Using Ionic Liquids for the Development of Renewable Biopolymer-Based Adsorbents for the Extraction of Uranium from Seawater and Testing Under Marine Conditions

Fuel Cycle Research and Development

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DOE-NEUP FINAL REPORT

Project Title:
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I. Abstract

The key goal of this project is to develop high-performance sorbents for extracting uranium from seawater by blending chitin with other additives and tailoring the materials architecture using ionic liquid (IL) technology. Use of IL for processing chitin and chitin-based blends made it possible to produce materials with the fiber at nano to micro-scale diameter. Advantage of this approach includes 1) tailoring materials composition and materials properties by using additives with unique properties which are insoluble in common organic solvents but solubilizing in IL, 2) low cost and sustainability of the sorbents via using shellfish waste as a source of chitin, and 3) chemical modification of surface of the composite materials through use of chitin as main structural biopolymer.

In the last several years, application of IL for developing high surface area materials was better understood and expanded. The fundamental parameters controlling fiber diameter during electrospinning were found and were shown to be related to polymer concentration, voltage and distance towards the collector bath. One of the key performance issues of chitin sorbents has been their low strength and fast biodegradation, which prevents their long-term durability and performance, was addressed through the preparation of composite materials. Electrospinning of chitin-based composite solutions, where chitin was co-dissolved with other biopolymer in IL was demonstrated and found to be efficient approach to improve mechanical properties of electrospun materials. The fundamental chemistry and selectivity of amidoxime groups towards uranyl ions was studied through isolation of the first analogs of uranyl and pervynadyl complexes of amidoxime and demonstration of the different coordination modes. Finally, the surface modification and uranium uptake of electrospun chitin mats was demonstrated under simulated seawater conditions.
II. Scope and Aims of the Proposed Work

The overall goal of this work is to apply ionic liquids technology to develop a high-performance chitin sorbents with desired properties by blending chitin with other additives, tailoring the materials architecture, improving economic performance through new functionalization chemistry, and understanding how these parameters affect performance in seawater. The work is divided into three important and interconnected tasks: 1) understand and control bulk material properties through blending of chitin with other additives and control of the material architecture; 2) understand how to use surface modification to improve sorbent economics by controlling metal ion selectivity and capacity; 3) understand how these modifications affect the critical performance properties by measuring the performance under simulated and actual marine conditions. The key scientific challenges which have to be overcome include developing materials with optimal structure-properties relationship and high surface area which are stable under seawater conditions and capable of selectively extract uranium.

The challenges mentioned above were approached through understanding of fundamental chemistry and reported in peer-reviewed publications. The work included comparison study of UO$_2^{2+}$ and VO$_2^{+}$ - amidoxime complexes and understanding their coordination modes (Chem. Commun. 2014, 50, 12504-12507), the development of parameters needed for obtaining nanofibers through electrospinning process (ChemSusChem 2017, 10, 106-111 and ACS Sustainable Chem. Eng. 2017, 5, 5512-5519) and demonstration of the uranium extraction from aqueous solution, and design of dry-wet spun and electropsun chitin-based composites with increased mechanical and antibacterial properties.
III. Technical Summary of the Work Accomplished

A. “Practical” Electrospinning of Biopolymers in Ionic Liquids


Structured networks of polymer nanofibers with fiber diameters below several micrometers have gained significant attention for a variety of applications due to their high surface area and porosity.¹ The diameter of fibers was shown to be crucial for metal-ion extraction efficiency, and one of the effective techniques to produce nanosize fibers is electrospinning.²,³ In our previous work we have demonstrated electrospinning of chitin directly from shrimp shell extract in 1-ethyl-3-methylimidazolium acetate ([C₂mim][OAc]) using a single needle syringe.² The resulting materials had fibers in the micron and sub-micron range. We sought to use electrospinning to improve the uranium adsorption capacity of our chitin based sorbent by further decreasing the size of fibers in our materials from micro to nanoscale, increasing the rate of material output, and controlling the architecture. We investigated this through modifying electrospinning parameters such voltage, distance from the tip of the needle to collector and to the electrode. In contrast to our previous work,⁴ here we have also use a system designed in-house equipped with a seven-needle spinneret positioned on a spinneret holding frame allowing for adjustable distance between the tips of the needles and the collector. This modifiable, high-throughput electrospinning device was tested with solutions of regenerated chitin at 0.5 wt% in [C₂mim][OAc].

First, we determined the optimal potential needed for fiber formation. Based on different attempts that are summarized in Table 1, the optimal voltage was found to be 27 kV, about 30% higher than the threshold voltage of 20 kV (the voltage at which the applied electrical force stretching the droplet at the needle equals the surface tension holding the droplet in place). Electrospinning was observed for voltages below 27 kV but above the 20 kV threshold; however, the fibers were not stretched sufficiently.

Next, we investigated the distance between the needle tip, the surface of the coagulation bath, and the electrode. The shortest distances (1.9 and 7.5 cm) to the water surface did not allow for proper fiber elongation, whereas at a distance of 17.8 cm the stretched fibers were too thin, and the material was scattered too far and not collected by the water bath (Table 2). We ultimately found that a 9.5 cm working distance from water surface to the needle tips and 19.0 cm from electrode provide the best balance between fiber elongation and thinning as well entanglement of the overall mat.
Table 1. Effects of Voltage on Electrospinning

<table>
<thead>
<tr>
<th>Voltage, kV[^a]</th>
<th>Observations[^b]</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>Drops, no spinning observed</td>
</tr>
<tr>
<td>10</td>
<td>Beaded thick short fibers</td>
</tr>
<tr>
<td>15</td>
<td>Beaded fibers, beads are smaller than at 10kV</td>
</tr>
<tr>
<td>20</td>
<td>Mixture of well-elongated fibers and tiny beads, mat formed on the water surface</td>
</tr>
<tr>
<td>25</td>
<td>Elongated thin fibers, mat formed on the water surface</td>
</tr>
<tr>
<td>27</td>
<td>Elongated thin fibers, mat formed on the water surface</td>
</tr>
</tbody>
</table>

[^a] Applied voltage. The setup was powered by UltraVolt High Voltage Power System Model HV-RACK-1-250-00382.  
[^b] Observations associated with electrospinning.

Table 2. Effect of Distance on Electrospinning

<table>
<thead>
<tr>
<th>Distance from needle tip to grounded electrode</th>
<th>Distance from needle tip to water surface, cm</th>
<th>Observations[^b]</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.5</td>
<td>1.9</td>
<td>Insufficient elongation</td>
</tr>
<tr>
<td>19.0</td>
<td>7.5</td>
<td>Jet formed fibers</td>
</tr>
<tr>
<td>19.0</td>
<td>9.5</td>
<td>Jet formed fibers</td>
</tr>
<tr>
<td>19.0</td>
<td>12.5</td>
<td>Jet was forming fibers that partially were breaking into the droplets</td>
</tr>
<tr>
<td>28.5</td>
<td>17.8</td>
<td>Fibers too thin, excessive ‘whipping’ motion</td>
</tr>
</tbody>
</table>

[^a] At applied voltage of 27 kV.  
[^b] Observations associated with electrospinning.

Next, we electrospun 0.5 wt% regenerated chitin solutions using the experimental parameters described above. Electrospinning resulted in bead-free thin fibers that were collected on the surface of coagulation bath. The collected mats were strong enough to be collected from the water surface and air-dried. The air-dried mats were transparent without any distinctive ‘fibrous’ structure. The surfaces of the mats were analyzed with scanning electron microscopy (SEM) and atomic force microscopy (AFM). SEM revealed randomly oriented fibers with 22 ± 7 nm diameter on the mat surface (Figure 1). The 2x2 µm surface area scan performed with AFM (Figure 2) showed randomly oriented nanofibers; consistent with the observed fiber morphology from SEM images. The surface microroughness determined from 1x1 µm² scans of electrospun nanofiber network was 4.2±0.7 nm.
In summary, we have found optimal electrospinning parameters (voltage and distance) needed to produce chitin nanofibers from solution of regenerated chitin in [C₂mim][AOc] through electrospinning process. The obtained results demonstrate that networks of extremely thin chitin fibers can be obtained from chitin without need for its derivatization, paving the way for high-surface area sorbents.
Having devised an optimized apparatus for electrospinning IL solutions, we proceeded to investigate how the solutions themselves could be used to control the nanomaterial properties. As known from extensive studies of electrospinning from volatile organic compounds (VOCs), electrospinability and fiber formation depend on solution properties.\(^5\)-\(^8\) For example, the proper chain entanglement during electrospinning from VOCs, needed for fiber stretching, is regulated by polymer concentration, viscosity, and polymer molecular weight (MW). On the other hand, the formation of either fibers or droplets is directed by the surface tension and conductivity.\(^9\),\(^10\) Therefore, we have investigated the effects of key solution parameters (viscosity, polymer concentration, conductivity, and surface tension) needed for electrospinning of chitin from ionic liquid (IL) and compared them to parameters determined for VOCs.

The use of an IL as solvent and a natural biomaterial as polymer feedstock both present differences from conventional spinning of well-controlled synthetic polymers in VOCs, and these differences needed to be understood. The viscosity and conductivity of pure [C\(_2\)mim][OAc] were measured to be 135(5) cP and 2.9 mS/cm, respectively, both of which are several orders of magnitude higher than that of VOCs. Typical VOCs used for electrospinning have low viscosity (0.5-3 cP), conductivities of 0-10 µS/cm and surface tension values of 17-34 dyne/cm.\(^9\) For the electrospinning study, we chose regenerated chitin that has high molecular weight (MW) and purity. The chitin was extracted from shrimp shell using [C\(_2\)mim][OAc] followed by coagulation in water and air-drying. Air-dried chitin was ground and thermally re-dissolved in [C\(_2\)mim][OAc] IL. As the biomass source, we have used two types of shrimp shells: 1) from seafood processor, which were thermally dried in a drying facilities (‘P-chitin’) and 2) shells obtained by peeling of commercially frozen shrimps (‘R-chitin’). The both types of chitin were prepared with 0.2 to 1 wt% load in IL.

All of the prepared chitin solutions had similar values of conductivity (2.5-2.6 mS/cm) and surface tension (35-38 dyne/cm) for chitin loads from 0.2 to 1.0 wt% and regardless of the chitin source (Table 3). On the other hand, viscosities of the chitin solutions were varied significantly with respect to chitin concentration. The chitin solutions had similar viscosity values which were increased from ~240 cP to ~2,500 cP with increasing chitin load from 0.2 to 1.0 wt%. This is consistent with the fact that chitin is a nonelectrolyte and, interestingly, suggests that chitin makes a solution-phase network that reduces bulk flow but does not greatly restrict the mobility of individual ions.
Table 3. Solution properties and electrospinning results obtained for regenerated and PG-chitin solutions.

<table>
<thead>
<tr>
<th>Chitin Source</th>
<th>Chitin Concentration (wt%)</th>
<th>Surface Tension (dyne/cm)</th>
<th>Conductivity x10 (mS/cm)</th>
<th>Viscosity (cP)</th>
<th>Solution Flow (Gravity or Pressure, psi)</th>
<th>Electrospun Fiber Morphology/Diameter† (nm)</th>
<th>Fiber Surface Microroughness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[C₂mim]-[OAc]</td>
<td>0.00</td>
<td>47(2)</td>
<td>29(1)</td>
<td>135(5)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>0.20</td>
<td>35(3)</td>
<td>26(2)</td>
<td>250(10)</td>
<td>Gravity</td>
<td>No mat formed</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>0.30</td>
<td>38(2)</td>
<td>29(1)</td>
<td>471(40)</td>
<td>Gravity</td>
<td>Nanofibers/20(10)</td>
<td>4.9(5)</td>
</tr>
<tr>
<td></td>
<td>0.50</td>
<td>34(1)</td>
<td>28(2)</td>
<td>1010(50)</td>
<td>Gravity</td>
<td>Nanofibers/22(7)</td>
<td>4.2(7)</td>
</tr>
<tr>
<td></td>
<td>0.75</td>
<td>35(3)</td>
<td>29(1)</td>
<td>1490(90)</td>
<td>Gravity/Pressure, 0.8</td>
<td>Nanofibers/30(10), randomly seen submicron fibers, gel particles</td>
<td>4.9(6)</td>
</tr>
<tr>
<td></td>
<td>1.00</td>
<td>-*</td>
<td>-*</td>
<td>2460(43)</td>
<td>Pressure, 2.0</td>
<td>Nanofibers, submicron fibers, gel particles</td>
<td>4.7(8)</td>
</tr>
<tr>
<td>“Processed”</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Biomass/P-</td>
<td>0.20</td>
<td>38(1)</td>
<td>25(1)</td>
<td>240(12)</td>
<td>Gravity</td>
<td>No mat formed</td>
<td>-</td>
</tr>
<tr>
<td>chitin</td>
<td>0.30</td>
<td>38(1)</td>
<td>26(2)</td>
<td>490(27)</td>
<td>Gravity</td>
<td>Nanofibers/20(10)</td>
<td>5.2(5)</td>
</tr>
<tr>
<td></td>
<td>0.50</td>
<td>-*</td>
<td>27(1)</td>
<td>1000(50)</td>
<td>Pressure, 0.5-1.0</td>
<td>Nanofibers/30(12), randomly seen submicron fibers, gel particles</td>
<td>4.9(3)</td>
</tr>
<tr>
<td></td>
<td>0.75</td>
<td>-*</td>
<td>-*</td>
<td>1520(80)</td>
<td>-</td>
<td>Gelation</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>1.00</td>
<td>-*</td>
<td>-*</td>
<td>2620(140)</td>
<td>-</td>
<td>Gelation</td>
<td>-</td>
</tr>
<tr>
<td>“Raw”</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Biomass/R-</td>
<td>0.75</td>
<td>34(3)</td>
<td>29(1)</td>
<td>950(30)</td>
<td>Gravity</td>
<td>No mat formed</td>
<td>-</td>
</tr>
<tr>
<td>chitin</td>
<td>1.00</td>
<td>33(2)</td>
<td>29(2)</td>
<td>1400(100)</td>
<td>Gravity</td>
<td>Beads, short fibers, unstable mat</td>
<td>-</td>
</tr>
<tr>
<td>PG-chitin</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Solution was too viscous at room temperature. The solutions did not rise in the capillary tube and gel was formed around the electrode.
†Measured from SEM images using ImageJ.
All electrospinning experiments were performed using the multi-needle spinneret and parameters such as voltage and distance described in Section IIIA. Briefly, the electrospinning was done at a spinning voltage of 25-27 kV and a needle-to-collector distance fixed at 9.5 cm. Chitin solutions were electrospun directly into an aqueous coagulation bath at ambient conditions and collected on the surface of the water.

We first determined the range of concentrations from which different biopolymer sources could be electrospun from [C$_2$mim][OAc]. The minimum chitin concentration that resulted in a stable jet and mat formation for was 0.3 wt%. The mass loading of P-chitin could be increased up to 1 wt% all resulting in a smooth electrospinning process. However, P-chitin at 0.75 and 1 wt% required application of external pressure and were accompanied by random formation of gel particles. By contrast, an increase of concentration of R-chitin from 0.3 to 0.5 wt% required application of external pressure to prevent gelation and 0.75 and 1.0 wt% solutions formed gels regardless of applied pressure.

Next, we correlated the fiber architecture with solution properties. For this, all electrospun mats were washed and air-dried. After the air-drying, the mats became thin and optically transparent (Figure 3), due to hydrogen-bonding between the fibers during the slow evaporation of the water.

The fiber morphology was investigated with scanning electron microscopy (SEM) and atomic force microscopy (AFM). The surface of all mats had randomly oriented fibers, regardless of starting chitin concentration. The mats obtained after electrospinning of 0.75 and 1.0 wt% solutions had combination of both fibers and gel particles on the surface.

The AFM images (Figure 4) additionally confirmed presence of nanofibers. However, as seen from large scan area (20 x20 µm$^2$), the mats obtained after electrospinning of 0.75 and 1.0 wt% solutions had a combination of nano and submicron fibers. Similar results were obtained for R-chitin.
To summarize, our results revealed that among all investigated solution parameters, electrospinning from IL is most strongly influenced by chitin concentration and molecular weight and influenced to a lesser extent by conductivity and surface tension of solutions, which are not themselves as strongly affected by the dissolution of chitin. We found that the biomass source used for chitin extraction is important and influences the concentration range suitable for electrospinning. Specifically, P-chitin formed fibers at chitin concentration from 0.3 to 1 wt%, while fiber formation from R-chitin was observed at 0.3 and 0.5 wt% load. Furthermore, the critical concentrations for both P- and R-chitin needed to spin fibers were found to be above 0.2 wt%. This work offers some insight into the effect of solution parameters on polymer electrospinning from ILs relevant not only for fundamental, but also important for applied research, when the control over the fiber diameter is needed.
C. Electrospinning of Chitin-Cellulose Nanofibers with Cellulose as Low Molecular Weight Additive using Ionic Liquid Platform

Zavgorodnya, O.; Shamshina, J. L.; Choudhary, H.; Rogers, R. D. Electrospinning of biopolymer composites from ionic liquids. (In preparation as a full article for ACS Sustainable Chem. Eng.)

Using the development of electrospinning parameters and investigated solution properties (Section III-A,B), we sought to improve mechanical properties, in particular elastic modulus of electrospun chitin mats without compromising materials biodegradability through adding microcrystalline cellulose. The microcrystalline cellulose was chosen as an additive to chitin due to its high Young modulus and ability to dissolve in 1-ethyl-3-methylimidazolium acetate IL, [C_{2}mim][OAc].

To find the optimal ratio between chitin and cellulose and test electrospinnability of composite solutions, the following chitin/cellulose ratios were used: 1/0, 9/1, 8/2, 7/3, 6/4, 5/5, 4/6 and 0/1. The solutions were prepared by thermal dissolution of cellulose in chitin solution in IL. Electrospinning was done using a multi-needle setup with the operating parameters described in Section III-A,B. The mats were obtained for solutions of chitin (1/0) and chitin/cellulose at 9/1, 8/2, 7/3 and 6/4 ratios. Decreasing chitin concentration (alternatively increasing cellulose content) resulted in jet breaking down into the droplets. The electrospun mats were collected from the water surface, washed and air-dried. The surface morphology was characterized with atomic force microscopy (AFM). As seen from Figure 5, all electrospun mats had combination of nano- and submicron fibers with the amount of visible submicron fibers decreasing with increasing cellulose content.

**Figure 5.** AFM images of air-dried electrospun mats obtained after electrospinning of chitin (1/0) (A,G), chitin/cellulose 9/1 (B,H), 8/2 (C,K), 7/3 (D, L), 6/4 (E,M) and cellulose film (F,N). Scan size is 20 µm x 20 µm (Z-scale is 450 nm for A-F) and 1 µm x 1 µm (Z-scale is 60 nm G-N).

Once we confirmed the successful fiber formation after electrospinning, we investigated mechanical properties of electrospun mats. Since the microcrystalline cellulose cannot be electrospun under investigated conditions, for comparison, we have prepared cellulose films, cast from IL. The films were washed and air-dried prior to characterization. The elastic moduli of materials were determined from force curves measurements obtained from AFM. As seen from Figure 6, the elastic modulus of electrospun mats gradually increased with increasing cellulose content. The lowest modulus of 4.3 GPa was observed for chitin mats and the highest value was achieved when 30 and 40 wt% of cellulose were added. The Young’s moduli of 7/3 and 6/4
electrospun mats were similar to the modulus determined for IL-regenerated cellulose film and were ~ 7GPa.

![Figure 6. Elastic moduli of electrospun chitin, chitin-cellulose (9/1, 8/2, 7/3 and 6/4 chitin to cellulose ratios) and IL-regenerated cellulose film.](image)

In this work, we have prepared electrospun chitin/cellulose mats with different ratios of chitin to cellulose. By blending with cellulose, we significantly improved value of elastic modulus for electrospun materials. Specifically, the modulus was increased from ~4.3 GPa (chitin mat) to ~ 7GPa (the mats with 30 and 40 wt% cellulose). The work shows that mechanical properties of chitin electrospun chitin materials can be improved by adding other biopolymers, while keeping chitin as a prime polymer needed for surface functionalization.

As we discovered, cellulose as an additive improves primarily plasticity of chitin fibers. Therefore, to improve the tensile strength of chitin fibers, we explored the use of cellulose-rich material (CRM) obtained directly from biomass by extraction from IL. Cellulose is renewable and biodegradable polymer that is known for its high strength and durability. Cellulose can be extracted from wood biomass using [C$_2$ mim][OAc] and blends of IL-extracted cellulose and chitin are not known in the literature. We have investigated the feasibility of their preparation and the physicochemical properties of the blends.

Blends of chitin and CRM with chitin/CRM mass ratios of 9/1, 8/2, 7/3 and 5/5 were successfully spun and their tensile strength properties have been determined (Figure 7). We observed that addition of CRM to the chitin fibers does not increase their strength, although it significantly increases their deformation capacity (shown on a plot as % strain) before fibers break.

![Image](http://example.com/image.jpg)

**Figure 7.** Photographs of blended composite chitin/CRM fibers with different ratio between chitin to CRM (left). The stress and deformation of blended chitin/CRM fibers (right).

While chitin will need to be the main component in the fiber as it is the source of uranium binding sites, the study shows that the composition range can be varied, and fibers can be tuned from brittle (100% chitin) to more flexible during handling and applying stress.
E. An Ionic Liquid Platform for Spinning Composite Chitin-Poly(lactic acid) Fibers

Zavgorodnya, O.; Shamshina, J. L.; Chhotaray, P. K.; Rogers R. D. An Ionic Liquid Platform for Spinning Composite Chitin-Poly(lactic acid) Fibers. (In preparation as a full article for ACS Sustainable Chem. Eng.)

Degradation, stability, and mechanical strength are two key components in designing sorbents for extraction under marine conditions. The ability of [C$_2$ mim][OAc] to dissolve and homogeneously blend chitin along with other additives is one the key advantages of our process, allowing us to adjust the properties of our chitin based sorbents to be competitive with synthetic resins yet without compromising biodegradability. Our prior proof-of-concept study showed that it was possible to co-dissolve chitin and other biopolymers, extracted directly from their biomass sources, and produce composite materials in a controlled architecture (fibers). To control both degradation and mechanical properties, we investigated chitin blending with poly(lactic acid) (PLA) of different molecular weight (MW). Structure of both polymers is shown on Figure 8.

![Figure 8](image)

**Figure 8.** Structures of chitin (A) and poly(lactic acid) (PLA) (B).

We have been motivated by the fact that PLA is a biodegradable semi-crystalline polymer with good mechanical properties depending on degree of crystallinity and MW.$^{12,13}$ Therefore, we have investigated PLA with average MW values of 2,400, 100,000 and 700,000 g/mol. On the other hand, chitin provides the surface groups suitable for functionalization with uranyl selective groups and was used as a primarily polymer in fiber spinning.

Blends of chitin and PLA were prepared by simultaneous thermal dissolution of chitin and PLA, keeping the chitin concentration fixed at 1.75 wt% relative to IL, while changing the amount of PLA in the blend from 10 to 33 % of that of chitin (or 0.175, 0.438 and 0.578 wt% of the chitin mass). PLA with MW of 2,400, 100,000 and 700,000 g/mol was used to investigate the effect of MW on fiber morphology and mechanical robustness. All prepared composite solutions were successfully spun to form fibers, regardless of composition and MW of PLA.

The structure and composition of spun fibers were confirmed by Fourier Transform Infra-Red (FT-IR) spectroscopy (Figure 9). The FT-IR spectrum of neat commercial PLA pellets (Figure 9) had two characteristic bands at 1753 cm$^{-1}$ and 869 cm$^{-1}$ corresponding to C=O and C-\text{COO} stretching, respectively. For neat chitin fibers, characteristic groups included acetamide group (-NH-C(O)-CH$_3$) which had a carbonyl C=O stretching band (amide-I) split into two components (due to hydrogen bonding between amide moieties), at 1646 and 1613 cm$^{-1}$, and an
amide-II band appearing at 1539 cm\(^{-1}\). The peak positions were consistent with those previously reported for chitin and PLA\(^{14,15}\). In blended fibers, the characteristic peaks for both PLA and chitin were also detected, but were slightly shifted compared to neat polymers.

**Figure 9.** FTIR spectra of chitin (blue), PLA (black) and chitin-PLA blended fibers with 10 (dark red), 25 (dark green) and 33 (dark pink) % of PLA. Blended chitin-PLA fibers are shown for fibers with PLA-700 (MW 700,000 g/mol).

Thus, the characteristic peak of PLA at 1753 cm\(^{-1}\) shifted to the lower frequency (\(\sim 1733\) cm\(^{-1}\)), while chitin amide-I band, originally split into two different intensity bands at 1646 and 1613 cm\(^{-1}\), approach nearly equal intensity in blended fibers, with the relative ratio between these two bands being dependent on the PLA loading. Such changes suggest the appearance of hydrogen-bonding between C=O groups of PLA and amide (-C(O)NH-) groups of chitin in the blended fibers. It should also be noted that the intensity of PLA peaks were significantly smaller than those of chitin due to the low quantity of PLA. Also, no peaks related to [C\(_2\)mim][OAc] IL were seen from FTIR spectrum, confirming complete removal of IL during washing steps.

The tensile strength measurements performed for all spun fibers showed that among all fibers, the lowest tensile strength (71 MPa) was observed for neat chitin fibers and composites with low amounts of PLA (10 % from chitin mass), independent of PLA MW (**Figure 10**). The strength of composites with higher amounts of PLA depended on the MW of the PLA. Chitin fibers blended with PLA of MW 100,000 showed only slightly improved strength and plasticity. The strongest effect of blending on mechanical properties was observed for chitin-PLA fibers using PLA with a MW of 700,000. The increase in tensile strength and plasticity was observed for PLA contents of 25 and 33 wt% with the highest improvement for composite fibers containing 33 wt% of PLA.
Figure 10. Stress-strain curves of 1.75 wt % chitin fiber blended with different amounts of PLA, (A) PLA MW is 2,400 g/mol, (B) PLA MW is 100,000 g/mol, (C) PLA MW is 700,000 g/mol.

The study shows that chitin can be blended not only with biopolymers but also with synthetic biodegradable polymers such as PLA. The mechanical properties of composite fibers can be adjusted by varied amount and MW of PLA in the structure. While chitin will need to be the main component in the fiber as it is the source of uranium binding sites, the study shows that the composition range can be varied, and fibers can be tuned from brittle (100% chitin) to more flexible during handling and applying stress.
F. Surface Functionalization for Additional Metal Targets.

Under Objective II, we investigated various ways to use the chemical modifiability of chitin fiber surfaces to further improve performance and properties. One of the advantages of chitin is its ability to introduce multiple functional groups on the surface in addition to amidoxime. This could be used for co-extraction of other metals alongside uranium, such as copper for anti-microbial properties using the same sorbent. Deacetylated chitin (chitosan) is known as a chelating polymer for removing heavy metals. The deacetylated amino group is a poor ligand for uranyl ions but bonds strongly to early transition metal ions, such as copper (II). By exposing only a portion of a surface-deacetylated chitin fiber to the amidoxime treatment bath, we expected that a sorbent would be made with segregated amino-rich regions for copper (II) extraction and amidoxime-rich regions for uranyl extraction.

The fibers with two different functional groups were prepared by deacetylation of chitin fibers in aqueous NaOH and then suspending the fibers from outside the reaction vessel so that only approximately half the length was immersed in the baths for the next two steps, treatment with chlorobutyronitrile followed by hydroxylamine. Following this procedure, the fibers were exposed to solutions of copper (II) and uranyl ions in deionized water at 2 ppm, spiked with $^{233}$U. Time to equilibrium and $^{233}$U $D_w$ were monitored radiochemically. $D_w$ values were intermediate between those reported previously by us for deacetylated and amidoxime-functionalized fibers, which supports partial surface modification.

To determine if uranyl and copper (II) ions were co-extracted randomly or segregated into discrete sections on the sorbent, X-ray photoelectron spectroscopy (XPS) was used. XPS was measured at two points on each of the fiber pieces. High resolution (0.1 eV) scans were conducted throughout the Cu 2p and U 4f energy ranges (925-975 and 355-405 eV, respectively). It was observed that only a signal for uranium or copper was observed for each spot (Figure 11), never both, which indicated segregation of the metals by specific copper or uranium selective regions on the fibers.

![Figure 11](image_url). X-ray photoelectron spectra of Cu 2p (left) and uranium 4f (right) regions. Traces of the same color are from the same ends of the fiber.

Of the four points sampled for each end of the fiber, two regions were rich in either copper or uranium, one region was rich in the opposite metal, and one region that gave no signal
for either metal. This supports that the partial surface treatment did impart bulk uranium ion selectivity to one half of the fiber while leaving the other half covered with copper selective amino groups. The presence of a copper-rich region on the uranium-selective half of the fiber (and vice versa) can be explained by failure of the surface to be fully functionalized, possibly due to incomplete exposure to the treatment baths. A deacetylated region which did not make sufficient contact with the amidoxime treatment baths would remain deacetylated and therefore have an affinity for copper over uranyl, whereas a region of the fiber which was never deacetylated in the first place would have an amide functional group, which is a hard Lewis base and would likely be selective for uranyl over copper. The regions with no metal absorption may have been damaged during handling of the fiber.

Next we determined Cu$^{2+}$ adsorption capacity of deacetylated fibers for later comparison with dual metal adsorption efficiency we measured Cu (II) weight distribution coefficient (D$_w$). A high sorption of Cu (high distribution ratios) was observed on deacetylated chitin in DI water (Figure 12).

![Figure 12](image)

**Figure 12.** Copper (II) uptake by deacetylated chitin fibers in deionized water presented as weight distribution coefficient (D$_w$). Measurements are done in 3 separated batch contact experiments.

The study shows possibility of making a dual-functionalized sorbents which can segregate metal ions via selective modification of surface of the sorbents.
G. Extraction of Uranium from Seawater using Electrospun Chitin Mats.

Under Objective III, we explored methods for screening the performance of our new sorbents and understanding their behavior in actual seawater. Our primarily goal was to develop electrospun chitin mats with high surface area capable of extracting uranium from seawater. Therefore, we have prepared electrospun chitin mats, which were surface treated to gain amidoxime functionality. The mats were characterized by light microscopy, IR spectroscopy, and uranium $D_w$ and uptake capacity from both batch contact and continuous flow experiments were determined.

The $D_w$ measurements were conducted for both surface functionalized and untreated electrospun chitin mats in simulated seawater (a solution of Instant Ocean® aquarium salt in DI water at 1.018 specific gravity). The obtained results revealed that both materials were capable of extracting uranium, but there were wide batch-to-batch variation between samples that underwent the same treatment with no clear difference in affinity (Figure 13). The obtained results might be due to contamination or loss of the high surface area originally present in the nanomaterial due to the intrinsic instability of such high surface area materials.

![Figure 13. $D_w$ values for uranium from simulated seawater for non-functionalized, electrospun chitin nanomats (red) and electrospun nanomats surface treated for amidoxime functionality (blue).](image)

Surface functionalized nanomats were also submitted for continuous flow uranium uptake studies at Pacific Northwest National Laboratory. During the course of the 40-day trial the materials were found to lose their integrity and wash into the glass frit that was originally used to hold them.
I. Blended Fibers with Antifouling Properties.

Surface functionalized nanomats were submitted for continuous flow uranium uptake studies at Pacific Northwest National Laboratory for 40 days trial. During the trial the materials lost their integrity and were washed into the glass frit that was originally used to hold them. These results served as important benchmarks on the stability of nanomaterials towards exposure ambient laboratory and marine conditions. The observed loss of integrity under marine conditions could be a result of biodegradation of the materials. As described in Sections C-E, we have sought to improve the physicochemical properties of our chitin based sorbents by identifying additives which can be co-dissolved in [C$_2$mim][OAc], allowing us to spin homogeneously blended chitin composite fibers directly from solution. Selection of additives was also governed by a need to preserve the renewability and ultimate biodegradability of chitin, which are major advantages of this platform. We investigated lignin as additive, which is an extremely abundant polyphenolic plant compound which acts as a cross-linking agent in wood and is known to have anti-microbial properties, possibly allowing it to control the biodegradation of the sorbent in seawater. It can be obtained renewably and dissolved in [C$_2$mim][OAc], but blends of natural lignin and chitin are not known in the literature.

Prior to preparing composite fibers, we investigated antibacterial properties of different type of lignin. We first developed protocols for testing antibacterial and antioxidant properties of our materials. To address the potential leaching of antifouling additives from the materials and strength of antibacterial properties we have developed agar diffusion test and shaking flask method, respectively. As an additive to our chitin materials, lignin, a chemical component of terrestrial plants which protects them from chemical and microbial attack, was investigated. Depending on lignin extraction procedure and source of the biomass, antifouling properties of lignin can vary significantly. In order to find the lignin with the strongest antifouling properties, lignins obtained from typical industrial pulping (Indulin-AT or often called Kraft lignin) and lignin, extracted from biomass, using ionic liquid (IL-lignin) were compared.

We found that all types of tested lignins had antibacterial properties (Figure 14). However, the IL-lignin, extracted from pine wood at low temperature (Treatment II) showed up to ~90% reduction of bacteria, while high temperature treatment decreased antibacterial activity (only ~30% reduction was seen). The antibacterial properties were tested against *E.coli*. We also observed that IL-lignin had stronger antioxidant properties, in comparison with Indulin-AT lignin.
Figure 14. Antibacterial properties of IL-lignin extracted from wood at 175°C (treatment I) and 80°C (Treatment II) using [C$_2$mim][OAc] vs. commercially available Kraft lignin. The antibacterial properties were tested using shake flask method and *E.coli* as a test culture.

Next, we investigated the spinning of chitin/lignin blends using chitin extracted from shrimp shells and indulin AT lignin. Lignin was found to be soluble in [C$_2$mim][OAc] but did not produce solutions with enough viscosity to pull fibers. We observed that chitin and lignin powders could not be co-dissolved into [C$_2$mim][OAc] despite their independent solubility, but solutions of chitin and lignin in [C$_2$mim][OAc] could be mixed at any ratio. The addition of chitin to lignin at only a 1.5:8.5 ratio (w/w) allowed continuous (though brittle) fibers to be pulled (Figure 15). Increasing the ratio of chitin to lignin resulted in fibers with increased strength and flexibility.

Figure 15. Chitin/lignin blended materials. Attempting to co-dissolve chitin and lignin powder directly into [C$_2$mim][OAc] results in a material made of pure lignin which cannot be pulled into fibers (left). Blending [C$_2$mim][OAc] solutions of chitin and lignin allows pulling of short fibers at a 1.5:8.5 chitin/lignin ratio (center) and meter-length fibers at a 4.5:5.5 chitin/lignin ratio (right).

Once we were able to prepare composite fibers, we tested possible leaching of lignins from the materials using an Agar diffusion test. We observed that lignin did not leach from
lignin-based membranes (Figure 16A) indicating that it should provide long term antibacterial stability. The prepared blended chitin/lignin fibers had the following ratios: 9:1, 8:2, 7:3 and 5:5 and were evaluated for their stability against the bacteria using shake Flask method (Figure 16B). We found that a minimum ratio of lignin/chitin needed to increase antibacterial properties is 7:3 (chitin/lignin).

**Figure 16.** Antibacterial testing of materials with different types of lignin as an additive. (A) Agar diffusion test for lignin-based membranes: KF-Kraft lignin, IL-lignin extracted from biomass using IL and KF+xy–Kraft lignin+xylan. (B) Antibacterial test (shake flask method) for chitin-lignin blended fibers with different chitin/lignin ratios.

Based on our findings, blending chitin with lignin resulted in a decrease in strength with increasing lignin content, and continuous fibers were produced at minimum 4.5:5.5 ratio of chitin to lignin. Addition of lignin into chitin fibers improved antibacterial properties, when the ratio of chitin to lignin was 7:3. Increasing lignin content in chitin fibers did not result in additional increase in antibacterial activity indicating that 7:3 is optimal ratio between chitin and lignin.
J. Structural Clues to UO$_2^{2+}$/VO$_2^+$ Competition in Seawater Extraction using Amidoxime-based Extractants


Amidoxime continues to be the center of efforts to design higher capacity extractants, as well as the benchmark against which new extractants are compared. Nevertheless, the present amidoxime-based sorbents do not yet perform well enough for seawater extraction to be competitive with terrestrial mining due to seawater ions (V, Cu and Fe) competition for amidoxime binding sites. Despite some progress made in the designing amidoxime-based sorbents, still little is known about the selectivity of amidoxime for the uranyl ([UO$_2$]$^{2+}$) ion that is crucial for adsorption in the seawater environment. This understanding will be important for making decisions on how to improve the capacity of the sorbent by modifying the extractant functionality, especially for chitin-based sorbents where the ability to freely attach new sorbent moieties is an important advantage. For instance, it is hypothesized that adjacent amidoxime functional groups may work together to form the actual active uranyl binding site on poly(acrylamidoxime)-based resins. Therefore, for better understanding of both the affinity and selectivity of extractants towards uranium, we were using small molecule analogs of sorbent binding sites to prepare crystalline metal complexes and characterize them through single crystal X-ray diffraction (SCXRD).

We identified 4,5-dicyanoimidazole as a commercially available precursor that can be converted to a diamidoxime ligand using an addition reaction with hydroxylamine. The conversion of 4,5-dicyanoimidazole yielded 4,5-(diamidoximyl)imidazole (4,5-(DAO)Im) (Figure 17), the structure of which was confirmed by SCXRD.

![Figure 17. Synthesis of 4,5-(diamidoximyl)imidazole (4,5-(DAO)Im) from dicyanoimidazole precursor.](figure)

The analysis of the crystal structure revealed that the adjacent functional groups did not react or tautomerize, but formed a strong intramolecular hydrogen bond. The 4,5-(DAO)Im ligand was poorly soluble in water and ethanol, but readily dissolved in aqueous solutions containing uranyl or pervanadyl ions. When co-dissolved with uranyl, the color was changed from yellow-green to dark-orange immediately and the metal complex with (4,5-(DAO)Im) crystallized spontaneously upon standing overnight. The complex of uranyl with (4,5-(DAO)Im) revealed that the ligand was doubly deprotonated to form a chelating dianion with both oxime groups bonding through both the N and O atoms (Figure 18, right). When 4,5-(DAO)Im was co-
dissolved with pervanadyl, no change in color was observed and crystals were formed after standing for several days. The obtained complex with VO$_2^+$ was found to form a dinuclear complex in which one of the oxime groups was deprotonated and strongly coordinating, while the other remained protonated. The strong intramolecular hydrogen bond was preserved in the pervanadyl complex, and basic nitrogen atom on the imidazole ring as also found to participate in coordination. (Figure 18 left).

Figure 18. Ball-and-stick representation of crystal structures of 4,5-(DAO)Im (top) and its complexes with pervanadyl (bottom left) and uranyl (bottom right) ions.

In this work, we have demonstrated a previously undiscovered cooperative binding mode between [UO$_2$]$^{2+}$ and the two amidoxime groups and provided the first direct comparison of analogous V$^{5+}$ and [UO$_2$]$^{2+}$ amidoxime complexes which show the effects of intramolecular hydrogen bonding on the geometry and coordination mode of the amidoxime ligand. In total, our findings indicate that ligands with multiple amidoxime groups can have significantly different selectivity to [UO$_2$]$^{2+}$ ions.
IV. Summary of Major Achievements

The successful demonstrations, achievements and important findings are summarized below:

- Demonstration of chitin nanofiber formation during electrospinning from ionic liquids through finding optimal electrospinning parameters such as voltage, distance from the tip of the needles to the collector and to the electrode.
- Discovered optimal solution properties (viscosity, surface tension, conductivity) needed for electrospinning of chitin obtained from different biomass source from ionic liquids to form nanofibers.
- Demonstration electrospinning of chitin-cellulose composites from ionic liquid into networks of nano- and submicron fibers with increased mechanical stability and chitin-lignin blends with increased antimicrobial activity.
- Demonstration of tensile strength and plasticity improvement of chitin-based dry wet-spun fibers through blending with other biopolymers.
- Explored various surface functionalization techniques to produce fibers with dual function.
- Isolate the first analogous of uranyl and pervanadyl complexes of amidoxime and demonstrated their structural difference and coordination modes.
- Successfully demonstrated surface modification of electrospun chitin mats and their uranium uptake from simulated seawater solutions using $^{233}$U as a marker.

V. Publications

7. Berton, P.; Kelley, S. P.; Rogers, R. D. Stripping uranium from seawater-loaded sorbents

8. Zavgorodnya, O.; Shamshina, J. L.; Choudhary, H.; Rogers, R. D. Electrospinning of biopolymer composites from ionic liquids. *In preparation as a full article for ACS Sustainable Chem. Eng.*


**VI. Presentations**


7. “If we are going to mine the oceans, let’s not make the same mistakes made in terrestrial mining,” R. D. Rogers, O. Zavgorodnya, J. L. Shamshina, Presented by R. D. Rogers before International Conference on Seawater Uranium Recovery, University of Maryland, College Park, MD USA. July 19-22, 2016


VII. References