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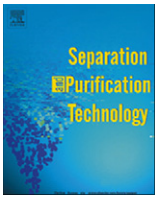

Novel N-methyl-D-glucamine-based water-soluble polymer and its potential application in the removal of arsenic

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ABSTRACT

A new water-soluble polymer based on the *N*-methyl-D-glucamine (NMG) group was prepared and characterized, and its arsenic retention capacity was studied using the liquid-phase polymer-based retention (LPR) technique.

The monomer glycidyl methacrylate-*N*-methyl-D-glucamine (GMA–NMG) was synthesized, and the polymer was subsequently obtained through radical polymerization using ammonium persulfate as an initiator reagent. The polymer was dissolved in water, purified and fractionated with ultrafiltration membranes with molecular weight cut-offs of 50,000 Da. The polymer was then characterized by potentiometric titration, FTIR and ^{1}H NMR spectroscopy.

The removal of arsenic was analyzed using the LPR technique with both the washing and enrichment methods. The removal experiments using the washing method were conducted by varying the pH, polymer:As(V) molar ratio, and concentrations of interfering ions. P(GMA–NMG) showed a high affinity for binding arsenate species (82% of removal) at pH 3.0. The optimum molar ratio was 70:1 polymer:As(V). Selectivity experiments showed that the presence of interferents gradually decreased the arsenic removal capacity. The maximum retention capacity was determined by the method of enrichment, obtaining a value of 45.9 mg As g^{-1} polymer.

Finally, the results showed that the combination of P(GMA–NMG) with ultrafiltration membranes is a potential alternative for the removal of hazardous As(V) species from aqueous solutions at acidic pH.

1. Introduction

Various technologies currently exist to remove arsenic using membranes or polymeric materials, including reverse osmosis, nano-, micro- and ultrafiltration processes, ion-exchange resins and fibers and water-soluble polymers.

Nanofiltration and reverse osmosis are the most commonly used techniques for the removal of arsenic. These processes use high pressure and therefore consume a considerable amount of energy [1]. Low-pressure membrane processes for arsenic removal include microfiltration and ultrafiltration. Nevertheless, these technologies are not adequate, because arsenical species are very small and can pass through the membranes. Currently, the available membranes are more expensive that other arsenic removal options, but they are more appropriate in municipal settings where very low arsenic levels are required.

Synthetic ion-exchange resins, generally polymers that are linked to charged functional groups, can also be applied to the removal of arsenic. Quaternary amine functional groups are commonly used for this purpose [2].

Ion-exchange fibers have many advantages when compared with traditional resins, such as their higher specific surface, smaller diameter and better elasticity. They can exist in the form of filaments and other textile articles and can be regenerated and reused [3].

Among the most recently developed materials for the removal of arsenic are water-soluble polymers, which, when combined with ultrafiltration membranes, can remove arsenic species from aqueous solutions [4–9].

The liquid-phase polymer-based retention (LPR) technique is a hybrid method of membrane separation in which a water-soluble polymer and arsenate ion are in contact on the feed side of a filtration system. The water-soluble polymer interacts with the arsenate ions, allowing the ions to bond to the polymer and create polymer-arsenate macromolecules that are then retained mainly by a size-exclusion mechanism. The unbound arsenic species, with diameters that are less than that of the membrane cut-off diameter, pass through with the permeate [10–13]. The great advantage of the LPR method is that it is performed in homogeneous media and largely avoids the phenomenon of mass transfer or diffusion that occurs with heterogeneous methods. Nevertheless, the fouling of the membrane is a

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disadvantage which must be minimized because the permeate flux decreases and, therefore, increases the processing time [12].

The LPR technique uses polymers with adequate molecular weights (i.e., higher than 50,000 Da) and membranes that have exclusion limits of 10,000 Da to interact with ions [10]. The membranes are typically composed of polycarbonate or cellulose esters, polyamides, or polysulfones. The ultrafiltration system consists of an ultrafiltration cell, membrane, stirrer, flow switch, reservoir, and pressure source [11].

Previous studies have reported the abilities of certain polymer-based ammonium salts to remove arsenate species from solution using the LPR technique. These cationic water-soluble polymers that contain different counterions have been synthesized, characterized and studied, demonstrating their different arsenic retention capabilities. Essentially, the capacity of the polymer to interact and retain arsenate anions depends on the pH [4], polymer:arsenic molar ratio [7], counterion of the quaternary ammonium group [6], ionic strength and the polymer concentration [9].

The *N*-methyl-D-glucamine (NMG) group consists of tertiary amine and sorbitol moieties. NMG is well known due to its high capacity and efficiency in removing boron from aqueous solutions [14–16]. Various resins and gels containing NMG have been developed to remove different oxyanions [17–19]. Recently, ion-exchange resins with NMG have been synthesized to selectively remove arsenic [20]. However, water-soluble polymers containing NMG have not yet been investigated.

The present study is focused on the removal of arsenic with a novel water-soluble polymer that is based on NMG in conjunction with ultrafiltration membranes. The NMG-containing water-soluble monomer was synthesized and subsequently polymerized through radical polymerization using amonium persulfate as an initiator. The polymer was then purified by ultrafiltration and characterized by potentiometric titration, FTIR and ^{1}H NMR spectroscopy. The arsenic retention capacities of poly(glycidyl methacrylate-*N*-methyl-D-glucamine) (P(GMA–NMG)) were studied with the LPR technique using a washing and enrichment method.

2. Materials and methods

2.1. Preparation and characterization of P(GMA–NMG)

Into a three-neck round bottom flask was added 60 mL of an aqueous solution (0.83 M) of *N*-methyl-D-glucamine (Sigma–Aldrich). Then, 6.8 mL (50.0 mmol) of glycidyl methacrylate (GMA) (Fluka) was slowly added to the NMG solution. The reaction was incubated for 5 h at 70 °C with powerful stirring. At the end of the reaction, only one aqueous phase was observed. The product was washed with diethyl ether to remove the excess GMA [18].

The reaction solution containing the GMA–NMG monomer in water was further polymerized by radical polymerization. The monomer solution was transferred to a polymerization tube, and the initiator ammonium persulfate (Sigma–Aldrich) was added (1 mol%). The solution was degassed with nitrogen gas for 20 min, and the reactor was placed in a thermoregulated bath at 70 °C for 24 h under a nitrogen atmosphere (see Fig. 1).

After the polymerization was complete, the polymeric solution was diafiltrated with twice-distilled water using a membrane with a molecular weight cut-off of 50,000 Da (Millipore). The solution containing the polymeric fraction that was greater than 50,000 Da was lyophilized. This polymeric fraction was then characterized by potentiometric titration, FTIR, and ^{1}H NMR spectroscopy.

For the potentiometric titration, 10 mL aliquots of 0.005 M P(GMA–NMG) were titrated with an aqueous solution of 0.005 M HNO_3. The aqueous solution of HNO_3 was prepared from Titrisol® (Merck). Potentiometric measurements were made using a pH meter (330 Inolab WTW). The FTIR spectra were obtained with a Nexus Nicollet spectrometer. For the FTIR analysis, 1 mg of sample was combined with 100 mg KBr. For the ^{1}H NMR analysis, the polymer was dissolved in D_2O, and the NMR spectra were recorded on a Bruker AC 250 spectrometer.

2.2. LPR Procedure

When arsenic ions and the water-soluble polymer are placed in contact and diafiltered by ultrafiltration, the arsenate ions are retained, whereas ions with low interaction rates pass through the membrane to the permeate stream.

The main features of our LPR system include a filtration cell (Amicon 8050) with a magnetic stirrer that contains a membrane filter of regenerated cellulose with a molecular weight cut-off of 10,000 Da (Ultracel PLGC, Millipore), a reservoir (Amicon RC800), a flow selector and a nitrogen gas cylinder as the pressure source (see Fig. 2).

Two types of experiments were investigated for the LPR technique. The first one was a washing method, which involved a constant dilution that was based on the continuous diafiltration by addition of solvent. In the feed, a certain amount of polymer was dissolved in twice-distilled water, and then a solution of sodium arsenate was added to the polymer solution, resulting in an arsenic concentration of 30 mg L^{-1}. Before performing the ultrafiltration procedure, the pH of the solution was adjusted. The resulting polymer/arsenate mixture was stirred for 1 h at room temperature and then placed in the ultrafiltration cell. The solution was submitted to ultrafiltration and was washed with reservoir twice-distilled water at the same pH. Ultrafiltration was performed under a total pressure of 3.5 bar and a stirring speed of 250 rpm. The total cell volume (20 mL) was kept constant during the filtration process. Fractions of 20 mL were collected to a total permeate volume of 100 mL. Results of the As(V) uptake were systematically presented as the percentage of retention (R(%)) versus the volume of permeate. The quantity of arsenic species that were retained was calculated as the difference from the initial concentration. For the selectivity assays, Na_2SO_4 (Fluka) and NaCl (Merck) solutions were used, and the results of the arsenic retention are shown in the column chart.

The second type was an enrichment method, which involved a method of concentration that was based on the continuous diafiltration by the addition of arsenic solution at constant volume. This method was used to determine the maximum retention capacity of the water-soluble polymer.

A solution that contained the arsenate was passed from the reservoir through the ultrafiltration cell containing a polymer solution. Both the cell and reservoir solutions were adjusted to the same pH values. The enrichment method was used with an aqueous solution of 30 mg L^{-1} As(V) and 189 mg of soluble polymer in 450 mL of total filtrate volume.

A blank experiment (in the absence of the water-soluble polymer) was performed with both experiments.

The arsenic concentration in the filtrate was measured by atomic absorption spectroscopy (AAS) using a Unicam Solaar spectrometer. The pH was measured using a pH meter (330 Inolab WTW). A solution of 500 mg L^{-1} of $Na_2HAsO_4 \cdot 7H_2O$ (Merck) was used. The pH was adjusted by adding 0.1 M HNO_3 (J.T. Baker).

3. Results and discussion

3.1. Characterization of P(GMA–NMG)

Potentiometric titration was performed in duplicate, and the obtained curves are shown in Fig. 3. The pK_a of the polymer was determined to be 6.19 from the curve, whereas the equivalence