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Fabrication and characterization of a boehmite nanoparticle impregnated electrospun fiber membrane for removal of metal ions

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Abstract:

The fabrication of a composite electrospun fiber membrane with sorptive characteristics intended for removal of heavy metals was investigated. The electrospun fiber membrane was impregnated with nano-boehmite particles. The latter had been selected to increase surface area of the active component. Cd (II) was chosen as the challenge bivalent cation. The sorption capacity of the nano-boehmite was studied as a function of pH and time. Electrospinning was used to prepare the composite submicron fiber membrane impregnated with boehmite nanoparticles. The later was blended with the polymer to produce a homogenous mixture before electrospinning. Two polymers, the hydrophobic /PCL/ and hydrophilic /Nylon-6/, were chosen to serve as the support for the boehmite. The nanoparticles and resulting composite membranes were characterized using SEM, TEM, and XRD techniques. XRD data confirmed the presence of nano-boehmite particles in the nanofibers membrane. The membranes so prepared were challenged with aqueous solutions of Cd in batch isotherm tests. Atomic absorption spectroscopy results show sorption of Cd (II) by boehmite impregnated electospun membrane was possible and a capacity of 0.20 mg/g was achieved.

Key words: Submicron fibers, Boehmite, Nanoparticles, Electrospinning, Membrane, Adsorption.

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Introduction

The contamination of water by toxic heavy metals is a world-wide environmental problem. Many industrial wastewater streams (e.g. metal working, semiconductor and copper industries, and mine water) contain such metals which must be removed prior to water discharge or water recycling [1-3]. The most commonly applied physico-chemical treatment methods are: (i) precipitation as hydroxides, carbonates or sulfides and subsequent liquid-solids separation by gravity settling, flotation or filtration, (ii) sorption (adsorption, ion exchange), (iii) membrane processes, (iv) electrolytic recovery and, (vi) liquid–liquid extraction. The adsorption process is arguably one of the more popular methods for the removal of heavy metal ions such as arsenic, zinc, cadmium, and lead [4-6].

Discharges containing cadmium are strictly controlled due to the highly toxic nature of this element and its tendency to accumulate in the tissues of living organisms. The harmful effects of cadmium include a number of chronic and acute disorders such as renal damage, emphysema, hypertension, and testicular atropy. The drinking water guideline value recommended by WHO (World Health Organization) is 0.005 mg/L. Waters with low concentrations (less that 5mg/L) of cadmium are difficult to treat economically using the existing methodologies [7,8].

It is well known that hydrated alumina or alumina hydroxide such as boehmite (AlOOH) and perhaps to a lesser extent iron compounds, which are widely used in ceramic materials, can be used in water applications [9]. However, the nano-size form of this alumina is anticipated to be more catalytically active than it’s presently more commonly used forms and if indeed sorption is the key mechanism, then the substantial increase in surface area of the nano form would increase capacities very significantly. There is therefore scope for development of such nano-boehmite materials for sorption of pollutants and in terms of an application platform could mean fabrication of affinity membranes. Besides metal ions, such membranes can also possibly attract and retain viruses, other macromolecules, and ions by electrostatic forces onto the material’s surface. While not necessarily for environmental applications, various methods have been reported for the fabrication of boehmite nanoparticles and nanofibers [10-12].

Electrospinning has been used as an efficient technique for preparing polymer fibers with diameters ranging from tens of nanometers to few micrometers. Since past few years various polymers have been successfully electrospun into ultra-thin fibers from their solvent solution and some in melt form [13]. This method is based on electrostatic surface charging of a polymer solution droplet, and drawing a jet moving at a high speed toward a grounded stationary or rotating surface. The highly extensional flow results in ultrahigh draw ratios, which lead to the formation of a continuous submicron / nanofiber. Recently, an overview of research activity on development of submicron fibers, fundamental understanding of electrospinning process, the properties and applications of electrospun fiber materials has been reported by Subbiah et al [14]. Thandavamoorthy et al., reported a novel and interesting phenomenon of self-assembly in the electrospinning of polyurethane nanofibers. The electrospun polyurethane nanofibers self-assemble into unique honeycomb patterns on the collector surface, which is important for enhanced filtration capability [15]. The electrospinning method has recently been adapted and further developed to enable synthesis of ceramics and organic-inorganic hybrid/composite fibers [16, 17]. Such composite eletrospun nanofibers membranes have shown significantly improved efficiency in membrane filter applications [18]. In a recent study, Son et al., (2006) have reported the antimicrobial application of electrospun cellulose acetate nanofibers containing Ag nanoparticles on their surface [19].

This paper reports the fabrication and characterization of submicron fiber membranes impregnated with boehmite nanoparticles using the electrospinning method. The polymer nanofibers serve as a carrier for the reactive boehmite nanoparticles. These organic-inorganic hybrid electrospun fibers were then used to study sorption of Cd (II) ions. The electrospinning process was selected for fabrication of the nanocomposite membrane because it can (i) generate ultra-fine fibers consistently and also (ii) it is feasible to produce submicron fibers impregnated with different nanoparticles in large quantities. The method also allows (i) retention of electrostatic charges and, (ii) generation of highly porous support as a carrier for reactive nanoparticles.

Materials and Methods:

Materials:

The boehmite (AlOOH) nano-powder was purchased from Argonide Corporation, Florida (USA). These nano-powders were of fiber like dimensions, having particle diameter 2 - 4 nm and length ranging from 50 to 100 nm. Nylon 6 polymer, polycaprolactone (PCL, MW = 80,000), hexafluoro-2-propanol (HFIP, 99%), chloroform (99.8%), methanol (99.9%), and cadmium nitrate tetra-hydrate solution (1000 mg/L) were purchased from various suppliers and used as received. Deionized water was used in all the experiments. Contact between the electrospun fibers and cadmium solution was conducted in acid-washed 25 ml glass vials.

Method:

Electro-spinning

Solutions of 8 wt% of Nylon-6 in HFIP, and PCL in chloroform and methanol (3:1) were prepared at room temperature (~24 ^{o}C). The boehmite nano-particles were blended into the above polymer solutions with constant stirring. The polymer to nano-particle weight ratio was maintained at 1:1 in both polymer systems. A polymer nano-particle blend was then loaded into a 3 ml plastic syringe connected with a 0.2 mm diameter needle. This was mounted vertically and connected to a KD programmable syringe pump. The latter delivered feed at 1.0 ml/hr. A Gamma high voltage supplier was used to apply voltages between 10-20 KV to the needle tip. This resulted in a jet of fluid being drawn towards the grounded rotating drum collector. The collector produced a boehmite-polymer nanofiber membrane of thickness between 80-100 μm. The electrospun membrane was kept under vacuum overnight to facilitate evaporation of the solvent and was thereafter used for sorption of Cd (II) ions.

Experimental Procedure

A 5 ppm solution of Cd^{+2} ions was prepared by diluting cadmium nitrate tetrahydrate (1000 mg/L) solutions with double distilled water in a 500 ml measuring flask. Batch experiments were performed in neat and clean small glass bottles. pH of the solution was adjusted to 4.0 by using 1 M NH_4OH solution. To the 20 ml of 5 ppm solution containing Cd^{+2} ions, 0.2 gm of electrospun membrane containing boehmite nanoparticles (1:1 weight ratio) was added. The bottles were equipped with glass screws and then were shaken for one hour. Then the electrospun composite membranes were separated by filtration and the residual concentration of Cd^{+2} ions in the supernatant solution were analyzed using atomic absorption spectroscopy. Controlled experiments were also carried out using blank electrospun membrane. The initial concentration of Cd^{+2} ions in the prepared solution was calculated from the atomic absorption spectra and was found to be 5.2 ppm.

Characterization

Microscopy

Surface morphology of the electrospun polymer membrane was observed using a scanning electron microscope (SEM) operated at 10 kV. SEM observations were carried out after gold sputtering the samples with a Joel JFC-1200 fine coater.

A JEOL 200 HR-TEM was used to characterize the nanoparticles and polymer membrane impregnated with nanoparticles. The electrospun fibers were directly collected on a carbon coated copper grid (300 mesh) and dried under vacuum for few hours before imaging at 100KV (to avoid sample damage).

Spectroscopy

Residual concentrations of cadmium following sorption experiments were determined using the Shimadzu AA-6701F atomic absorption flame emission spectrophotometer fitted with a Cd- Lamp.

X-ray Diffraction

An x-ray diffractometer XRD (Shimadzu XRD-6000) with Cu Kα source was used to detect the crystalline phases of the original nano-particles and nanoparticles impregnated onto the polymer membrane.

Results and Discussions

The steps of preparation and characterization of the electrospun nanocomposite membrane and its subsequent contact with the challenge solution is shown in Figure 1.

Morphology of the nanoparticles immobilized on the elctrospun submicron fibers is observed by SEM. Figure 2 shows SEM micrographs of the electrospun nylon-6 (8 wt%, Fig. 2a) and boehmite impregnated nylon-6 (1:1 wt ratio) fibers (Fig 2b). It may be observed from the micrographs the resulting nylon and nylon-boehmite composite fiber membranes are highly porous, and the fibers are generally uniform in dimensions. The fiber diameters, as calculated from the SEM micropgrahs, are found to be in the range of 300-600 nm for nylon 6 and 400-850 nm for nylon-boehmite. The SEM micrographs also show the nylon-boehmite fiber surfaces to be relatively rougher and with a somewhat “beaded” morphology as compared to the nylon nanofibers. Since morphology of the electrospun fibers depend on the solution’s properties (eg. viscosity, surface tension, conductivity, and concentration - Huang et al. [13]) blending nanoparticles into the polymer solution would have changed these, and hence the change in morphology as observed in Fig 2b.

The SEM micrographs of electrospun PCL and PCL-Boehmite composite fibers are shown in Fig 3a and 3b respectively. The fiber diameters, as calculated from SEM micrographs, were in the range of 0.9-1.2 μm for PCL (Fig 3a) and 1.0-1.5 μm for PCL-boehmite composite fibers (Fig. 3b). The SEM images shows an even more “beaded” morphology and rougher surface in the case of PCL-boehmite as was first observed for the nylon-boehmite. The individual boehmite nanoparticles could not, however, be visually detected; in large part this would be because in the SEM micrographs the fiber diameters are very large relative to the nanoparticle diameters.

Figure 4 shows the TEM micrographs of boehmite (AlOOH) nanoparticles and boehmite impregnated nylon submicron fiber. From Fig 4a, it is observed the boehmite nanoparticles used had a flake-like shape. These nanoparticles are 60-80 nm wide and 100-120 nm long as measured from the TEM micrograph. Figure 4b shows the presence of such a boehmite nanoparticle flake mounted on an electrospun nylon fiber.

The X-ray diffraction spectra of the nano-boehmite particles and boehmite impregnated nylon fiber membrane are shown in Fig 5. Fig. 5a indicates the beoehmite nanoparticles are highly crystalline in nature. All the peaks can be indexed to the boehmite (AlOOH) phase of Al_2O_3. No peaks from any other phase of alumina or impurities were found, indicating the purity of the boehmite nanoparticles used in these experiments. Fig 5b shows the XRD spectra of the nylon-boehmite composite fiber membrane. All peaks for the crystalline phase of boehmite nanoparticles were also found along with the crystalline peak of nylon. This confirmed the presence of crystalline boehmite nanoparticles in the electrospun composite fiber membrane. However, less intense XRD peaks were observed in case of the nylon-boehmite system. This indicated the boehmite nanoparticles were present on and inside the polymer matrix. For the latter, the polymer fibers would have acted like a “protective” layer.

The present study evaluated the use of nanoparticles of alumina (AlOOH) for the removal of Cd(II) in terms of pH and time of contact. To faciliatate comparison with data in the literature on the removal of Cd (II) ions by activated alumina, [4] the experimental conditions in this study were as follows: 20 ml of a solution containing 5.2 mg/L Cd (II) contacted with 0.2 gm of boehmite nanoparticles and the mixture was shaken for 1.0 hr.

Figure 6 shows the effect of pH and time on the adsorption of Cd(II) by using the boehmite nanoparticles. It may be observed sorption capacity increased with increase in pH from 4-7 (Fig 6a). Since there is possibility of chemical precipitation of Cd (II) with increase in pH, a low pH (4.0) was selected for this study. Fig 6b shows the effect of time on the adsorption of Cd (II) using nano-boehmite particles at pH 4.0. It may be observed sorption increased with time from 0.3 mg/g after 30 min of contact to 0.48 mg/g after 12 hrs.

Boehmite impregnated nylon and PCL electrospun fiber membranes were then investigated using the above experimental conditions and sorption capacities are as tabulated below (Table 1).

Table 1: Adsorption of Cd^{+2} ions by electrospun composite fiber membrane

Materials	Initial Cd(II) Concentration	Final Conc. AAS	Sorption Capacity(mg/g)
Nylon electro-spun fibers	5.20 ppm	5.19 ppm	0.001
PCL fibers	5.20 ppm	5.17 ppm	0.003
Nylon-Boehmite	5.20 ppm	3.02 ppm	0.21
PCL-Boehmite	5.20 ppm	3.18	0.20

The sorption capacities of the hydrophobic and hydrophilic composite electrospun fiber membranes were similar but there was a 30-40% decrease in sorption capacity compared to the boehmite nanoparticles. This was likely due to the polymer coating on the surface of the nanoparticles. Diffusion limitations could have affected the transfer of Cd from the bulk solution to the nano-boehmite particles embedded within the polymer matrix.

Conclusions:

The study demonstrated the ease with which fabrication of submicron sized composite fiber membranes could be achieved with the electrospinning technique. Boehmite nanoparticles could be embedded on and within the polymer matrix. The inclusion of boehmite nanoparticles was possible with both the hydrophilic nylon and hydrophobic PCL polymer. However, sorption capacity of the boehmite nanoparticles was compromised as it declined from 0.34 mg/g to 0.20-0.21mg/g following its inclusion in the polymer matrix. Thus, it is concluded here that although there is a reduction in sorption capacity in case of nanoparticle embedded polymer fiber membrane due to the inclusion of the nanoparticles in a polymer matrix, it would nevertheless help to prevent release of such particles into the environment with the treated effluent, and avoid or reduce the cost associated with separation of nanomaterials from treated water. Hence, it may be useful for commercial filtration application.

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Figure Captions:

Figure 1: Schematic of formation, characterization and use of the electrospinning nanocomposite membrane.

Figure 2: SEM Images of Nylon-6 and Nylon-Boehmite composite elctrospun fibers.

Figure 3: SEM images of PCL and PCL-Boehmite composite electrospun fibers.

Figure 4: TEM Micrographs of Boehmite and Nylon-Boehmite electrospun fiber.

Figure 5: XRD spectra of Boehmite nanoparticles and nanocomposite membrane.

Figure 6: Effect of pH and time on the sorption of Cd (II) from aqueous solution.

References

1. M. Hodi, K. Polyak, and J. Hlavay, *Environment International,* 21 (1995) 325.
2. M.J. Demarco, A.K. Sengupta, and J.E. Greenleaf, *WaterResearch* 37 (2003) 164.
3. R. Sierra-Alvarez, J. A. Field, I. Cortinas, G. Feijoo, M. T. Moreira, M. Kopplin, and A. J. Gandolfi, *Water Research,* 39 (2005) 199.
4. M. L. Cervera, M. C. Arnal and M. D. L. Gurdia, *Anal. Bioanal. Chem.*, 375 (2003) 820.
5. N. R. Bishnoi, M. Bajaj, N. Sharma and A. Gupta, *Bioresource Tech.,* 91 (2004) 305.
6. J. H. Potgieter, S. S. Potgieter-Vermaak, and P. D. Kalibantonga, *Mineral Engg.,* 19 (2006) 463.
7. C. A. Christophi and L. Axe, *J. Environmental Engg.,* 126 (2000) 66.
8. D. Tilaki and R. Ali, *Diffuse pollution conference Dublin,* (2003) 8-35.
9. Y. Xu and L. Axe, *J. Colloid. Interface Sci.,* 282 (2005) 11.
10. M. K. Naskar and M. Chatterjee, *J. Am Ceram. Soc.,* 88 (2005) 3322.
11. J. H. Park, M. K. Lee, C. K. Rhee and W. W. Kim, *Mater. Sci. & Engg. A,* 375-377 (2004) 1263.
12. H. Y. Zhu, X. P. Gao, D. Y. Song, Y. Q. Bai, S. P. Ringer, Z. Gao, Y. X. Xi, W. Martens, J. D. Riches and R. L. Frost, *J. Phys. Chem. B,* 108 (2004) 4245.
13. Z. M. Huang, Y. Z. Zhang, M. Kotaki, S. Ramakrishna, *Composites Sci. & Tech.* 63 (2003) 2223.
14. T. Subbiah, G. S. Bhat, R. W. Tock, S. Parameswaran, S. S. Ramkumar, *J. Appl. Polm Sci.*, 96 (2005) 557.
15. S. Thandavamoorthy, N. Gopinath, S. S. Ramkumar, *J. Appl. Polm Sci.*, 101 (2006) 3121.
16. I. S. Chronakis, *J. Mater. Processing Tech.,* 167 (2005) 283.
17. W. Sigmund, J. Yuh, H. Park, V. Maneeratana, G. Pyrgiotakis, A. Daga, J. Taylor, and J. C. Nino, *J. Am. Ceram. Soc.,* 89 (2006) 395.
18. K. Yoon, K. Kim, X. Wang, D. Fang, B. S. Hsiao, and B. Chu, *Polymer,* 47 (2006) 2434.

W. K. Son, J. H. Youk, and W. H. Park, *Carbohydrate Polymer,* 65 (2006) 430.

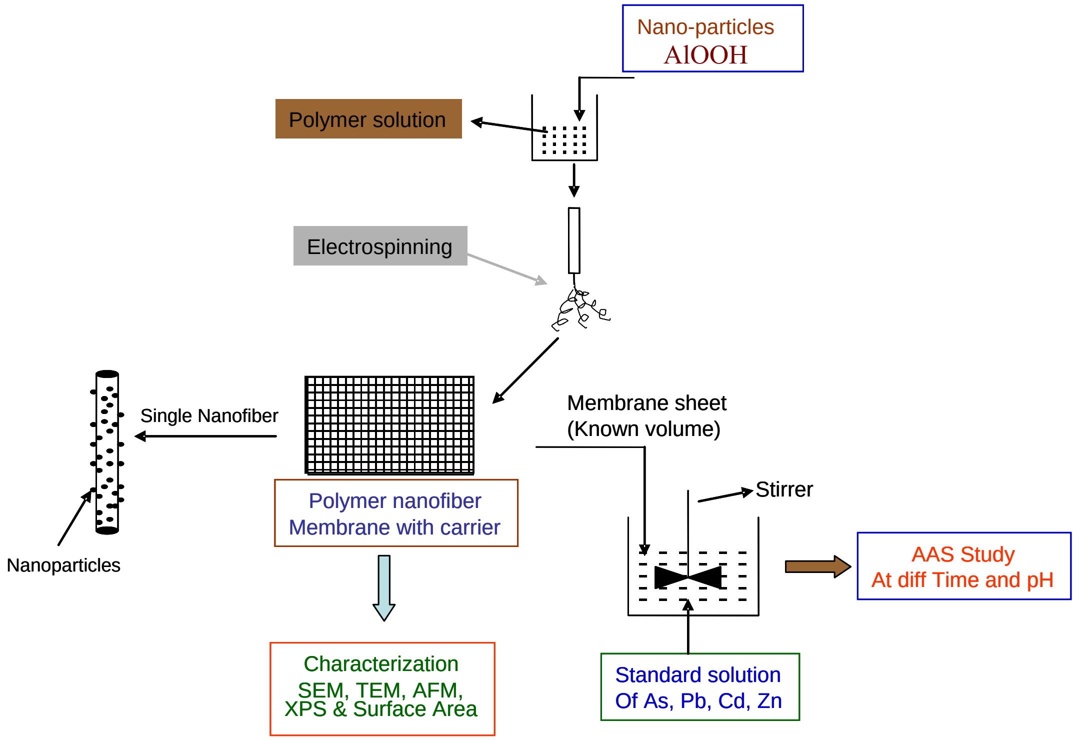

Figure 1: Schematic of preparation, characterization, and use of the electrospun nanocomposite membranes

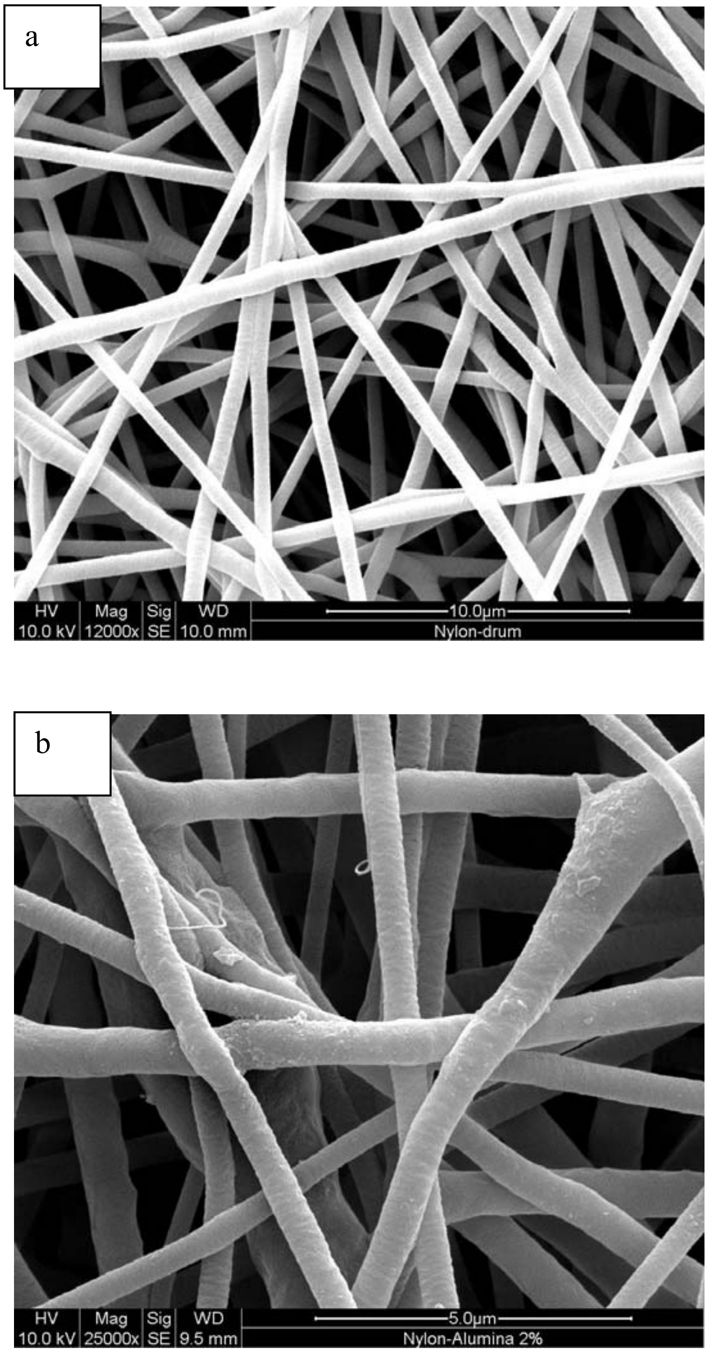

Figure 2. SEM images of electrospun (a) Nylon and (b) Nylon-Boehmite composite fibers.

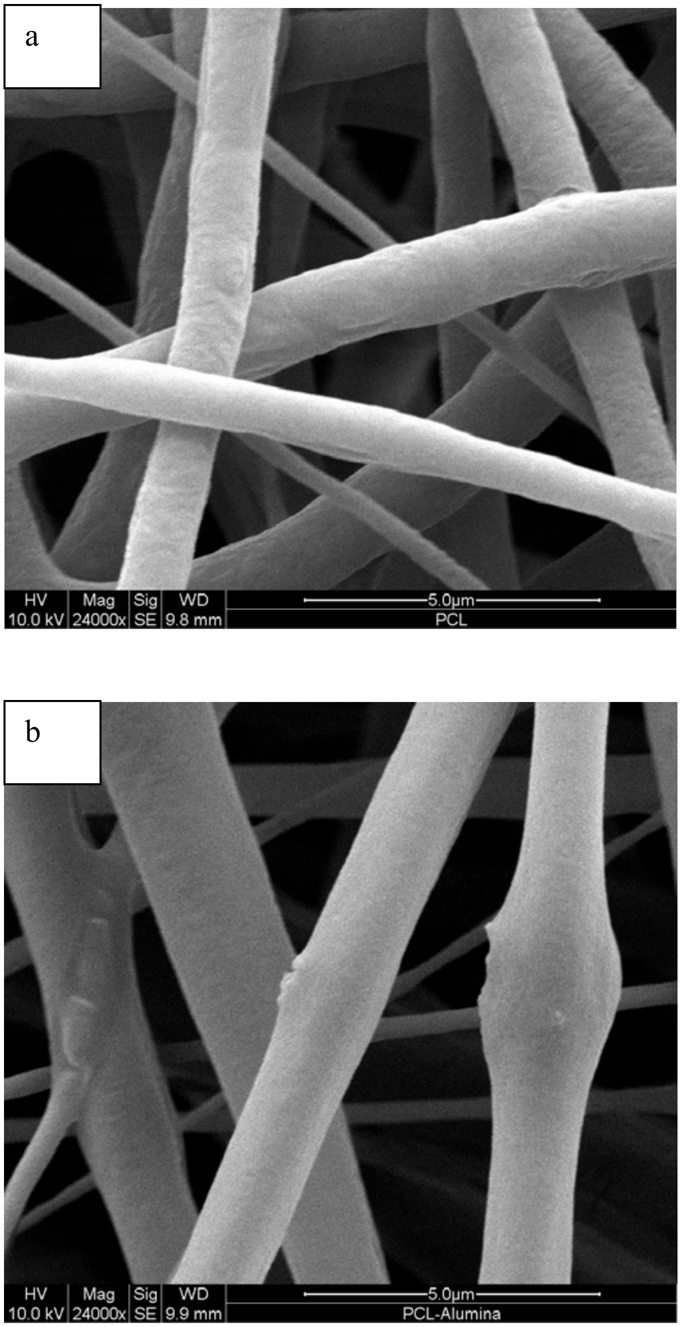

Figure 3. SEM images of electrospun (a) PCL and (b) PCL-Boehmite composite fibers.

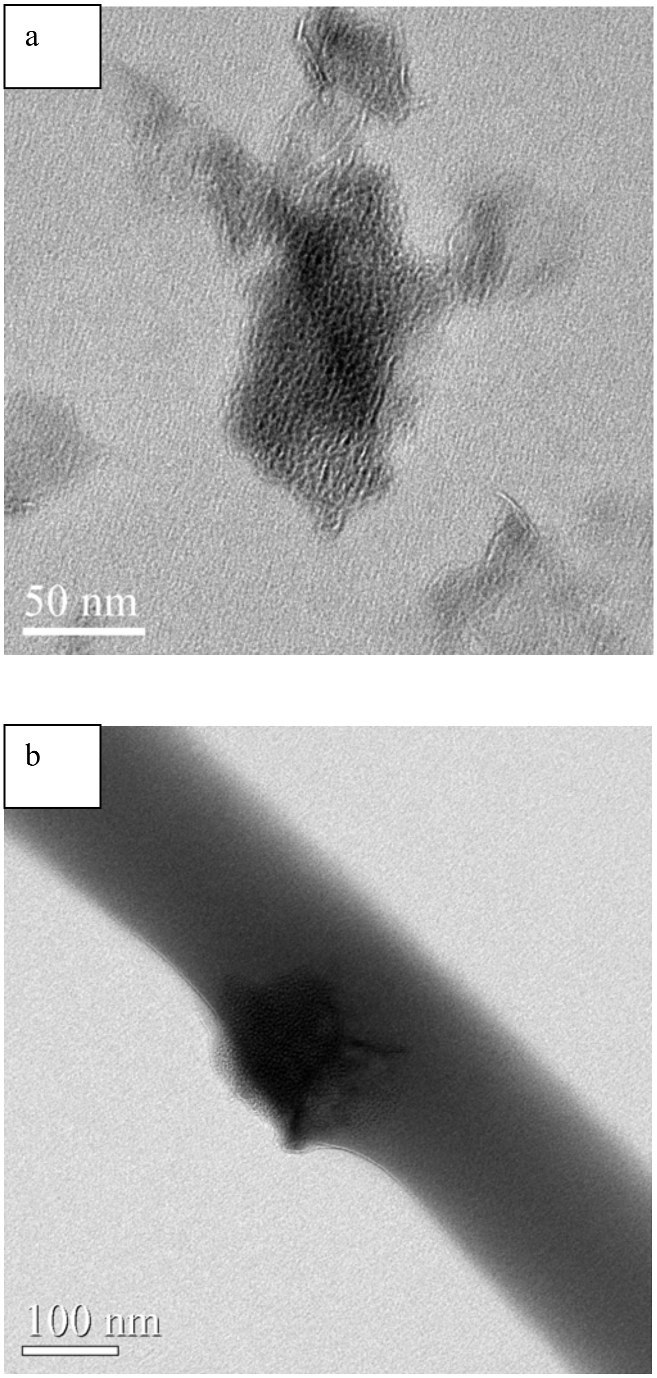

Figure 4: TEM micrographs of (a) a boehmite nanoparticle and (b) such a particle on a Nylon –boehmite electrospun fiber.

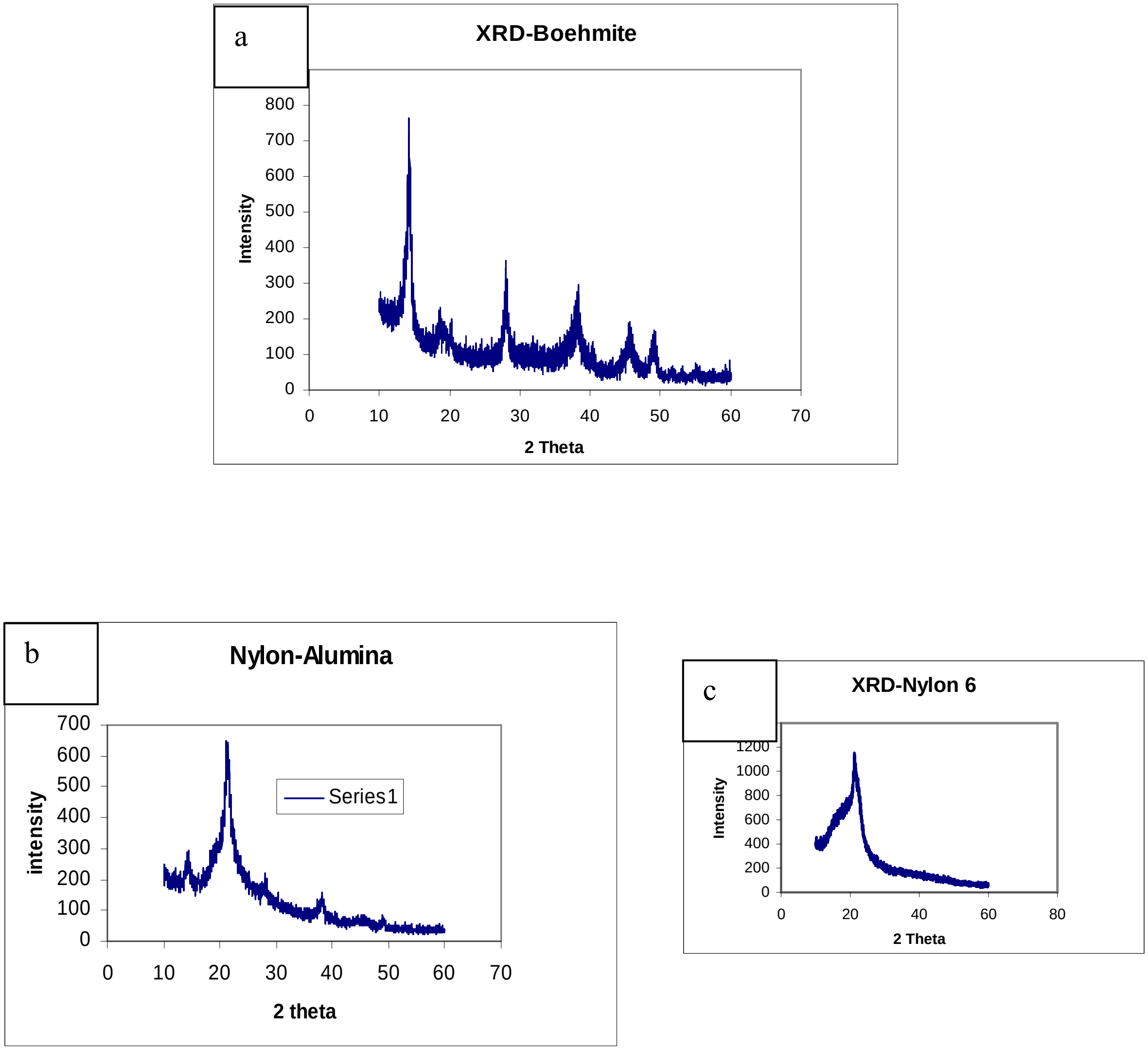

Figure 5: XRD spectra of (a) Boehmite nanoparticles, (b) nylon-boehmite nanocomposite membrane and, (c) electrospun nylon membrane.

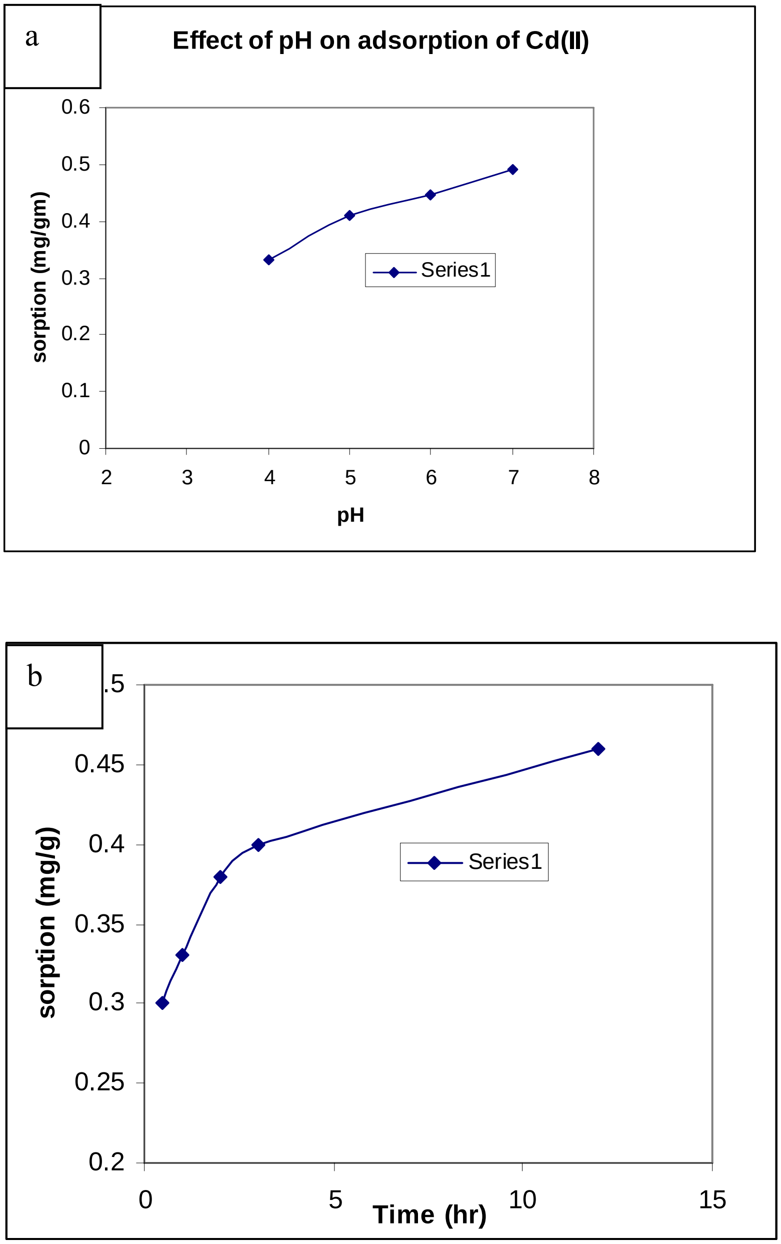

Figure 6: (a) Effect of pH and (b) time on the sorption of Cd(II) from aqueous solution at Room temperature, initial Concentration 5.2 ppm.