



Crosslinked polyDADMAC gels as highly selective and reusable arsenate binding materials



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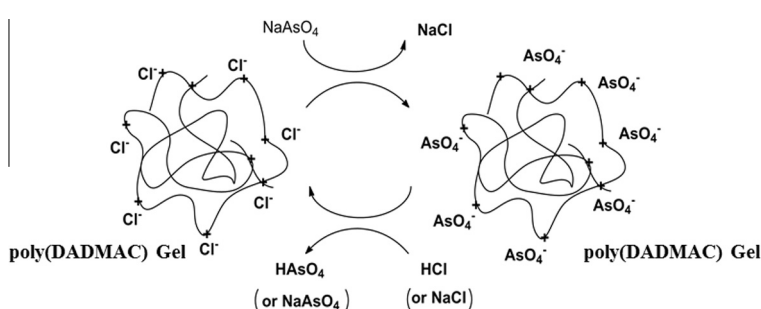
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HIGHLIGHTS

- Crosslinked DADMAC polymer gel is excellent sorbent for removal trace arsenic.
- The arsenate removal is based on the ion exchange mechanism.
- The arsenate exchange is highly selective over sulfate and chloride ions.
- Equilibration with arsenate at pH 7 takes place within 10 min.
- The gels loaded can be recovered either by acidifying (0.1 M) or treatment with brine.

GRAPHICAL ABSTRACT



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ABSTRACT

High porosity cationic hydrogels synthesized via crosslinking co-polymerization of diallyldimethylammonium chloride (DADMAC) with N,N'-tetraallylpiperaziniumdichloride (TAP) showed high affinity towards arsenate anions over a wide pH range within notably short periods. Batch tests indicated that poly(DADMAC) hydrogels removed 99% of the arsenate anions from aqueous solutions at pH 6–10 and exhibited a maximum arsenic removal capacity of 0.12 g arsenic per gram of hydrogel. DADMAC hydrogels performed well at various pH levels after a short contact time (*i.e.*, 10 min). Evidence of the ion exchange mechanism was based on experiments with solutions containing competing chloride and sulfate ions. An “intra-particle diffusion model” was proposed for the kinetics of arsenic removal. This gel was determined to be a good candidate for use in practice due to its easy regeneration either by treating with a 8.24 g/L of NaCl solution or by reducing the pH of the medium to below 1.0.

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1. Introduction

The shortage of usable water resources is one of the most challenging issues currently facing the world. In this respect, arsenic contamination in ground and surface waters is considered to be

one of the major problems contributing to this shortage. Arsenic is a highly toxic element [1–13] that may cause cancer malignancies, vascular diseases, and non-malignant skin tumors [1]. The acceptable limit for arsenic in drinking water is 10 µg/L according to the World Health Organization (WHO) [6–11]. The US Environmental Protection Agency (EPA) set the arsenic standard for drinking water in the US at 10 µg/L in 2001; the previous standard was 50 µg/L [2]. Arsenic is a naturally occurring element in rocks, soil,

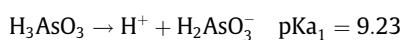
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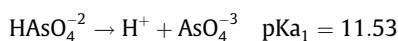
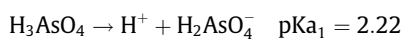
air, and so on and can be found in ground and surface waters due to the corrosion, dissolution, and microbial activity of these natural sources. In addition, arsenic can be transferred to surface and ground waters due to industrial processes. Industries, such as mining, petroleum refining, and pesticide production, are other sources of arsenic contaminations in water bodies [13,14].

Inorganic arsenite (oxidation state +3) and arsenate (oxidation state +5) ions are the most common arsenic species in nature and generate the greatest environmental concern [10–13]. As(V) is more abundant in oxidizing environments, such as surface water, rivers, and lakes; however, As(III) is more abundant in reducing environments, such as ground water. Based on the pH and redox potential of the environment, As(III) can be observed to occur as arsenious acid (H_3AsO_3) and arsenite ions, whereas As(V) can occur as arsenic acid (H_3AsO_4) and arsenate ions [7]. The dissociation constants of these species are as follows [13]:

Arsenious acid:



Arsenic acid:



The pKa value represents the pH value at which 50% of a reactant dissociates. As(III) species do not form anions easily at neutral pH values; however, the anionic forms of As(V) species can be observed at neutral pH values. Consequently, As(V) can be treated more easily than As(III). The most common practice in traditional arsenic treatment is the pre-oxidation of As(III) species and removal of the more accessible As(V) species.

The effective removal of arsenic from water sources to meet the established standards has remained a hot topic after the regulations were established in the early 2000s. Both traditional and innovative methods for arsenic removal have been successful, including polymer-enhanced ultrafiltration (still in the development stage) [2–6], adsorption, ion exchange, coagulation/filtration, and reverse osmosis [8].

Polymer-assisted removal processes have been extensively studied for the removal of arsenic using both soluble and insoluble polymers [1–6,13–18]. In particular, it was observed that polymers with quaternary amine groups were effective for removing As(V) during membrane-assisted studies [1–6,13–15]. Rivas et al. [5] reported the successful removal of arsenic with various water-soluble polymers combined with ultra-filtration using $(\text{R})_4\text{N}^+\text{X}^-$ groups. Linear poly(diallyldimethylammonium chloride) (DADMAC) is included among the polymers with proven effectiveness for removing As(V). Pookrod et al. [2,13,15] also studied linear, water-soluble DADMAC for the removal of As(V), demonstrating that the polymer was indeed effective in this respect. The literature reveals several studies dedicated to the arsenic removal efficiency of hydrogels, such as poly(3-acrylamidopropyl) trimethylammonium chloride (p(APTMAC)) hydrogels [19] and vinyl pyridine-based hydrophilic polymers that can absorb water up to a thousand times their dry weight in water and thus have various applications [20]. The use of hydrogels to remove other metals from aqueous solutions has also been investigated [21–24].

In this study, cross-linked poly(diallyldimethylammonium chloride) (DADMAC) hydrogels were synthesized using the TAP cross-linker introduced by Bicak et al. [25] according to the recipe reported by Korpe et al. [26]. Copolymers of DADMAC were first synthesized in hydrogel form by Korpe et al. [26] as super absorbents. Similarly prepared hydrogels derived from N-glucidol-N-methyl-2-hydroxypropyl methacrylate with the TAP cross-linker have also been used for boron extraction [27]. Cationic hydrogels constituting with DADMAC and TAP was considered as an alternative sorbent for arsenic removal. In this structure not only the monomer, DADMAC but also crosslinker, TAP contains quaternary ammonium groups. Therefore cationic charges on each repeating unit of their hydrogels were considered to provide efficient arsenic exchange in swollen state. Such a fully cationic hydrogel has not been studied as arsenic sorbent.

The results of this study should also enrich the limited literature related to hydrogels used in arsenic removal by introducing a new material that has been demonstrated to be superior based on its renewability, pH tolerance, and removal capacity.

2. Experimental

2.1. Materials

All chemicals used in this study were reagent-grade chemicals. Hydrochloric acid (HCl) (Sigma Aldrich 37%, Germany) and sodium hydroxide (NaOH) pellets (Sigma–Aldrich, Czech Republic) were used for pH adjustment and arsenic analysis; sodium borohydride (NaBH_4) (Merck, Germany) and potassium iodide (KI) (Sigma–Aldrich, Germany) were used for arsenic analysis. Arsenic standard solutions (Merck, Germany) were used during calibration and $\text{Na}_2\text{HASO}_4 \cdot 7\text{H}_2\text{O}$ (Sigma, India) were used during the preparation of arsenic solutions. Monomeric DADMAC (Aldrich, USA 65% in water), 2,2'-azo bis-(2-methyl propionamide) dihydrochloride (Aldrich, USA) and tetraallyl piperazinium dibromide (TAP) were synthesized according to the previous report [26] for use in gel synthesis.

2.2. Synthesis of polyDADMAC hydrogels

PolyDADMAC hydrogels were synthesized by copolymerization of DADMAC monomers with tetraallyl piperazinium dibromide (0.05 mol) (TAP) by radical initiation. Polymerization was conducted in a three-necked round bottom flask. The procedure employed was exactly the same as reported in the literature [20]. A 1:9 M ratio of crosslinker to DADMAC was chosen. In a typical procedure, 47.2 g of DADMAC (65%) solution (0.2 mol) and 20.4 g of solid tetraallyl piperazinium dibromide (0.05 mol) (TAP) were introduced to the flask together with 0.678 g of 2,2'-azo bis-(2-methyl propionamide) dihydrochloride (2.5 mmol) and Pluronic F68 (2.1 g). The flask was placed in an oil bath and equipped with a reflux condenser and a nitrogen inlet. Nitrogen was flushed through the system and the temperature of the bath was adjusted to 70 °C. The mixture underwent sudden gelation within 30–60 min and stirring was stopped. The reaction content was kept at this temperature for an additional 12 h to increase the monomer conversion efficiency.

The gel product was transferred into a purse and dialyzed under flowing water using 10 Volt DC biases to remove linear fractions of DADMAC. This was conducted until the conductivity of washings was reduced to 10 $\mu\text{S}/\text{cm}$ (~ 1 h). At the end, the product was leached in acetone twice (2×80 mL) and washed with ether (50 mL). Dried gel weighed 64.7 g.

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