Adsorptive removal of copper ions in water using electrospun cellulose acetate / chitosan nanostructured membrane

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Abstract. Nanostructured membranes from cellulose acetate (CA) reinforced with chitosan (CS) were developed using electrospinning process and characterized in order to obtain the best blend for the removal of Cu$^{2+}$ ions in wastewater. Different CA/CS ratios of 95:5 (w/w), 90:10 (w/w), and 85:15 (w/w), respectively, were prepared and electrospun on a constant voltage of 30 kV and a tip-to-collector distance of 18 cm, which are the optimum conditions for this blend. Scanning Electron Microscopy (SEM) and Fourier Transform Infrared Spectroscopy (FTIR) were used to characterize the membrane in terms of its morphology and molecular structure. Among the three (3) blends prepared, CA with 15% load of chitosan had exhibited better membrane properties and therefore was utilized in the removal of Cu$^{2+}$ ions in wastewater. The effect of contact time on the adsorption capacity at constant fiber dosage (0.05 g) in a 50 mL copper nitrate solution containing an initial concentration of 100 ppm Cu(II) was investigated. A strong affinity of Cu$^{2+}$ ions for pure CA than CA/CS was observed after 4 hours of contact time. However, as equilibrium was established for CA/CS blend, the highest adsorption capacity was recorded. Adsorption kinetics studies were best fitted to pseudo-second-order model describing a chemisorption process that showed a covalent or electrostatic chemical bond between the adsorbent and adsorbate. CA loaded with CS in adsorption of Cu$^{2+}$ ions in water showed that it is a novel process that could be widely used in the industry.

1. Introduction

One of the main causes of pollution in bodies of water is the presence of trace metals, particularly heavy metals, since these have significant effects on ecological quality. Heavy metal contamination of different water resources poses a major environmental problem, considering its lethal effect to flora and fauna, particularly to human beings. Among the listed heavy metals, copper pollution is of critical concern. Copper is deemed toxic beyond acceptable levels which could trigger vomiting, cramps, convulsions, and even death. Copper-contaminated drinking water could come from the erosion of natural deposits, corrosion of plumbing systems and contaminant seepage from disposal sites.
Conventional techniques of treating heavy metals in water is limited and not capable of diminishing concentrations of heavy metal content down to necessary levels, and usually entail excessive operational cost and high capital. Membrane adsorption may present superiority over conventional methods because of its good hydrodynamic property, high removal efficiency, suitable reusability, and minimal footprint.

The application of membrane technology can bring a considerable improvement in industrial production through lowering the cost of production and energy consumption, reducing equipment size and minimizing waste generation, and enhancing the flexibility of the process [1]. Adsorptive membranes can form bonds with heavy metal ions by means of surface complexation mechanism. Its porous property and the functional groups present, such as -COOH, -SO\textsubscript{3}H, or -NH\textsubscript{2}, are responsible for its affinity to heavy metals. A study conducted by Liu and Bai (2006) used highly porous hollow fiber membranes, and were prepared using cellulose acetate (CA) and chitosan (CS). The study resulted to an adsorption capacity of 35.3 – 48.2 mg/g copper ions [2].

At the moment, indigenous cheaper materials are being used as the main component in membrane fabrication [3]. Incorporation of a biopolymer would result in improvements in the physical properties of the natural fibers and chemical modification can improve remarkably fiber properties through application of electrospinning. In most cases, CA membrane modifications are required to be able to obtain higher selectivity, porosity, and higher flux. Chitin is an abundant, accessible, and renewable natural polymer. It exists in various species of Zygomycetes in its deacetylated form which is chitosan (CS) [4]. CS possesses excellent binding capacities for many heavy metals including Cu, Cd, Hg, and Pb. Because of its high amine content, the reactive sites, it can even surpass the performance of expensive ion exchange resins [5]. Currently, CA and CS have been combined to merge the desirable properties of the two [6]. The blended material shows a wide array of physical properties that are favorable because of its versatility and simplicity. Numerous researchers have performed experiments on the combination of CA and CS [7]. Novel adsorptive membranes made of CS/CA blend have been studied and developed, using CA to improve the mechanical strength of the support matrix and utilizing CS to functionalize CA for the adsorption of heavy metal ions. The CS/CA membrane produced was effective for the adsorptive removal of Cu\textsuperscript{2+} ions [8,9].

Previous membrane systems for Cu\textsuperscript{2+} ion removal have only considered membrane fabrication within the micro-scale. Electrospinning as a technique is one of the promising candidates for various applications of membrane fabrication because it is simple, versatile, cost-effective, and can produce fibers in the nano-scale. As such, it would be the method that will be used to fabricate the CA/CS nanostructured membrane in this study.

The main objective of this research was to determine the adsorption performance of CA pristine and the best CA/CS blend for the removal of Cu\textsuperscript{2+} ions in water. Specifically, the objectives of this study were as follows: to develop an electrospun CA/CS nanofibrous membrane; to characterize and obtain the best blend based from the Scanning Electron Microscopy (SEM) (membrane morphology – that of which has the smallest fiber diameter) and Fourier Transform Infrared Spectroscopy (FTIR); and, to determine the kinetics of the adsorption based from the results obtained.

2. Methodology

2.1. CA/CS blend preparation

CA/CS blends were measured through weight ratio containing varying amounts of CS at 0%, 5%, 10%, and 15%. A basis of one (1) gram of CA for each blend was used in the entire experiment. CA was dissolved in a reagent-grade acetone at 12% (w/w) ratio. Also, with the same weight ratio, CS was dissolved in a reagent-grade acetic acid. Both solutions were then mixed in a beaker and then prepared for sonication. The sonicator was set for five minutes in order to eliminate bubbles in the solution. Three (3) ml dichloromethane (DCM) was added to the homogenized solution before subjecting it to electrospinning. The following parameters were used in the electrospinning process: temperature during processing is at 25°C room temperature, 30 kV voltage applied and 18 cm tip-to-collector
distance.

2.2. Characterization of nanostructured membranes

Fourier Transform Infrared Spectroscopy (FTIR) was used to identify the unique combination of atoms of the material, and to identify the infrared spectrum of the produced sample. Subsequently, the surface topography of the nanostructured membrane were measured and analyzed in a Scanning Electron Microscope (SEM).

2.3. Adsorption kinetics

For the adsorption experiment, pure CA was used, together with CA/CS nanostructured membrane with the smallest average fiber diameter were used in the analysis. A constant fiber weight of 0.05 g was placed in a beaker flask (250 mL) that contains 50 ml of 100 ppm of Cu(NO$_3$)$_2$ solution. Using the Atomic Absorption Spectrophotometer (AAS), different samples were analyzed to determine Cu$^{2+}$ ions concentration in the solution.

The influence of contact time on the adsorption capacity of the optimum CA/CS blend for Cu$^{2+}$ ions was observed. The kinetics uptake of Cu$^{2+}$ ions by these nanofiber blends was fitted with respect to pseudo-first-order of Lagergren and Kungliga and pseudo-second-order of Ho and McKay. First-order model of Lagergren is expressed in this equation:

$$\frac{dq_t}{dt} = k_1(q_e - q_t)$$

(1)

where $q_e$ is the quantity of Cu$^{2+}$ ions adsorbed at adsorption equilibrium, mg/g; $q_t$ is the quantity of Cu$^{2+}$ ions adsorbed at time t, mg/g; and $k_1$ is the rate constant of first order sorption, min$^{-1}$. The value of $k_1$ was calculated using slopes of the straight-line plots of log ($q_e - q_t$) versus t at different temperatures. The pseudo-second-order kinetic equation by Ho and McKay is expressed as:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2$$

(2)

where $k_2$ is the rate constant of second order sorption, min$^{-1}$. The value of $k_2$ was calculated using slopes of the straight-line plots of ($t/q_t$) versus t.

3. Results and discussion

3.1. Fiber structure: effect of CS content

Electrospinning CA and CA/CS produced fine fiber diameter. Noticeable effect on the nanofibrous membrane was observed upon varying amounts of CS were added on the blends. As the CS loading increases, smaller fiber diameter was achieved. Functioning as a partial polyelectrolyte, CS intensifies the conductivity of the polymer solution; thus, reducing the diameter of the fibers [10,11]. Figure 1 shows the tabulated average diameter and the SEM images for all the fiber blends.

3.2. Fiber molecular structure

Using Fourier Transform Infrared Spectroscopy (FTIR), the chemical bond interactions and functional groups that exist in the electrospun nanostructured membrane were determined. IR can be utilized to do quantitative and qualitative analyses to ascertain compounds and molecules and to establish the presence of functional groups. The presence of a specific chemical bond can be determined by looking at the peak at a specific wave number. Table 1 shows the significant adsorption peaks for chemical groups associated with CA and CS.

Figure 2 displays characteristic adsorption band peak at 1504 cm$^{-1}$ which is attributed to the distortion of the N-H bond that is present in the amide (I) of the -CONH- plane. Similar observations can be incurred for the adsorption band peak at 1661 cm$^{-1}$, but this time, for amide (II) groups of CS. The amide (I) and amide (II) adsorption bands also suggest that CS is a partially deacetylated product.
[12]. Broad adsorption band peak seen at 3293 cm$^{-1}$ is attributed to the O-H and N-H stretching which corresponds to the presence of the-OH and -NH$_2$ groups in CS.

| Compound    | Chemical Group                              | Wave Number | Interpretation                      |
|-------------|---------------------------------------------|-------------|-------------------------------------|
| Cellulose   | Carbon-carbon bonds                          | 1000 - 1100 | -C-C- bending                       |
| acetate     | (-C-C, C=C)                                  | 1210 - 1300 | -O-C stretching                     |
|             | Carbon-oxygen bonds (-O-C-)                  |             |                                     |
|             | Carbon-hydrogen bonds                        | 2850 - 3000 | -C-H- stretching                    |
|             | (C-H, C-H$_2$) bending                      | 1375 - 1420 | -C-H$_2$-, -C-H$_3$-                |
|             | Acetyl-Carbonyl (-COCH$_3$) groups           | 1738 - 1750 | -C=O stretching                     |
|             | Hydroxyl groups (-OH)                       | 3000 - 3500 | -OH stretching of intra-molecular hydrogen bonds |
| Chitosan    | Amine (-NH$_2$) and hydroxyl groups (-OH)   | 3000 - 3500 | -N-H stretching and O-H- stretching |
|             | Amine groups (-NH$_2$)                      | 1550 - 1590 | -NH$_2$ - scissoring                |
|             | Amide (-CONH-)                               | 1640 - 1690 | -C=O stretching of amide            |

Figure 1. Average diameters in nanometers of pure CA and different CA/CS blends. SEM micrographs at low and high magnifications (first row and second row, respectively).

Table 1. Peak wave numbers of infrared adsorption bands of cellulose acetate and chitosan.
Figure 2. FTIR results for a) pure CA, b) 95% CA / 5% CS, c) 90% CA /10% CS, d) 85% CA /15% CS, and e) pure CS.

The data showing important adsorption peaks for the -NH$_2$ and –OH groups of CS located in the 3000-3500 cm$^{-1}$ wavenumber range, with the carbon-hydrogen bonds (-C-H, -C-H$_2$) attributed to CA at 2850-3000 cm$^{-1}$ were monitored through changes in the wavenumber and sharpness of peaks. Shifting in the band peaks at lower frequencies was observed from 3000-3500 cm$^{-1}$ wave numbers as CS was added up to 15%. As the amount of CS is increased, shifting of band peaks from 3216 cm$^{-1}$ to 3208 cm$^{-1}$ up to 3192 cm$^{-1}$ was observed. The addition of CS increases the amount of -NH$_2$ groups that interacted with the -OH groups. The carbon-hydrogen bonds (C-H) deformation in CA caused a shift in the adsorption band peak observed at around 2900 cm$^{-1}$. At around 1754 cm$^{-1}$, the shifting of the adsorption band peak represents the overlapped ester-carbonyls (acetyl groups) in CA.

3.3. Adsorption process: Kinetic study

Upon the characterization of the fibers produced, 85:15CA/CS blend possessed the smallest average fiber diameter of all the blends produced. Smaller diameter means larger surface area thus increasing the adsorption sites for the attachment of the heavy metals.

3.3.1. Influence of contact time. Investigation on the influence of contact time to the nanofiber adsorption capacity at constant fiber dosage (0.05 g) in a 50 mL Cu(NO$_3$)$_2$ solution with an initial concentration of 100 ppm Cu$^{2+}$ was done.

Based on the results presented on figure 3, the maximum adsorption capacity occurred on the 12$^{th}$ hour. The rapid uptake was due to the hydroxyls, carbonyls and amines present. It was determined that maximum Cu$^{2+}$ uptake for the CA/CS blend is 52.15 mg/g which occurred on the 16$^{th}$ hour. There is strong affinity of Cu$^{2+}$ ions for pure CA than that of CA/CS which explains the higher adsorption capacity of pure CA than CA/CS (4$^{th}$ hour, Q$_{CA}$ = 42.945 mg/g and Q$_{CA/CS}$ = 17.29 mg/g). Previous transport studies suggested that metal ion is being chelated with the-NH$_2$ and -OH groups in the CS chain. In a study by Chui and colleagues in 1996, the amino sugars present in chitin and chitosan effectively function as major binding sites in forming stable complex for metal ions by means of coordination. The transition metals can form dative bonds with the lone pair electrons present in nitrogen of the amino and N-acetyl amino groups. Also, some -OH groups in these biopolymers can serve as proton donors; hence, deprotonated -OH groups can be included in the coordination with the
metal ions.

![Figure 3](image_url)

**Figure 3.** The adsorption capacities versus time graph of pure CA and CA/CS (85/15%) membranes for Cu$^{2+}$ adsorption.

3.3.2. Kinetic models for pseudo first-order and pseudo second-order. The order of adsorption of Cu$^{2+}$ ions in the CA/CS nanostructured membrane was investigated by means of Lagergren pseudo first-order kinetic model and Ho pseudo second-order kinetic model. Figure 4 shows the fitted adsorption experimental data for CA/CS. Based on the graph, it clearly shows that the Cu$^{2+}$ uptake fits well with pseudo second-order kinetic model, which gives a better correlation for Cu$^{2+}$adsorption compared to the pseudo first-order kinetic model. The Ho pseudo second-order kinetic model describes the adsorption process assuming that the rate limiting step would be chemisorption in which the adsorbent-adsorbate attraction is governed by covalent bond or electrostatic chemical bond between atom shaving higher bond energy or shorter bond length. Since Cu$^{2+}$ may dissociate first from its parent molecules and form mostly covalent bonds with the probable functional group, the assumption might be possible. This possibility supported the occurrence that the membrane had been able to adsorb Cu$^{2+}$ from wastewater, and the binding sites are potentially present as amines and hydroxyls of CA and CS, correspondingly. This study indicated that the fabricated nanostructured membranes could be utilized as an efficient adsorbent for the removal of Cu$^{2+}$ ions from wastewater.

![Figure 4](image_url)

**Figure 4.** Pseudo first-order kinetic model and pseudo second-order kinetic model for pure CA and CA/CS nanostructured membrane.

Based on the results, pseudo second-order kinetic model shows that for CA/CS (85/15%) membrane, chemisorption is the rate-limiting step for Cu$^{2+}$ adsorption. In this regard, the Cu$^{2+}$ ions attach to the membrane binding sites via covalent bond between the sorbent and sorbates. In this case, binding sites can be searched, maximizing the coordination number with the adsorbent’s surface. The rate constant from the nanostructured membrane was determined from the best fitted model which is pseudo second-order kinetic model. The linearization of both pseudo first-order and pseudo second-order kinetics of the nanostructured membrane was done to determine the rate constants. The rate
constants $k_1$ and $k_2$ were calculated from the slopes of pseudo first-order and pseudo-second-order equations. Kinetic constants for pseudo second-order show a larger value for pure CA (0.0471 min$^{-1}$) compared to 85%CA/15%CS (0.7816 min$^{-1}$). This result aligns with the influence of contact time on the CA and CA/CS adsorption capacities.

4. Conclusion

By means of the electrospinning technique, nanostructured membranes produced from varying CA/CS blend were fabricated in an efficient, cost effective and convenient manner. By subjecting each blend of CA/CS, namely, 95/5 %, 90/10 % and 85/15 %, respectively for testing using SEM and FTIR, it could be said that the 85/15 % blend of CA/CS is the optimum/best blend in order to carry out the adsorption process. Reinforcing CA with CS decreases the average fiber diameter of the membrane produced which corresponds to the increase in the membrane surface area thus increasing the adsorption sites. Subsequently, CS was able to add additional functional groups which helped in sequestering Cu$^{2+}$ ions from water. Considering the adsorption study, it showed that there has been a considerable increase in the adsorption capacity of the CA/CS blend which transpired up to the 12th hour. In relation to this, it was shown that the equilibrium state was obtained nearly beyond the 12th hour. Based on the graph given, the maximum Cu$^{2+}$ uptake for the CA/CS blend is 52.15 mg/g. From the study conducted by Liu and Bai in 2006, the Cu$^{2+}$ uptake for the CA/CS blend ranged from 35.3-48.2 mg/g for Cu$^{2+}$ ions at pH 5 using fibers in micro-scale. Based on this literature, this study would prove to be more effective since it involved nanofibers, thus increasing Cu$^{2+}$ uptake. Pseudo-second order kinetic model best fitted the data acquired in the adsorption of Cu$^{2+}$ ions using CA and CA/CS nanostructured membrane.

References

[1] Drioli E and Fontanova E 2004 Membrane technology and sustainable growth Chem. Eng. Res. Des. 82(A12) 1557-26
[2] Liu C and Bai R 2006 Adsorptive removal of copper ions with highly porous chitosan/cellulose acetate blend hollow fiber membranes J. of Membr. Sci. 284 68-77
[3] Akhtar M et al 2007 Sorption of potential of moringa oleifera pods for the removal of organic pollutants from aqueous solutions J. of Hazard. Mater. 141 546-56
[4] Kafetzopoulos D, Martinou A and Bouriotis V 1993 Bioconversion of chitin to chitosan: Purification and characterization of chitin deacetylase from Mucor rouxii Appl. Biol. Sci. 90 2564-8
[5] Bailey S et al 1999 A review of potentially low-cost sorbents for heavy metals Water Res. 33 2469-79
[6] Du J and Hsieh Y 2008 Cellulose/chitosan hybrid nanofibers from electrospinning of their derivatives Cellulose 16 247-60
[7] Tsekova K et al 2010 Removal of heavy metals from industrial wastewater by free and immobilized cells of aspergillusniger Int Biod Boricha Exterior Biodegradation 64 44-51
[8] Zhang Q et al 2011 Heavy metals chromium and neodymium reduced phosphorylation level of heat shock protein 27 in human keratinocytes Toxic. In Vitro. 24 1098-104
[9] Liu N and Bai R 2005 Copper adsorption on chitosan-cellulose hydrogel beads: Behaviors and mechanisms Sep. Purif. Technol. 42 237-47
[10] Huang Y et al 2010 Electrospun membrane of cellulose acetate for heavy metal ion adsorption in water treatment Carb. Poly. 83 743-8
[11] Aquino R, Tolentino M, Amen S, Arceo M, Dolojan M and Basilia B 2018 Preparation of cellulose acetate blended with chitosan nanostructured mebrane via electrospinning for Cd$^{2+}$ adsorption in artificial wastewater IOP Conf. Series: Earth and Environmental Science 191 012137
[12] Chen Z et al 2004 Preparation and performance of cellulose acetate/polyethyleneimine blend microfiltration membranes and their applications J. of Membr. Sci. 235 73-86