Electrospun PLA/α-Fe_2O_3 Chitosan Fiber Composite for Removal of Selected Heavy Metals in Aqueous Solution

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ABSTRACT— ***Heavy metals released into the environment pose significant threat to the environment and public health because of their toxicity and persistence. Thus, the contamination of wastewaters and surface waters by toxic heavy metals became a worldwide environmental problem. Recently, extensive efforts have been made on remediation of soils and wastewater polluted by toxic metals; several approaches for remediation of aqueous systems contaminated with heavy metals have also been reported. In addition, different nanomaterials with specific morphology and structure are widely explored as adsorbents or nanocatalysts to remove heavy metal ions, and organic dyes. In this study, electrospun PLA/modified α-Fe_2O_3 chitosan fiber composite was made by impregnating α-Fe_2O_3 into low viscous chitosan, and adding the mixture into dissolved polylactic acid (PLA). Preliminary characterization of the electrospun fiber composite was done using FTIR and SEM. The electrospun fiber composites were soaked into aqueous solutions of Ni^{2+} and Pb^{2+} at 25 ppm and 75 ppm concentration and their capacity to adsorb heavy metal cations was measured using ICP-MS. The fibers produced showed both the chemical characteristics of chitosan and PLA with diameter sizes ranging from 0.578 µm to 1.263 µm. Further, they manifested high adsorption efficiency for both Ni^{2+} and Pb^{2+} at low and high concentration, but not showing significant differences in the adsorption efficiency. Results also show that the fibers were produced by electrospinning the PLA/ modified α-Fe_2O_3 chitosan composite blend. The obtained fibers efficiently adsorbed Ni^{2+} and Pb^{2+}. However, the addition of α-Fe2O3 showed no significant contribution to the adsorption of heavy metals.***

Keywords— α-Fe_2O_3, chitosan, electrospinning, nanosorbent

1. INTRODUCTION

One of the worldwide environmental issues and problems we encounter today is the release of heavy metals into the environment which pose significant threat to public health because of their toxicity and persistence. The contamination of wastewaters and surface waters is brought about by rampant use of heavy metals. These toxic metal ions commonly exist in process waste streams from mining operations, metal plating facilities, power generation facilities, electronic device manufacturing units, and tanneries.

Industrial effluent streams can introduce heavy metal contamination into aqueous systems. Heavy metals (such as mercury, lead, cadmium, arsenic, copper, and nickel) can then migrate to any plant or animal life which uses this water. Fish and other aquatic life are obviously the most affected. Since heavy metals do not break down, they will bio-accumulate up the food chain.

The use of heavy metals in industry has lead to widespread environmental contamination. In this study, two of the heavy metals, lead and nickel, were selected on account of their toxicity and ubiquity. Moreover, they are known to remain stable in the aquatic environment (Fernandez, et al., 1992; Ayas & Kolankaya, 1996; Heiny & Tate, 1997; Samanta, et al., 2005; and Singh & Singh, 2006 as cited by Zafer, Guler, Sedat & Murat, 2007). Lead is a heavy metal that affects the functioning of the blood, liver, kidney and brains of human beings. Lead is a component of most industrial and domestic paints. Nickel which causes gastrointestinal irritation and lung cancer is often obtained from

Ni/Fe storage batteries. Also, it is used to produce ferrous steel cutlery (Greenwood & Earnshaw, 1993 by as cited Abia & Asuquo, 2006).

Recently, considerable efforts have been made on remediation of soils and wastewater polluted by toxic metals. Moreover, several approaches for remediation of aqueous systems contaminated with heavy metals have been reported. The use of adsorbent is considered as an effective and economical method for the removal of pollutants from wastewater due to easy handling.

With the development of nanoscience and nanotechnology, many of the new nanosorbents have been created for current water-treatment problems. Different nanomaterials with specific morphology and structure have been widely explored as adsorbents or nanocatalysts. The unique characteristics of enhanced huge planar surfaces of nanosorbents can enable and increase interface reactions with pollutants in environment (Wang & Chen, 2012).

Several studies on nanomaterials (NMs) have demonstrated that they are cost-effective, efficient and environment-friendly alternative to existing treatment materials from the standpoints of both resource conservation and environmental remediation (Friedrich, et al., 1998; Dimitrov, 2006; and Dastjerdi & Montazer, 2010 as cited by Xu, et al., 2012). Nanotechnology holds out the promise of immense improvements in manufacturing technologies, electronics, telecommunications, health and even environmental remediation (Gross, 2001; Kim et al., 2005; and Moore, 2006 as cited by Xu, et al., 2012). It involves the production and utilization of a diverse array of NMs, which include structures and devices with sizes ranging from 1 to 100 nm, and display unique properties not found in bulk-sized materials (Stone, et al., 2010; Wang, et al., 2010 as cited by Xu, et al., 2012).

In this study, α-Fe_2O_3 was impregnated into low viscosity chitosan, and blended with PLA using electrospinning apparatus to produce composite fiber. The obtained composite fiber was used for heavy metal residue removal of Pb^{2+} and Ni^{2+} in aqueous solutions.

2. METHODOLOGY

2.1 Materials

PLA (*polylactic acid*) in commercial grade with a molecular weight of 160,000 g / mole, low viscous chitosan from crab shell (≤12% loss on drying), α-Fe_2O_3 (97% trace metals basis), dichloromethane (>99.9% purity, volatile and high toxicity), and methanol (95% purity, volatile) were purchased from Sigma Aldrich Corporation.

An optimum power supply of 30kV was employed to charge the polymer solution. Ordinary aluminum foil was used to collect the nanofibers.

$Pb(NO_3)_2$ and $Ni(NO_3)_2$ in analytical grade reagents were used for the removal of heavy metals in aqueous solution.

2.2 Modification of Chitosan with α-Fe_2O_3

Five hundred milligrams of chitosan was dispersed in five milliliter (5mL) methanol and mixed with different amounts of α-Fe_2O_3 (0.25g, 0.50g, and 0.75g). Then, it was heated in a boiling tube, and stirred using auto-sonicator repeatedly until the mixture became homogenous.

2.3 Preparation of PLA/Modified α-Fe_2O_3 Chitosan Blend

Two grams of PLA was weighed using analytical balance, and then dissolved in fifteen milliliter (15mL) of dichloromethane (CH_2Cl_2). The PLA pellets were stirred until completely dissolved. Modified α-Fe_2O_3 chitosan solution was added directly to the PLA solution. The solution was stirred using auto-sonicator until homogenous solution was obtained.

2.4 Electrospinning of PLA/Modified α-Fe_2O_3 Chitosan Blend

The fully dissolved solution was drawn into the syringe; then, the needle was attached to the set-up. Air from the needle was removed, and the polymer solution was pushed manually through the syringe until it emerged at the end of the needle. The solution was electrospun at room temperature.

When droplets of the polymers solution appeared at the end of the needle, the 30 kV power supply was turned on, and the polymer solution was pushed for slight pressure. This electrospinning process was continued until desired collection was established, and solid products samples were visible in the collector plate covered by aluminum foil.

2.5 Optimization Parameters

Parameters were varied based on the resulting range of fiber diameter and fiber uniformity. Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscope (SEM) were used to interpret the outcome of electrospinning.

2.6 Evaluation of the Fibers

The fibers obtained after electrospinning were cut approximately 1cm x 1cm. The fiber diameter and fiber consistency were determined by randomly selecting three representative fibers from each sample at different locations. For sample selection, samples with abnormal structures were avoided. Scanning Electron Microscope (SEM) was used to examine the morphology of the fibers, while the different functional groups present in the fiber were analyzed using Fourier Transform Infrared Spectrophotometer (FTIR).

2.7 Preparation of Aqueous Solutions Containing Heavy Metal Ions

The nitrate salts of Pb^{2+} and Ni^{2+} in analytical grade were used without further purification. Stock solutions of 1000 ppm of each nitrate salts were prepared. From 1000 ppm stock solutions of nitrate salts, 150 ppm and 50 ppm concentrations of Ni^{2+} and Pb^{2+} nitrate solutions were prepared.

To produce a solution with concentration of 25 ppm Pb^{2+} and 25 ppm Ni^{2+}, twenty five milliliter (25 mL) of 50 ppm Ni^{2+} and twenty five milliliter (25 mL) of 50 ppm Pb^{2+} solutions were mixed. Another test solution was prepared by mixing twenty five milliliter (25 mL) of 150 ppm Ni^{2+} and twenty five milliliter (25 mL) of 150 ppm Pb^{2+} solutions to produce a solution with concentration of 75 ppm Pb^{2+} and 75 ppm Ni^{2+}.

2.8 Batch Removal of Heavy Metal Ions from Aqueous Solutions

The adsorption of heavy metal by PLA/modified α-Fe_2O_3 chitosan fiber composite was studied through a batch operation chosen due to its simplicity at room temperature. 0.5 g of each fiber was suspended in a one hundred milliliter (100 mL) test solution containing 25 ppm Pb^{2+} and 25 ppm Ni^{2+}. The same procedure was applied for a test solution containing one hundred milliliter (100 mL) of 75 ppm concentrations of Pb^{2+} and Ni^{2+}. The samples were drenched for 24 hr at room temperature. After 24 hr, the soaked fibers were pulled out from the solutions, after which the solutions were stirred for 90 min at 150 rpm. After a time period of agitation, the suspensions were centrifuged at 2500 rpm for 5 min. The supernatants were collected and stored in the refrigerator until the day of analysis.

The supernatants were analyzed for the decrease in Pb^{2+} and Ni^{2+} concentrations through Inductively Coupled Plasma-Mass Spectrometer (ICP-MS). The effects of the experimental parameters on the adsorption capacity of PLA/modified α-Fe_2O_3 chitosan blend in the experiments were also investigated. The percent of removed metal ions by the adsorbent was calculated by the following equation:

$$R\ (\%) = \left[\frac{Co - Ct}{Co}\right] x\ 100$$

where R is the removal efficiency of the metals ions, C_0 is the initial concentration of the metal ions in ppm, and C_t is the concentration of the metal ions at any time in ppm.

3. RESULTS AND DISCUSSION

3.1 Electrospun PLA/Modified α-Fe_2O_3 Chitosan Blend

Polylactic acid and α-Fe_2O_3-modified chitosan were blended together using needle type electrospinning apparatus. Fibers were successfully produced at optimum electrospinning parameters such as voltage required (30 kV), needle tip size (21 gauge), and tip-to-collector distance (20 in.). The produced fiber from PLA/chitosan blend alone was white in color and had fine texture, while the fibers produced from PLA/modified α-Fe_2O_3 chitosan blend had gray to black color with fine texture. Blended polymer solution was employed to improve the properties of the polymers since its potential

application is for heavy metal residue removal in aqueous solution. Each of the blended polymer solution contained varying amount of α-Fe_2O_3 to assess the effect of α-Fe_2O_3 concentration in removing heavy metal residues. The amount of α-Fe_2O_3 in each blend varied from 0 gram, 0.25 gram, 0.50 gram, and 0.75 gram, respectively. The potential of PLA/modified α-Fe_2O_3 chitosan fiber composites in removing heavy metal residues was tested by soaking the fibers in 25 ppm and 75 ppm aqueous solutions of nickel (II) nitrate and lead (II) nitrate.

3.2 Fourier Transform Infrared Spectroscopy Analyses

The FTIR spectrum (Figure 1) of the fiber produced from PLA/modified α-Fe_2O_3 chitosan blend shows the characteristic bands that belong mainly to PLA, and intersecting with the chitosan. It can be observed that pure chitosan had peaks on 3357 cm^{-1} (-OH stretching), 2877 cm^{-1} (-CH_2 asymmetric stretching), 1645 cm^{-1} (-NH bending), and 1027 cm^{-1} (-CN bending) which represented the functional groups of the chitosan. PLA/modified α-Fe_2O_3 chitosan blends had characteristic peaks with vibrational frequencies of 1749 cm^{-1} (C=O stretching), 1455 cm^{-1} (-CH_3 asymmetric stretching), and 1180 cm^{-1} (C-O-C asymmetric stretching in ester).

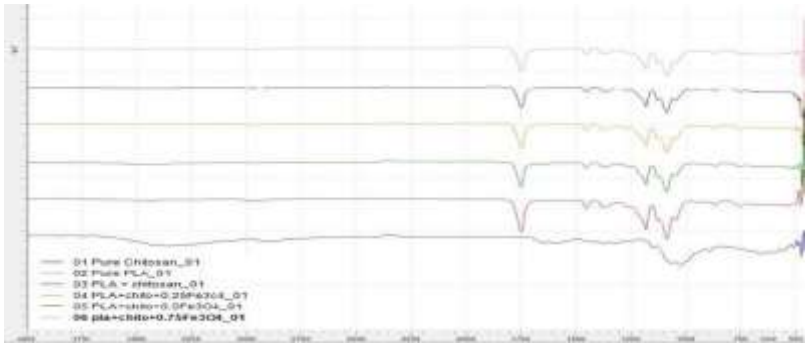


Figure 1. The FTIR spectra of PLA/modified α-Fe_2O_3(0.75g) chitosan (top 1st), PLA/modified α-Fe_2O_3(0.50g) chitosan (2nd), PLA/modified α-Fe_2O_3(0.25g) chitosan (3rd), PLA/Chitosan (4th), pure PLA (5th), and pure chitosan (bottom last).

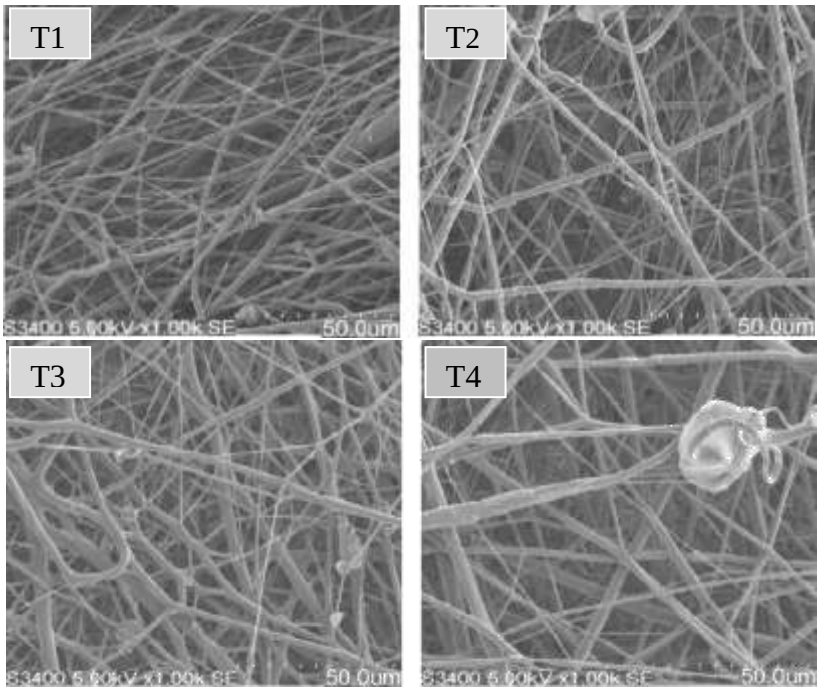


Figure 2. Scanning Electron Microscope Images of Electrospun Fibers: (T1) PLA/Chitosan, (T2) PLA/modified α-Fe_2O_3 (0.25g) chitosan, (T3) PLA/modified α-Fe_2O_3(0.50g) chitosan, and (T4) PLA/modified α-Fe_2O_3(0.75g) chitosan.

3.3 Scanning Electron Microscopy Analyses

The SEM images of PLA/modified α-Fe_2O_3 chitosan fiber composite are shown in Figure 2. The fibers were analyzed by SEM using 5.00 kV supply and 1000 magnification in all three randomly chosen areas of sample. Thirty six measurements (twelve measurements per area) were made for each fiber. The diameter sizes of the fiber ranged from 0.578 μm to 1.263 μm. The smaller sizes of the fibers were suitable for the removal of heavy metals because they could influence high adsorption capacity for heavy metal ions indicating their unique morphology which could bring much larger surface area per unit mass, and high effectivity for the removal of heavy metal ions from aqueous solutions (Min, et al., 2011).

The mean average diameter size of the electrospun fibers is presented on Table 1. As can be seen, the fiber diameter decreased as the amount of α-Fe_2O_3 in the blend increased. According to Liu, Luo, & Zhou (2013), the size of the α-Fe_2O_3 nanoparticles is far smaller than the macropores of the wet polymer solution. Magnetic nanoparticles could rotate freely, and randomly align within the pores at wet state. When they are fixed and dried in the air with the supply of voltage, the composite fibers shrink in the longitudinal direction resulting in the decrease in size of the fiber in dry state.

Table 1. Mean average diameter size and measure of significance of the electrospun fibers: (T1) PLA/chitosan, (T2) PLA/modified α-Fe_2O_3 (0.25g) chitosan, (T3) PLA/modified α-Fe_2O_3 (0.50g) chitosan, and (T4) PLA/modified α-Fe_2O_3 (0.75g) chitosan.

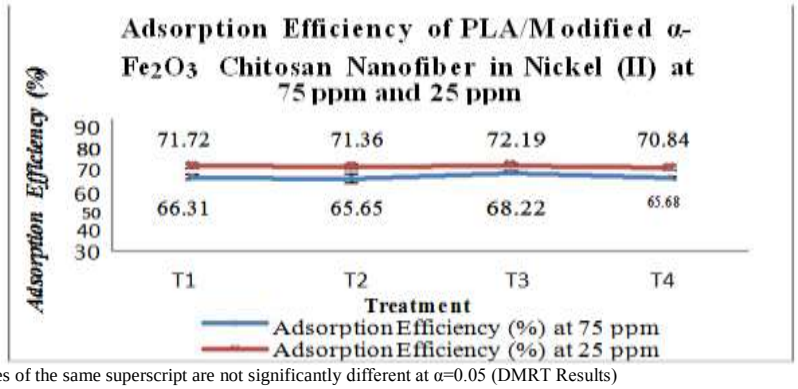
Treatment	Average Diameter (μm)
T1	1.263^{a}±1.408
T2	0.955^{b}±0.986
T3	0.659^{b}±0.787
T4	0.578^{b}±0.776

*Values of the same superscript are not significantly different at α=0.05 (DMRT Results)

Table 1 further reveals that T1 was significantly different from T2, T3, and T4. However, T2, T3, and T4 were not significantly different with each other. This data suggests that the addition of α-Fe_2O_3 significantly reduced the diameter size of the fibers. Although the size of the fiber decreased with increased concentration of α-Fe_2O_3, the decrease in size of the fiber was not significantly different with increase in the amount of α-Fe_2O_3.

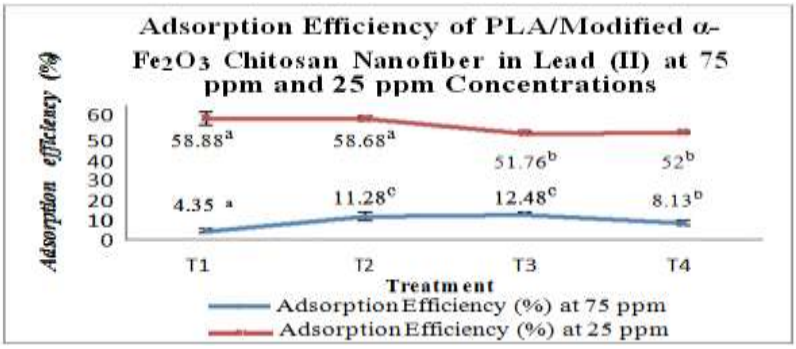
3.4 Inductively Coupled Plasma – Mass Spectrophotometer Analyses (ICP-MS)

The analyses of the adsorption efficiency of the fibers in Ni^{2+} and Pb^{2+} using ICP-MS are revealed in Figures 3 and 4. At 75 ppm concentration of Ni^{2+} (Figure 3), it can be observed that T1 had the highest adsorption efficiency followed by T3, while T2 had the lowest adsorption efficiency. At 25 ppm concentration of Ni^{2+}, T3 had the highest adsorption efficiency followed by T1, while T4 had the lowest adsorption efficiency. In both high and low concentrations of Ni^{2+}, no significant differences manifested among the treatments which means the addition of αFe_2O_3 had no effect on the adsorption of Ni^{2+}in fiber blends.



*Values of the same superscript are not significantly different at α=0.05 (DMRT Results)

Figure 3. Adsorption Efficiency of Electrospun Fibers in Ni^{2+} at 75 ppm and 25 ppm Concentrations: (T1) PLA/chitosan, (T2) PLA/modified α-Fe_2O_3 (0.25g) chitosan, (T3) PLA/modified α-Fe_2O_3(0.50g) chitosan, and (T4) PLA/modified α-Fe_2O_3(0.75g) chitosan.



*Values of the same superscript are not significantly different at α=0.05 (DMRT Results)

Figure 4. Adsorption Efficiency of Electrospun Fibers in Pb^{2+} at 75 ppm and 25 ppm Concentrations: (T1) PLA/chitosan, (T2) PLA/modified α-Fe2O3 (0.25g) chitosan, (T3) PLA/modified α-Fe2O3(0.50g) chitosan, and (T4) PLA/modified α-Fe2O3(0.75g) chitosan.

At 75 ppm of Pb^{2+}, T3 had the highest adsorption efficiency followed by T2, while T1 had the lowest adsorption efficiency. Further, the adsorption efficiency of both T2 and T3 were not significantly different, while T1 was significantly different with T2, T3 and T4. In this graph (Figure 4), the presence of α-Fe_2O_3 showed slight difference in adsorption efficiency of fibers to Pb^{2+}. At 25 ppm concentration of Pb^{2+}, T1 showed the highest adsorption efficiency followed by T2, while T3 had the lowest adsorption efficiency. Moreover, it can be noted from the plot that the adsorption efficiency of both T1 and T2 were not significantly different, but was significantly different in both T3and T4.

In both low and high concentrations of Pb^{2+}, the adsorption efficiency of the fibers varied with the presence of α-Fe_2O_3. In 75 ppm of Pb^{2+}, the fibers with α-Fe_2O_3 adsorbed higher concentration of Pb^{2+}, but in 25 ppm of Pb^{2+} only T1(PLA/chitosan) and T2 (PLA/chitosan /0.25g α-Fe_2O_3) showed high adsorption efficiency.

The adsorption efficiency of the fiber composites as shown in Figures 3 and 4 was higher at lower concentrations of Ni^{2+} and Pb^{2+} (25 ppm) in the aqueous solution. This observation was made to account for the saturation of the adsorbent fibers at higher concentration (75 ppm) of heavy metals. Since the addition of α-Fe_2O_3 in the fibers did not show significant contribution in adsorbing the Pb^{2+} and Ni^{2+}, the adsorption efficiency can be due to the added chitosan, which was also present in the produced fibers. Chitosan was found to be effective in removing anionic dyes and cationic heavy metals from wastewater (Ngah, Teong, & Hanafiah, 2011) because the amine groups of chitosan can bind with the metal cations (Guibal, 2004 as cited by Sewvandi & Adikary, 2013).

It is also evident in Figures 3 and 4 that the adsorption efficiency of the produced fibers on Ni^{2+} was higher than the adsorption efficiency on Pb^{2+} in both high and low concentration of heavy metals. This was due to the competition of the metals in binding with the adsorbent chitosan since Pb^{2+} and Ni^{2+} were in the same aqueous solution. Nickel (II) ion was adsorbed with higher percentage removal than lead (II) ion. This may be explained by considering the ionic radii of the two metals: Ni^{2+} (0.72Å) and Pb^{2+} (1.20Å). Since Ni^{2+} ions had a smaller ionic radius, it was possible that Ni^{2+} ions diffused through the adsorbent pores faster than the bulkier Pb^{2+} ions (Abia & Asuquo, 2006). Moreover, as cited by Abia and Asuquo (2006), Atkinson et al., (1998) stated that during sorption of metal ions, the ions of smaller ionic radii tend to move faster to potential adsorption sites.

4. CONCLUSION

Based on the results of this study, the α-Fe_2O_3 was successfully incorporated into a low viscous chitosan blended with PLA using electrospinning process. Fibers with diameter sizes ranging from 0.578 µm-1.263 µm were produced. The fibers obtained were efficient in adsorbing Ni^{2+} and Pb^{2+} in both high (75ppm) and low (25 ppm) heavy metal concentrations. However, the addition of α-Fe_2O_3 in the fibers did not show contribution and significant difference in removing Ni^{2+} and Pb^{2+} in both high and low concentrations of heavy metals.

5. ACKNOWLEDGMENT

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