

Article

Electrospun Zeolite/Cellulose Acetate Fibers for Ion Exchange of Pb²⁺

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Abstract: The ion exchange capability of electrospun cellulose acetate (CA) fibers containing zeolite A nanoparticles is reported. Solid and porous CA fibers were used to make a zeolite-embedded filter paper, which was then used to ion exchange Na⁺ with Cu²⁺ and Pb²⁺. The composite Linde Type A (LTA) zeolite CA fibers exchanged 0.39 mmol/g more Pb²⁺ than LTA nanoparticles in the solid CA fibers. These fibers could provide a simple and effective method for heavy metal ion removal in water.

Keywords: ion exchange; electrospinning; heavy metal removal; lead removal

1. Introduction

The high toxicity of lead makes it vitally important to remove it from the environment [1]. Lead poisoning can result from physical inhalation or from ingestion from contaminated food and water sources. However, lead in water is absorbed more efficiently and poses an additional threat [2]. The methods of lead removal include chelation, precipitation, adsorption and filtration [3–8]. These processes can often be inefficient and generate secondary pollutants [5]. Ion exchange is a simple technique that does not have high requirements to operate. In this paper, we report the

preparation of electrospun zeolite polymer composite fiber mats that have been used as an ion exchange microfiltration system for the removal of lead.

Zeolites are microporous aluminosilicates that have ordered structures, uniform pore sizes, good thermal stability and chemical resistance and have been extensively studied for their ion exchange properties [9]. The widespread commercial use of zeolites is as ion exchangers in detergents and water softeners. The application of zeolites is typically in powder form, but other configurations, such as fibers, hollow fibers or membranes, are also possible [10–13]. The incorporation of zeolites into a fiber structure can be easily achieved through electrospinning, which allows for the zeolite to be easily processed and handled, whereas a zeolite powder would require additional equipment to recover and reuse. Electrospinning is a non-mechanical technique to generate fibers with diameters from the nano- to micro-meter range [14,15]. By applying a high voltage to a polymer solution, a charged polymer jet can form. As it is traveling to a grounded target, the polymer jet will stretch and elongate from electrostatic repulsions, while the solvent evaporates. The fiber is then deposited as a free standing paper. This would provide a suitable matrix for ion exchange as a membrane filter. Zeolites have been incorporated within electrospun fibers before [16,17]; however, their applications as ion exchangers has not been explored. Zeolite A has been electrospun and used as a nitric oxide delivery vehicle for wound healing applications [16]. Other work with electrospinning zeolites involves dye-loaded zeolite L encapsulated within electrospun fibers for imaging purposes [17]. The zeolite used in this study, zeolite A, exhibits the Linde Type A (LTA) framework and is cubic structured with a pore opening of 4 Å. The polymer used in this study is cellulose acetate. Modified cellulosic materials have been made into composites for heavy metal removal [18–20]. The proposed system would provide a simple way to generate ion exchange filters in one step without the further need for modification.

2. Materials and Methods

2.1. Materials

Alumina isopropoxide, fumed silica, tetramethylammonium hydroxide pentahydrate, copper sulfate, lead nitrate, cellulose acetate (M_n 50,000) and 2,5-dimercapto-1,3,4-thiadiazole (DMT) were purchased from Sigma Aldrich (St. Louis, MO, USA) and used as received. Copper nitrate trihydrate was purchased from Acros and used as received.

2.2. Experimental

Nano-sized zeolite A (LTA) crystals were synthesized according to a published procedure [21]. Two separate solutions were prepared in polypropylene bottles. Solution 1 consisted of 0.75 g of alumina isopropoxide and 5.0 g of tetramethylammonium hydroxide pentahydrate, dissolved by stirring in a 1 M NaOH solution (0.58 mL) at 50 °C until clear. Solution 2 consisted of a 30% silica solution prepared by stirring 0.675 g of fumed silica 1.575 mL 1 M NaOH in 2 mL DI water (pH 10) at 50 °C. The two solutions were then combined into one polypropylene bottle and placed in an oven at 80 °C for 24 h. The resulting nanoparticles were repeatedly washed with a 3:1 ethanol/water mixture, then collected through centrifugation and dried overnight at 80 °C.

For electrospinning, a dispersion of LTA in acetone was first prepared. A cellulose acetate/acetone solution was prepared and slowly added to the LTA dispersion with stirring and sonication. The final solution obtained was a 5% cellulose acetate with 10% by weight LTA (with CA) loading, which was used to electrospin fiber mats. The use of a 1:1 acetone:chloroform solvent mixture was used in place of acetone to generate porous fibers. The solution was fed in a syringe using a pump with a 16 gauge flat tipped needle as the spinneret. A voltage of 15 kV was applied from an external power source (ES50P-5W, Gamma High Voltage Research) with a distance of 10 cm between the spinneret and a grounded collector.

Samples of LTA powder and CA/LTA fibers were mounted on an aluminum stud and coated with Au/Pd for SEM imaging (Zeiss SUPRA 40 field emission scanning electron microscope, Zeiss SMT AG, Oberkochen, Germany). Powder X-ray diffraction patterns were recorded using a Rigaku Ultima IV diffractometer ($\text{Cu K}\alpha = 1.54 \text{ \AA}$) at a scan rate of $1^\circ/\text{min}$.

The ion exchange capacity was tested by soaking of the CA/LTA fibers and LTA in solutions for 20 min and using CA/LTA fibers as a filter membrane. Solutions of CuSO_4 and $\text{Pb}(\text{NO}_3)_2$ in water (pH 6.6) were used for ion exchange. A 1:1 Cu^{2+} (copper nitrate trihydrate) and Pb^{2+} (lead nitrate) mixture was also used for ion exchange. UV-Vis was obtained using a spectrophotometer (Shimadzu UV-1601PC, Shimadzu, Kyoto, Japan) to determine concentrations of CuSO_4 ($\lambda_{\text{max}} = 810 \text{ nm}$) and $\text{Pb}(\text{NO}_3)_2$ after ion exchange. Detection of Pb^{2+} was achieved through UV detection after complexation with DMT ($\lambda_{\text{max}} = 395 \text{ nm}$) [22].

3. Results

The SEM in Figure 1 shows that the LTA crystals were uniform, ranging from 100 to 300 nm in size with an average size of $175 \pm 43 \text{ nm}$, measured with ImageJ. The powder XRD pattern for the as-synthesized LTA crystals (Figure 2) are in good agreement with the reported diffraction pattern. The crystal size calculated from the XRD pattern (216 nm) is in good agreement with the observed size.

Figure 1. SEM image of Linde Type A (LTA) crystals as synthesized (inset: LTA structure). Crystals had an average size of $175 \pm 43 \text{ nm}$.

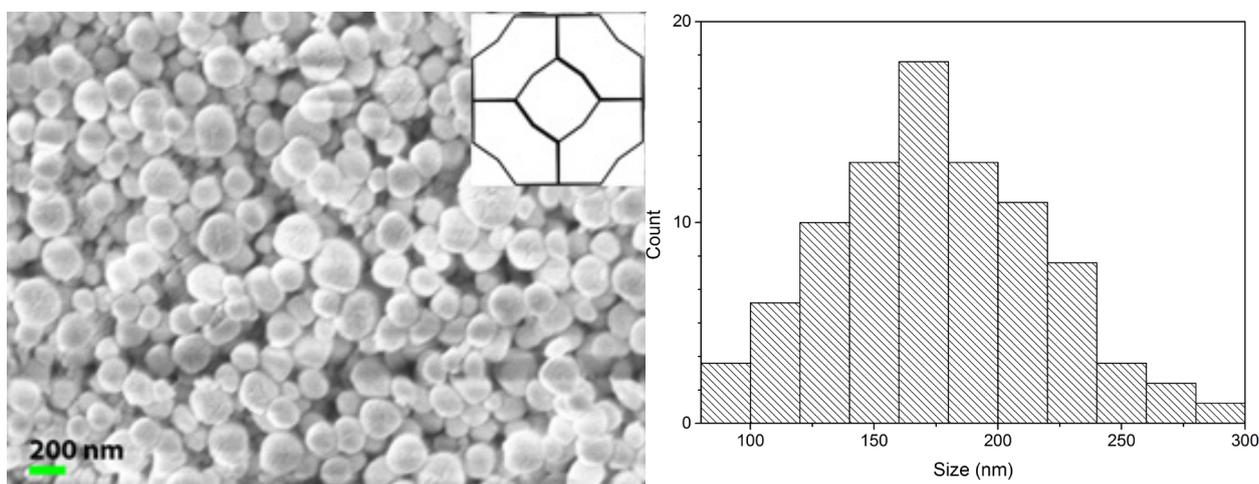
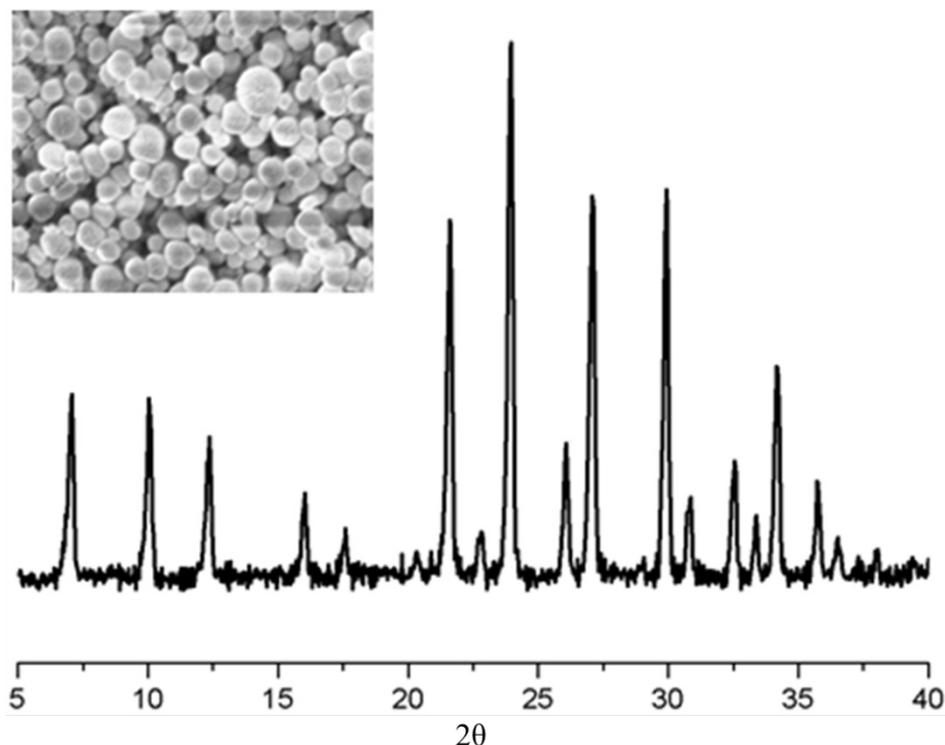


Figure 2. XRD pattern of LTA crystals as synthesized (inset: SEM of LTA crystals).

The electrospinning of cellulose acetate (CA)/LTA fibers requires a uniform dispersion of LTA.

The mixing of LTA powder with a CA solution results in aggregated LTA particles, which can be within electrospun fibers (Figure 3). Smaller aggregates can be seen within electrospun fibers in Figure 3A, while large aggregates can be seen in the background of the same sample in Figure 3B. By first dispersing the LTA in acetone or a 1:1 acetone/chloroform mixture and slowly adding (1 mL/5 min) the polymer solution to it, the aggregation of LTA seen within fibers is not as prevalent. Loadings higher than 10% by weight of LTA did not result in fibers, but electro spray of CA coated LTA. The best fibers (high loading, uniform fiber diameter, ease of handling, and minimized aggregation) were produced using 10% dispersed LTA in 5% CA solution. Fibers with diameters smaller than the LTA size could be seen covered by the CA fiber (Figures 4 and 5). The use of acetone as the solvent produced non-porous CA/LTA fibers (Figure 4). With an average fiber diameter smaller than the LTA size, the LTA crystals could be seen in the fiber in Figure 4A. At higher magnification (Figure 4B), the larger LTA crystals (350 nm) can be seen within the larger diameter (250 nm) fibers. The electrospun fibers ranged from 50 to 300 nm in diameter and had an average diameter of 118 nm (Figure 4C). Porous fibers were generated by using a chloroform/acetone mixture at a 1:1 ratio, as seen in Figure 5A,B. The pores are created when solvents evaporate at different rates from the solvent mixture [23]. The use of highly volatile solvents, such as chloroform for electrospinning CA, also leads to ribbon-like fibers (Figure 5A) [24]. LTA crystals were also embedded within the porous fibers without much aggregation (Figure 5B). The porous fibers are expected to allow for better access to the embedded LTA, increasing the ion exchange rates. The porous CA/LTA fibers had diameters ranging mostly from 50 to 200 nm with an average diameter of 139 ± 54 nm (Figure 5C).

Figure 3. SEM image of LTA aggregates within electrospun CA fibers from solutions without uniform dispersion of LTA. (A) Small LTA aggregates can be seen within the fiber; (B) while larger aggregates of polymer-coated LTA can be seen.

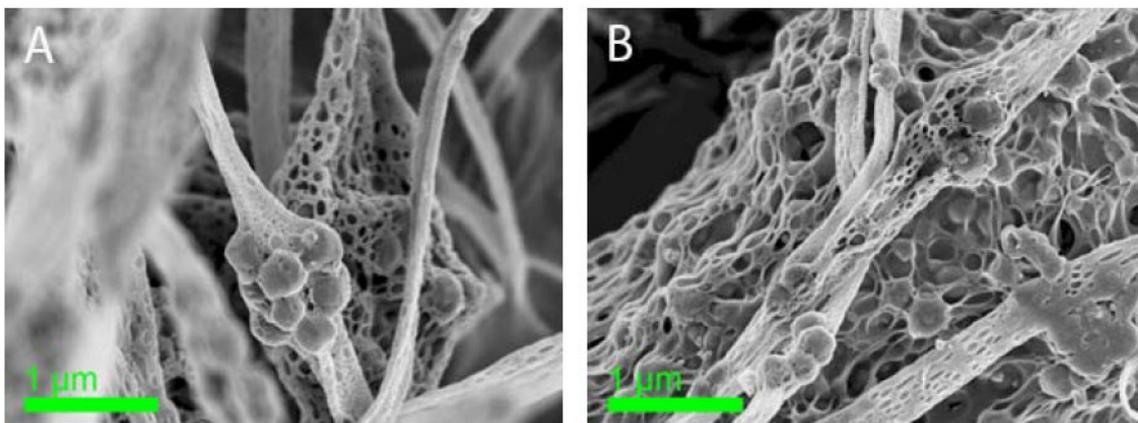


Figure 4. SEM image of Electrospun 10% by weight cellulose acetate (CA)/LTA non-porous fibers (A) and at higher magnification (B) with the measured fiber diameter distribution shown in the histogram (C).

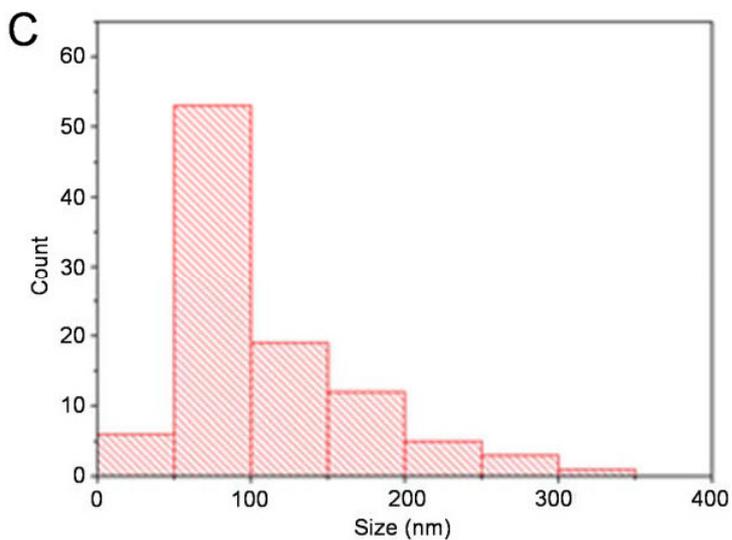
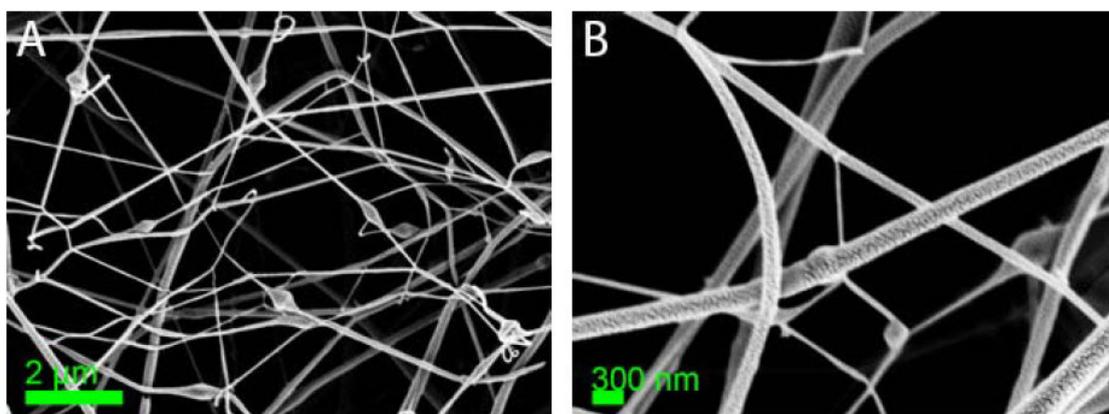
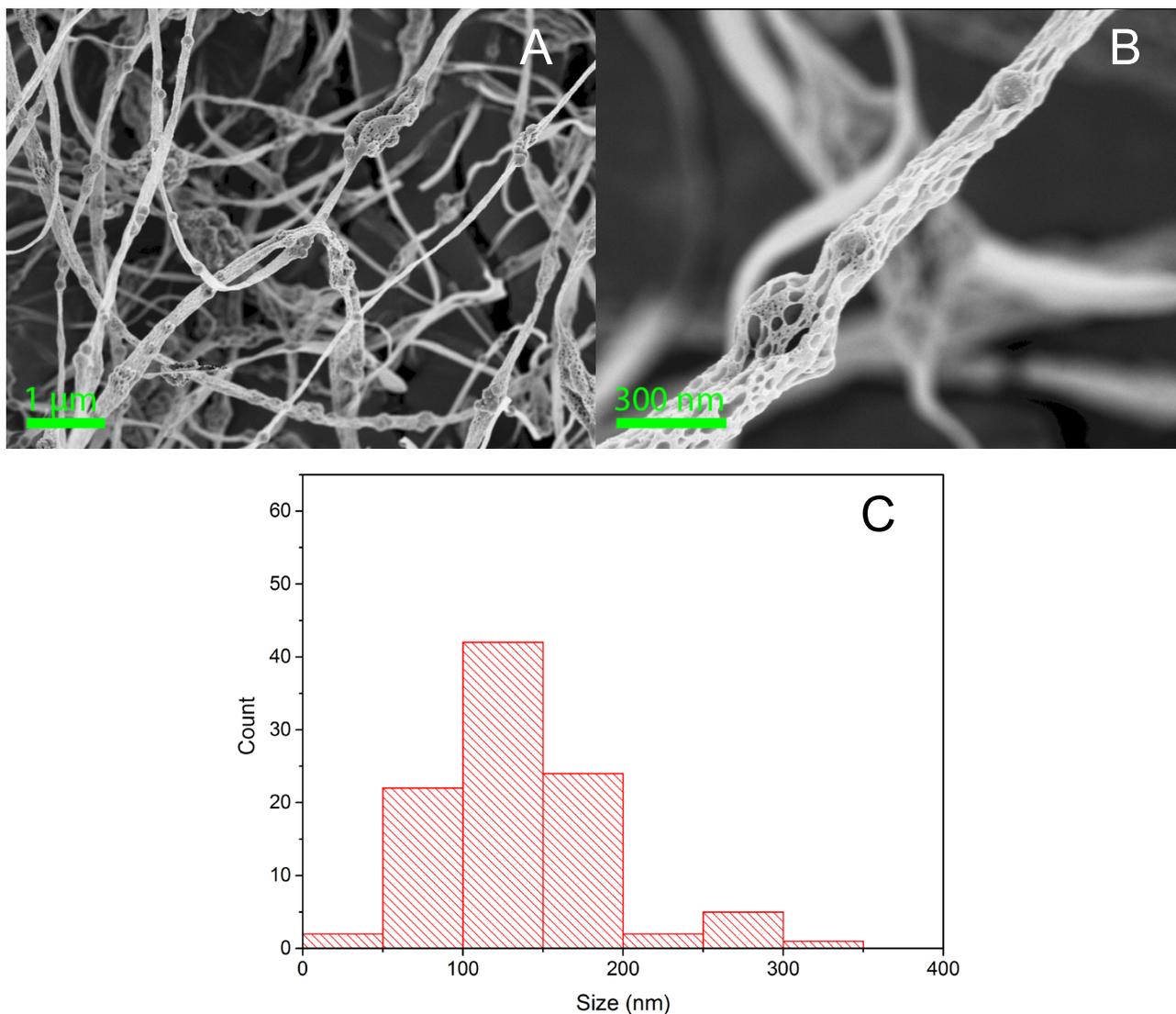


Figure 5. SEM image of Electrospun 10% by weight CA/LTA porous fibers (A) and at higher magnification (B) with the measured fiber diameter distribution shown in the histogram (C).



Ion exchange was performed for both the LTA powder and CA/LTA fibers with copper sulfate and lead nitrate, and they both readily dissolve and disassociate in water. The use of copper sulfate provided a quick colorimetric method of confirming if ion exchange occurred. The light blue color of copper sulfate ($\lambda_{\max} = 810 \text{ nm}$) can be easily detected by UV-Vis and was used to determine the ion exchange of Cu^{2+} ions. Ion exchange of electrospun solid and porous CA/LTA fibers is seen in Figures 6 and 7, respectively. Electrospun CA/LTA solid fibers could exchange $0.98 \pm 0.24 \text{ mmol/g}$ when soaked in a CuSO_4 solution, a little over half of the capacity of the free powder. While ion exchange is observed, the lowered capacity is most likely due to inaccessible LTA within the CA matrix. When a CA/LTA fiber mat was used as a filter membrane to filter the same solution, the LTA exchanged Cu^{2+} at $0.81 \pm 0.38 \text{ mmol/g}$. Diffusion of ions and their exchange is not expected to be greatly affected for hydrated cellulosic membranes [25]. It should be noted that no exchange or adsorption was seen for CA fibers. When LTA was embedded within porous CA fibers, 1.22 ± 0.25

and 1.01 ± 0.31 mmol/g Cu^{2+} were exchanged when soaked and used as a membrane, respectively. A summary of the measured ion exchange capacities (IEC) is shown in Table 1.

Figure 6. Ion exchange capacity of LTA in solid CA fibers for Cu^{2+} and Pb^{2+} .

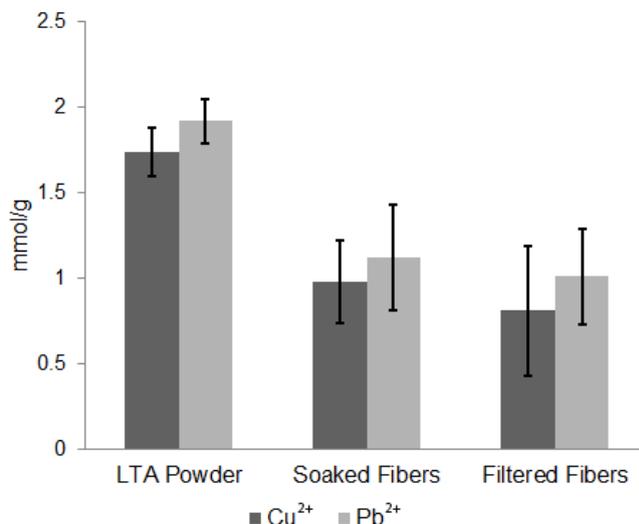


Figure 7. Ion exchange capacity of LTA in porous CA fibers for Cu^{2+} and Pb^{2+} .

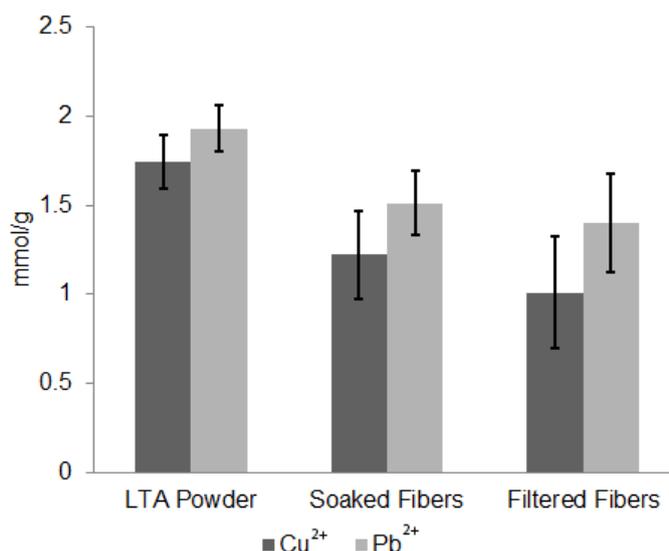


Table 1. Summary of ion exchange for LTA powder and CA/LTA fibers for Cu^{2+} and Pb^{2+} .

Sample	Cu^{2+} (mmol/g)	Pb^{2+} (mmol/g)
LTA Powder	1.74 ± 0.14	1.92
Solid CA/LTA Fibers Soaked	0.98 ± 0.24	1.12 ± 0.31
Solid CA/LTA Fibers Filtered	0.81 ± 0.38	1.01 ± 0.28
Porous CA/LTA Fibers Soaked	1.22 ± 0.25	1.51 ± 0.18
Porous CA/LTA Fibers Filtered	1.01 ± 0.31	1.4 ± 0.28

As it is not possible to detect Pb^{2+} with UV-Vis, complexation with DMT allows for the detection of the Pb(II) -DMT complex in aqueous environments at concentrations up to $80 \mu\text{M}$ [26]. The addition of Pb^{2+} at concentrations greater than $100 \mu\text{M}$ to DMT results in a yellow colored precipitate. The

exchange capacity with Pb^{2+} determined by UV-Vis of the Pb(II) -DMT absorbance was 1.92 ± 0.13 , 1.12 ± 0.31 and 1.01 ± 0.28 mmol/g for the LTA powder, soaked fibers and filtered fibers, respectively. The increased ion exchange seen with Pb^{2+} when compared to Cu^{2+} is expected, as the selectivity is a big part of the ion exchange, and the LTA ion exchanges more selectively with Pb^{2+} than Cu^{2+} .

The loss in ion exchange between CA/LTA fibers and LTA powder is due to the restricted access to the LTA within the fibers. Free powder would not have this limitation, as it would not be constricted by a polymer matrix, limiting access to the inner surface of the zeolite. This is evident when comparing ion exchange between LTA powder, LTA embedded in solid fibers and LTA embedded in porous fibers. Ion exchange with LTA in porous CA fibers is higher for both Cu^{2+} and Pb^{2+} . An improvement of 14% is seen for the exchange of Cu^{2+} -soaked fibers and 12% for filtered fibers, while the exchange of Pb^{2+} is improved by 20%. The open pores allow for greater access to the anionic zeolite framework for exchange. Previous studies show that zeolite A is strongly selective for heavy metal cation exchange, such as with lead and cadmium [4,24,27]. This can be used as an advantage, as heavy metal removal is the greater concern in contaminated samples where competing ions for ion exchange are present. A solution mixture of copper nitrate and lead nitrate was used to test for selective ion exchange between two competing ions. Copper nitrate was used for the copper ion source, as lead salt (lead sulfate) forms when mixed with copper sulfate, which is not water soluble and precipitates. When using the porous CA/LTA fiber mats for ion exchange with the Cu/Pb mixture, lead exchanged 1.34 ± 0.24 mmol/g, while copper only exchanged 0.14 ± 0.05 mmol/g. This high selectivity of zeolite A to ion exchange of lead over copper is seen here, as over 90% of the ion exchange is with lead.

4. Conclusions

The use of cellulose acetate fibers as a host matrix for zeolite A allows for a free standing ion exchange filter membrane. LTA embedded within solid CA fibers exhibited 56% of the ion exchange capacity of the free powder. Utilizing a porous CA fiber support increased the ion exchange to 78% of the free powder. When used to filter a copper and lead mixture, over 90% of the ion exchange was for lead. These CA/LTA fiber mats could be used as a cheap and efficient way to selectively remove heavy metal from water through ion exchange. Though regeneration and reuse still requires further testing, it should only be limited by the stability of the matrix fibers.

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Author Contributions

Kenneth J. Balkus Jr. and Daniel N. Tran conceived of and designed the experiments. Anne M. Marti synthesized and characterized the nano-LTA crystals. Daniel N. Tran performed all other experiments and wrote the paper.

Conflicts of Interest

The authors declare no conflict of interest.

References

1. Needleman, H. Lead poisoning. *Annu. Rev. Med.* **2004**, *55*, 209–222.
2. Goyer, R.A. Toxic and essential metal interactions. *Annu. Rev. Nutr.* **1997**, *17*, 37–50.
3. Sharma, A.K.; Lee, B.-K. Lead sorption onto acrylamide modified titanium nanocomposite from aqueous media. *J. Environ. Manag.* **2013**, *128*, 787–797.
4. Wiers, B.H.; Grosse, R.J.; Cilley, W.A. Divalent and trivalent ion exchange with zeolite A. *Environ. Sci. Technol.* **1982**, *16*, 617–624.
5. Fu, F.; Wang, Q. Removal of heavy metal ions from wastewaters: A review. *J. Environ. Manag.* **2011**, *92*, 407–418.
6. An, H.; Shin, C.; Chase, G.G. Ion exchanger using electrospun polystyrene nanofibers. *J. Membrane Sci.* **2006**, *283*, 84–87.
7. Li, H.; Wang, J.; Xu, J.; Meng, X.; Xu, B.; Yang, J.; Li, S.; Lu, J.; Zhang, Y.; He, X. Synthesis of zeolite NaA membranes with high performance and high reproducibility on coarse macroporous supports. *J. Membrane Sci.* **2013**, *444*, 513–522.
8. Alexandratos, S.D. Ion-Exchange resins: A retrospective from industrial and engineering chemistry research. *Ind. Eng. Chem. Res.* **2009**, *48*, 388–398.
9. Mauritz, K.A.; Moore, R.B. State of understanding of Nafion. *Chem. Rev.* **2004**, *104*, 4535–4585.
10. Abels, C.; Carstensen, F.; Wessling, M. Membrane processes in biorefinery applications. *J. Membrane Sci.* **2013**, *444*, 285–317.
11. Liu, B.S.; Tang, D.C.; Au, C.T. Fabrication of analcime zeolite fibers by hydrothermal synthesis. *Microporous Mesoporous Mater.* **2005**, *86*, 106–111.
12. Di, J.; Chen, H.; Wang, X.; Zhao, Y.; Jiang, L.; Yu, J.; Xu, R. Fabrication of zeolite hollow fibers by coaxial electrospinning. *Chem. Mater.* **2008**, *20*, 3543–3545.
13. Ke, C.; Yang, W.L.; Ni, Z.; Wang, Y.J.; Tang, Y.; Gu, Y.; Gao, Z. Electrophoretic assembly of nanozeolites: Zeolite coated fibers and hollow zeolite fibers. *Chem. Commun.* **2001**, *2001*, 783–784.
14. Reneker, D.H.; Fong, H.; Koombhongse, S.; Yarin, A.L. Bending instability of electrically charged liquid jets of polymer solutions in electrospinning. *J. Appl. Phys.* **2000**, *87*, 4531–4547.
15. Li, D.; Xia, Y. Electrospinning of nanofibers: Reinventing the wheel? *Adv. Mater.* **2004**, *16*, 1151–1170.
16. Liu, H.A.; Balkus, K.J., Jr. Novel delivery system for the bioregulatory agent nitric oxide. *Chem. Mater.* **2009**, *21*, 5032–5041.
17. Cucchi, I.; Spano, F.; Giovanella, U.; Catellani, M.; Varesano, A.; Calzaferri, G.; Botta, C. Fluorescent electrospun nanofibers embedding dye-loaded zeolite crystals. *Small* **2007**, *3*, 305–309.

18. Tian, Y.; Wu, M.; Liu, R.; Li, Y.; Wang, D.; Tan, J.; Wu, R.; Huang, Y. Electrospun membrane of cellulose acetate for heavy metal ion adsorption in water treatment. *Carbohydr. Polym.* **2011**, *83*, 743–748.
19. Xiang, T.; Zhang, Z.; Liu, H.; Yin, Z.; Li, L.; Liu, X.M. Characterization of cellulose-based electrospun nanofiber membrane and its adsorptive behaviours using Cu(II), Cd(II), Pb(II) as models. *Sci. China Chem.* **2013**, *56*, 567–575.
20. Zhou, W.; He, J.; Cui, S.; Gao, W. Preparation of electrospun silk fibroin/Cellulose Acetate blend nanofibers and their applications to heavy metal ions adsorption. *Fibers Polym.* **2011**, *12*, 431–437.
21. Mintova, S.; Olson, N.H.; Valtchev, V.; Bein, T. Mechanism of zeolite a nanocrystal growth from colloids at room temperature. *Science* **1999**, *283*, 958–960.
22. Vasimalai, N.; John, S.A. Spectrofluorimetric determination of picogram level Pb(II) using a dimercaptothiadiazole fluorophore. *Spectrochim. Acta Part. A* **2011**, *82*, 153–158.
23. Megelski, S.; Stephens, J.S.; Chase, D.B.; Rabolt, J.F. Micro- and nanostructured surface morphology on electrospun polymer fibers. *Macromolecules* **2002**, *35*, 8456–8466.
24. Cerjan-Stefanovič, S.; Kaštelan-Macan, M. The effect of temperature on the ion-exchange of Cd(II) and Pb(II) from waters. *Fresenius Zeitschrift Anal. Chem.* **1988**, *332*, 817–818.
25. Reid, C.E.; Breton, E.J. Water and ion flow across cellulosic membranes. *J. Appl. Polym. Sci.* **1959**, *1*, 133–143.
26. Wu, Y.; Li, N.B.; Luo, H.Q. Electrochemical determination of Pb(II) at a gold electrode modified with a self-assembled monolayer of 2,5-dimercapto-1,3,4-thiadiazole. *Microchim. Acta* **2008**, *160*, 185–190.
27. Dąbrowski, A.; Hubicki, Z.; Podkościelny, P.; Robens, E. Selective removal of the heavy metal ions from waters and industrial wastewaters by ion-exchange method. *Chemosphere* **2004**, *56*, 91–106.