

Preparation of cellulose acetate blended with chitosan nanostructured membrane via electrospinning for Cd^{2+} adsorption in artificial wastewater

R R Aquino^{1,3}, M S Tolentino^{1,3}, S C S Amen¹, M A V Arceo¹, M E S Dolojan¹ and B A Basilia^{1,2}

¹School of Chemical, Biological, and Materials Engineering and Sciences, Mapúa University, 658 Muralla St., Intramuros, Manila 1002, Philippines

²Industrial Technology Development Institute, Department of Science and Technology, Bicutan, Taguig City, Metro Manila 1631, Philippines

E-mail: rraquino@mapua.edu.ph/marvstolentino@yahoo.com

Abstract. This study focused on using chitosan (CS) as the functional polymer in the cellulose acetate (CA) matrix to provide reactive ion exchange sites for heavy metal ions. Pure CA and CA/CS blends (wt % 95:5, 90:10 and 85:15) were electrospun to determine the most qualified blend for the adsorption experiment. The morphologies of the electrospun nanostructured membranes were investigated using Scanning Electron Microscopy. The average fiber diameter was found to decrease with increasing CS concentration. CA and CS interaction was confirmed using Fourier Transform Infrared Spectroscopy. Upon characterization, the blend with 15% CS had the best properties for the adsorption process. The adsorption capacities of pure CA and CA/CS blend at different membrane loading and initial concentration showed a significant increase from 67.25 mg Cd^{2+} /g pure CA membrane to 110.48 mg/g CS doped membrane. The experiment revealed that the adsorption kinetics of pure CA and CA/CS blend for Cd^{2+} were described by the pseudo-second order reaction model. The adsorption isotherm data for Cd^{2+} on the surface of pure CA and CA/CS blend best fit the Freundlich isotherm and can be used to describe adsorption of Cd^{2+} . This study produced an innovative nanostructured membrane for the removal of Cd^{2+} in wastewater.

1. Introduction

It is a fact that living organisms, specifically humans, need varying amounts of some heavy metals such as iron, copper, zinc, cobalt, manganese and molybdenum. These heavy metals help in maintaining body metabolism. However, most of these elements are only required by humans and other living organisms in minute amounts because excessive quantities can be harmful to the organism [1]. Contamination of aquatic media by heavy metal loaded effluents from mining, smelting, electroplating operations, and other industrial sources is a serious environmental problem that is very difficult and expensive to tackle because these heavy metals are toxic, persistent, and non-biodegradable [2].

Remediation of heavy metals from different water sources could be a challenge because unlike organic pollutants, these heavy metals do not deteriorate. Various methods such as membrane filtration, ion-exchange, chemical precipitation/coagulation, electrolytic reduction, solvent extraction, and absorption techniques have been used to treat effluents loaded with heavy metals; but most of



them are either too expensive or incapable of eliminating trace levels of heavy metal ions, especially from very dilute solutions [3].

A developing technology being used in water treatment for the removal of heavy metals is biosorption which overcomes the selective disadvantage of usual adsorption processes. It involves the use of different biological materials as adsorbents or ion exchange media for chelating heavy metals [4]. In this regard, biopolymers, which are renewable and more environment friendly, became the interest of recent studies for the adsorption of heavy metals.

In the discipline of nanotechnology, nanocomposites with polymer matrices have become an important area of current research and development. Polymers combine a number of favorable features, including flexibility, processability, low cost, size in the nanometer range, diverse functionalities, and microphase separation. Many commercial polymeric membrane materials have good mechanical, thermal and chemical properties, but the lack of reactive functional groups on the polymer backbones is a drawback. Due to this reason, membranes which are made from these materials often need to be enhanced and modified. Cellulose and its derivatives contain reactive hydroxyl groups, which can be modified with other reactive functional groups to obtain adsorptive membranes. One method to fabricate adsorptive membranes can be the introduction of amine groups into cellulose or its derivatives such as cellulose acetate (CA). However, CA membranes lack of reactive functional groups on the polymer backbones which affects the separation efficiency of the membranes. Hence, other materials are blended with CA to overcome this disadvantage and to enhance the CA membrane's adsorption capacity. More recently, chitosan (CS) which is a promising adsorptive material for various applications, have been combined to CA due to its abundance of the free amine groups for the adsorption of heavy metal [5].

In this study, researchers aimed to produce an electrospun CA/CS blend nanostructured membrane for Cd^{2+} removal in synthetic wastewater. The morphology, molecular properties, and mechanical properties of the resulting nanostructured membrane were characterized using Scanning Electron Microscopy (SEM), Fourier Transform Infrared (FTIR) Spectroscopy, and Universal Testing Machine (UTM). Kinetic studies for the adsorption process and adsorption isotherms were also investigated. The ability of the produced nanostructured membrane in removing Cd^{2+} ions in wastewater was studied. However, this study only utilized synthetic wastewater containing Cd^{2+} . Furthermore, it is not concerned with the mechanism of the adsorption process, effect of solvent and with the organic materials that would be collected upon experimentation.

2. Methodology

The polymers were dissolved first in their corresponding solvent in 70:30 ratio, CA in trichloroacetic acid and CS in dichloromethane. The CA/CS blend were then prepared with concentrations of 100%-0%, 95%-5%, 90%-10% and 85%-15% CA to CS solution concentration, respectively. The solution was stirred continuously until a viscous solution was obtained. The blended solutions of varying concentration underwent the electrospinning process utilizing the following parameters: processing conditions at room temperature (25°C), applied voltage at 30 kV and the tip-to-collector distance was fixed at 18 cm. The electrospun CA/CS nanostructured membranes were characterized using different analytical techniques; namely, scanning electron microscopy (SEM), Fourier transform infrared (FT-IR) spectroscopy and testing of mechanical strength using the universal testing machine (UTM). Pure CA dope and CA/CS fibers, that satisfied the most desired properties, were used for adsorption experiment. The pure CA membrane and the best CA/CS blend membrane of different amounts (from 0.025 g to 0.0875 g with 0.0125 g interval) were used as adsorbent in a 250 mL Erlenmeyer flask containing 50 mL of 50 ppm concentration of Cd^{2+} solution. From these fiber dosages and volume, the liquor to sorbent ratio ranges from 500:1 to 2000:1. Different sample preparations were conducted and the samples were subjected to Atomic Absorption Spectrophotometer (AAS) analyzer to determine the effect of adsorbent dosage, adsorption kinetics (from the effect of contact time on adsorption capacity of the membranes for Cd^{2+} ions), and adsorption isotherm (fitted to Langmuir and Freundlich isotherm models).

3. Results and discussion

3.1. Effect of CS content on fiber structure

The SEM images were obtained at different magnifications for all electrospun CA/CS blends which confirmed the effects of CS content on the surface characteristics of the membranes. As can be seen on figure 1, varying the amount of CS in the CA/CS blend established a visible effect in the generated nanostructured membrane. It was observed that as the CS concentration increases, smaller fiber diameter is obtained. This behavior between nanostructured membrane diameter and concentration is because CS acts as a partial polyelectrolyte and increases the polymer solution conductivity, thereby decreasing the diameter of the nanostructured membranes [6,7]. Another reason for this decrease in diameter with increase in concentration can be observed due to the partial clogging or restriction to flow at the tip of needle. This clogging can be attributed to higher viscosity of the solution of CS in acetic acid [8].

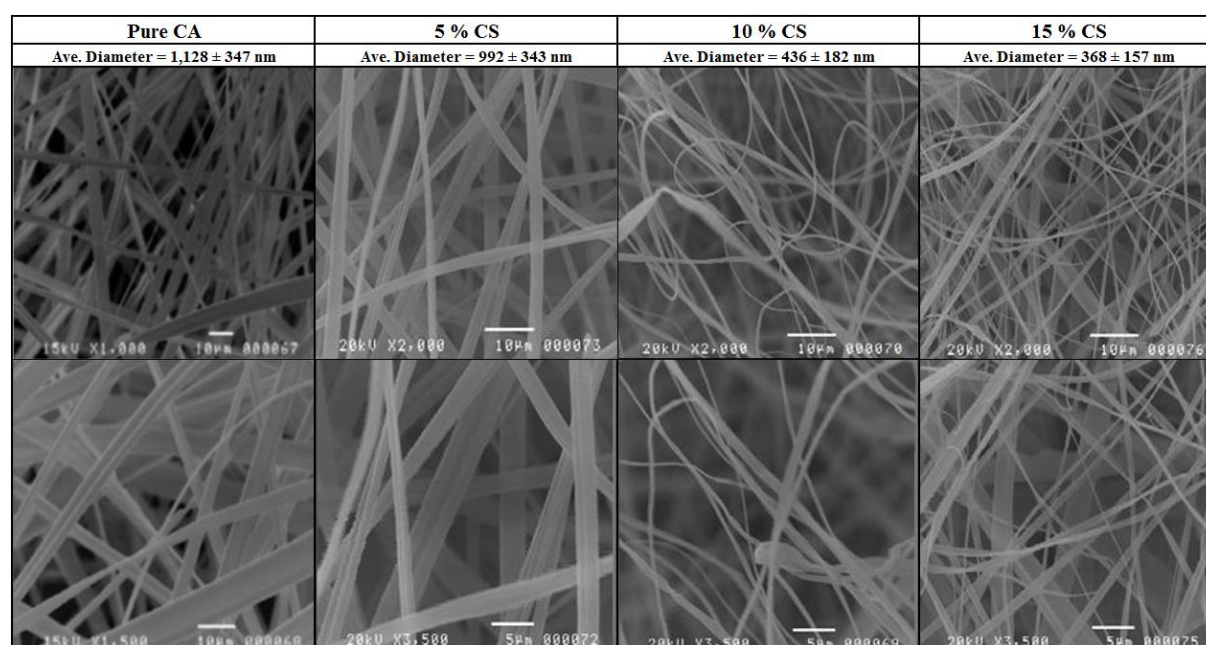


Figure 1. SEM micrographs of electrospun pure CA and CA/CS blends at low (first row) and high (second row) magnifications, with their corresponding average diameters in nanometers.

3.2. Molecular structure of the fibers

The electrospun nanostructured membranes were subjected to FTIR analysis and based on the results (figure 2), interaction took place between CA and CS polymers. This was evident due to the significant difference in the appearance of new peaks and shifting of existing peaks. As CS was added up to 15%, noticeable shifting at lower frequencies were observed at wavenumbers ranging from $3000\text{--}3500\text{ cm}^{-1}$. Increasing the amount of CS present in the matrix created a shift from 3216 cm^{-1} to 3208 cm^{-1} up to 3192 cm^{-1} which indicates that an increased amount of amine groups promotes its interaction with the OH groups and signifies its incorporation into the CA matrix. The shifting of the absorption band seen at around 1754 cm^{-1} for the 5%, 10% and 15% membrane represents the characteristic absorption band attributed to the coincided ester-carbonyls (acetyl groups) in cellulose acetate, while the shifting of the absorption band observed at around 2900 cm^{-1} is attributed to the carbon-hydrogen bonds (C-H) carbon-hydrogen deformation in cellulose acetate.

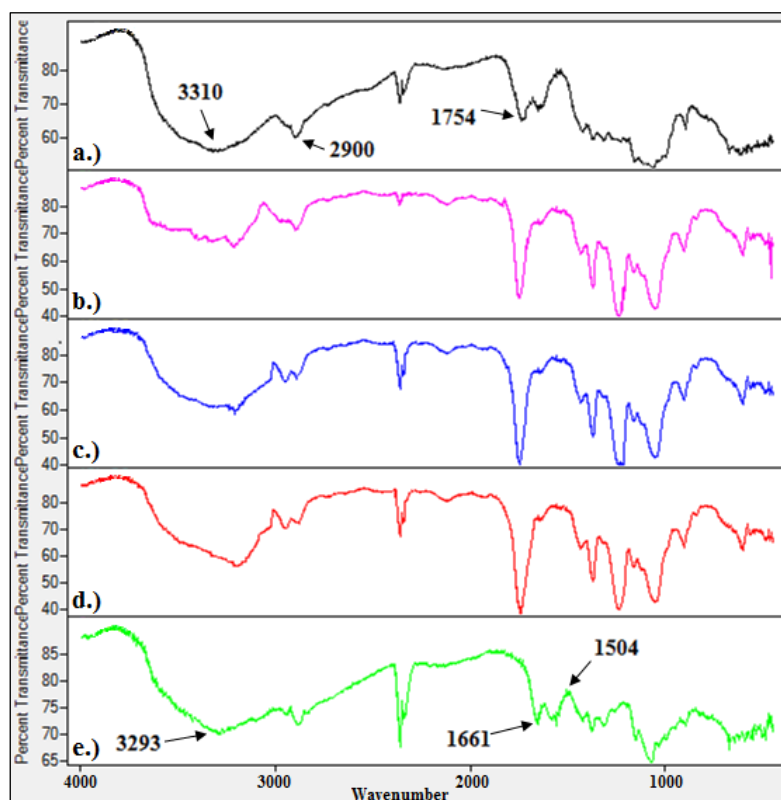


Figure 2. FTIR spectra for a.) pure CA; CA/CS blends b.) 5% CS, c.) 10% CS, d.) 15% CS; and e.) pure CS.

3.3. Mechanical analysis of membrane

Based on the results obtained from UTM as shown in table 1, it can be observed that the values for the mechanical properties decrease with the increase of amount of CS in the membrane. The decrease in the mechanical strength of the different CA/CS blend nanostructured membrane may be attributed to the decrease in intermolecular attraction between the molecules of the blended polymers. CS shows a good performance in adsorption of heavy metal [9]; however, it is also known to have poor mechanical strength [10] so the decrease in the mechanical properties was already expected. The fiber mechanical properties are dependent on fiber orientation and as the fiber disorientation increases, mechanical properties decrease. Based on SEM results (figure 1), as CS increases, the disorientation of the fibers also increases resulting in the decrease of mechanical properties of the CA/CS blend. Upon performing ANOVA, the values of the mechanical properties of the nanostructured membrane displayed no significant difference since its F critical value (3.490) is greater than F value (0.1328), and P value (0.9387) is greater than 0.05 significance level. Nevertheless, the mechanical properties of the fabricated nanostructured membrane were not given emphasis and were not considered in the determination of the best blend to be used in the adsorption study.

Table 1. Mechanical properties of electrospun pure CA and CA/CS blends.

Blend	Stiffness (MPa)	Elongation (mm)	Tensile Stress at Yield (MPa)	Tensile Strain at Yield (mm/mm)
0%	0.31255 ± 0.122423	33.32755	0.02085	0.17175
5%	0.15336 ± 0.103723	39.08769	0.01207	0.21691
10%	0.20900 ± 0.057700	19.07539	0.01232	0.13714
15%	0.21755 ± 0.187500	18.08215	0.01515	0.14167

3.4. Adsorption study

Based on the fiber characterization, blend with 15% CS loading had the best properties needed for the adsorption process. This CS blend was used together with pure CA nanostructured membranes to compare the adsorption capacity of both fibers at different dosage.

3.4.1. Effect of adsorbent dosage. Figure 3 shows that the adsorption of Cd^{2+} increases rapidly as the amount of the fibers increases. This is due to the presence of larger surface area for adsorption at higher adsorbent concentration. For pure CA (figure 3(a)), a considerable increase in uptake was observed when the amount was increased from 0.025 g to 0.05 g and addition of adsorbent beyond this point result in a decrease of adsorption capacity. The decrease in adsorption capacity as adsorbent dosage increased is because the adsorption equilibrium may not have been attained. It also means that all the Cd^{2+} ions from the solution adhered to the adsorbent while there were still available sites for adsorption [11]. The result also shows that 50 ppm of Cd^{2+} was enough to saturate 0.05 g of pure CA fiber. The same behavior was observed for CA/CS blend (figure 3(b)). The adsorption capacity of the fiber increases up to 0.0375 g then decreases with further increase in the adsorbent dosage. The results obtained imply that 0.0375 g of CA/CS blend was enough to attain equilibrium at 50 ppm concentration compared to 0.05 g of pure CA.

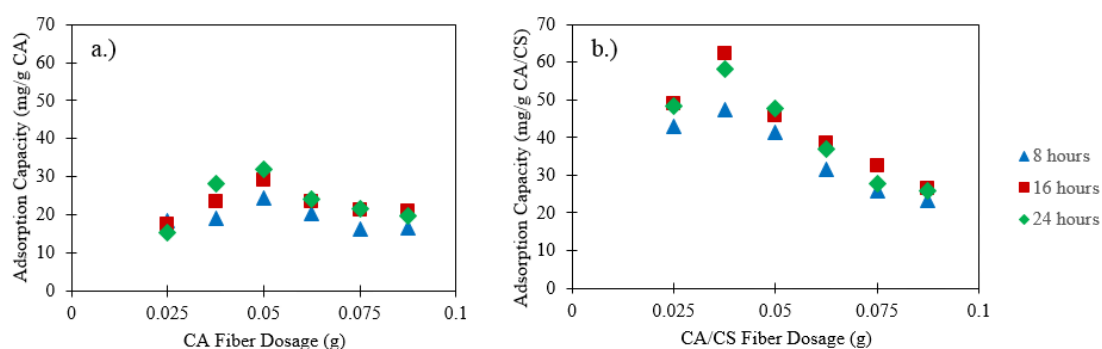


Figure 3. Adsorption capacity of a.) pure CA and b.) CA/CS (15%) fibers for Cd^{2+} as a function of adsorbent dosage at different time intervals.

3.5. Kinetics study

3.5.1. Effect of contact time. As can be seen from figure 4(a), CA/CS blend has higher adsorption capacity than pure CA. The adsorption of Cd^{2+} on fibers reached equilibrium after 6 hours wherein the adsorption capacity curve flattens. The adsorption occurred rapidly during the first 6 hours, which was possibly because of the active sites abundantly available on the adsorbent [12]. As the final concentration decreases, it lowers the concentration gradient which leads to a decrease and steadiness on the rate of adsorption [11].

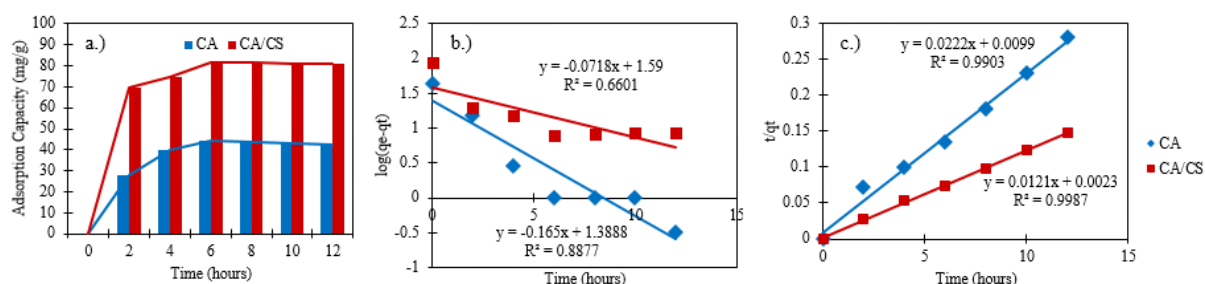


Figure 4. a.) Effect of contact time on the adsorption capacity of the fibers for Cd^{2+} , b.) pseudo first-order and c.) pseudo second-order model plots for the adsorbents.

The experimental data for the adsorption kinetics were fitted using the pseudo first-order and pseudo second-order kinetic models to identify whether physical or chemical mechanism governs the adsorption process. The results in figures 4(b) and 4(c) clearly show that the pseudo second-order model provides a better correlation for the adsorption kinetic data obtained than the pseudo-first order model. This means that the rate limiting step in the adsorption of Cd^{2+} would be chemisorption or chemical sorption which involves valency forces from the exchange and sharing of electrons between the adsorbent and adsorbate [12]. The potential binding sites that are present are the amines of CS and hydroxyls of CA.

3.6. Equilibrium study

The results in figure 5 demonstrate that for both fibers, at a fixed adsorbent dose, the adsorption capacity is linearly increasing with the initial concentration of Cd^{2+} for the reason that raising the Cd^{2+} concentration speeds up the diffusion of Cd^{2+} ions from solution to the adsorbent surface due to the concentration gradient factor; thus, increasing the driving force for adsorption. For pure CA adsorbent, an increase in adsorption capacity was observed from 3-6 hours of immersion and decreases at 9 hours of immersion due to reversibility in the adsorption process. On the other hand, the adsorption capacity of CA/CS blend was observed to be steady and decreases slightly which suggests that CS dope fibers was more stable adsorbent for metal species at longer times. It can be seen that CS doped fibers have higher adsorption capacities for all varied initial concentration of Cd^{2+} solution compared with the fiber of pure CA.

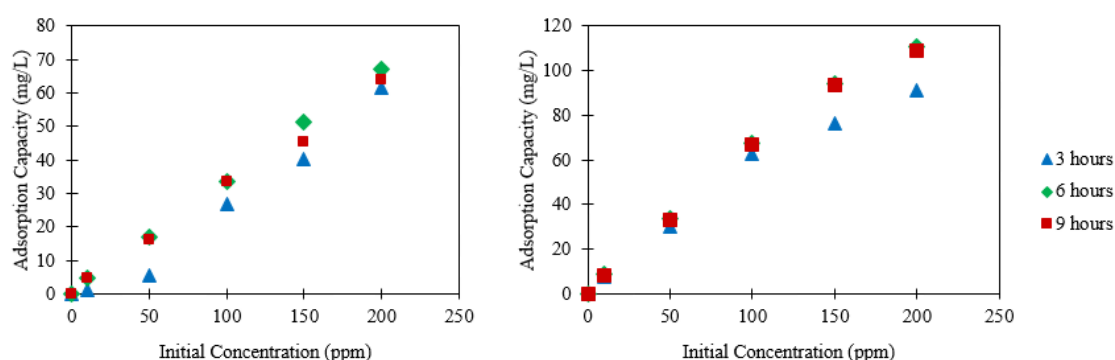


Figure 5. Effect of contact time on the adsorption capacity of a.) pure CA and b.) CA/CS (15%) fibers for Cd^{2+} at different initial Cd^{2+} concentrations.

3.7. Isotherm fitting

The equilibrium data were analyzed using Langmuir and Freundlich equilibrium models to obtain the best fit isotherm. Based on the results obtained (figure 6), the regression coefficients R^2 of linear Freundlich isotherm for Pure CA and CA/CS were found to be both equal to 0.989.

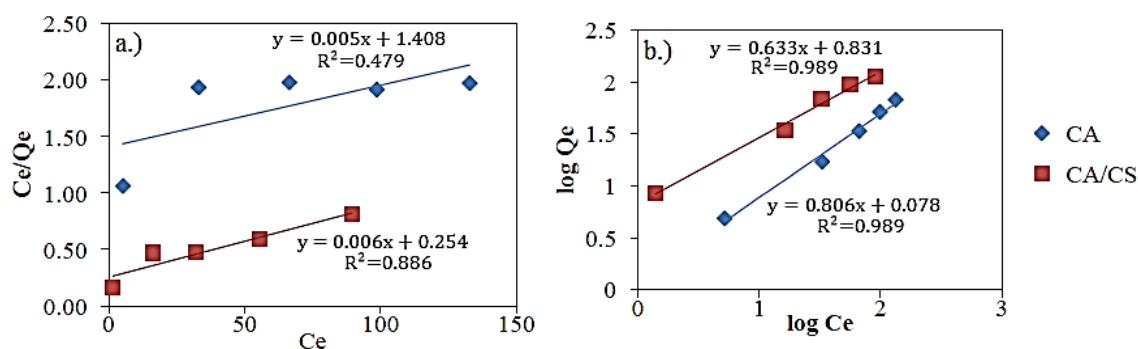


Figure 6. Adsorption isotherm fitting; a.) Langmuir isotherm and b.) Freundlich isotherm.

This suggests that Freundlich isotherm is the best-fit model for the experimental data obtained. The Freundlich isotherm illustrates that the adsorption of Cd^{2+} happened on a heterogenous multi-layer surface with uniform energy [12].

4. Conclusion

Nanostructured membrane from CA/CS nanofibres at different CS loading have been successfully fabricated through electrospinning technique. It was found that the average fiber diameter of the electrospun nanostructured membranes decreases with increasing CS contents in the polymer blend. FTIR results showed the interaction between CA and CS with the consistent shifts of hydroxyl, amine and carbonyl peaks from 5% to 15% CS loading. For the mechanical properties, the decrease in the mechanical strength of the different CA/CS blend nanostructured membrane may be attributed to the decrease in intermolecular attraction between the molecules of the CA polymer matrix and CS. Based on the adsorption study, it was found that the adsorption capacity of the two adsorbents at different membrane loading and initial concentration showed a significant increase from 67.25 mg Cd^{2+} /g pure CA nanostructured membrane to 110.48 mg Cd^{2+} /g of CS doped fibrous membrane. Data obtained from kinetics experiment were best fitted to pseudo second-order model. In varying the initial concentration of the Cd^{2+} solution, the adsorption data at equilibrium were best fitted to the Freundlich isotherm model.

References

- [1] O'Connell D, Birkinshaw C and O'Dwyer T 2008 Heavy metal adsorbents prepared from the modification of cellulose: A review *Bioresour. Technol.* **99** 6709-24
- [2] Zhang G, Qu R, Sun C, Ji C, Chen H, Wang C and Niu Y 2008 Adsorption for metal ions of chitosan coated cotton fiber *J. Appl. Polym. Sci.* **110** 2321-7
- [3] Kurniawan T A, Chan G Y S, Lo W H and Babel S 2006 Physicochemical treatment techniques for wastewater laden with heavy metals *Chem. Eng. J.* **118** 83-98
- [4] Volesky B and Holan Z 1995 Biosorption of heavy metals *Biotechnol. Prog.* **11** 235-50
- [5] Liu C and Bai R 2005 Preparation of chitosan/cellulose acetate blend hollow fibers for adsorptive performance *J. of Membr. Sci.* **267** 68-77
- [6] Huang C, Chen S, Lai C, Reneker D, Qiu H, Ye Y and Hou H 2006 Electrospun polymer nanofibres with small diameters *Nanotech.* **17** 1558-63
- [7] Jia Y, Gong J, Gu X, Kim H, Dong J and Shen X 2007 Fabrication and characterization of poly (vinyl alcohol)/chitosan blend nanofibers produced by electrospinning method *Carb. Polym.* **67** 403-9
- [8] Arayanarakul K, Choktaweasap N, Aht-ong D, Meechaisue C and Supaphol P 2006 Effects of poly(ethylene glycol), inorganic salt, sodium dodecyl sulfate, and solvent system on electrospinning of poly(ethylene oxide) *Macromol. Mater. Eng.* **291** 581-91
- [9] 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
- [10] Shu X and Zhu K 2002 The release behavior of brilliant blue from calcium-alginate gel beads coated by chitosan: the preparation method effect *Eur. J. Pharm. Biopharm.* **53** 193-201
- [11] Millare J 2010 Chitosan reinforced polycaprolactone nanostructured membrane: fabrication and adsorption kinetics for Cu(II) removal from wastewater (Manila, Philippines: School of Chemical, Biological, and Materials Engineering and Sciences)
- [12] Qu R, Sun C, Wang M, Ji C, Xu Q, Zhang Y, Wang C, Chen H and Yin P 2009 Adsorption of Au(III) from aqueous solution using cotton fiber/chitosan composite adsorbents *Hydrometallurgy* **100** 65-71