PHOSPHATE REMOVAL FROM AQUEOUS SOLUTION USING A QUATERNIZED ELECTROSPUN CELLULOSE NANOFIBER AS AN ANION EXCHANGE RESIN

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EXTENDED ABSTRACT

Nutrient pollution is a serious problem that is threatening water quality worldwide. Phosphate in high concentrations is the leading contributor to the degradation of estuaries, lakes and reservoirs, and consequently to the creation of hypoxic zones, where fish and aquatic life cannot survive. A quaternized cellulose nanofiber mesh was prepared using a choline-based ionic liquid to serve as an anion exchange resin for the removal of phosphate from aqueous solutions. A 17% cellulose acetate (CA) solution in a mixture of acetic acid and water (75/25% v/v) was electrospun into nonwoven fiber mesh. The latter was heat-treated at 195ºC for 1 hour and then alkali-treated to obtain regenerated cellulose (RC) mesh. The RC mesh was then quaternized in a mixture of a choline chloride derivative and urea in the presence of imidazole. The structure and morphology of the functionalized mesh were characterized using Fourier Transform Infrared Spectroscopy (FTIR) and polarization microscopy. Batch tests were performed to evaluate the adsorption capacity of the mesh for the removal of phosphorus as phosphate (PO₄³⁻-P). The preliminary results showed a maximum uptake for PO₄³⁻-P in the order of 55 mg/g mesh. The Langmuir isotherm adsorption model fit the adsorption data best, suggesting a monolayer adsorption mechanism. The developed anion exchange resin can potentially be useful for other water purification purposes mainly the removal of other anions of environmental concern.

Keywords: Phosphate, Cellulose, Nanofibers, Adsorption, Quaternized, Electrospun

1. INTRODUCTION

Nutrient pollution is a serious problem threatening water quality worldwide. It is the leading factor for the degradation of estuaries, lakes and reservoirs, and for the creation of hypoxic zones, where fish and aquatic life cannot survive (EPA, Nutrient Pollution and Numeric Water Quality Standards). High phosphorus and nitrogen loadings stimulate the growth of blue-green algae [they are not plants!!]. In the presence of nutrients, these organisms consume large amounts of dissolved oxygen, suffocating fish and other marine animals.

To overcome these problems, chemical precipitation and biological nutrient processes are the most commonly used methods for nutrients removal from municipal and industrial wastewaters (Metcalf, 2003). Generally, these processes give effective and steady results. However, they produce sludge with very high concentrations of nutrients that require subsequent disposal. Commercial ion-exchange resins and adsorbents are materials that have been used to remove nutrients from effluents. These commercial ion exchangers have good adsorption properties, but they are very expensive.
The use of biopolymers has been suggested as a possible method for the removal from water of contaminants. Two attractive features of biopolymers are that they are biodegradable and they can be regenerated. Previous studies have shown that lignocellulosic adsorbents can be chemically modified by adding cationic groups through quaternization to enhance their adsorption capacities towards anions such as phosphate, nitrate, sulfate and others. The quaternization involves reacting these biopolymers with quaternary ammonium compounds. These compounds react with –OH group in the glucose moieties of cellulose. Most of the derivatizations involve first the crosslinking the cellulose material, then converting into a quaternary amine (L.H. Wartelle, W.E. Marshall). W.-Y. Wang et al successfully treated giant reed for the removal of phosphate by reacting it with epichlorohydrin, ethylenediamine (EDA) and triethylamine in the presence of N,N-dimethylformamide (DMF). X. Xu et al. prepared amine-crosslinked wheat straw that showed high removal capacities for phosphate and chromium (VI) from aqueous solutions.

The preparation of nanofibers from cellulose through electrospinning poses challenges, as cellulose dissolves in few solvents. Cellulose derivatives can be better alternatives to prepare nanofibers. Among the cellulose derivatives, cellulose acetate (CA) is an essential ester used in many applications such as films, reverse osmosis and nanofiltration membranes due to its good physical properties (Y. Tian et al. / Carbohydrate Polymers 83 (2011) 743–748). Unlike cellulose, CA is soluble in various solvents, forming gels that are suitable for electrospinning and can later be deacetylated to regenerate cellulose fibers. The regenerated cellulose (RC) can be surface-modified by adding functional groups to produce adsorbents for the removal of anions from aqueous solutions.

Electrospinning is a versatile method to produce continuous fibers with diameters ranging from micrometers to submicrons (Wang et al., 2002). The electrospun fibers possess high specific surface area and can be functionalized to provide adsorbents with better adsorption capacities towards anions.

In this study, regenerated cellulose (RC) nanofibers from cellulose acetate non-woven mesh were quaternized using green chemistry. The RC nanofibers were functionalized by the introduction of quaternary amines to the backbone of the RC using chlorocholine chloride (ClChCl) and urea in the presence of imidazole. The quaternized RC nanofibers were then used as an ion exchange resin to remove PO$_4^{3-}$ -P from water.

2. MATERIALS AND METHODS

Cellulose acetate (CA) (Molecular Weight (MW) =30,000 and % acetyl content=39.8)), imidazole and chlorocholine chloride were purchased from Sigma-Aldrich (WI, USA). Potassium hydroxide, ethanol, acetic acid and urea were purchased from Fisher Scientific (PA, USA). All chemicals were of analytical grade and were used without modification.

2.1. Electrospinning and Deacetylation of Cellulose Acetate Nanofibers

The electrospinning was carried out at room temperature. The polymer solution was prepared by mixing CA 17% (w/v) in a mixture of acetic acid/distilled water (75/25% v/v) (S.O. Han et al.) for 48 hours to ensure the complete gelation of the polymer. The polymer solution was placed in a syringe. The solution was pumped horizontally at a flow rate of 20 µl/min through a stainless-steel needle (ID=0.84 mm) at 15 kV using a direct-current power source. The electrospun nanofibers were collected on a grounded aluminum-foil collector. The needle-tip-to-collector distance, was 10.0 cm. After electrospinning, the CA nanofibers were heat-treated at 195 °C to improve their physical characteristics; then they were carefully detached from the aluminum foil. The heat-treated CA nanofibers were deacetylated at room temperature for 4 hours with 0.5 M KOH solution in ethanol to produce RC nanofibers (S.O. Han et al.). After the alkali treatment, the RC nanofibers were copiously washed with water followed by ethanol, and were air-dried for 24 hours.
2.2. Functionalization of RC nanofibers
An ionic liquid (IL) analogue was prepared following the procedure by Abbott et al (2006). First, 12.96 g of chlorocholine chloride was mixed with 10.27 g of urea at 75 °C with continuous stirring for 30 min to produce a clear transparent solution. Then the IL was cooled to room temperature. The functionalization of RC nanofibers was carried out by mixing 0.1 g of RC with 5 ml of IL in the presence of 0.392 g of imidazole and heated for 15 hours at 150 °C in a Fisher Scientific HiTemp Bath filled with Lab Armor thermal beads. After functionalization, the nanofibers were copiously washed with water and air-dried for 24 hours.

2.3. Characterization
The morphology of the electrospun cellulose nanofibers was observed using a polarized-light microscope (Nikon Eclipse e600). The infrared spectra of the functionalized nanofibers were obtained with a Thermo Nicolet NEXUS 670 FTIR spectrometer equipped with a Centaurus microscope. The spectra were collected in transmission mode at a resolution of 4 cm⁻¹ with averaging 400 scans.

2.4. Sorption Isotherms:
The adsorption isotherms were constructed based on batch equilibrium tests using phosphate as the target contaminant. The experiments were carried out in 30 mL plastic bottles using PO₄³⁻P solutions of 20, 40, 80, 160, 320 and 400 mg/L with a dosage of 1 g of the functionalized resin per 1 liter of solution. The PO₄³⁻-P stock solution was prepared by dissolving the set amount of sodium phosphate monobasic (NaH₂PO₄) (Fisher Scientific) in deionized water. NaCl was added to adjust the ionic strength of the solutions to 0.01 M. The bottles were sealed and placed on a planetary shaker table for 24 hours. The solutions were then filtered through a 0.45 µm filter. The filtrates were analyzed using the Molybdovanadate method for phosphate.

The sorption amount q (mg/g) of adsorbed PO₄³⁻-P anions at any time were calculated as:

\[ q = \frac{(C_0 - C_e)V}{m} \]

Where:  
- \( C_0 \) = initial concentration of contaminant (mg/L)  
- \( C_e \) = equilibrium concentration of contaminant (mg/L)  
- \( V \) = volume of the solution (L)  
- \( m \) = functionalized regenerated cellulose (FRC) dosage (g)

3. RESULTS AND DISCUSSION:
3.1. Morphology of the nanofibers:
Figure 1 shows photomicrographs of the CA, RC and FRC nanofibers. The electrospun CA as shown in Figure 1(a) are long uniform nanofibers. Only few short fibers or beads were observed. Fiber diameters were measured by image processing software (ImageJ, NIST). Fiber diameters were measured from the micrographs by drawing straight lines along the diagonals of an image (to avoid counting the fibers twice) and measuring fibers that crossed the lines. To generate reliable statistics, fibers were imaged from different parts of a 1 cm × 1 cm sample area. CA, RC and FRC nanofibers are a nonwoven mesh of fibers with submicron diameters ranging from 400 nm to 1µm. The nonwoven mat structure of the nanofibers was maintained during deacetylation and functionalization processes as shown in Figure 1(b) and (c).
3.2. Fourier-transform infrared spectroscopy

The FTIR spectra of CA, RC, and FRC are presented in Figure 2. The untreated CA spectrum is characterized by a broad peak at 3250-3650 cm\(^{-1}\) attributable to the hydrogen-bonded-OH-stretching vibration. The characteristic peaks at 1766 cm\(^{-1}\)(\(\nu_{\text{C}=\text{O}}\)) and 1274 cm\(^{-1}\)(\(\nu_{\text{C}-\text{O}-\text{C}}\)) representing the acetyl group in the spectra of untreated CA are not present in the spectra of RC and FRC, indicating that the CA fibers were converted to RC (Z.Ma et al). The peaks at 1647 cm\(^{-1}\) and 2943 cm\(^{-1}\) correspond to carbonyl stretching and C-H stretching, respectively (T.S.Anirudhan et al). In the FRC spectrum, there are additional peaks at 1421 cm\(^{-1}\) and 1084 cm\(^{-1}\), characteristic of C-N vibration and \(-\text{CH}_2-\text{N}^+\text{H R}_2\) type nitrogen (T.S.Anirudhan, M.R.Unnithan).
3.3. Adsorption tests

The adsorption test of the functionalized NRC was investigated with a synthetic solution for PO₄³⁻·P with concentrations ranging from 20 to 400 mg/l (which salt used to generate the solution). The results are shown in figure 3. An increase of removal of the anions is observed with increasing concentration until a plateau is reached corresponding to the maximum uptake at site saturation of the FRC.
Langmuir and Freundlich models were used to interpret the equilibrium data. The linearized form of the Langmuir isotherm is governed by the following equation:

\[
\frac{1}{q_e} = \frac{1}{b q_m C_e} + \frac{1}{q_m C_e}
\]

And the linear form of Freundlich adsorption equation is

\[
\log q_e = \log K_F + \frac{1}{n} \cdot \log C_e
\]

where, \( q_e \) (mg/g) and \( C_e \) (mg/L) are the equilibrium concentrations of \( PO_4^{3-} \) in the solid and liquid phase, respectively, \( q_m \) (mg/g) is the Langmuir monolayer sorption capacity, \( b \) (L/mg) is the equilibrium constant, \( K_F \) [mg/g(L/mg)^1/n] is the relative sorption capacity of the sorbent, and \( 1/n \) is the intensity of sorption.

The parameters of the isotherms for the removal of \( PO_4^{3-} \) are listed in Table 1. The values of \( R^2 \) for the Langmuir isotherm are higher than those obtained with the Freundlich model. This indicates that the adsorption mechanism was most likely a monolayer adsorption mechanism onto the surface of FRC.

<table>
<thead>
<tr>
<th>Langmuir</th>
<th>Freundlich</th>
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<tbody>
<tr>
<td>( q_m ) (mg/g)</td>
<td>( b ) (mg/L)</td>
</tr>
<tr>
<td>56.59</td>
<td>0.006</td>
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4. CONCLUSION
In the present study, RC nanofibers from electrospun CA were functionalized by the addition of quaternary amines to the cellulose moiety. The functionalized regenerated cellulose showed great potential for the removal of \( PO_4^{3-} \) from water. The Langmuir
isotherm adsorption model provided a better fit for the adsorption data, suggesting a monolayer adsorption mechanism. The developed biosorbent can potentially be useful for water purification purposes mainly to remove other anions of environmental concern such as chromate, arsenate and others.

REFERENCES

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