

Adsorptive removal of lead (Pb^{2+}) ion from water using cellulose acetate/polycaprolactone reinforced nanostructured membrane

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Abstract. Nanostructured membranes of cellulose acetate (CA) with various polycaprolactone (PCL) loadings (0%, 10%, 20% and 30%) were produced via electrospinning process for the removal of Pb^{2+} ion from wastewater. Optimized electrospinning parameters were utilized: voltage supply (30 kV), temperature (25 °C), tip to collector distance (18 cm) and needle size (25 G). Certain characterization techniques were used to investigate the effect of PCL addition on CA nanostructured membranes. The surface morphology was examined through Scanning Electron Microscopy (SEM), and chemical composition and molecular structure were determined using Scanning Electron Microscope – Energy Dispersive X-ray Spectroscopy (SEM-EDX) and Fourier Transform Infrared Spectroscopy (FTIR), respectively. Results showed that the incorporation of PCL in CA produced finer fiber diameter which gave the membrane a larger surface area; thus, increasing the adsorption sites. Based on the results, adsorption capacity was improved from 43.96 mg Pb^{2+} /g of pure CA membrane to 70.50 mg Pb^{2+} /g of CA/PCL doped membrane. Moreover, the results of this experiment best fitted the pseudo second-order kinetics, and the Freundlich isotherm which appropriately describe the adsorption process. CA membranes are widely used in several separation processes, and the results showed, its capability can be further enhanced by the incorporation of PCL to produce nanostructured membranes.

1. Introduction

The presence of heavy metals in different water sources can pose a great threat to various living organisms, specifically to humans. With this as a problem, many researches in the past years focused on the removal of certain heavy metals in water [1]. Several processes are being conducted to treat wastewater to remove heavy metals, and protect further water resources [2]. Emerging treatment techniques such as adsorption using different adsorbent media, namely, modified natural materials [3], industrial by-products [4], agricultural wastes [5], biological wastes (bio-sorption) [6], and modified biopolymers and hydrogels [7], are commonly used in the removal of heavy metals from water. Furthermore, other techniques include membrane filtration using different membrane blends [8], electro dialysis [9] and photocatalysis [10].



Among the known water treatment techniques, adsorption process is widely used because of its versatile applications other than heavy metal adsorption. Its applications also include adsorptive removal of nitrogen contamination [11] and organic pollutants [12]. In addition to adsorption is membrane technology, which is also known for its significant contribution in the field of water treatment processes [13]. Furthermore, distinct advantages in applying membrane processes compared to other water treatment processes include low energy consumption, membrane separations with mild operating conditions, possible optimization of different membrane properties to satisfy various requirements, minimal footprint, and most importantly, the feasibility to combine membrane processes with other processes [14]. Several ways can be utilized in producing membranes, but a prominent method is the electrospinning process, wherein nanofibers can be produced exhibiting special properties such as large surface area to mass ratio, low density, high pore volume and tight pore size make them suitable for a wide range of applications [15]. With the flexible uses of adsorption together with the unique properties of electrospun membranes, an innovative technique for water treatment applications [16], specifically the removal of heavy metals from wastewater [17], can be achieved.

Cellulose acetate (CA) is mostly used as membrane in several separation and water treatment processes because of its desirable properties, mainly low cost/benefit ratio [18]. Its competence in sequestering heavy metals in water had been proven because of the presence of different functional groups such as $-\text{COOH}$, $-\text{SO}_3\text{H}$ and $-\text{NH}_2$ groups, which are naturally grafted on CA. Hence, heavy metals ions can attach and form bonds on the surface of CA through complexation mechanisms [19]. Studies had been made wherein reinforcement of synthetic polymers with CA were done to improve its adsorption capability. In the study conducted by Tian and co-workers [20], electrospun CA was surface-modified using poly (methacrylic acid) (PMAA). The results of their study showed an increased adsorption capacity for Cd^{2+} , Cu^{2+} and Hg^{2+} upon modification of CA. For instance, it was found that there is the shifting of adsorption peak for $-\text{COO}^-$ from 1734 cm^{-1} to 1730 cm^{-1} . This signifies the decrease in the electronegativity of $-\text{COO}^-$ which is the main reason in the attraction of electropositive heavy metal ions.

Other than water treatment, electrospun membranes are also significant in the biomedical field, usually used as wound dressing [21]. One of the promising materials being used to fabricate biocompatible membranes is the polycaprolactone (PCL), mainly because of its outstanding structure, and excellent mechanical and physical properties [22].

In this study, it was aimed to fabricate a novel electrospun CA nanostructured membrane impregnated with PCL to remove toxic Pb^{2+} from wastewater by means of membrane adsorption. The material that produced underwent a series of characterizations using Scanning Electron Microscopy (SEM) and Fourier Transform Infrared Spectroscopy (FTIR) to investigate its acquired properties. The ability of the nanostructured membrane in removing Pb^{2+} metal ions from wastewater was investigated. The adsorption kinetics, equilibrium, and adsorption isotherm were also studied.

2. Experimental

CA (65,000 g/mol) and commercial grade PCL (60,000 g/mol) utilized in this study were provided by Chemline Enterprises. Acetone and dichloromethane (DCM) were used as solvents for CA and PCL, respectively. Pure CA and CA/PCL blends of different PCL loading (0%, 10%, 20%, and 30%) were electrospun and the following parameters were applied: room temperature ($25\text{ }^\circ\text{C}$), 30 kV applied voltage and the distance from the tip to the collector was fixed at 18 cm. The nanostructured membranes produced were characterized using the following techniques: Fourier Transform Infrared Spectroscopy (FTIR) to confirm the presence of organic molecules and provides a direct evidence of PCL and CA attachment, Scanning Electron Microscope (SEM) for the morphological investigation of the material, SEM–Energy Dispersive X-ray Spectroscopy (SEM-EDX) – with SEM in combination to determine the elemental composition of the sample. Afterwards, the adsorption analysis was performed making use of the best CA/PCL blend membrane and pure CA membrane as adsorbent at various amounts (0.05 g to 0.15 g at 0.025 g interval) in a 250 mL flask having 200 mL Pb^{2+} solution with 100 ppm concentration. From these

fiber dosages and volume, the liquor to sorbent ratio ranges from 500:1 to 2000:1. The set up was then placed in a water bath shaker for 24 hours. Then every 8 hours, a 50 mL aliquot was collected and digested. Analysis of each solution was conducted using Absorption Spectrophotometer analyzer (AAS) to determine the following: the effect of contact time and Pb^{2+} initial concentration on the adsorption capacity, adsorption kinetics (the best fit between pseudo first-order and pseudo second-order kinetic model), and adsorption isotherm (Langmuir and Freundlich isotherm model).

3. Results and discussion

3.1. Effect of PCL on fiber structure

Figure 1 shows the SEM micrograph of pure CA membrane having uniform and straight fiber morphology. The incorporation of PCL to CA reduced the fiber diameter of the membrane produced which can be observed from the morphologies of the CA/PCL blends and their corresponding average fiber diameters. Since PCL has a better conductivity compared to CA, and has good adhesion to a broad spectrum of substrates [23], it provides better stretching of the solution which produced finer fiber diameter [24]. Based from the obtained micrographs, CA with 10% PCL produced the nanostructured fiber with the minimum average fiber diameter (570 ± 188 nm).

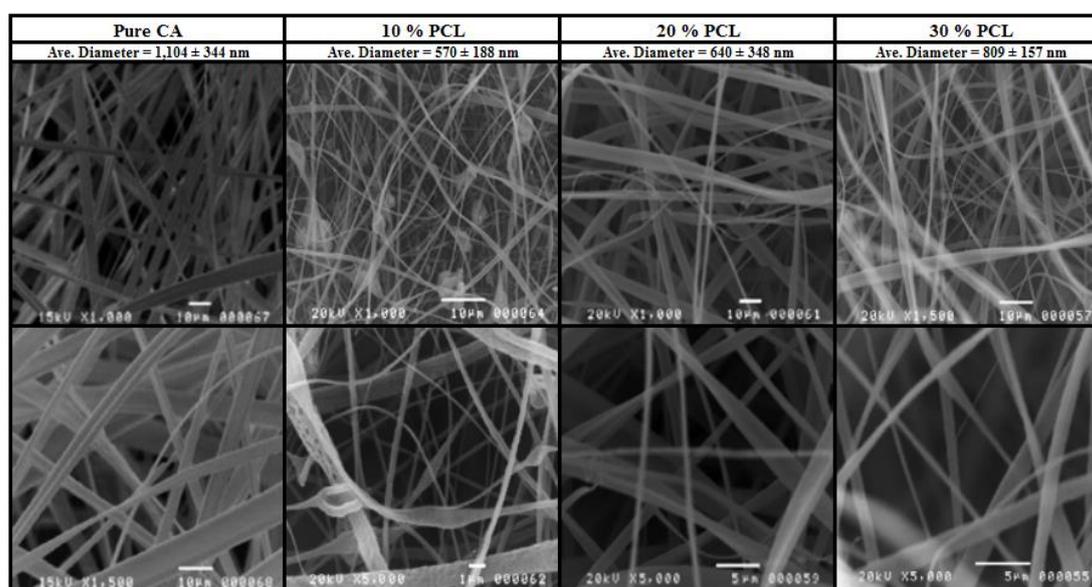


Figure 1. SEM micrographs of electrospun pure CA and CA/PCL blends at low (first row) and high (second row) magnifications, with their corresponding average fiber diameters.

3.2. Molecular structure of the fibers

The FTIR results of the electrospun membranes were presented in figure 2.a. For pure PCL, at around 2900 cm^{-1} and 1700 cm^{-1} , the spectrum indicates the presence of carbon-hydrogen (C-H) stretching and carbonyl (C=O) stretching of carboxylic acid, respectively. For pure CA, the carbonyl (C=O) group stretching is found at 1748.26 cm^{-1} . The three changes or shifting of peaks for pure CA as shown in figure 2.a shows the effect of adding PCL in the solution. The continuous increase in peaks upon PCL addition implies the successful bonding of the CA with the PCL in the membrane.

3.3. Adsorption analysis

As observed from the SEM micrographs (figure 1), the CA/PCL (10%) blend produced, has the finest fiber diameter among the different blends. Finer fiber diameter would mean larger surface area which would, in turn, mean larger adsorption area. Hence, the said blend and pure CA were used in the adsorption experiment to compare the adsorption capacity as well as the kinetics of both fibers.

Furthermore, based on the results of the SEM-EDX as seen on figure 2.b and 2.c, traces of Pb^{2+} were detected after the adsorption process which proved the effectivity of the membrane produced.

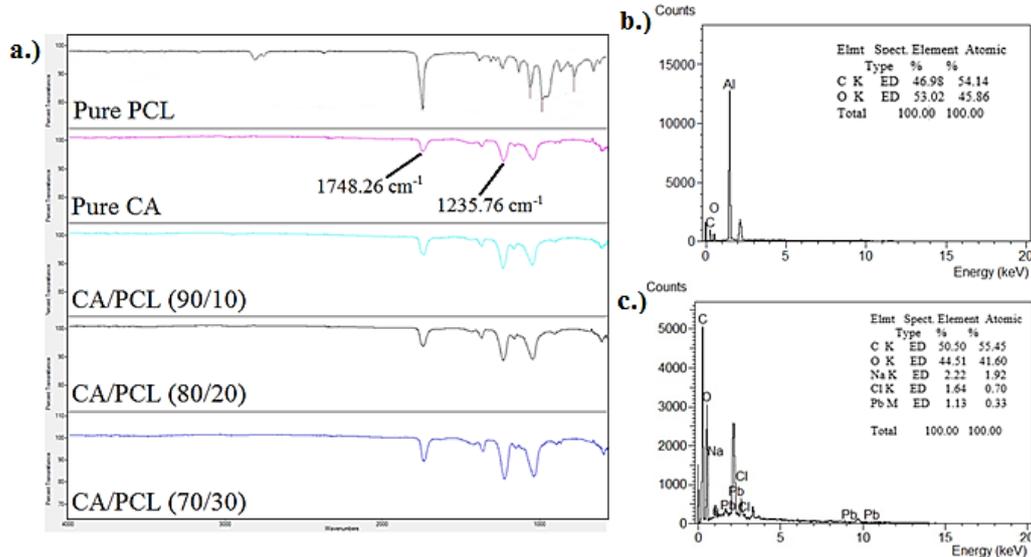


Figure 2. a.) FTIR spectra of the different membrane blends, and SEM-EDX results for CA/PCL (10%) blend b.) before and c.) after Pb^{2+} adsorption.

3.3.1. Effect of adsorbent dosage. For pure CA, based on the graph on figure 3.a, there is a noticeable increase in the Pb^{2+} uptake when the CA fiber dosage was increased from 0.05 g to 0.075 g. As for the CA/PCL (figure 3.b), similar characteristics and behavior could be observed. In this case, the optimum adsorption dosage was determined to be 0.075 g. For both membranes, decrease in the adsorption capacity can be observed when the fiber dosage exceeds 0.075 g. The decrease in adsorption capacity could mean two things. First, adsorption equilibrium may not have been attained as the fiber dosage was increased. Second, it is also possible that all Pb^{2+} ions from the solution adhered to the adsorbent while there were still available sites for adsorption [23]. Thus, the results show that 100 ppm of Pb^{2+} was enough to saturate 0.075 g of pure CA, and CA/PCL blend.

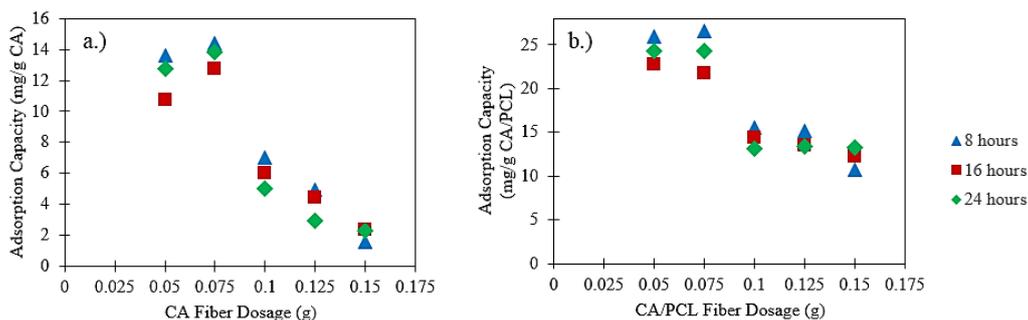


Figure 3. Adsorption capacity of a.) pure CA and b.) CA/PCL (10%) fibers for Pb^{2+} as a function of adsorbent dosage at different time intervals.

3.4. Kinetics study

3.4.1. Effect of contact time. As can be seen on figure 4.a, equilibrium state was reached after 6 hours for pure CA. Increasing trend for the adsorption capacity with time was observed up to 6 hours but at time values greater than 6 hours, the adsorption capacity remained constant. This is most possibly due to the large amount of active sites in the adsorbent [25] initially available, before the fiber started to become saturated. In addition, initially there exist a high concentration gradient which aids the fast

diffusion of Pb^{2+} onto the surface of the adsorbent. Conversely, for CA/PCL blend, equilibrium was not attained. Based figure 4.a, even at 10 hours, the adsorption capacity still tends to increase. In this case, due to the interaction of CA and PCL, and also because of finer fiber diameters produced, higher amount of active sites became available for the adsorption of Pb^{2+} on the membrane.

3.4.2. Adsorption kinetics. Based on the results of the experimental data fitting (figure 4.b and 4.c), pseudo second-order was found to be the model that best fitted the adsorption of Pb^{2+} onto fibers with R^2 value of 0.9174 for pure CA and 0.9934 for CA/PCL (10%) blend, compared to that of the pseudo first-order model with R^2 value of 0.2502 and 0.1598 for pure CA and CA/PCL (10%), respectively. This means that the Pb^{2+} ion first dissociate from its parent molecule and form a chemical bond, likely dipolar covalent, with the potential functional group of the fibers thereafter. These potential binding sites are the amines, hydroxyls and carbonyls from CA and PCL. Also, the pseudo second-order kinetics reveals that for both pure CA and CA/PCL (10%) membranes, the chemisorption is the rate-limiting step for the adsorption of Pb^{2+} , wherein the Pb^{2+} ions affix to the membrane with a covalent bond among the sorbent and sorbates. Here, sites may be searched to which maximizes the coordination number with the surface [26].

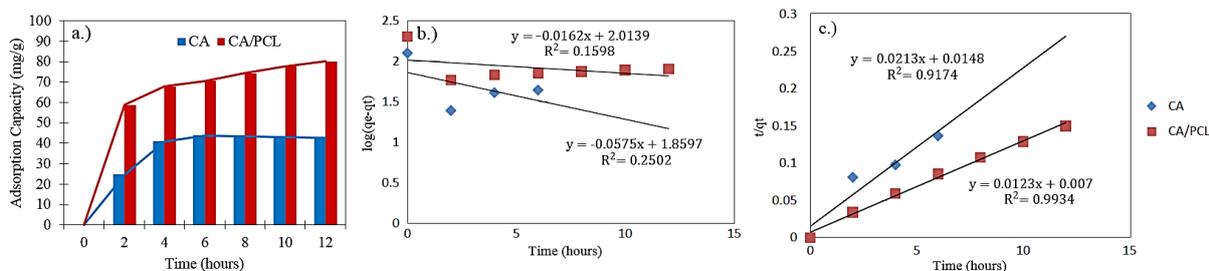


Figure 4. a.) Effect of contact time on the adsorption capacity of the fibers for Pb^{2+} , b.) pseudo first-order and c.) pseudo second-order model plots for the adsorbents.

3.5. Equilibrium study

Based from the gathered results (figure 5), the adsorption capacity is linearly increasing with initial concentration of Pb^{2+} for both fibers at a fixed adsorbent dosage. This is due to the increase in the driving force of the concentration gradient which accelerates the diffusion of Pb^{2+} from the solution to the adsorbent surface. For pure CA adsorbent, an increase in the 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, it was observed that the adsorption capacity of PCL is steady and decreases slightly which suggests that PCL dope fibers were more stable adsorbent for metal specie at longer times. In addition, it can be seen that PCL doped fibers have higher adsorption capacities compared to pure CA for all varied initial concentration of Pb^{2+} solution.

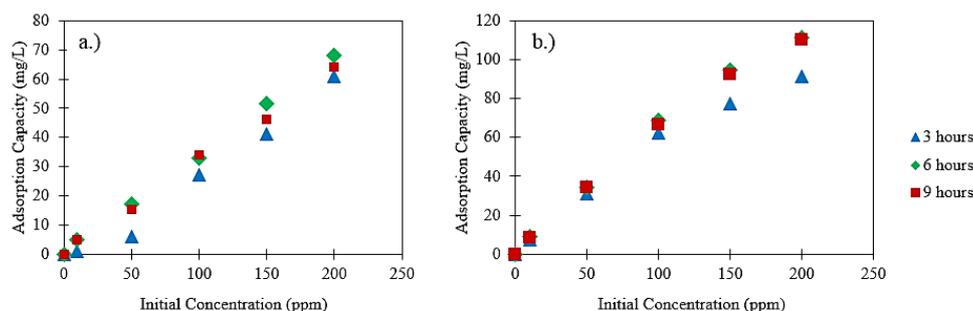


Figure 5. Effect of initial Pb^{2+} concentration on the adsorption capacity of a.) pure CA and b.) CA/PCL (10%) fibers at different time intervals.

3.6. Adsorption isotherm

Based on the results in figure 6, the regression coefficient R^2 of linear Freundlich isotherm for pure CA and CA/PCL were found to be 0.9957 and 0.994, respectively. The experimental data best-fitted the Freundlich isotherm model because it has the best R^2 compared to Langmuir isotherm model. This explains that the adsorption process occurred on a heterogenous (multiple layer) surface with uniform energy [25]. Also, physisorption and chemisorption occur at low coverages.

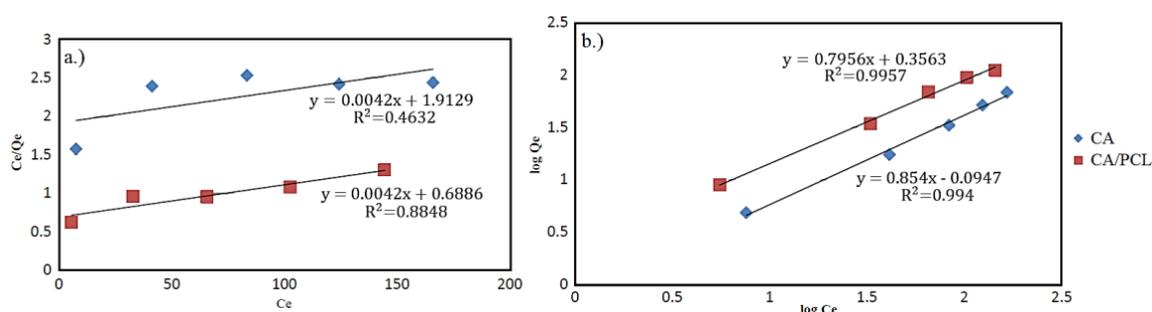


Figure 6. Adsorption isotherm fitting; a.) Langmuir isotherm and b.) Freundlich isotherm.

4. Conclusion

Electrospun CA/PCL nanostructured membranes for the adsorption of Pb^{2+} were successfully produced. The SEM results showed that CA/PCL (10%) exhibited the smallest average fiber diameter, which means larger adsorption surface area. Interaction between CA and PCL was supported by the results of FTIR analysis. For the adsorption experiment, based from the gathered results, it was observed that the incorporation of 10% PCL improved the adsorption capacity of pure CA from 43.96 mg Pb^{2+} /g membrane of pure CA to 70.50 mg Pb^{2+} /g of PCL doped fibrous membrane, after 6 hours in which the saturation of pure CA had occurred. The adsorption data of the study were best fitted in the pseudo-second order model and Freundlich isotherm model. In general, it had been observed that the incorporation of PCL can improve the adsorption capacity of pure CA, which shows that the CA/PCL (10%) blend is a more suitable adsorbent for heavy metals at longer time intervals and can be a promising material for wastewater treatment.

References

- [1] Barakat M A 2011 New trends in removing heavy metals from industrial wastewater *Arab. J. Chem.* **4** 361-77
- [2] Fu F and Wang Q 2011 Removal of heavy metal ions from wastewaters: A review *J. Environ. Manage.* **92** 407-18
- [3] Pham T D, Nguyen H H, Nguyen N V, Vu T T, Pham T N M, Doan T H Y, Nguyen M H and Ngo T M V 2017 Adsorptive removal of copper by using surfactant modified laterite soil *J. Chem.* **2017** 1-10
- [4] Ma J, Qin G, Zhang Y and Jiang L 2018 Heavy metal removal from aqueous solutions by calcium silicate powder from waste coal fly-ash *J. Clean. Prod.* **182** 776-82
- [5] Renu M A, Singh K, Upadhyaya S and Dohare R K 2017 Removal of heavy metals from wastewater using modified agricultural adsorbents *Mater. Today* **4** 10534-38
- [6] Tran H T, Vu N D, Matsukawa M, Okajima M, Kaneko T, Ohki K and Yoshikawa S 2016 Heavy metal biosorption from aqueous solutions by algae inhabiting rice paddies in Vietnam *J. Environ. Chem. Eng.* **4** 2529-35
- [7] Zhou G, Liu C, Chu L, Tang Y and Luo S 2016 Rapid and efficient treatment of wastewater with high-concentration heavy metals using a new type of hydrogel-based adsorption process *Bioresour. Technol.* **219** 451-7
- [8] Feng Q, Wu D, Zhao Y, Wei A, Wei Q and Fong H 2018 Electrospun AOPAN/RC blend

- nanofiber membrane for efficient removal of heavy metal ions from water *J. Hazard. Mater.* **344** 819-28
- [9] Nemati M, Hosseini S M and Shabanian M 2017 Novel electro dialysis cation exchange membrane prepared by 2-acrylamido-2-methylpropane sulfonic acid; heavy metal ions removal *J. Hazard. Mater.* **337** 90-104
- [10] Ihsanullah, Abbas A, Al-Amer A M, Laoui T, Al-Marri M J, Nasser M S, Khraisheh M and Atieh M A 2016 Heavy metal removal from aqueous solution by advanced carbon nanotubes: Critical review of adsorption applications *Sep. Purif. Technol.* **157** 141-61
- [11] Pham T D, Do T T, Ha V L, Doan T H Y, Nguyen T A H, Mai T D, Kobayashi M and Adachi Y 2017 Adsorptive removal of ammonium ion from aqueous solution using surfactant-modified alumina *Environ. Chem.* **14** 327-37
- [12] Pham T D, Bui T T, Nguyen V T, Bui T K V, Tran T T, Phan Q C, Pham T D and Hoang T H 2018 Adsorption of polyelectrolyte onto nanosilica synthesized from rice husk: characteristics, mechanisms, and application for antibiotic removal *Polym.* **10** 220
- [13] Palma P, Alvarenga P, Brás T, Cavaco C, Neves L A, Fialho S, Santos C, Palma G and Gomes R 2016 Membranes technology used in water treatment: Chemical, microbiological and ecotoxicological analysis *Sci. Total Environ.* **568** 998-1009
- [14] Liao Y, Loh C H, Tian M, Wang R and Fane A G 2018 Progress in electrospun polymeric nanofibrous membranes for water treatment: Fabrication, modification and applications *Prog. Polym. Sci.* **77** 69-94
- [15] Aquino R R, Tolentino M S, Angeles J V and Millano H A 2018 Fabrication and Characterization of Electrospun Polysulfone (PSF)/Organo-Montmorillonite (O-MMT) Nanostructured Membranes *Mater. Sci. Forum* **916** 125-9
- [16] Aquino R R, Tolentino M S, Crisogono B M Z and Salvacion S K V 2018 Adsorption of Methylene Blue (MB) Dye in Wastewater by Electrospun Polysulfone (PSF)/Organo-Montmorillonite (O-MMT) Nanostructured Membrane *Mater. Sci. Forum* **916** 120-4
- [17] Haider S and Park S Y 2009 Preparation of the electrospun chitosan nanofibers and their applications to the adsorption of Cu(II) and Pb(II) ions from an aqueous solution *J. Memb. Sci.* **328** 90-6
- [18] Aoki D, Teramoto Y and Nishio Y 2007 SH-containing cellulose acetate derivatives: Preparation and characterization as a shape memory-recovery material *Biomacromolecules* **8** 3749-57
- [19] Liu C X and Bai R B 2006 Adsorptive removal of copper ions with highly porous chitosan/cellulose acetate blend hollow fiber membranes *J. Memb. Sci.* **284** 313-22
- [20] Tian Y, Wu M, Liu R, Li Y, Wang D, Tan J, Wu R and Huang Y 2011 Electrospun membrane of cellulose acetate for heavy metal ion adsorption in water treatment *Carbohydr. Polym.* **83** 743-8
- [21] Nhi T T, Minh H H, Nam T M P, Thien D B T, Hoai N T T, Phuoc T V, Thai D M, Hai N D, Toi V V and Hiep N T 2018 Optimization and characterization of electrospun polycaprolactone coated with gelatin-silver nanoparticles for wound healing application *Mater. Sci. Eng. C* (In Press)
- [22] Croisier F, Duwez A S, Jérôme C, Léonard A F, van der Werf K O, Dijkstra P J and Bennink M L 2012 Mechanical testing of electrospun PCL fibers *Acta Biomater.* **8** 218-24
- [23] 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)
- [24] Ramakrishna S, Fujihara K, Teo W, Lim T and Ma Z 2005 *An Introduction to Electrospinning and Nanofibers* (Singapore: World Scientific)

- [25] 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
- [26] Kumar J, Kim J, Lee J and Yoon H 2010 Solvent extraction of uranium(VI) and separation of vanadium(V) from sulfate solutions using Alamine 336 *J. Radioanal. Nuc. Chem.* **285** 301-8