Chitosan/silica composite membrane: Performance on water permeability and rejection of lead(II) ion from aqueous solution

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INTRODUCTION

Contaminants of heavy metals in wastewater, as a result of industrial and technological advancements, become a major concern nowadays. Although some of the heavy metals are essential for growth of living organisms, but mostly, they possess toxic and carcinogenic properties which can harm living things and environmental system (Zamani et al., 2012). Lead metal (Pb) is one of the examples of harmful heavy metals which can be found in any aqueous wastewater effluent from industries (Nasef and Yahaya, 2009). It will be deposited on soil and water before reaching human via food chain (Järup et al., 2003). However, its toxicity is depended on the concentration levels of Pb(II) metal ions in the ecosystem. World Health Organization (WHO) allows the limit amount of Pb(II) metal ions to be discharged into surface water, which is 0.015 ppm (Cotruvo et al., 2011).

With this concern, different techniques have been employed for removal of heavy metal ions from wastewater. It includes chemical precipitation, ion exchange, adsorption, membrane filtration, flotation, coagulation, flocculation and electrochemical treatment (Carolin et al., 2017; Azimi et al., 2017). In recent years, membrane filtration receives great attention from researchers because of its capability to remove suspended solid, organic compound and inorganic contaminants (Gunatilake, 2015). Besides, membrane can be simply designed with low production cost and excellent efficiency for the removal of metal ions (Habiba et al., 2017).

Presently, natural bio-polymer chitosan has been widely used in membrane fabrication to remove heavy metals since chitosan possesses high quantity of amino and hydroxyl groups, which makes it significant in adsorption process (Budnyak et al., 2015). However, chitosan-based membranes needs further modification due to their low structural and physical properties, which limits their potential applications in membrane filtration systems (Behera et al., 2017; Rekik et al., 2017).

Rice husk is an agricultural waste derived from rice production. In Malaysia, the production of rice increases every year as well as the production of rice husk. This situation may lead to the space limitations when the waste is disposed to landfills (Pode, 2016). In a previous study, Battegazzore et al. (2014) discovered about 80-90% of silica can be obtained from incineration process of rice husk. The obtained silica can be used in various applications such as plastic and rubber reinforcement. However, silica generally can be converted into...
sodium silicate since it is more convenient to be used in wastewater treatment applications (Pode, 2016). Therefore, sodium silicate tends to be added in chitosan membrane to enhance the properties of chitosan membrane.

In this study, chitosan/silica composite membranes were fabricated using sodium silicate that derived from rice husk ash and characterized using SEM and FTIR-ATR. Then, the membranes were used to investigate the rejection of Pb(II) metal ions from aqueous solution via filtration.

EXPERIMENTAL

Materials
Rice husks were collected from Kilang Beras Jelapang Selatan (M) Sdn Bhd., Muar, Johor. A commercial chitosan in powder form (75-85% deacetylated) with medium molecular weight (190, 000 – 310, 000 Da.) was purchased from Sigma Aldrich®. Acetic acid glacial (≥99.85%) that acted as a solvent was acquired from HmbG® Chemicals. Both, sodium hydroxide (NaOH, 99%) and lead(II) nitrate (>99.5%) were purchased from Sigma Aldrich®. Lead nitrate solution (Pb(NO3)2, ≥99.5%) were obtained from QREC™.

Synthesis of silica source
White rice husk ash that obtained from incineration process of rice husk at 600°C for 3 h was mixed with 1 M NaOH solution (molar ratio Si/Na = 1) by heating and stirring the solution. The product, white-grey powder was sintered at 800°C for 2 h to produce solid sodium silicate, Na2SiO3. This sodium silicate was then used as a silica source in the fabrication of chitosan/silica composite membranes.

Preparation of chitosan/silica composite membranes
Sodium silicate was first dissolved in 50 mL of 0.1 M acetic acid. 1 g of chitosan was later added and stirred until it was completely dissolved to obtain homogenous chitosan/silica solution, followed by sonication for 90 min. A yellowish colour dope solution was casted on the clean glass plate and left at room temperature for 24 h to allow the solvent to evaporate. Then, the dried membranes were immersed into 1 M NaOH solution to make it neutral. Distilled water was used to remove the excess of NaOH prior to drying at room temperature. The preparation of chitosan/silica dope solution was followed the formulation as described in Table 1.

Table 1 Chitosan/silica membrane formulation.

| Sample | Chitosan (g) | Sodium silicate (g) |
|--------|--------------|---------------------|
| CHSi0  | 0.09         | 1                   |
| CHSi3  | 0.06         | 1                   |
| CHSi6  | 0.03         | 1                   |
| CHSi9  | 0.09         | 1                   |

Membrane characterization
The morphologies of the composite 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.

The determination of functional groups in chitosan/silica composite membranes was recorded by using Fourier Transform Infrared-Attenuated Total Reflectance Spectrometer (FTIR-ATR), (JASCO, FTIR-4200IF). The samples were scanned at a wavelength of 400 to 4000 cm⁻¹.

The concentration of Pb(II) metal ions was measured by Atomic Adsorption Spectroscopy (AAS), (Shimadzu AAS, AA-7000 model). All the reported data was in the average of five replicates.

Membrane performance
The pure water permeability (PWP) and Pb (II) ion rejection were measured using membrane filtration process (effective membrane area: 10.18 cm²) at room temperature with applied pressure of 0.5 bar. The membrane samples were firstly pressurized at 1 bar for 30 min to avoid any compaction effects. Meanwhile, the output pressure was exposed to the atmospheric conditions. In case of PWP, distilled water was used to circulate through the membrane permeation system until constant flux was observed. Meanwhile, for rejection of Pb(II) metal ions from aqueous solution, permeate samples were collected after 30 minutes of operation with feed containing 10 ppm of Pb(II) solution. As previously described (Ma et al., 2012), flux (F) and rejection (R) were calculated by using equations, in which F was calculated using Eq. (1).

\[ F \left( \text{Lm}^{-2}\text{h}^{-1} \right) = \frac{V}{t \times A} \]  

Where, F is the flux, V (L) is the volume of permeate through the membrane, A (m²) and t (h) are the area of the membrane and time, respectively. Rejection of Pb(II) metal ions was calculated by Eq. (2).

\[ R \left( \% \right) = \left( 1 - \frac{C_P}{C_F} \right) \times 100 \]  

Where, R is the percent of rejection, \( C_P \) (mg L⁻¹) and \( C_F \) (mg L⁻¹) are the lead concentration in permeate and feed stream, respectively. All recorded data was the average values of five replicates.
FTIR-ATR analysis

The fabrication of chitosan/silica composite membranes involved the changes of functional groups. Therefore, the pure chitosan membrane and composite membranes were characterized using FTIR-ATR as shown in Fig. 4. Broad adsorption bands were observed at 3363 and 3282 cm\(^{-1}\) which corresponded to the vibration of O-H hydroxyl groups that bonded to carbon atoms and silica atoms (Budnyak \textit{et al.}, 2015). The stretching vibrations of N-H were overlapped with the adsorption band of O-H at the wavenumber area of 3500-3100 cm\(^{-1}\) and the intensity of the peak was decreased in the CHSi9 membrane spectrum due to the interaction of silica with amide and hydroxyl groups of chitosan. The C-H stretching vibration peaks were recorded at 2904 and 2891 cm\(^{-1}\) (Abu-Saied \textit{et al.}, 2017). The bands at 1645, 1560 and 1550 cm\(^{-1}\) of both spectra indicated the deformation of N-H bond of amino groups (Budnyak \textit{et al.}, 2015). The peaks of C-H bending vibrations were observed at 1381 and 1367 cm\(^{-1}\). Besides, the band at 1024 cm\(^{-1}\) represented the vibrations of C-O of CH-OH groups (Mahatmanti \textit{et al.}, 2016). The new adsorption peak was observed at 1041 cm\(^{-1}\) and a shoulder was detected at 779 cm\(^{-1}\) of CHSi9 membrane, corresponding to the asymmetric Si-O-Si and symmetric Si-O-Si bonds of chitosan/silica membrane, respectively (He \textit{et al.}, 2016).

Membrane performance

The membrane permeation performance data with different silica contents was reported in Table 2. As presented, the flux and rejection of Pb(II) metal ions were increased with the addition of silica. This results was expected based on the SEM images and spectra from FTIR analysis. Since CHSi9 membrane contained microvoids, it allowed more water molecules to pass through the membrane (Vlotman \textit{et al.}, 2018). Furthermore, the amount of active sites for Pb(II) metal ions to adsorb onto the surface of the membrane during the filtration process was also increased. Thus, the rejection of Pb(II) metal ions from aqueous solution was also increased.

| Sample  | Water flux (L/m²h) | Rejection of Pb(II) (%) |
|---------|--------------------|------------------------|
| CHSi0   | 37.36              | 11.72                  |
| CHSi9   | 42.43              | 13.78                  |

CONCLUSION

In this study, the chitosan/silica composite membranes were successfully fabricated. Based on the characterization results, it was found that the presence of silica in chitosan/silica composite membrane enhanced the physical and structural characteristics of chitosan membrane. The composite membrane provided more active sites and created microvoids to increase Pb(II) metal ions rejection through membrane. The rejection of Pb(II) ions showed an improvement in the chitosan/silica composite membrane as compared to pure chitosan membrane. Therefore, it was suggested that the silica derived from rice husk ash could be used to improve the properties of chitosan based membrane and enhanced the rejection of Pb(II) metal ions.

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