Novel Polymeric Filtration Devices for Arsenic Removal from Water

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Abstract

The work focuses on the development of supermacroporous polymeric cryogels as filtration devices for the capture and removal of arsenic, microbial contaminations and other heavy metals from different sources of potable water. Cryogels are macroporous polymeric gels with interconnected pores with a size range upto 200 μm and can be synthesized in any format like, monoliths, discs and beads. These gels were incorporated with iron by employing iminodiacetic acid coupling on the cryogels. They show high efficiency of arsenic capture along with other heavy metals and microbial contaminants. We have optimized these devices at different scale of operation as domestic water filters, devices for the filtration of water reservoirs and for filtration of ground water. These provide novel and cost effective approach for the removal of arsenic contamination from drinking water.

Keywords: Arsenic, cryogels, magnetite-chitosan beads, filtration devices, microbial contaminants.

1. INTRODUCTION

Treatment technologies for the removal of arsenic from water typically rely on its adsorption or filtration. Methods such as coagulation with ferric sulphate, lime softening, activated alumina, ion exchangers, reverse osmosis, electrodialysis, and nanofiltration have been tested with various degrees of success (EPA 2009). Research is also being done on combination treatments with coagulation and filtration. Presently, the major challenge is to design suitable filtration matrix with or without surface modifications for removal of air/water contaminants. Most of the filtration membranes available at present in the market are specific according to their applications, so there is no generalized filtration aids available which can cover a broad range of applications and can be at the same time cost effective. Limitations also exist in these membranes with respect to their appropriate chemistry and physical properties which otherwise could have made them applicable for general use.

In the present work, an attempt was made to use cryogel technology and immobilized metal affinity chromatography to remove arsenic and microorganisms present in water and make it potable. The cryogel filtration membrane can be a suitable choice for efficient and cost effective water filtration aid for heavy metal, microbial and other toxin removals. Cryogels are hydrogels which are synthesized at sub-zero temperatures and have supermacroporous structure with interconnected pores, thus offering a unique combination of high interconnected porosity with high mechanical strength (Kumar 2010). The binding of arsenic to the column was found to be due to ionic interactions. The binding capacity of the columns can be modified using different concentrations of the monomers. Also, the level of arsenic in water could be brought down to the acceptable limits by the passage of a spiked solution through the column. The interaction was found to be independent of the ionic concentration of the suspension. A complete separation of microbes was obtained by a single pass through the column.

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2. MATERIALS AND METHODS

Preparation of metal loaded-poly(AAm) cryogel filters and poly (DMAEMA) cryogel filters

Two types of cryogels were developed to exploit the principle of immobilized metal affinity chromatography for removal of arsenic and bacteria: metal loaded poly(AAm) cryogels and poly(DMAEMA) cryogels. Metal was loaded onto poly(AAm) cryogels by employing IDA coupling on these columns. Poly(DMAEMA) cryogel was used as such as it had positively charged groups and thus metal immobilization was not needed.

The epoxy-containing supermacroporous cryogel matrix was prepared as described. Monomers (0.95 grams of acrylamide, 0.25 grams of methylene-bis-acrylamide, and 0.2 ml of allyl glycidyl ether) were dissolved in deionized water (final concentration 6%). The free radical polymerization was initiated using 20 µl of TEMED and 22 mg of APS. The mixture was poured in 5 ml plastic syringes plugged at bottom, and was frozen at – 12 °C for 16 h. Then the columns were washed with warm water to remove any unreacted monomers and were stored at 4 °C till further use. The coupling of IDA and metal was done as described previously (Arvidsson 2003). The cryogels were washed each with 30 ml of 0.5 M sodium carbonate solution for 30 min in 50 ml centrifuge tubes. Each cryogel was equilibrated with 30 ml IDA (0.5 M in 1M sodium carbonate, pH 10). It was then incubated with a fresh solution of IDA for 48 h at room temperature on a rotating mixer. The cryogels were washed with distilled water till the pH came down to about 8. Copper / Iron was loaded in the form of 30 ml 1M CuSO4 / $FeCl_3$ for 2 h and kept for shaking The cryogels were washed with water to remove unbound metal ions. These were then washed with imidazole buffer (15 mM in 20 mM HEPES and 0.2 M NaCl, pH 7). The cryogels were repacked in syringes and equilibrated with 5 bed volumes of the loading buffer or binding buffer, as the case may be, at the rate of 1 ml/ min.

The charged DMAEM cryogel was prepared as follows. DMAEMA (0.6 ml), 200 mg of bis-acrylamide were dissolved in 20 ml water. After cooling in an ice bath, 11 mg of APS and 10 µl of TEMED were added to start polymerization. The solution was dispensed into 5ml plastic syringes sealed at bottom. The syringes were capped at the top with parafilm and stored at -12 °C for 16 h in a cryostat. After the stipulated period, the cryogels were taken out and washed with sufficient amount of water. They were then dried and stored till further use.

Detection and quantification of arsenic

The quantification of arsenic was done as described elsewhere (Merry and Zarcinas, 1980, DGHS, 2005). Silver diethyldithiocarbamate solution (3 ml) was introduced into the bubbler of a modified Gutzeit apparatus. Potassium iodide (2 g) and 50 ml of sample were introduced in to the 100-ml conical flask, swirl until dissolved, and mixed with 2 ml of stannous chloride solution and 10 ml of concentrated hydrochloric acid. After mixing well, 10 g of granulated zinc was added. The blubber was positioned in place and all joints were sealed. The reaction was allowed to proceed for 20 min. The generated arsine gas was passed through a solution of lead acetate by the passage of nitrogen through the apparatus. The absorption of the resulting solution was measured at 540 nm against standards to determine the amount of arsenic in the sample.

Testing the arsenic retention capacity of cryogel filter

The columns were washed with 3 column volumes of distilled water. A diluted solution of sodium arsenite (5ppm) was loaded into the columns at a low linear flow rate of 2 cm/min. The aliquots of flow-through through the column were collected. The amount of arsenic in the flow-through was determined by the silver diethyldithiocarbamate method. The difference in the amount of arsenic loaded and that in the flow-through gave the amount of arsenic retained in the column.

Testing of bacterial retention capacity on metal loaded cryogels

The columns were first washed with 2 column volumes of 70% ethanol. These were then washed with 1 column volume of distilled autoclaved water. A diluted bacterial suspension was loaded onto the columns at a low linear flow rate of 2 cm/min. The aliquots of flow-through through the column were collected. Sample (50 µl) was then plated on to nutrient agar plates. After an incubation of 2 days at 37 °C, the number of colonies appearing on the plates was counted.

3. RESULTS AND DISCUSSION

Supermacroporous monolithic cryogel filters

Supermacroporous, continuous, monolithic, cryogel filters have large continuous interconnected pores. These macroporous matrices can be synthesized in different formats i.e. monoliths, disc shaped (Figure 1 A, B), etc. High porosity with pore size up to 200 µm as confirmed by scanning electron microscopy (Figure 1 C, D) enables the cryogel to be employed for filtration purposes. As a result of the convective flow of the solution through the pores, the mass transfer resistance is practically negligible. The flow pass characteristics are extremely good; the water flow rate through the monoliths estimated at a hydrostatic pressure equal to 1 m of water column (about 0.01 MPa) is in the

range of 2000–2500 cm/h. The gel phase (polymer with tightly bound water) composes only 10% of the total cryogel volume, and the most part of the monolithic column (90%) is an interconnected system of supermacropores filled with water. Contrary to the bead-packed columns where one could distinguish between the pore volume inside the beads and interstitial volume in between beads, in monoliths, pores are uniformly permeate through the whole column volume. The pores are equally accessible for the substances of different molecular weights, tyrosine (Mw 181), bovine serum albumin (Mw 69 000) and Blue Dextran (Mw 2000000) (Arvidsson et al, 2003) indicating highly interconnected structure. The large pore size in cryogel in

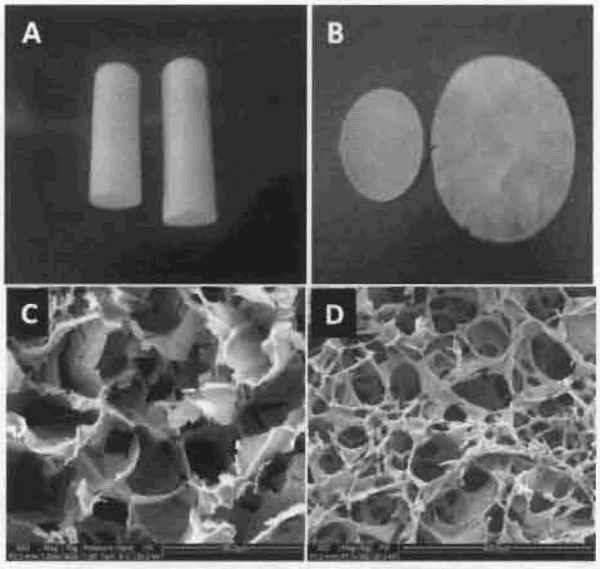

Figure 1. Supermacroporous polymeric filters. A) Monolith format of polymeric filter, B) Disc/sheet format of polymeric filter. C) & D) Scanning electron microscopic image of supermacroporous polymeric filters.

combination with highly interconnected pore morphology and hydrophilic nature of the pore walls formed from a gel warrants their use for filtration devices.

Arsenic retention capacity of cryogel filters

To find the amount of arsenic binding to $FeCl_3$ and DMAEM gels, a load solution of known concentration was passed through the columns. The concentration of arsenic in the flow through was measured (Figure 2). Since the binding of arsenic is due to ionic interactions, it was hypothesized that arsenite / arsenate ions will be displaced if some other negative ions are made to compete with them. Thus, a 4 M NaOH solution was passed through the column, and the concentration of arsenic in the resulting elution was measured. Finally, the column was stripped of the bound iron by passing a 5 M HCl solution.

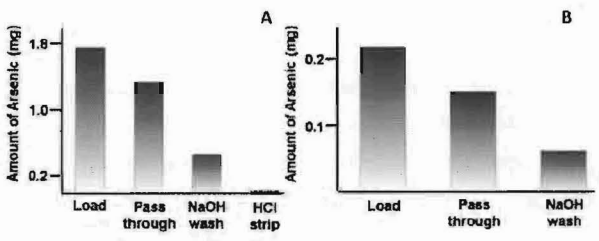

Figure 2. Binding of Arsenic to A) iron loaded cryogel filter, b) DMAEM cryogel filter.

The concentration of arsenic in this elution was also measured. The same process was carried out with DMAEM gels, with the exception of the HCl step, since here the whole column is positively charged, and is devoid of any other positively charged ions. It was found that the capacity of the $FeCl_3$-cryogel column is 0.1 mg / ml, and the capacity of DMAEM column is 0.01mg / ml. Thus the iron columns can hold 10 times as much arsenic as can the DMAEM columns.

Effect of pH on the arsenic removal capacity of the columns

The pH of most raw water is between 6.5 and 8.5 (APHA, 1989). Thus, our filtration system should not have a large variation in arsenic retention capacities between these pH; which could result in leaking of arsenic in to the water supply. To test this, water samples spiked with arsenic were maintained at different pH using phosphate and tris buffers. To cover the entire range, we maintained the pH at 6, 7, 8 and 9. These samples were then passed through the columns and the arsenic retention capacities were measured. It was found that the capacity of the column is invariant of the pH of the solution (Figure 3).

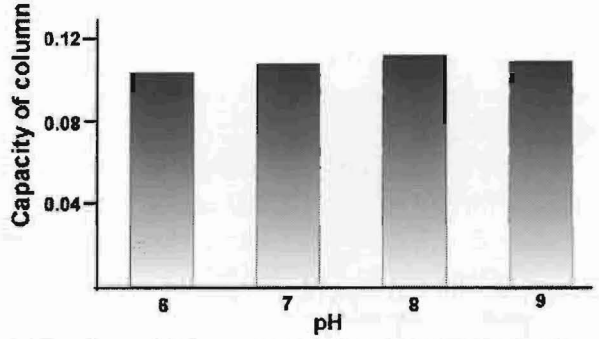

Figure 3.Effect of pH on arsenic removal capacity of cryogel column. Capacity is defined as mg of arsenic retained per ml of column.

Demonstration of the capability of the column to completely clean a sample of water

The water sources found practically may be contaminated by

both bacteriological and mineral agents. Thus, we wanted to determine if the column can bring the levels of both these types of contaminants to acceptable limits. The WHO recommends that no bacteria of enteric origin should be detected in 100 ml of potable water. Since 1993, the limit for arsenic is 10ppb (Johnston et al, 2008). Also, the natural water might contain upto 10 mg/liter of iron salts, which could interfere with the column operation. To test this, we took a water sample with a bacterial concentration of 14000 cfu/ml, and an arsenic concentration of 5 ppm. $FeCl_3$ was added to a concentration of 20 mg/liter. This sample was then passed through a 20 ml $FeCl_3$ loaded poly(AAm) cryogel filter at a flow rate of 5 cm/min. The bacterial and arsenic concentrations in the resulting flow through were found. No bacterial colonies were found when any of the resulting flow-throughs were plated.

For arsenic, the following results were found (Figure 4):

- Amount of arsenic loaded: 0.85 mg (concentration ~5ppm)
- Amount of arsenic in the flow-through of first pass: 0.04 mg (concentration 214 ppb)
- Amount of arsenic in the flow-through of second pass: negligible (concentration 2.8 ppb)
- Amount of arsenic in the flow-through of first pass with $FeCl_3$: negligible (concentration 7 ppb)

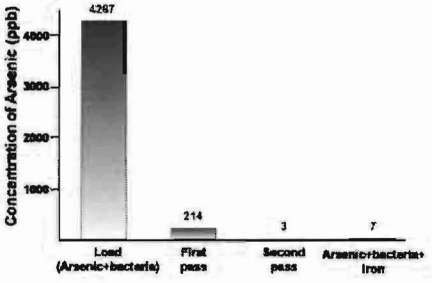

Figure 4. Removal of arsenic and bacteria from spiked water sample by Fe-loaded cryogel filter

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