecular interaction between chitosan and PEG, as suggested in the literature [10,15-16]. Hence, the intermolecular interaction between chitosan and PEG may be ascribed to the hydrogen bond.

Structure of the membranes is examined based on XRD patterns presented in Fig. 2. The peaks around 2ϴ = 9.26, 20.37, and 22.06° should be assigned to chitosan: the peak around 2ϴ = 22.06° corresponds to the amorphous structure. The diffraction of chitosan blending with silica tends to crystallize in the form hydrated crystalline structure (2ϴ = 9.87) and amorphous structure (2ϴ = 22.02°). Once blending with amount of PEG, the main crystalline structures changes into hydrated one (2ϴ = 11.1°). Three produced membranes (Ch, Ch/Si and Ch/Si/P) give similar peaks with 2ϴ around 9.80, 20.445 and 10.46° which should be assigned to an amorphous solid structure. The addition of silica and PEG in Ch does not

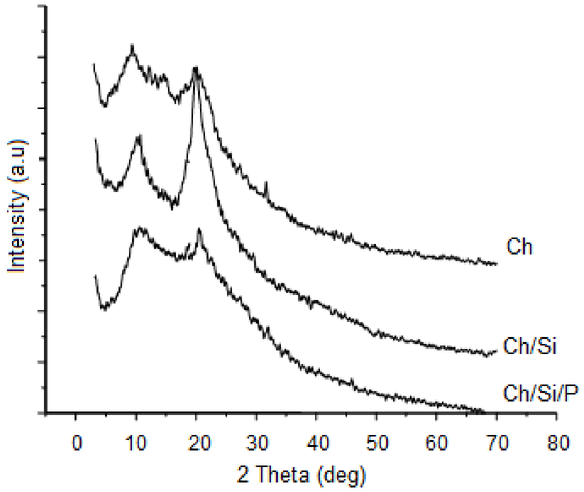

Fig 2. XRD patterns of Ch, Ch/Si, and Ch/Si/P membranes

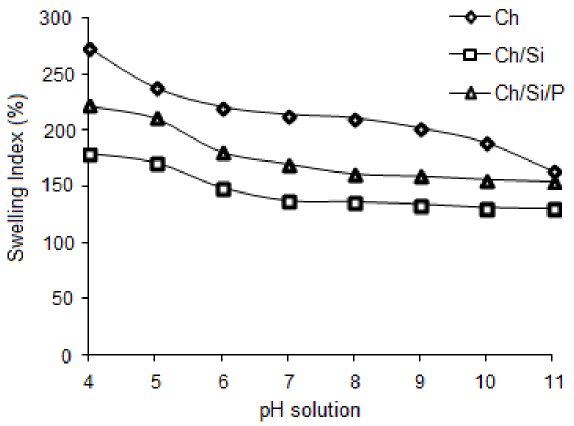

Fig 4. Plot of swelling index (%) for Ch, Ch/Si, and Ch/Si/P membranes in a buffer solution with various pHs

change significantly the crystalline; Ch/Si/P membrane is an amorphous solid structure; it is relevant to the result reported by He et al. [10].

The morphology of the chitosan membranes is evaluated based on the scanning electron microscopy (SEM) images presented in Fig. 3. It is observed that the surface of chitosan membrane is smooth and the texture is plain without pores. Chitosan membrane gives a dense structure and very small porosity. Blending sodium silicate with chitosan membrane (Ch/Si) improves the porosity of membrane and the morphology of blending PEG (Ch/Si/P). Addition of PEG causing the pores in the Ch/Si membrane is reduced due to the physically trapped PEG on the solid surface. PEG is likely to accumulate on the top surface of the membrane, where maximum contact with water is possible during phase inversion [15-16]. SEM is a powerful tool to characterize the microscopical pore structure of membrane in qualitative manner. In order to provide quantitative data of surface and cross-sectional pores computer image analysis can be used. Ch/Si and Ch/Si/P membrane have pore size of 2.2 and 1.9 μm respectively. This result supports the conclusion based on the FTIR spectra showing that the possibility of interaction between component molecules is very small and does not significantly affect material properties.

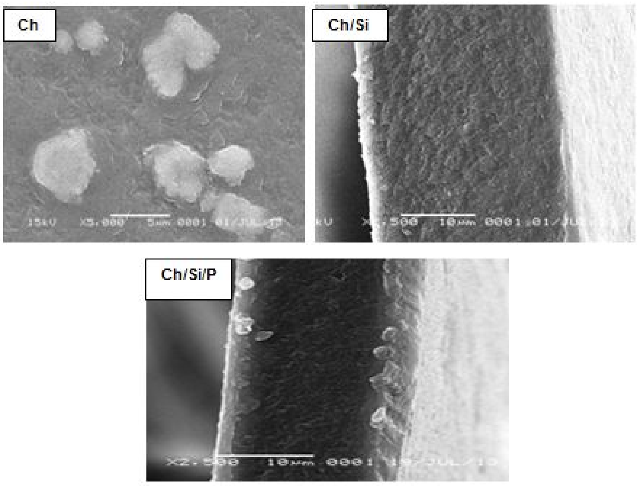

Fig 3. SEM images of membrane surface of Ch, Ch/Si and Ch/Si/P. Superscript shows image of cross surface

Water content of the membranes depends on silica and PEG content. The results are presented in Fig. 4. Addition of silica (Ch/Si) causes the capability to absorb water decreases. Water content inclines with increasing PEG content in the blend (Ch/Si/P). The enhanced hydrophilicity is caused by the addition of PEG attributing to the immobilization of PEG chains on the material surface. Acidic media gives a pronounced effect on the swelling behavior compared to the neutral and basic media; swelling index decreased with increasing pH value. The water affinity improvement may increase the possibility of ion uptake into the internal active site of the membrane leading to absorption enhancement [16].

Adsorption of Metal ions

Effect of pH

The pH value is one of the most important factors in the interaction a metal ion with a binding polymer [9]. Effect of solution pH on the adsorption ability of heavy metal ions was expressed in Fig. 5. The metal ion adsorption on Ch membrane has similar pattern to that on Ch/Si and Ch/Si/P ones. The adsorption inclines with pH increment. In acidic conditions, competition of H_3O^+ and heavy metal ions reduces adsorption of the target ions [6]. Moreover, in acidic solution protons on the membrane surface weakens electrostatic interactions between metal ions and membrane surface leading to sorption reduction. Increasing adsorption

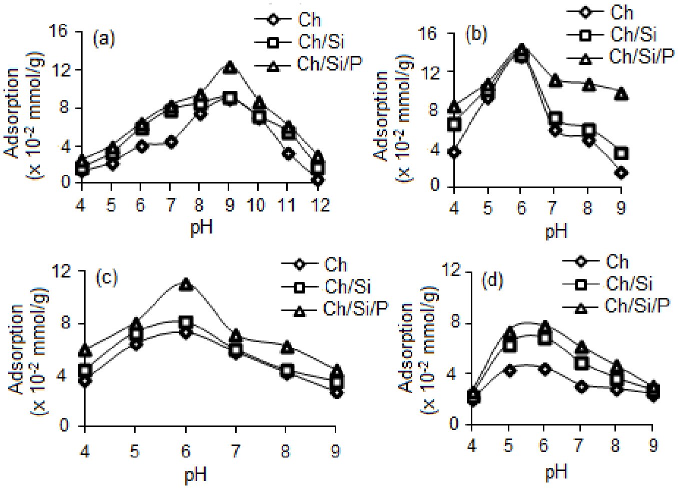

Fig 5. Effect of various pHs on adsorption of metal ions (a) Ca(II), (b) Mg(II), (c) Zn(II), and (d) Cd(II) onto membranes

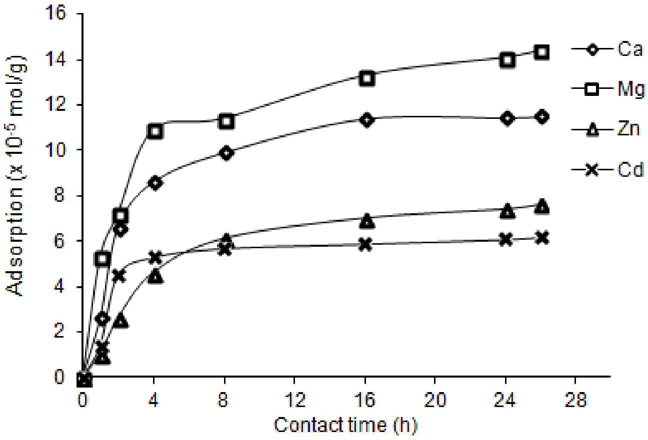

Fig 6. Adsorption curve of metal ions on Ch/Si/P membrane at various contact times

versus pH is presumably attributed to the formation of metal hydroxides in adsorption system. Therefore, precipitation-assisted adsorption arises at alkaline pHs leading to enhancement of loading capacity. The solution pH for pure adsorption (without precipitation) of metal ions on membrane Ch, Ch/Si and Ch/Si/P are commonly adjusted in the range of 5-6. Except Ca(II), the metal ion adsorption at pH of 9 is higher than that at 5-6 (Fig. 5 a). In the case, adsorption shows different trend especially at higher pH. Calcium may form monovalent ionic pairs such as $CaCl^+$, $CaOH^+$ before being adsorbed. At pH 12.56 (pK_{sp} = 5.89), the obvious increase in adsorption is due to precipitation of $Ca(OH)_2$, not due to real adsorption [17].

The order of adsorption capability for metal ions on the membrane is Ch/Si/P > Ch/Si > Ch. In Ch/Si membrane, blending sodium silicate with chitosan membrane improves the porosity of membrane. High porosity of Ch/Si membrane resulted in a larger surface area, also leading to increasing the adsorption of metal ions. In Ch/Si/P membrane, swelling degree increases with presence of PEG. The enhanced wettability caused by the addition of PEG can be attributed to the immobilization of PEG chains on the material surface. In the polymer science, hydrophilic chains can be stabilized by the polymer surface through physical adsorption during blending and formation of hydrophilic polymer surface network [7]. Therefore, porogens not only plays role in formation of the porous structure of membranes (by phase separation) but also affects the wettability as discussed previously. Water affinity improvement increases the possibility of ion uptake into the internal active site of the membrane leading to adsorption enhancement.

It is well accepted that amine sites are the main reactive groups for metal ions, though hydroxyl groups (especially in the C-3 position) may contribute to sorption. These reactive groups may interact with metal ions through different mechanisms depending on the metal, the pH, and the matrix of the solution. The free electron doublet on nitrogen may bind metal cations at pH close to neutrality (or weak acidity) [18]. Hence, Ch/Si/P membrane was used determination contact time and initial concentration effects.

Kinetics adsorption

The effect of contact time on the adsorption of 50 mL solution of metal ion 25 mg/L at a room temperature and optimum pH on 0.12 g Ch/Si/P membrane is shown in Fig. 6. It is obvious that the adsorption of metal ions on Ch/Si/P achieves equilibrium within 24 h. The kinetics of the metal ion adsorption have been described on the basis of the pseudo-first-order and pseudo-second-order models [19]. A simple kinetic model given by Lagergren for the pseudo-first order is presented in Eq. (2).

$$\frac{dQ}{dt} = k_1(q_e - q) \tag{2}$$

And the pseudo-second-order model is given in Eq. (3).

$$\frac{dQ}{dt} = k_2(q_e - q)^2 \tag{3}$$

where q and q_e are the adsorbed metal ions onto the membrane at time t and equilibrium, respectively; k_1 and k_2 are the kinetic rate constants of pseudo-first-order and pseudo-second-order models, respectively. One can obtain a linear equation for the pseudo-first-order and pseudo-second-order modes by integrating Eq. (2) and (3), respectively:

$$\ln(q_e - q) = \ln q_e - k_1 t \tag{4}$$

$$\frac{t}{q} = \frac{1}{k_2 h} + \frac{t}{q_e} \tag{5}$$

Table 1. Fitting results of the pseudo-first-order and pseudo-second-order kinetic models for adsorption of heavy metal ions onto Ch/Si/P membrane

Metal ion	pseudo-first-order Lagergren model			pseudo-second-order kinetic model		
	k_1 (h^{-1})	q_e(mmol/g)	R^2	k_2 (g $mmol^{-1}h^{-1}$) (10^{-3})	q_e (mmol/g)	R^2
Ca(II)	0.231	0.116	0.919	2.0	0.127	0.995
Mg(II)	0.146	0.085	0.944	5.1	0.154	0.999
Zn(II)	0.270	0.075	0.998	0.5	0.093	0.985
Cd(II)	0.702	0.070	0.928	1.3	0.063	0.999

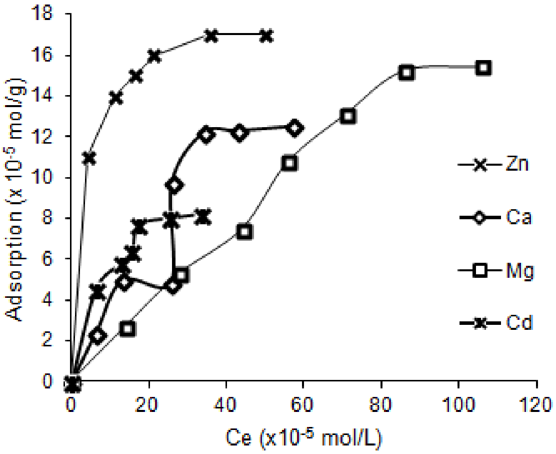

Fig 7. Adsorption curve of metal ions on Ch/Si/P membrane at various metal ion concentrations

Fitting result for the kinetic models are given in Table 1. Pseudo-second-order model well represented the kinetic data on the basis of the excellent goodness of the fit (R^2) as well as the agreement of the equilibrium adsorption capacity predicted by the model (q_e) with the experimental ones. Pseudo-first-order model does not give an acceptable fit to the kinetic data. Moreover, equilibrium sorption capacity estimated by the first-order model is not comparable to the experiment ones. Therefore, the pseudo-second-order model tends to be more favorable for adsorption of ions on Ch/Si/P membrane.

The value order of second-order rate constant (k_2) is Cd(II) > Zn(II) and Mg(II) > Ca(II). The phenomenon can be explained by considering the ionic radii. Ionic radii (Å) of metal ions Zn(II) 4.19, Ca(II) 4.12, Mg(II) 4.28, and Cd(II) 4.26 [20]. Since Zn(II) is smaller radii than Cd(II) and ion Ca(II) is smaller radii than Mg(II) ion. It leads to hydrate water molecule in the large number and form bulky hydrated metal ions. The metal ions with small ionic radii may form a large hydrate water molecules resulting in low mobility.

Adsorption isotherm models (single metal ion system)

The adsorption isotherm was studied by varying the initial concentration of metal ions (20 to 70 mg/L) at pH optimum. The effect of concentration of metal ions on the adsorption is shown in the Fig. 7. An adsorption isotherm describes the fraction of adsorbate molecules that are partitioned between liquid and solid phases at equilibrium. Adsorption of metal ions by adsorbent was modeled using two adsorption isotherms. Langmuir isotherm assumes mono-layer adsorption on a uniform surface with a finite number of adsorption sites that are saturable. Maximum capacity of adsorption is achieved when all the sites are saturated with adsorbates. The linear form of the Langmuir isotherm model is described as:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \qquad (6)$$

where K_L is Langmuir constant related to the energy of adsorption and q_m is the maximum adsorption capacity (mol/g). The slope and intercept of plot of C_e/q_e vs C_e at room temperature were used to calculate q_m and K_L.

The Freundlich isotherm is applicable to both mono-layer (chemisorptions) and multilayer adsorption (physisorption) and is based on the assumption that the adsorbate adsorbs onto the heterogeneous surface of an adsorbent. The linear form of Freundlich equation is expressed as:

$$\log qe = \log K_F + \frac{1}{n}\log Ce \qquad (7)$$

where K_F and n_F are Freundlich isotherm constants related to adsorption capacity and adsorption intensity, respectively and Ce is the equilibrium concentration (mmol/L). The Freundlich isotherm constants K_F and n are determined from the intercept and slope of log qe vs. log Ce.

The sorption isotherm constants, according to these two isotherms, were summarized in Table 2. After comparing the linear correlation coefficients in Table 2, the sorption of the Zn(II) and Cd(II) ions on Ch/Si/P membrane were found to follow the Langmuir isotherm equation accurately under the concentration range studied. The q_m (mmol/g) values of the Langmuir sorption were as follows: Zn(II) > Cd(II) on Ch/Si/P membrane.

The sorption of the Ca(II) and Mg(II) ions on Ch/Si/P membrane is found to follow the Freundlich isotherm equation accurately under the concentration range studied. Meanwhile, for Freundlich isotherm the magnitude of the exponent n_F value gives an indication of the favorability of adsorption. Based on Table 2, it can be seen that Ch/Si/P membrane had n_F values greater

Table 2. Isotherm constant for adsorption of heavy metal ions onto Ch/Si/P membrane

Metal ion	Langmuir Isotherm			Freundlich Isotherm		
	q_m *(mmol/g)*	*E (KJ/mol)*	R^2	K_F	n_F	R^2
Ca(II)	0.317	17.8	0.255	0.485	1.266	0.855
Mg(II)	0.748	14.0	0.512	0.223	1.099	0.985
Zn(II)	0.182	26.0	0.999	6.163	5.319	0.927
Cd(II)	0.105	29.0	0.975	2.459	2.626	0.915

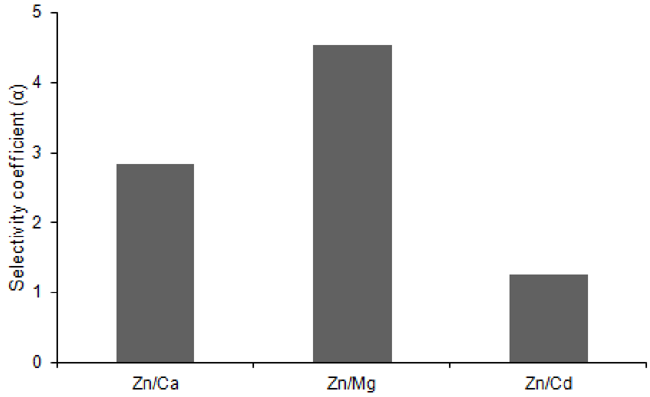

Fig 8. Selectivity coefficient of Zn(II) onto Ch/Si/P membrane

than 1, which represents a favorable adsorption condition [21]. The order of n_F values for the Freundlich sorption is Ca(II) >Mg(II) on Ch/Si/P membrane.

The membrane showed different affinities for the various metal ions; Zn(II) is the best ion to form complex with the Ch/Si/P membrane compared to Ca(II), Mg(II), and Cd(II) ions. This behavior can be explained in the framework of the concept developed by Pearson about the softness and the hardness of chemical species [22]. Pearson determined a scale of hardness (or softness) of a species according to its electronegativity, its polarizability, its size and its charge (for the ions). This theory is not quantitative but gives information about the ability for a species to be bound preferably with another. Thus, the acid defined as a hard one reacts preferably with a hard base. A soft acid preferably reacts with a soft base.

Chitosan, due to the presence of hydroxyl (OH^-) and amine (NH_2) groups, is widely used for the adsorption of metal ions. Hydroxyl (OH^-) and amine (NH_2) groups are hard bases. The metal ions of Ca(II) and Mg(II) are a hard acids, Zn(II) metal ions a borderline, Cd(II) metal ion is soft acid. The Hydroxyl and amine group on the Ch/Si/P membrane will bind with Ca(II) and Mg(II) is better than Zn(II). This theory explains the high efficiency of the Zn(II) complexation by the Ch/Si/P membrane. It is probably due to the bonding type of Ca(II) and Mg(II) ionic and incompleteness of oxidation. Ionic bond may be ready to be broken down in aqueous (polar) solution via solvation and the amine groups interact with Zn(II) and Cd(II) than Ca(II) and Mg(II) [23].

Adsorption isotherm models (quaternary metal ion system)

In addition to the research of adsorption of single metal ions, the possible competition between several metal ions has been considered. The presence of multiple competitive ions is more frequent than the presence of a single ion, and adsorption in multi-component systems is complicated due to the variety of solute-surface interactions involved. For this purpose, the membrane selectivity for mixtures of four metal ions has been studied. The adsorption equilibria of quaternary Ca-Mg-Zn-Cd mixtures were studied, using the same initial concentration of 25 mg/L for each ion. Since the ions were used in equal mass concentrations, they were not in equimolar proportions, since the molecular weights are different. Selectivity coefficient (α) was determined using Equation 8 [24].

$$\alpha_{(M1/M2)} = D_{M1}/D_{M2} \qquad (8)$$

where distribution ratio D = q/C_e, q is adsorption capacity (mmol/g), C_e is the adsorbate concentration in the aqueous phase at equilibrium (mmol/L), and α is selectivity coefficient.

A comparison of capability of Ch/Si/P membrane in adsorbing Ca(II), Mg(II), Zn(II), and Cd(II) in quaternary metal ions system represented as selectivity coefficient is expressed in Fig. 8. As can be seen in Fig. 8, selectivity coefficient (α) of Zn(II) toward other ions is in order of Cd(II) < Ca(II) < Mg(II). This phenomena indicates that Zn(II) shows much greater affinity with membrane when competing with Ca(II), Mg(II), and Cd(II). Thus, more Zn(II) ion combines with hydroxyl and amine groups on the membrane surface. Zn(II) is the best ion to form complex with the Ch/Si/P membrane compared to Ca(II), Mg(II), and Cd(II) ones, Ca (II) and Mg (II) ions tend to form ionic bonds with -NH_2 groups.

CONCLUSION

Chitosan-silica-PEG membrane (Ch/Si/P) has been successfully synthesized. Blending chitosan with polyethylene glycol and silica enhances adsorption behavior probable due to pore size and water affinity of membrane. Zn(II) is the best ion to form complex with the Ch/Si/P membrane compared to Ca(II), Mg(II), and Cd(II) ones, Ca (II) and Mg (II) ions tend to form ionic bonds with -NH_2 groups. The adsorption capacity of metal ions with the order of Zn(II) > Cd(II) for transition metal ions and Ca(II) > Mg(II) for the alkali earth metal ions. The adsorption of Ca(II) and Mg(II) is the best described with pseudo-second order kinetic model and Freundlich adsorption isotherm. Meanwhile, the adsorption of Zn(II), and Cd(II) follows pseudo-second order kinetic model and Langmuir adsorption isotherm. The adsorption capacity (μmol/g) of Ch/Si/P membrane for Zn(II) and Cd(II) were 182 and 106 respectively. The affinity Freundlich (n_F) of Ch/Si/P membrane for Ca(II) and Mg(II) were 1.266 and 1.099, respectively. Further work is still going on to evaluate the probability of membrane to separate selected metal ion in flow system.

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