Chitosan/Silica Composite Membrane: Adsorption of Lead(II) Ion from Aqueous Solution

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ABSTRACT

Chitosan membrane has the potential to separate lead(II) ions from aqueous solution. However, the kind of membrane has a drawback due to the low structural properties. Thus, this study investigates the role of silica in improving chitosan-based flat sheet membrane for removal of lead(II) ions from aqueous solution. The functional groups and structural morphologies were characterized using Fourier Transform Infrared-Attenuated Total Reflectance (FTIR-ATR) spectrometer and Scanning Electron Microscope (SEM), respectively. The membrane performance in terms of adsorption study was conducted at different pHs and initial concentration of lead(II) solution. The FTIR-ATR spectrum showed the existence of new absorption peak of chitosan/silica membrane. SEM images revealted the presence of microvoids on the cross-section of the chitosan/silica membrane whereas pure chitosan membrane possessed dense structure. The adsorption study showed that the composite membrane exhibited higher efficiency of lead(II) removal at optimum pH of 7.0 which was 89.27% as compared to 11.50% of pure chitosan membrane. The amount of lead(II) adsorbed onto the membrane was 57.60 mg/g. Therefore, it indicates the potential use of silica to improve the properties of chitosan membrane for removal of heavy metal from water solution.

Keywords: Chitosan, silica, membrane, lead(II), adsorption

1.0 INTRODUCTION

The metal-contaminated wastewater still represents a worldwide environmental problem due to the industrialization and technological advances [1]. The lead metals are among the well-known heavy metal that are toxic and carcinogenic [2]. Due to their high solubility, living organisms can easily absorb the heavy metals that entering the eco-system. The accumulation in human body may occur if the amount of metals consumed beyond the limits, either by ingestion or food chain [3]. This will cause serious health problem such as cancer, damage of organ and nervous system, which can disrupt the growth and development of human body [4]. Therefore, it is essential to treat the metal-contaminated wastewater before being discharge to the environment.

There are several techniques that can be implied for removal of lead from water streams but one of the most convenient operations was membrane adsorption [5]. Membrane have its own advantages such as low production cost, easy to handle, high flow rate and possess excellent efficiency for removal of metal ions [6, 7].

Previously, researcher used synthetic polymer such as polyacrylonitrile (PAN) and polyethylene terephthalate (PET) for

membrane fabrication [8]. Recently, natural bio-polymer such as chitosan has gained increasing attention to be used as adsorptive membrane since it contains hydroxyl and amine groups that acts as active sites for adsorption process [9]. However, chitosan membrane have low structural and physical properties which limits their potential use to remove lead metal ions [10].

Rice husk is the agricultural waste that most abundantly found in rice production country. In Malaysia, it is estimated that about 1, 564, 604 tons of rice will be produced in year 2020 [11]. As the production of rice increases, so does the production of rice husk. This circumstance can lead to the space limitation when it disposes to the landfills [12]. In a previous study, Battegazzore *et al*. [13] found that 80-90% of silica can be obtained from thermally treated rice husk. Theoretically, silica can interact with hydroxyl and amine groups of chitosan due to the presence of silanol groups [14]. However, in wastewater treatment application, sodium silicate was commonly used as a silica source [15].

Thus, in this study, sodium silicate was synthesized from agricultural waste of rice husk and used in the fabrication of chitosan/silica composite membrane to improve the properties of chitosan membrane. Then, the membranes were characterized by using FTIR-ATR and SEM analysis. Several parameters were investigated in adsorption study of the pure chitosan and chitosan/silica membrane which were pH effect and initial concentration of the lead(II) solution. The adsorptive performance was further evaluated by Langmuir and Freundlich isotherm model to identify their adsorption behaviour.

2.0 METHODS

2.1 Materials

Commercial chitosan (75-85% deacetylated) with medium molecular weight was purchased from Sigma Aldrich®. Rice husks were collected from Kilang Beras Jelapang Selatan (M) Sdn Bhd., Muar, Johor. Acetic acid glacial ($\geq$99.85%) was obtained from HmbG® Chemicals. Both, sodium hydroxide (NaOH, 99%) and lead(II) nitrate (Pb(NO$_3$)$_2$, $\geq$99.5%) were purchased from QRëC™.

2.2 Silica Source Preparation

Rice husks were incinerated at 600˚C for 3 h to produce rice husk ash which was then mixed with 1 M NaOH solution (molar ratio Si/Na = 1). The product was sintered at 800˚C for 2 h to produce sodium silicate.

2.3 Membrane Fabrication

In this study, membrane preparation consists of pure chitosan and chitosan/silica membrane fabrication.

For chitosan/silica membrane, sodium silicate (0.2 g) was first dissolved in 50 mL of 0.1 M acetic acid. 1 g of chitosan were later added and stirred until it is completely dissolved to obtain homogeneous dope solution, followed by sonication. A yellowish colour solution was then casted onto the clean glass plate and left for at least 24 h at room temperature to allow the solvent to evaporate. The dried membrane was then immersed in 1 M NaOH solution and followed by a rinse with distilled water to make it neutral prior to drying at room temperature.

For pure chitosan membrane, similar method was used as chitosan/silica membrane fabrication with the absence of sodium silicate addition.

2.4 Characterization

The chemical composition in rice husk ash obtained from incineration process was examined by using X-ray Fluorescence (XRF), (Bruker, S4-Pioneer model). The samples were prepared by press powder method prior to analysis. The physical interactions between chitosan and silica were determined by using Fourier Transform Infrared-Attenuated Total Reflectance Spectrometer (FTIR-ATR), (JASCO, FT/IR-4200IF). The samples were scanning at a wavelength of 400 cm^{-1} to 4000 cm^{-1}. The surface and cross-sectional morphology of the membranes were observed under Scanning Electron Microscopy (SEM), (Hitachi, TM3000 model). All the samples were cut into smaller pieces and sputter with gold prior to observation.

2.5 Membrane Performance

The adsorption study of the chitosan/silica membrane on lead removal was conducted at different pH and initial concentration of lead(II) solution. To each sample, 0.05 g of pure chitosan and chitosan/silica membrane were used.

For the pH study, membranes were added into 50 mL of lead(II) solution (100 mg/L) at various pH (5.0, 6.0, 7.0 and 8.0) and agitated for 24 h. The pH was adjusted by using 0.01 M HCl and 0.1 M NaOH solutions. The removal efficiency, R was calculated by using Equation 1.

The adsorptive performance of the membranes at different initial concentration (60, 80, 120, 140, 160, 180, 200, 220 and 240 mg/L) was done with 50 mL of lead(II) solution at optimum pH. The adsorption capacity, q_e was calculated by using Equation 2.

$$R(\%) = \frac{C_o - C_e}{C_o} \times 100\% \qquad (1)$$

$$q_e\left(\frac{mg}{g}\right) = \frac{(C_o - C_e)V}{m} \qquad (2)$$

where C_o and C_e (mg/L) are initial concentration and equilibrium concentration of metal, respectively; V (L) is the volume of the solution and m (g) is the dry mass of the membrane used.

The adsorption isotherm mechanism of the chitosan/silica membrane for removal of lead(II) metal ions from aqueous solution were evaluated based on the Langmuir and Freundlich isotherm models as described in Equations 3 and 4, respectively.

$$\frac{C_e}{q_e} = \frac{1}{Q_{max}b} + \frac{C_e}{Q_{max}} \qquad (3)$$

$$\ln q_e = \ln K_F + \left(\frac{1}{n}\right)\ln C_e \qquad (4)$$

where q_e (mg/g) is amount of lead(II) adsorbed onto the membrane; C_e (mg/L) is equilibrium concentration of metal; Q_{max} (mg/g) is maximum adsorption capacity; b is Langmuir constant; K_F (mg/g) is Freundlich constant and $1/n$ is parameter related to adsorption intensity. Throughout the study, equilibrium concentration of the metal for each sample was analysed by using Atomic Adsorption Spectroscopy (AAS), (Shimadzu AAS, AA-7000 model).

3.0 RESULTS AND DISCUSSION

3.1 Characterization

3.1.1 XRF Analysis

White rice husk ash was obtained from the burning process of rice husk at 600°C. The chemical composition was
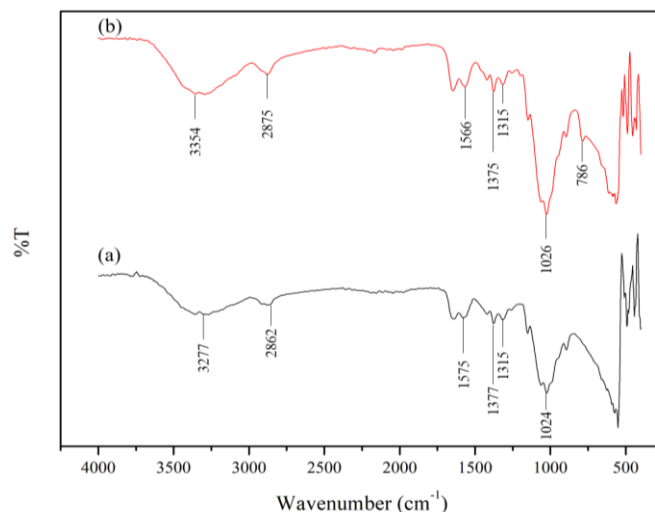
Figure 1 FTIR-ATR image of (a) chitosan membrane (b) chitosan/silica membrane

determined by XRF analysis as shown in Table 1. It specifies that silica, SiO_2 act as the major ingredient in the rice husk ash along with other metal oxides such as alumina, ferric oxide, titanium oxide, calcium oxide, magnesium oxide, zinc oxide, manganese(II) oxide, phosphorus pentoxide and others. It was noteworthy to make a good used of agriculture waste to yield silica. Besides, it can solve the environmental problems due to the limitation of waste disposal space.

Table 1 Chemical composition of rice husk

Element	Mass Percent (%)
SiO_2	87.4
Al_2O_3	0.5
Fe_2O_3	0.2
TiO_2	0.0
CaO	1.4
MgO	0.6
K_2O	4.1
ZnO	0.0
MnO	0.2
P_4O_{10}	0.5
Others	5.1

3.1.2   FTIR-ATR Analysis

In Figure 1, the spectra showed broad adsorption band at 3277 and 3354 cm^{-1}. It corresponds to the vibration of hydroxyl groups that bonded to carbon atoms and silica atoms [16]. Between wavenumber area of 3500-3100 cm^{-1}, there was stretching vibrations of N-H that was overlap with the adsorption band of O-H. Both bands at 2862 and 2875 cm^{-1} are due to the C-H stretching vibrations [17]. The deformation of N-H bond of amino groups of pure chitosan and chitosan/silica membrane were observed at 1575 and 1566 cm^{-1}, respectively [18]. The peaks at 1377, 1375 and 1315 cm^{-1} were observed due to the C-H bending vibrations. The band at 1024 cm^{-1} represents the vibrations of C-O of CH-OH groups, same as proposed by Mahatmanti *et al.* [19]. Meanwhile, the appearance of band at 1026 cm^{-1} and 786 cm^{-1} correspond to the asymmetric Si-O-Si bond and symmetric Si-O-Si bond of chitosan/silica composite membrane, respectively. Similar results were reported by He *et al.* [20].
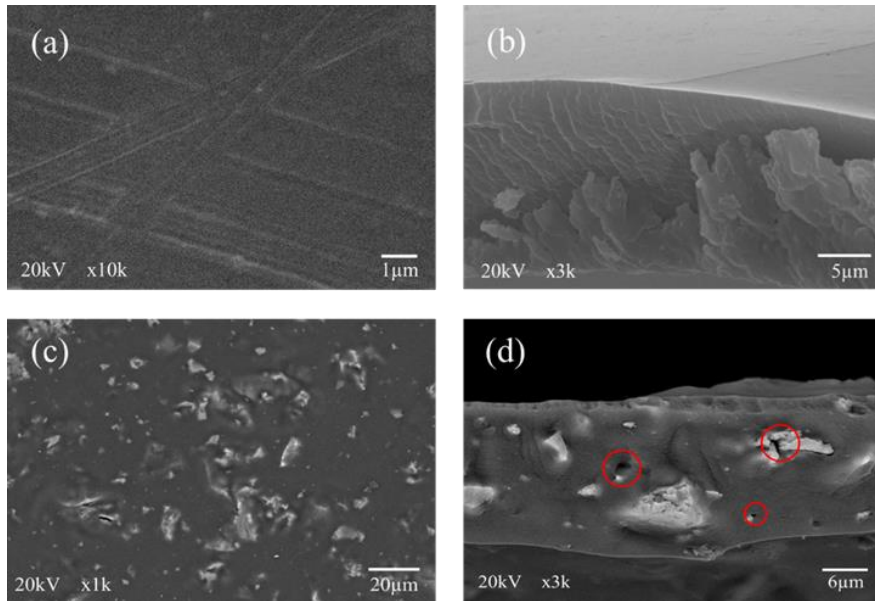
Figure 2 SEM images of (a) surface and (b) cross-section of pure chitosan membrane; (c) surface and (d) cross-section of chitosan/silica composite membrane
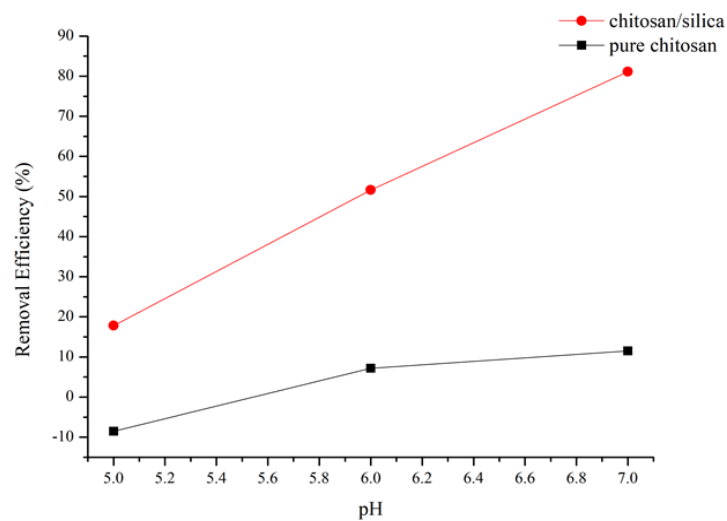

Figure 3 The effect of pH on the removal of lead(II) from aqueous solution

3.1.3   SEM Analysis

The structural morphologies of the membranes are presented in Figure 2. The pure chitosan membrane showed dense cross-sectional structure. This result was supported by Rekik *et al*. [10] who observed pure chitosan membrane has a uniform, smooth, flat surface and displays a homogeneous structure. However, the surface of the membrane became more rougher after the addition of sodium silicate in chitosan dope solution and some microvoids were presence in inner structure of the membrane which can help in the separation of lead(II) metal ions from aqueous solution.
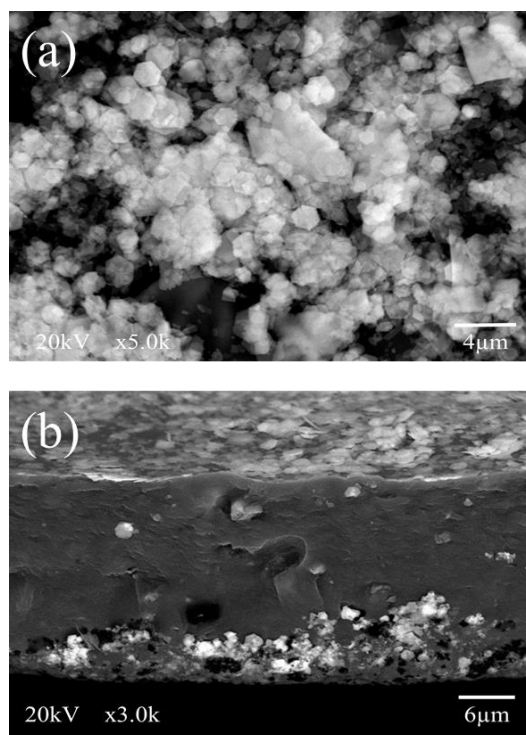
Figure 4 Structural morphologies of (a) surface and (b) cross-section of chitosan/silica membrane after adsorption study at pH 7.0

3.2 Membrane Performance on Lead(II) Removal from Aqueous Solution

3.2.1 Effect of pH

The pH effect on the adsorption of lead(II) ion onto pure chitosan and chitosan/silica membrane was presented in Figure 3. As shown in the figure, the adsorption of metal ions increased as the increasing of pH. This finding proved that the adsorption efficiency of lead(II) metal ions was strongly dependent on the pH. In acidic condition, there was counteraction between metal ions, Pb^{2+} and H^+ which leading to the low adsorption efficiency of lead(II) metal ions onto the membrane [21]. The optimum pH was found at pH 7.0 with chitosan/silica composite membrane exhibited 89.27% of adsorption efficiency. It was slightly higher as compared to pure chitosan membrane which exhibited 11.50% of removal efficiency of lead(II) metal ions. At pH 8.0, instead of adsorption, chemical precipitation was taking place. This is due to the formation of lead hydroxide ion such as $Pb_4(OH_4)^{4+}$, $Pb_6(OH_8)^{4+}$ and $Pb_4(OH_4)^{2+}$ in basic condition [22]. The adsorption of lead metal ions onto chitosan/silica membrane were further supported with SEM analysis of the membrane after adsorption at pH 7.0. As seen in Figure 4, the presence of hexagonal structure on the membrane surface can be observed and some of the lead(II) metal ions were adsorbed onto the microvoids that exists in the cross-section of the membrane. Then, it is further investigated by SEM-EDX mapping as displayed in Table 2. From the data obtained, it is confirmed that the hexagonal structure was lead(II) metal ions with 67.24 wt.% , besides other elements of the composite membrane which are oxygen, carbon and silicon.

Table 2 SEM-EDX analysis of chitosan/silica composite membrane after adsorption study pH 7.0

Element	AN	Series	norm. C (wt. %)	Atom. C (at. %)
Lead	82	M-series	67.24	12.39
Oxygen	8	K-series	17.22	41.09
Carbon	6	K-series	13.96	44.37
Silicon	14	K-series	1.58	2.15
		Total	100.00	100.00

3.2.2 Effect of Initial Concentration of Lead(II) solution and Adsorption Isotherm

The adsorption capacity of the chitosan/silica composite membrane at optimum pH and room temperature was studied by varying the initial concentration of lead(II) solution (60, 80, 120, 140,160, 180, 200, 220 and 240 mg/L). The obtained results were plotted in Figure 5. From the data plotted, it was found that the adsorption of metal ions increased with the initial concentration of lead(II) solution. The composite membrane achieved the highest adsorption of lead(II) metal ions at initial concentration of 220 mg/L with 57.60 mg/g of adsorption capacity. However, the adsorption capacity of the lead(II) ions decrease at the initial concentration of 240 mg/L. According to the study by Farghali *et al.* [23], this behaviour is probably due to the increasing of the chemical driving force of concentration gradient. The evaluation on the adsorption mechanism of composite membrane was based on R^2 value of Langmuir and Freundlich isotherm model. The Langmuir model assumes that the surface topography was uniform which leading to the monolayer coverage of adsorbate on the adsorbent surface. Thus, no adsorption will take place at

equilibrium condition. Meanwhile, Freundlich model assumes that the surface topography was rough and optimum adsorption capacity was achieved when there is no functional group available as active site for adsorption to take place [24]. The results of the experiment of this study were demonstrated in Table 3. As can be seen clearly from the table, the experimental data showed R^2 value of Freundlich model was higher than Langmuir model. Thus, the adsorption behaviour that occur between chitosan/silica composite membrane and lead(II) metal ions fitted better with Freundlich isotherm model. This model suggested that the adsorption process happened on the surface of the membrane due to interaction between metal ions and several functional groups of the composite membrane and the process assumed was taking place on heterogenous surface of the membrane with different adsorption energy due to the surface roughness. [25, 26]
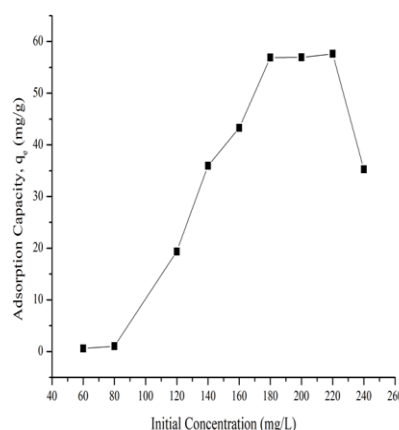
Figure 5 The effect of initial concentration of lead(II) solution

4.0 CONCLUSION

In this study, chitosan/silica composite flat sheet membrane was successfully

Table 3 Langmuir and Freundlich isotherm parameters

Membrane	Langmuir Model			Freundlich Model		
	Q_{max} (mg/g)	b (L/mg)	R^2	K_F (mg/g)	1/n	R^2
Chitosan/silica membrane	-2.3137	-5.82×10^{-3}	0.3918	1.41×10^{-6}	3.4427	0.6449

fabricated via casting technique. The SEM images revealed that the structural properties of pure chitosan membrane can be improved with silica addition. Based on the adsorption study, the removal of lead(II) metal ions have relied on the pH of lead (II) solution. At optimum pH=7.0, 89.27 % of lead (II) metal ions removal was achieved. Furthermore, the highest adsorption capacity of 57.60 mg/g was achieved at initial concentration of 220 mg/L. It is suggested that the adsorption mechanism was following Freundlich isotherm model.

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