CHITOSAN-SILICA RICE HUSK COMPOSITE MEMBRANE FOR REMOVAL OF LEAD(II) ION FROM AQUEOUS SOLUTION

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ABSTRACT

Heavy metal such as lead can be classified as non-biodegradable inorganic pollutants which can contaminate the ground and surface water. It cannot be breakdown or decomposed by living organism and continues to exist over a prolonged period which can generate harmful effects to the living things. Hence, lead removal is necessary in order to diminish the amount of heavy metals contaminating the water. The purpose of this study was to fabricate chitosan-silica flat sheet composite membrane for removal of lead(II) metal ions from aqueous solution via phase inversion technique by using sodium silicate from rice husk. The chemical composition of rice husk ash was determined by X-ray fluorescence (XRF) analyzer and the crystallinity of rice husk ash and sodium silicate were observed from X-ray diffraction (XRD) analyzer. The functional groups and structural morphologies were characterized using Fourier transform infrared-attenuated total reflectance (FTIR-ATR) spectrometer and scanning electron microscopy (SEM), respectively. The membranes were also subjected to swelling and tensile analysis to identify their mechanical properties. The membrane performance in terms of adsorption study was conducted at various pHs, initial concentrations of lead(II) solution and contact times as well as membrane recoveries. The membrane performance in terms of ultrafiltration study was evaluated using membrane cross-flow permeation system. XRF analysis confirmed that the rice husk ash had high silica content (87.4%). XRD analysis revealed the rice husk ash was present in amorphous phase while sodium silicate was in crystalline phase. The FTIR-ATR spectra showed the presence of new adsorption peaks (Si-O-Si bond), contributed by silica interaction with hydroxyl group of chitosan. Meanwhile, SEM images revealed the presence of microvoids on the cross-section of the CHSi20 membrane which improved the morphology of pure chitosan membrane and helped in the removal of lead(II) metal ions. Although, the swelling degree of chitosan membrane declined with the addition of sodium silicate, the tensile strength of chitosan membrane increased up to 0.2 g addition of sodium silicate. The adsorption study showed that CHSi20 membrane exhibited higher efficiency of lead(II) removal at optimum pH of 7.0, initial concentration of 220 mg/L of lead(II) solution and achieved equilibrium contact time after 16 h. In addition, the composite membrane behaviour was best fitted to Langmuir isotherm model and pseudo second-order model. However, the CHSi20 membrane had low membrane recovery due to the adsorption behaviour and kinetic mechanism of the membrane. Furthermore, the rejection of lead(II) metal ions by CHSi20 membrane was 97.56% at 0.5 bar applied pressure as compared to CHSi0 which was 11.72%. Therefore, these findings indicate the potential use of silica-derived rice husk to improve chitosan membrane properties, reduce agricultural waste dumping as well as reducing lead(II) metal ions polluted in water.

ABSTRAK

Logam berat seperti plumbum boleh diklasifikasikan sebagai bahan cemar tidak organik dan tidak biodegradasi yang boleh mencemari air bawah tanah dan permukaan air. Ia tidak boleh dimusnahkan atau terurai oleh organisma hidup dan akan terus wujud selama tempoh yang panjang yang menyebabkan kesan merbahaya kepada makhluk hidup. Oleh itu, penyingkiran plumbum adalah satu keperluan untuk mengurangkan jumlah logam berat yang telah tercemar dalam air. Kajian ini bertujuan untuk menghasilkan membran komposit lembaran rata kitosan-silika untuk menyingkirkan ion logam plumbum daripada larutan berair melalui teknik fasa penyongsangan dengan menggunakan natrium silikat daripada sekam padi. Komposisi bahan kimia dalam abu sekam padi ditentukan oleh penganalisa pendarfluor sinar-X (XRF) dan pengkristalan abu sekam padi dan natrium silikat dilihat oleh penganalisa pembelauan sinar-X (XRD). Kumpulan berfungsi dan struktur morfologi telah dicirikan menggunakan spektrometer infra merah transformasi Fourier-dilemahkan refleksi keseluruhan (FTIR-ATR) dan mikroskop imbasan elektron (SEM). Kesemua membran melalui analisis pengembangan dan ketegangan untuk mengetahui sifat mekanik. Prestasi membran dari segi kajian penjerapan telah dilakukan pada pelbagai nilai pH, kepekatan awal larutan plumbum(II) dan masa sentuh serta perolehan membran. Prestasi membran dari segi kajian proses turasan ultra dikendalikan dengan menggunakan sistem penelapan merentas aliran membran. Analisis XRF mengesahkan bahawa abu sekam padi mempunyai kandungan silika yang tinggi (87.4%). Analisis XRD menunjukkan abu sekam padi hadir dalam fasa amorfus dan natrium silikat dalam fasa kristal. Spektrum FTIR-ATR menunjukkan kehadiran puncak penjerapan baharu (Si-O-Si) yang disumbangkan oleh interaksi silika dengan kumpulan hidroksil kitosan. Sementara itu, imej SEM mendedahkan kehadiran liang-liang mikro pada keratan rentas membran CHSi20 yang memperbaiki morfologi membran kitosan tulen dan membantu dalam menyingkirkan ion logam plumbum(II). Walaupun darjah pengembangan membran kitosan menurun dengan penambahan natrium silikat, kekuatan tegangan membran kitosan meningkat sehingga penambahan natrium silikat sebanyak 0.2 g. Kajian penjerapan menunjukkan bahawa membran CHSi20 mempamerkan kecekapan yang tinggi dalam penyingkiran plumbum pada pH optima 7.0, kepekatan awal larutan plumbum 220 mg/L dan mencapai masa sentuh yang seimbang selepas 16 jam. Tambahan, kelakuan membran komposit bersesuaian dengan model isoterma Langmuir dan model tertib kedua pseudo. Walaubagaimanapun, membran CHSi20 mempunyai perolehan membran yang rendah disebabkan oleh sifat penjerapan dan mekanisma kinetik membran. Selain itu, penolakan ion logam plumbum(II) oleh membran CHSi20 adalah sebanyak 97.56% pada tekanan 0.5 bar berbanding dengan membran CHSi0 adalah sebanyak 11.72%. Justeru, penemuan ini menunjukkan potensi penggunaan silika daripada sekam padi dapat memperbaiki sifat-sifat membran kitosan, mengurangkan pelambakan buangan pertanian dan juga mengurangkan pencemaran logam plumbum(II) dalam air.

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LIST OF ABBREVIATIONS

AAS	-	Atomic Adsorption Spectroscopy
Al_2O_3	-	Aluminium oxide
CaO	-	Calcium oxide
Co	-	Cobalt
Cu	-	Copper
EDX	-	Energy Dispersive X-ray
Fe_2O_3	-	Iron(III) oxide
FTIR-ATR	-	Fourier Transform Infrared-Attenuated Total Reflectance
HCl	-	Hydrochloric acid
K_2O	-	Potassium oxide
MgO	-	Magnesium oxide
MnO	-	Manganese oxide
Na	-	Sodium
Na_2SiO_3	-	Sodium silicate
NaOH	-	Sodium Hydroxide
NO	-	Nitric oxide
NO_2	-	Nitrogen dioxide
Pb	-	Lead
$Pb(NO_3)_2$	-	Lead(II) nitrate
PWP	-	Pure water permeability
SEM	-	Scanning Electron Microscopy
Si	-	Silica
SiO_2	-	Silicon dioxide
SO	-	Sulphur oxide
TiO_2	-	Titanium oxide
UO	-	Uranium oxide
XRD	-	X-ray Diffraction
XRF	-	X-ray Fluorescence
ZnO	-	Zinc oxide

LIST OF SYMBOLS

%	-	Percent
˚C	-	Celsius
cm^{-1}	-	Per centimetre
cm^2	-	Centimetre square
cm^3	-	Cubic centimetre
Da	-	Dalton
g	-	Gram
h	-	Hour
L	-	Litre
M	-	Molarity
m^2	-	Metre square
mg	-	Milligram
min	-	Minute
mL	-	Millilitre
ppm	-	Part per million
R^2	-	Correlation coefficient

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CHAPTER 1

INTRODUCTION

1.1 Research Background

Environmental pollution is one of the real facts that world facing today. Among all, heavy metal pollution become major concern nowadays due to the rapid grows of industrialization [1]. Although heavy metals can naturally find throughout the earth's crust, it can also be found from different sources such as mining operations, painting and printing process, discharge of domestic waste, agricultural manufacturing, pharmaceutical, automobile exhaust and metal-based industrial operations. Most of the heavy metals from wastewater that release into eco-system are from human activities [2]. Heavy metals especially lead (Pb) can be classified as non-biodegradable inorganic pollutants which can contaminate the soils, sediments, ground water and surface water. It is because, they cannot be breakdown or decomposed by living organism. On the other hand, it will continue exist over a prolonged period which can generate to the harmful effects to the living things [3]. Thus, heavy metal treatment is necessary to reduce the amount of metal ions contaminated in wastewater.

Numerous studies have been done to discover the potential technique for removal of heavy metal from wastewater. One of them was membrane adsorption [4] because of its advantages such as low production cost, simple design, easy to handle, high flow rate and have excellent efficiency for removal of metal ions [5]. Recently, natural polysaccharide chitosan gained researcher interest and attention in polymer composite membrane manufacturer [6] to remove heavy metal such as cobalt, nickel [7], mercury [8] and copper [9] from polluted water. Beside its biopolymer properties, chitosan act as a functional polymer by providing the active sites in adsorption process [10] through huge quantity of amino and hydroxyl groups [11].

These functional groups can adsorb metallic ions selectively [12]. Thus, make it significant in membrane adsorption application for heavy metal removal.

In Malaysia, the rice production rose year by year and it was estimated that about 1, 564, 604 tons of rice will be producing in year 2020 [13]. Since the production of rice increases, so does the production of rice husk which can lead to the great environmental problem due to the space limitations when it disposes to the landfills [14]. Thermally treated rice husk will be obtained rice husk ash that contains about more than 90 % of silica with other metal oxides [15].

This amorphous silica already been used in various application such as plastic and rubber reinforcement, pulp and paper processing, high performance concrete, green concrete, carrier for pesticides, catalyst, coatings, anticaking agent for packing and oil spill absorbent. However, in wastewater treatment application, liquid sodium silicate was more suitable to be used as silica source [16]. It is expected that silica from the rice husk can be added in chitosan membrane in order to enhance the properties of chitosan. Therefore, finding a good use of the rice husk from agricultural waste industry will reduce the waste dumping problem as well as other environmental problem.

1.2 Problem Statement

The metal-contaminated wastewater still represents a worldwide environmental problem nowadays due to the industrialization and technological advances [17]. The lead metals are among the well-known heavy metal that are toxic and carcinogenic [18]. Due to their high solubility, living organisms can easily absorb the heavy metals that entering the eco-system. The accumulation in human body can occur if the amount of metals consumed beyond the acceptable limits, either by ingestion or food chain [19]. 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. Death also can happen in extreme cases [20].

Therefore, it was essential to carried out the treatment of metal-contaminated wastewater before being discharge to the environment.

Microfiltration, ultrafiltration, reverse osmosis, nanofiltration, polymer-supported ultrafiltration, complexation-ultrafiltration and electrodialysis are the examples of membrane technologies that had gained attention for removing heavy metal from inorganic contaminants due to its convenient operation [21]. Previously, researchers suggested that chitosan membrane can be used as absorbent for heavy metal ions since chitosan has hydroxyl (-OH) and amine ($-NH_2$) groups that act as chemical reactive group for sorption [22].

However, chitosan-based membrane needs further modification due to low structural and physical properties where chitosan own dense structure and need plasticizer agent to improve the mechanic properties [23]. These drawbacks limit its use for membrane adsorption. To improve, chitosan itself often been coated or blended with additives to make composite chitosan membrane. Moreover, Sumarni *et al*. [24] used silica (SiO_2) from rice husk ash as additives or filler in enhancing the properties of chitosan membrane due to silica have high porosity, good mechanical strength and high thermal stability properties. From the physical characteristic analysis results, they conclude that silica provide the pores on chitosan membrane and suggested that chitosan-silica composite membranes possess high potential to be used for heavy metal removal.

Wang *et al*. [25] has been evaluated that chitosan-silica composite membrane can be used as membrane adsorber to remove copper ions in low concentration. After all, not much study has been reported to evaluate the performance of chitosan-silica composite membrane for other heavy metal removal. To overcome the shortcoming as well as to extend our knowledge, further study regarding silica as additives in chitosan membrane manufacture and further information will be needed to confirm their potential application in removing heavy metal from aqueous water by adsorption, recovery and ultrafiltration test.

Therefore, in this study, sodium silicate from rice husk ash was used in the fabrication of chitosan-silica rice husk based composite membrane. The investigation on the morphological studies and the physicochemical properties of chitosan-silica composite membranes to remove lead(II) metal ions was conducted. Furthermore, the performance of composite membranes in terms of adsorption, recovery and ultrafiltration study on the removal of lead(II) metal ions from aqueous solution was evaluated.

1.3 Objective of Study

This study was accomplished by fulfilling the following research objectives:

i. To investigate the effect of sodium silicate composition on the physicochemical properties and membrane performance of chitosan-silica rice husk composite membrane.
ii. To evaluate the effect of operating conditions on the performance of the chitosan-silica rice husk composite membrane.

1.4 Scope of Study

In order to achieve the objective of the study, the scope of the study involved of:

i. The preparation of rice husk ash from the rice husk by incineration process at 600 ˚C for 3 h and the determination of its compound composition by using X-ray fluorescence (XRF).
ii. The production of sodium silicate as silica source by calcinate the mixture of rice husk ash with sodium hydroxide solution at 800 ˚C for 2 h.
iii. The characterization of rice husk ash and sodium silicate in term of crystallinity by using X-ray Diffraction (XRD).
iv. The fabrication of chitosan-silica composite membrane by phase inversion method with different loading of sodium silicate (0, 0.1, 0.2 and 0.3 g).

v. The physical characterization of chitosan-silica rice husk composite membrane by swelling test, tensile strength test, Fourier Transform Infrared-Attenuated Total Reflectance Spectrometer (FTIR-ATR), Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray (EDX).

vi. The examination of membrane performance on the removal of lead(II) metal ions from aqueous solution through adsorption study at various pH (5.0, 6.0, 7.0), initial concentration (60, 80, 100, 120, 140, 160, 180, 200, 220 and 240 ppm) and contact time (0, 2, 4, 6, 8, 10, 12, 14, 16, 18, 20, 22 and 24 h) as well as recovery study.

vii. The determination of the membrane filtration adsorption capabilities by measuring the pure water flux and rejection of lead(II) metal ions using cross-flow ultrafiltration system as well as the analysis of lead(II) metal concentration by using Atomic Adsorption Spectroscopy (AAS).

1.5 Significance of Study

Despite the numerous researches on wastewater treatment that had been conducted by researcher, only a few of them focused on using natural biopolymer such as chitosan and rice husk from agricultural waste in composite membrane manufacture. This combination between chitosan and rice husk not only derived from biological resources but benefit to the environment by reducing the waste problem. Results of the morphology, physical characteristics and performance test of chitosan-silica rice husk composite membrane will give information to confirm whether silica from rice husk can improve the properties and performance of the membrane for removal of lead(II) metal ions since it has tendency to increase the porosity of the composite membranes. The innovative from this investigation can improve the membrane technologies in wastewater treatment field for removal of heavy metal. Besides, it will prevent health disorder due to the accumulation of metal ions in human bodies as well as create green and sustainable life that surrounded by unpolluted environment.

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