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# FABRICATION AND CHARACTERISATION OF CHITOSAN/COCONUT FIBER COMPOSITE MEMBRANES FOR ELIMINATING $CU^{2+}$ AND $PB^{2+}$ FROM AQUEOUS SOLUTIONS

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Abstract

**Coconut fiber was chemically modified by NaOCl/NaOH, and then was composited through a cross-linking reaction with glutaraldehyde. The chitosan/coconut fiber (CTS/CF) composite membranes were prepared at various ratios of coconut fiber (CF) and then tested to determine their ability to eliminate aqueous heavy metals. The results showed that CTS/CF composite membranes having CF ratio of 80 wt% exhibited good mechanical strength as 89.8 MPa. In the elimination experiment of heavy metal ions, the CTS/CF 20/80 also showed that the removal capacity of Cu (II) and Pb (II) were over 90%.**

Keywords: **Chitosan; Coconut fiber; Membrane; Heavy metals.**

## 1. INTRODUCTION

Heavy metals play an important role as "trace elements" in biochemical reactions and are essential elements for the body in low concentrations [1]. However, at higher concentrations, heavy metals cause serious toxicity. When heavy metals enter the human body, they affect the sulphate groups in enzymes, enabling enzymatic deactivation or membrane blockade, preventing the transport of materials through the cell membrane and metabolism, potentially resulting in poisoning. In addition, the accumulation of heavy metals can lead to bone, liver, kidney, and nervous system disorders and diseases which can cause chronic poisoning for humans and other organisms. Therefore, the removal of heavy metal ions from water sources is a crucial scientific and practical problem [2]. Various methods have been studied to eliminate heavy metals from water, including chemical, electrochemical, physical, and biological, as well as precipitation, adsorption, ion exchange, and membrane filtration. Based on these, biomass materials have many advantages and are less expensive. An emerging method has been to remove heavy metals from water by using natural materials or agricultural industrial waste. Most of these biomasses have economic and environmental benefits. The use of biofilm membranes has been an especially effective research direction in this regard [3]. Chitosan (CTS), a derivative of chitin as displayed in Fig. 1a, is an organic

composition found in crustaceans and can be prepared from fish waste materials [4]. It has strong metal ion-absorption properties and is considered an important biomass material for the preparation of a wide range of compounds in various forms with properties suitable for applications in medicine, agriculture, and environmental treatments [5]. However, the aqueous solubility of CTS is not conducive to membrane preparation. Therefore, this work focused on a composite membrane with coconut fiber (CF), an agricultural waste product with the ability to absorb heavy metals effectively [6]. Combining these two materials to create a metal-separating membrane is a promising new direction in wastewater treatment technology [7]. Utilising activated carbon fiber from natural cellulose/coconut fiber in the process of removing heavy metals from water undergoing physical and chemical treatment, exhibits advantageous properties such as large surface area (> 1000 $m^2/g$) and high porosity (> 80%). These attributes highlight CF's potential as a heavy metal adsorbent in water [7, 8, 9]. The adsorption capacity of modified CF for Cu, As, and Pb ions and the biomass maximum adsorption capacity for Pb (II) followed by Cu (II) and As (III) has been studied. An emerging composition method for biomass materials seeks to achieve more efficient adsorption capacity for heavy metal ions by blending CFs and CTS. Recent studies have discussed the incorporation of membranes and adsorbents, such as CTS membranes and zeolites. However, the results of these studies have shown that these methods are inefficient at removing heavy metals. Therefore, this paper aims to further research in this area by fabricating a composite membrane of CTS/CF cross-linked with glutaraldehyde (Fig. 1b) that can effectively adsorb heavy metals. A biomass membrane that more efficiently removes heavy metals and is environmentally friendly would be a breakthrough in research technology of heavy metal pollution. This paper describes the preparation and properties of a biomass membrane of CTS/CF and its heavy metal elimination performance by pervaporation (PV) process. PV, non-energetic process, is a method for the separation of mixtures of liquid by partial vaporization through a non-porous or porous membranes. PV is a relatively new membrane separation process that has elements in common with reverse osmosis and membrane gas separation. In PV, the liquid mixture to be separated (feed) is placed in contact with one side of a membrane and the permeated product (permeate) is removed as low-pressure vapour from the other side. The permeated vapour can be condensed and collected or released as desired. The chemical potential gradient across the membrane is the driving force for the mass transport. The commercialization of the PC technique will have a large extent, attributed to the engineering approach of making thin membrane in asymmetric and composite forms. For that reason, in this research, PV process has been used for the separation of heavy-metal-contained solutions through CTS/CF membrane cross-linked with glutaraldehyde.

## 2. MATERIALS AND METHODS

### 2.1. Chemicals

CTS was purchased from Spectrum Chemical & Laboratory Products Co., Ltd (Japan). Glutaraldehyde, $H_2SO_4$, and HCl were purchased from Merck (Germany). A salt solution containing heavy metals was prepared in the laboratory at 50 ppm.

CF was harvested in the Ben Tre province of Vietnam, separated by machine. This CF was washed with distilled water to remove impure matters, and then dried for 24 h. Before being chemically modified, the CF was cut into < 2 mm lengths and screened through a 45 mm sieve.

### 2.2. Pre-treatment of CFs

For the pre-treatment of CF, 5 g of chopped CF (< 2 mm) was immersed in 100 ml of NaOCl 4–6% solution (v/v): $H_2O$ (1:1) for 2 h at 30°C. Then the CF was washed with distilled water and stirred in 100 ml of NaOH 10% for 1 h at 30°C. After each step, the CFs was filter up and washed in distilled water to neutral pH. Finally, the treated CF was dried at room temperature. The yield of the modified CF was calculated by the following equation:

$$\text{Yield (\%)} = \frac{m_0}{\text{m}} \times 100\% \qquad (1)$$

where $m_0$ is the initial mass of the raw CF (g), and $m$ is the mass after the chemical modification (g).

### 2.3. Preparation of CTS/CF membranes

First, CTS was dissolved in 2 vol% of acetic acid at room temperature. After 24 h, the 2 wt% of CTS solution was obtained. Then, the treated CF was added to the CTS solution at ratios of 100/0, 80/20, 50/50, 20/80 (CTS/CF). These mixtures were stirred under mechanical rotation. After 24 h, 10 mL of glutaraldehyde 2 vol% and 5 mL HCl 0.5 M were added

for the cross-linked reaction. A35 mL of the CTSCF solution for each ratio was poured into petri dishes of equal size to ensure consistent membrane thickness in subsequent tests. The dried composite membranes were resoaked in 0.5 M $H_2SO_4$ for 1 h, washed with distilled water to remove the acid, and dried at room temperature. Membranes at the appropriate composition ratios with diameters of 60 mm were cut to be fitted into the processing model and the properties of the CTSCF composite membranes could be investigated. The appearance of the CTS/CF membrane was displayed in the Fig. 1c.

### 2.4. Characterisation of the CTS/CF composite membranes

Scanning electron microscopy (SEM) was used to characterise the resultant CTS/CF membranes by observing the morphology of their surfaces and cross-sections. The surfaces and the cross-sections of the CTS/CL membranes were observed with a JSM-5300LV (JEOL, Japan). A Fourier transform infrared (FT-IR) analysis was carried out using a Spectrometer Model 4000 (Shimadzu, Japan) to study the interaction of the composite's components. The physical properties of the membranes were examined to verify the addition of the treated CF at the different mixing ratio. The swelling degree (SD) and mechanical strength of the membranes were checked. The dried membranes were immersed in water in a sealed vessel at room temperature for 24 h to observe the SD of the CTS/CF membranes. Then, the membranes were quickly removed from water, wiped with filter paper, then their length was measured quickly by comparing the volume of the membranes before and after immersion in water [9]. The SD of the CTS/CF membranes was calculated by the following equation:

$$SD\ (\%) = \frac{D - D_0}{D_0} x\ 100\% \qquad (2)$$

where *SD* is the swelling degree (%), $D_0$ is the initial diameter of the membrane (mm), and *D* is the average diameter of the membrane (mm) after 24 h.

The equilibrium water content (EWC) of the membranes was measured at room temperature by immersing 30 mm × 10 mm strips of the dry membranes in distilled water. After a soaking period of 24 h to ensure equilibrium sorption, the hydrogels were removed, quickly wiped with tissue paper, and weighed. The value of EWC was calculated for each sample by the following equation:

$$EWC\ (\%) = \frac{100(m - m_0)}{m_0} \qquad (3)$$

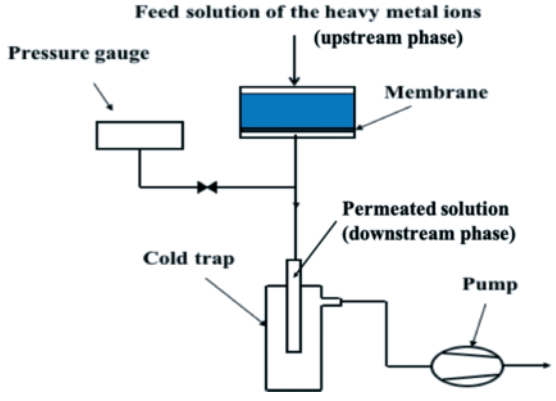
where $m_0$ was the dry weight and *m* was the weight of the composites after being immersed in distilled water for 24 h.

The tensile strength (TS) of the CTS/CF membranes was measured using a universal testing machine LTS-500N-S20 (Minebea, Japan) with an opening load of 500 N. Cross-sectional areas of the samples of known width (10 mm) and thickness (0.1 mm) were used in the calculations. The value of the TS was calculated by using the following equation:

$$\text{Tensile strength} = \frac{\text{Maximum load}}{\text{cross} - \text{sectional area}}\ (\text{N/mm}^2) \qquad (4)$$

### 2.5. The metal ions adsorption of the CTS/CF membranes

PV process was used to test the elimination of the heavy metal ions through the CTS/CF membrane as shown in Scheme 1. The effective area as Φ = 60 mm, where the CTS/CF membrane was place onto. For the separation process, 50 mL of metal solution containing of $Cu^{2+}$ and $Pb^{2+}$ at an initial concentration of 50 ppm was placed as the feed solution. After 1 h, the solution on the upstream phase would permeate through the CTS/CF membrane by the pressure offered by the vacuum pump. The permeated solution was collected from the lower chamber, and chromatographic analysis was carried out to evaluate the removal efficiency of heavy metals by the CTS/CF membrane. The chromatographic method used for the analysis was ICP-MS as measured by the "Standard Method for the Examination of Wastewater" on the Agilent 7700x ICP-MS.




**Scheme 1.**
**The pervaporation apparatus of the elimination process of the heavy metal ions**

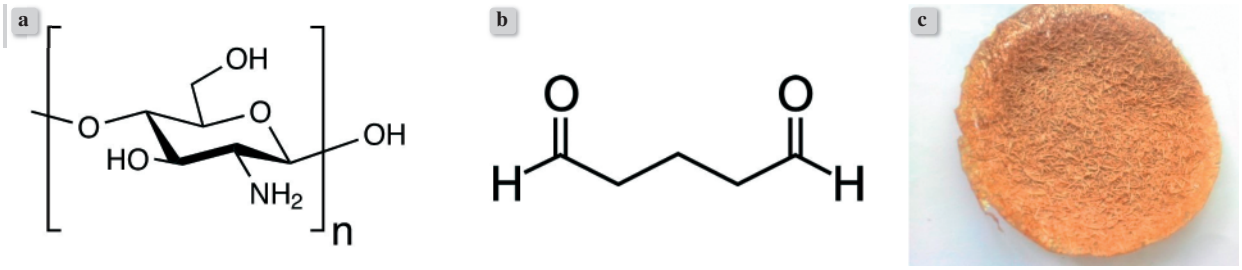



**Figure 1.**
**The chemical structure of (a) CTS, (b) Glutaraldehyde and the appearance of the CTS/CF ratio of 20/80 membrane cross-linked with Glutaraldehyde (c)**

## 3. RESULTS AND DISCUSSION

The structure and appearance of chitosan and the membrane could be found in Fig. 1.

### 3.1. Characteristic properties of CTS/CF membrane

***The FT-IR spectra***

Normally, cellulose, lignin, and hemicellulose are the main components of the biomass. It is established that NaOCl/ NaOH conversion of CF yields a yellowish colour. NaOCl/ NaOH also removes fatty acids, wax, and lignin from the CF's surface. Using NaOCl/ NaOH significantly reduced the volume of coir fiber compared to other processes; it was also the only process to reduce the number of hemicelluloses [6]. Here, the yield of the treated CF gained was about 80%. As shown in Fig. 2c, the FT-IR spectra of the treated CF confirmed that there were no peaks of the lignin and hemicellulose recorded [10], they are normally found at wavelengths of 1735 and 1536 $cm^{-1}$, respectively. The IR spectra indicated that chemical modification with NaOCl/NaOH eliminated the lignin and hemicellulose completely. In addition, the broad and intense peak at 3442 $cm^{-1}$ showed that the hydrogen-bonded (O–H bond) stretching vibration was from the cellulose, while the peak at 1632 $cm^{-1}$ showed that the O–H bond was from absorbed water, suggesting the hydrophilicity of the cellulose. The peak at 2899 $cm^{-1}$ was assigned to C–H stretching vibration. In the case of CTS (Fig. 2a), the peak recorded at 1652 $cm^{-1}$ was attributed to amide I (N–H vibration). However, the IR spectra of the CTS/CF 20/80 membrane (Fig. 2b) had a peak at 1507 $cm^{-1}$ that was assigned to N–H stretching, which strongly indicates interaction between CTS and CF when glutaraldehyde was used as the cross-linking agent.

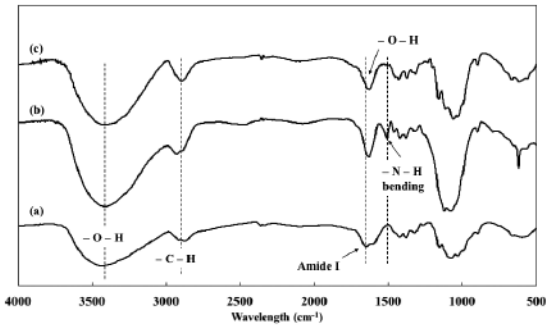



**Figure 2.**
**(a) The FT-IR spectra of the CTS, (b) the cross-linked CTS/CF 20/80 membrane, and (c) the CF modified with NaClO/NaOH**

***Scanning electron microscopy (SEM)***

As shown in Fig. 3a, there were several voids on the surface of the treated CF, meaning that the chemical modification with NaOCl/NaOH was successful. In the case of the surface of the CTSCF 20/80 membrane showed that the observed CF was distributed consistently on the surface of the membrane with a diameter of about 70 μm (Fig. 3b). In addition, the cross-section showed the existence of pores in the structure of the membrane composite of the CTS/CF 20/80. This observation suggests that CTS/CF membranes will have better surface morphology when combined with CF, with improved compatibility between biopolymers. Inorganic adsorbents will increase the membrane's output and selectivity.

***SD and water content of the CTS/CF composite membranes***

The SD of the CTS/CF membranes are shown in Figure 4a. The membranes swelled mainly in the first 2 h and attained stability about 24 h after immersion. This result indicates low levels of swelling in these membranes followed as order: M1 < M3 < M4. The lowest amount of swelling (6.3%) occurred in the M1 membrane. This result suggests that if the CF to CTS

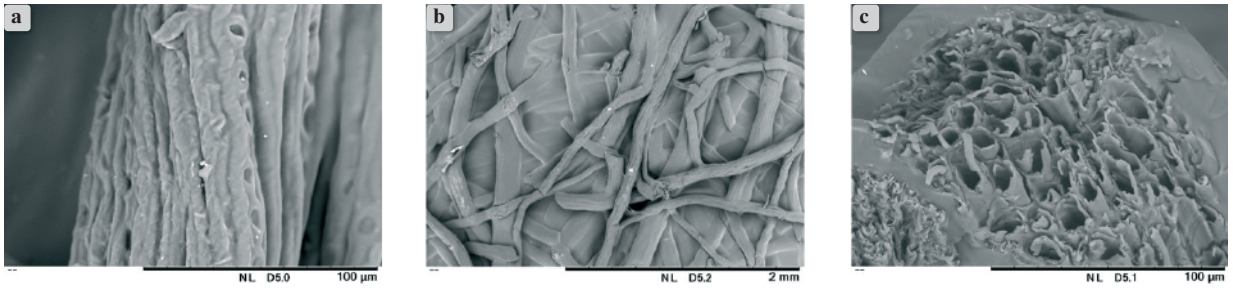



**Figure 3.**
**(a) SEM of the CF treated with NaClO/NaOH, (b) the CTS/CF 20/80 membrane surfaces, and (c) the cross-sectional area of the CTS/CF 20/80 membrane**

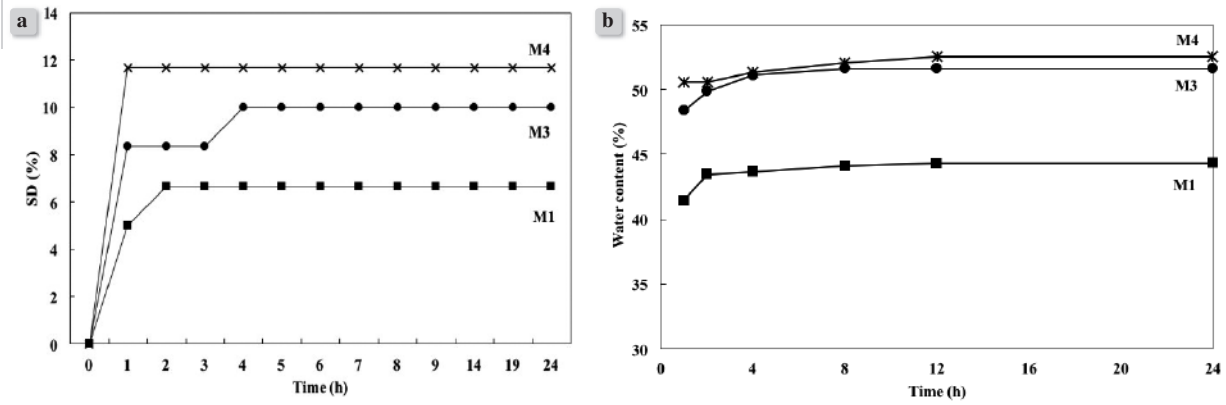



**Figure 4.**
**(a) SD (%) and (b) EWC (%) of the CTS/CF membranes M1: CTS/CF (100/0), M3: CTS/CF (20/80), and M4: CTS/CF (50/50)**

ratio in the membrane is approximately equal, the stability of the membrane will be higher due to the CF's physical interaction with CTS, which reduced the ability of the polymer to expand in the membrane. Membranes with low-level swelling indicated that the film had high stability and better physicochemical properties than other membranes [9]. The EWC illustrated in Fig. 4b, showed a similar tendency to those recorded for the CTS/CF composite membranes. This result shows that glutaraldehyde is closely bound to CTS molecules and that CTS molecules form hydrogen bonds with the cellulose molecules present in CF [11].

***Mechanical properties of the CTS/CF composite membrane***

Tests of the TS of the CTS/CF composite membranes at different ratios of CF were carried out to incorporate the treated CF into the CTS membrane. The results were listed in Table 1. As the amount of CF increased, the TS of the membranes dramatically increased. For example, the value of the TS increased from 45.6 to 89.8 MPa for the CTSCF 100/0 and CTS/CF 20/80 composite membranes, respectively. This result strongly indicates that increasing the relative amount of the CF improves the TS of the composite membranes.

**Table 1.**
**Physical properties of the CTS/CF composite membranes at various ratios of CF**

| Sample | Ratio CTS:CF | SD (%) | EWC (%) | TS (MPa) |
|---|---|---|---|---|
| M1 | 100:0 | 6.3 | 41.6 | 45.6 |
| M2 | 80:20 | 7.5 | 46.0 | 55.6 |
| M3 | 20:80 | 10.1 | 52.5 | 89.8 |
| M4 | 50:50 | 11.9 | 51.6 | 75.2 |

### 3.2. Membrane behaviour in the removal of heavy metal ions

The results in Fig. 5 demonstrated the differences in the ability of specific membranes to remove heavy metals using various denaturation methods. The M3 CTS/CF membrane was the most effective at removing Cu and Pb. This membrane contained a CTS/CF ratio of 20/80, with CF denatured by NaOCl/NaOH and a removal efficiency for Cu and Pb of 95.07% and 92.27%, respectively. The M4 and M1 membranes were the next highest in removal efficiency; the M2 membrane had the lowest removal efficiency, with a yield of 15.15% for Pb and 4.63% for Cu. The

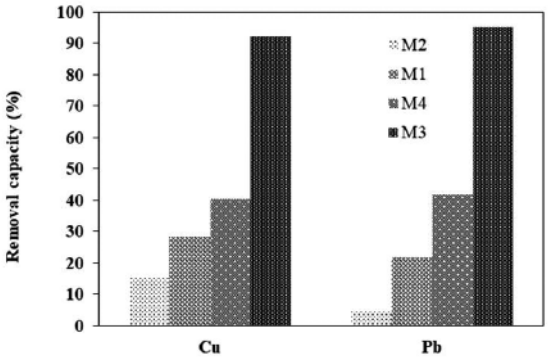



**Figure 5.**
**Efficiency of CTS/CF membranes in heavy metal removal, M1: CTS/CF (100/0), M2: CTS/CF (80/20), M3: CTS/CF (20/80), and M4: CTS/CF (50/50)**

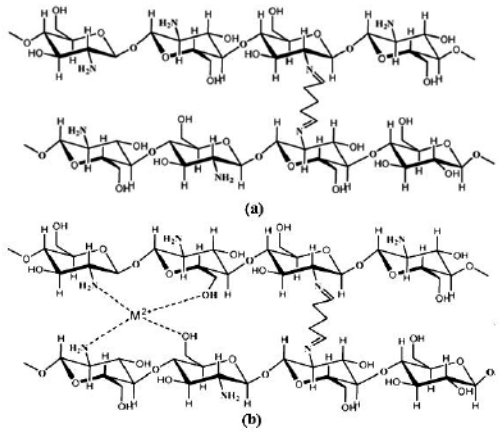



**Figure 6.**
**(a) Interaction between CTS/CF and glutaraldehyde and (b) the complexing mechanism of CTS/CF membranes with cations**

efficiency of the various membranes to separate heavy metals in wastewater can be summarised as follows: M3 > M4 > M1 > M2. This result shows that a CTS/CF ratio of 20/80 is optimal.

-$NH_2$ and -OH groups exist in the CTS/CF membranes. These groups are capable of complexing with heavy metals. The mechanism for complexing with metals is shown in Fig. 6. In addition, the relatively high metal content of the water combined with the hydrophilic nature of the membrane results in competition between the metal ions and water molecules as they pass through the membrane, causing space constraints. When this occurs, the metal ions do not bond with -$NH_2$ and -OH groups, resulting in poor separation efficiency. Interaction of metal ions such as Cu and Pb with the -$NH_2$ groups in polymer molecules can occur, and their resulting hydrated radiuses are large, making it more difficult for them to pass through the membrane than other ions. The diffusion of metal ions through the membrane is also affected by a number of factors including size selection, structural tightness and shape, and the distribution of the cellulose constituents in the CF network resulting in the variable separation efficiencies seen in different metals.

## 4. CONCLUSIONS

The process of studying CTSCF membranes with cross-linking reaction by glutaraldehyde was initially successful. CF can be denatured by NaClO/NaOH to increase its membrane strength and mechanical stability. The CTS/CF 20/80 membrane also showed relatively high heavy metal removal capacity; the removal efficiencies for Cu (II) and Pb (II) were 95.07% and 92.27%, respectively. The CTSCF 20/80 membranes had the highest processing efficiency when they were denatured by NaClONaOH.

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