Adsorptive removal of Ni$^{2+}$ ions in wastewater using electrospun cellulose acetate / iron-modified nanozeolite nanostructured membrane

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Abstract. Release of heavy metal contaminated wastewater is one of the major problems being encountered by many industries due to its hazardous effect on the ecosystem, specifically its negative impacts on human health. Although essential in small quantities, nickel (Ni) and other heavy metals could be very dangerous to human health when uptaken at high concentrations. In this regard, this undertaking focused on the fabrication of nanofibers of cellulose acetate (CA) with varying concentrations (0, 1.0, 1.2 and 1.4 wt%) of iron-modified nanozeolite (Fe-MNZ) through electrospinning technique for the adsorption of Ni$^{2+}$ ions in simulated wastewater. The membranes produced underwent different characterization techniques to determine the effect of Fe-MNZ addition on the nanofibers. FTIR result showed changes in the broadness of some bank peaks which signifies the interaction between CA and Fe-MNZ. SEM results showed increasing fiber diameter with increasing Fe-MNZ concentration having an 848.08 nm maximum diameter. Lastly, Freundlich isotherm and pseudo-first order kinetics govern the adsorption of the Ni$^{2+}$ ions, with the highest adsorption capacity of 7.46 mg Ni$^{2+}$ / g membrane.

1. Introduction
As humans continue to develop through the years, rapid industrialization inevitably affects the environment and poses major problems such as pollution, specifically in different bodies of water. In particular, untreated wastewater discharges from different industries and human activities such as mining and smelting, and fossil fuel combustion were some of the main causes of heavy metal contamination [1]. Heavy metal such as nickel (Ni), could be very hazardous if present in large amounts, due to high phytotoxicity and can damage fauna in the ecosystem. Also, being exposed to high quantities of Ni can cause eczema and DNA damage to humans [2]. Conventional technologies,
techniques and methods have been studied and employed for the remediation and removal of heavy metals from the wastewater. But most of the processes involving physico-chemical treatment need large amount of expensive chemicals [3] and require high energy consumption [4], which turned to be unideal and non-economical.

Apart from the disadvantages of the conventional techniques for the removal of heavy metals from water, the use of adsorptive electrospun membranes could be considered as a promising technique because of membranes’ high adsorption efficiency. Electrospun nanofibers produced exhibit desirable properties in terms of durability and high adsorption capacity [5,6]. Properties of electrospun nanofibers with regards to metal ions sorption performance can be enhanced further by functionalization and modification by the incorporation of mineral fillers [7]. In this regard, cellulose acetate (CA) has a great potential in this specific application, because aside from being economical, the presence of many functional groups in CA is a significant property, which makes its surface reactive, further results to its high adsorption capacity [8,9]. In addition to this, the incorporation of nanoparticles, specifically iron-modified nanozeolite (Fe-MNZ) to adsorptive membranes could be of great importance in the field of wastewater treatment wherein great amounts of heavy metals are needed to be removed before its discharge to the environment.

This study aimed to perform Ni$^{2+}$ ions adsorption using membrane-reinforced nanoparticles to understand more evidently the Ni$^{2+}$ heavy metal ion adsorption that happens in real industrial effluent systems. Generally, the main objective of this study was to investigate the adsorption of Ni$^{2+}$ heavy metal ions using electrospun CA reinforced with (Fe-MNZ). Specific objectives of this study were as follows: a.) to fabricate CA/Fe-MNZ nanostructured membrane using the electrospinning technique at optimized electrospinning conditions; b.) to characterize the electrospun CA/Fe-MNZ nanofibers using Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM); and lastly, c.) to determine the applicable isotherm model and kinetics for the adsorption of Ni$^{2+}$ heavy metals ions.

This research only focused on the adsorption of the Ni$^{2+}$ heavy metal ions. Adsorption experiment utilizing real samples of wastewater was not conducted. The Fe-MNZ that was used in this study was synthesized by the researchers from the Materials Science Division of the Department of Science and Technology, Philippines. For the electrospun CA/Fe-MNZ, all blends underwent characterization and were used for the adsorption experiments. Desorption and recyclability of the electrospun nanofibers were not investigated.

2. Methodology

2.1. Fabrication of the electrospun CA/Fe-MNZ nanostructured membrane

CA/Fe-MNZ nanofibers for the adsorption of Ni$^{2+}$ heavy metal ions were fabricated using the electrospinning technique. Firstly, the CA (MW = 50,000) was dissolved using 1-Methyl-2-pyrrolidinone, C$_5$H$_9$NO (NMP) as the solvent, and the resulting solution was continuously stirred using a sonicator until viscous and homogeneous solution was obtained. Four different blends were made with the following compositions (wt%) of CA/Fe-MNZ/NMP: Blend 1 – 15/0/85, Blend 2 – 14/1/85, Blend 3 – 13.8/1.2/85 and Blend 4 – 13.6/1.4/85. Upon producing four different blends of solutions, each blend was subjected to electrospinning process utilizing the following parameters: feed rate of 1.1 mL/hr, a tip-to-collector distance of 200 mm, 10 mL syringe with 17 mm diameter and 23G needle, a spinneret width of 110 mm, 25°C room temperature, and 20 kV applied voltage. Aluminum foil was used to collect the electrospun membranes.

2.2. Characterization of the electrospun CA/Fe-MNZ nanostructured membrane

Fourier Transform Infrared Spectroscopy (FTIR), which was used to determine the interaction between CA and fired Fe-MNZ based on the changes in their spectra, was conducted at the Chemistry Laboratory of Mapúa University using Perkin Elmer FTIR Spectrometer. Scanning Electron Microscopy (SEM), which was used to determine the surface morphologies of the nanofibers produced.
and to relate the results to their adsorption capability, was provided by Nanotech Analytical Services and Training Corporation (NASAT Labs).

2.3. Adsorption experiment

The Ni$^{2+}$ heavy metal ions stock solutions were prepared by the dissolution of 10 mg of NiCl$_2$·6H$_2$O in 1 L volumetric flask using ultrapure water producing 10 ppm (mg of Ni$^{2+}$/L of solution) heavy metal ion stock solution. For the adsorption experiment, four (4) 1 L beakers were filled with 10 ppm prepared solution containing Ni$^{2+}$. Then for each beaker, nanofibers produced using different blends were placed: M1 (membrane produced using Blend 1) to beaker 1; similar thing was done to other blends (M2, M3, M4). The solutions with their respective membranes were allowed to be in contact and stirred (400 rpm) for 2 hours. In that duration of time (2 hours), 15 mL aliquot of the solution from each beaker was obtained for every 24 minutes interval starting from time equals zero. Each 15 mL aliquot was diluted to 140 mL using ultrapure water, and then filtered using size 42 Whatman filter paper. After filtration, each solution was digested and the pH of each resulting solution was adjusted to 5.5 using 0.1 M HCl and 0.1 M NaOH and the pH was verified using a pH meter. Three 10 mL samples (triplicates) were obtained from the 35 mL digested solution and subjected to Perkin Elmer Optima 8000 Inductively Coupled Plasma – Optical Emission Spectrometer (ICP-OES) to determine the concentration of the solution after each adsorption time.

The concentration obtained from the ICP-OES were adjusted considering the dilution factor used and the adsorption capacities for each adsorption time were calculated and a graph was generated by plotting the adsorption capacity versus time for each heavy metal, for each membrane blend. From the graph generated, the equilibrium adsorption capacities were determined and were fitted to Langmuir and Freundlich adsorption isotherms, and Pseudo-first-order and pseudo-second-order kinetic models.

3. Results and discussion

3.1. CA/Fe-MNZ nanostructured membrane characterization

3.1.1. Fourier-transform infrared spectroscopy (FTIR). Different CA membrane blends (e.g., M1, M2, M3 and M4) were electrospun with varying concentrations of Fe-MNZ. FTIR analysis for each membrane blend was conducted to determine the effect of the addition of Fe-MNZ on CA. Changes in band peaks from the FTIR result signifies the interaction between CA and Fe-MNZ. Figure 1 shows the FTIR result for the different blends of the electrospun nanofiber membranes. Based on the results of FTIR, considering the diagnostic region of the IR spectra presented, a broad signal can be observed between 3200 cm$^{-1}$ and 3600 cm$^{-1}$. This is the characteristic signal for the O–H (hydroxyl group) present in pure CA. The changes in the broadness in the said range of frequency for O–H correspond to the weakening of the bond between O and H of O–H due to hydrogen bonding present. This can be observed for all the membrane blends upon the addition of Fe-MNZ. Increasing the concentration of Fe-MNZ made the signal broader since the iron (Fe) in Fe-MNZ is present as akageneite/ferric oxyhydroxide ($\beta$-FeOOH) [10]. The presence of O–H from $\beta$-FeOOH increases the species participating in hydrogen bonding which made broader signals in the range being considered. In reference to pure CA (M1), it is evident that the signal became weaker for M2 and M3. This is because of the low dipole moment present. The amount of O–H from pure CA was compensated by the amount of O–H from $\beta$-FeOOH, wherein hydrogen bonding governs preventing the oscillation of the dipole moment. Thus, producing a weak signal. For M4, it can be seen that it has the strongest signal for O–H. Broad signal can also be observed but its strong signal can be attributed to the presence of more O–H which does not participate in hydrogen bonding due the increase in concentration of the Fe-MNZ. Moreover, a distinct change in band peak between 1700 cm$^{-1}$ and 1750 cm$^{-1}$ can be seen. At this range of frequency, it is expected to be an ester group from pure CA (M1). Slight weakening of the signal can be observed for M2, M3 and M4 due to hydrogen bonding between the O–H of $\beta$-FeOOH and O from the C=O of the ester group of pure CA (M1), which further resulted to a low dipole moment for
the ester group. Hence, resulting to a weaker signal. This is also the reason for the decrease in the signal between 1250 cm\(^{-1}\) and 1350 cm\(^{-1}\) for the C–O in the ester group. For the band peak changes between 1000 cm\(^{-1}\) to 1100 cm\(^{-1}\), this refers to the interaction in the C–O bond present in between the repeating units of pure CA.

![FTIR result for electrospun CA nanofibers with varying concentrations of Fe-MNZ.](image)

**Figure 1.** FTIR result for electrospun CA nanofibers with varying concentrations of Fe-MNZ.

3.1.2. **Scanning electron microscopy (SEM).** Morphological structure is very important for electrospun nanofibers since it greatly affects the properties of the said nanofibers. In this study, each membrane blend was subjected to SEM analysis to determine the effect of the addition of Fe-MNZ on the pure CA, specifically with regards to the fiber diameters of the nanofibers that were produced. Based on the result of SEM (Figure 2), it can be visibly observed that the fiber diameter increases with Fe-MNZ concentration. This means that the incorporation of Fe-MNZ nanozeolite could greatly affect the fiber diameter of the nanofibers produced. With regards to the solution preparation before electrospinning, it was observed that the viscosity of the solution increases and Fe-MNZ are not easily dispersed evenly in the solution at higher amounts of Fe-MNZ. The more viscous the solution is, the larger the fiber that will be produced upon electrospinning. Similarly, this was also observed in the study of Ji et al, wherein the membrane produced via wet spinning method exhibited a decrease in pore size upon the incorporation of nanozeolite [11]. Relating their result in this study, the pore size could be regarded as the spaces between the intertwined nanofibers, since there is the addition of Fe-MNZ, the fiber diameters increases. Thus, resulting in the decrease in the spaces in between the nanofibers or the pore size of the fabricated membrane.

In addition, statistical analysis using one-way ANOVA, considering the increasing fiber diameter with increasing Fe-MNZ concentration, was performed. The \( p \)-value (3.59x10\(^{-5}\)) was less than the significance level \( \alpha \) (0.05) meaning the null hypothesis, which was the fiber diameters for all the membrane blends were equal or insignificantly different with respect to the Fe-MNZ concentration, was rejected. In this case, the differences in the fiber diameters obtained can be considered to be statistically significant. Hence, the concentration of Fe-MNZ on the nanofibers has a significant effect on the fiber diameters.
3.2. Adsorption isotherm and kinetics

Since this study was about the development of a new combination of materials, CA and Fe-MNZ, for the adsorption of Ni\(^{2+}\) heavy metals, adsorption isotherm and kinetic modelling are of great importance. The adsorption isotherm is needed to determine the governing interaction between the adsorbate and the adsorbent. The adsorption capacities of the different membrane blends were calculated using the results from the ICP-OES. It can be observed from Figure 3(a) that for all the blends, equilibrium was attained after 95 minutes. But it was distinct that starting from time equals zero, the adsorption capacities abruptly increased for M3 and M4 having more amounts of Fe-MNZ compared to M1 and M2. The presence of Fe-MNZ affected the adsorption of Ni\(^{2+}\) ions on the nanofibers produced. CA was further functionalized by the addition of Fe-MNZ resulting to the abrupt increase in the adsorption capacity as seen for M3 and M4.

Furthermore, M3 had exhibited the best fit for the isotherm and kinetics of Ni\(^{2+}\) adsorption among the other blends. Figures 3(b) and 3(c) show that Freundlich isotherm and pseudo-first order kinetics describe the adsorption of Ni\(^{2+}\) ions on the said membrane blend. In this regard, multilayer adsorption of Ni\(^{2+}\) occurred on the heterogeneous surface of the electrospun nanofibers with Fe-MNZ. Also, pseudo-first order kinetics suggests that there was only physical adsorption involved wherein, mainly the adsorption was due to the intermolecular forces present between the heavy metal and the electrospun nanofiber.

| Membrane Blend | Fiber Diameter | Magnification |
|----------------|---------------|---------------|
| M1             | 568.55 nm     | 5000x         |
| M2             | 608.17 nm     | 10000x        |
| M3             | 745.08 nm     | 20000x        |
| M4             | 848.09 nm     |               |

**Figure 2.** SEM images of the electrospun nanofibers of CA with varying amounts of Fe-MNZ at 5000x, 10000x and 20000x magnifications.
4. Conclusion
Upon the performance of the study, it can be said that the objectives are well met and satisfied. Electrospun CA/Fe-MNZ nanofibers were successfully produced under optimized conditions. Characterizations of the nanofibers were done to determine the effect of the Fe-MNZ addition to the pure CA. FTIR results showed the interaction between CA and Fe-MNZ through the changes in the strength of the signals at different frequencies. SEM images showed that incorporating Fe-MNZ in CA could result to the increase in the fiber diameter of the electrospun nanofibers. This was further supported by statistical analysis wherein the increasing fiber diameters with increasing Fe-MNZ concentration were found to be statistically significant. Moreover, Freundlich isotherms also governed the adsorption process of the Ni$^{2+}$ under pseudo-first order kinetics.

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References
[1] Dong C, Zhang F, Pang Z and Yang G 2016 Efficient and selective adsorption of multi-metal ions using sulfonated cellulose as adsorbent Carbohydr. Polym. 151 230–6
[2] Liu L, Luo X-B, Ding L and Luo S-L 2019 Application of Nanotechnology in the Removal of Heavy Metal From Water (Elsevier Inc.)
[3] Chiang Y W, Ghyselbrecht K, Santos R M, Martens J A, Swennen R, Cappuyns V and Meesschaert B 2012 Adsorption of multi-heavy metals onto water treatment residuals: Sorption capacities and applications Chem. Eng. J. 200–202 405–15
[4] Hossain M A, Ngo H H, Guo W S, Nghiem L D, Hai F I, Vigneswaran S and Nguyen T V. 2014 Competitive adsorption of metals on cabbage waste from multi-metal solutions Bioresour. Technol. 160 79–88
[5] Koushkbaghi S, Zakialamndari A, Pishnamazi M, Ramandi H F, Aliabadi M and Irani M 2018
Aminated-Fe3O4 nanoparticles filled chitosan/PVA/PES dual layers nanofibrous membrane for the removal of Cr(VI) and Pb(II) ions from aqueous solutions in adsorption and membrane processes Chem. Eng. J. 337 169–82

[6] Ge J C and Choi N J 2019 Performance of electrospun nanofibrous membranes for trapping of BTX aromatic hydrocarbons and heavy metal ions: Mechanisms, isotherms and kinetics J. Clean. Prod. 217 388–97

[7] Deng J, Liu Y, Liu S, Zeng G, Tan X, Huang B, Tang X, Wang S, Hua Q and Yan Z 2017 Competitive adsorption of Pb(II), Cd(II) and Cu(II) onto chitosan-pyromellitic dianhydride modified biochar J. Colloid Interface Sci. 506 355–64

[8] Adam M R, Hubadillah S K, Esham M I M, Othman M H D, Rahman M A, Ismail A F and Jaafar J 2018 Adsorptive Membranes for Heavy Metals Removal From Water (Elsevier Inc.)

[9] Liu R and Lian B 2019 Non-competitive and competitive adsorption of Cd 2+, Ni 2+ , and Cu 2+ by biogenic vaterite Sci. Total Environ. 659 122–30

[10] Wang T, Zhang P, Ni S, Huang Y, Qiu K, Li J, Zhang M, Yin H and Li J 2019 Synthesis of nano-akaganeite powder and its chromium adsorption behavior Ferroelectrics 540 184–92

[11] Ji F, Li C, Tang B, Xu J, Lu G and Liu P 2012 Preparation of cellulose acetate/zeolite composite fiber and its adsorption behavior for heavy metal ions in aqueous solution Chem. Eng. J. 209 325–33