



# Organic–inorganic interpenetrated hybrids based on cationic polymer and hydrous zirconium oxide for arsenate and arsenite removal



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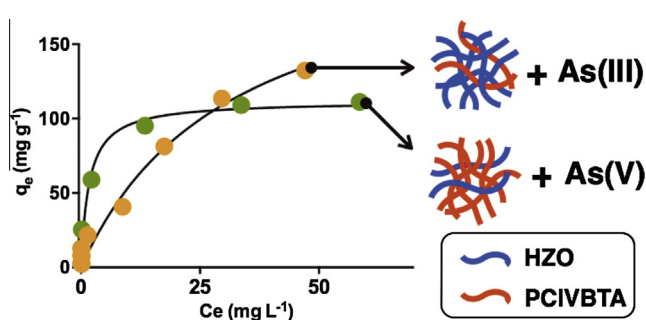
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## HIGHLIGHTS

- Cationic polymer-hydrous zirconium oxide hybrids retain arsenite and arsenate.
- The higher the hydrous zirconium oxide content the more arsenite sorption.
- Hybrid sorbent exhibits selectivity toward arsenite and arsenate sorption.
- Inorganic precursor and monomer mole ratio produces changes in the surface composition.

## GRAPHICAL ABSTRACT



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## ABSTRACT

In this study, the synthesis of interpenetrated hybrid materials capable of removing arsenic from water is reported. These novel hybrid sorbents consisted of a polymeric matrix with quaternary ammonium groups and zirconium oxide as the organic and inorganic phase, respectively. Furthermore, a coupling agent was used to enhance the compatibility between the polymeric matrix and the metal oxide, creating a covalent bond between them. The hybrid sorbents were prepared by varying the mole ratio of the zirconium oxide precursor and the monomer to provide different surface compositions, and their effect on arsenic sorption was investigated. The hybrids were characterized by spectroscopic analysis such as, Fourier transform infrared spectroscopy (FTIR), <sup>13</sup>C, and <sup>29</sup>Si solid-state nuclear magnetic resonance (NMR), thermal analysis (TGA), transmission and scanning electron microscopy (TEM, SEM–EDS), and FTIR microspectroscopy. Arsenite and arsenate sorption experiments were conducted under different experimental conditions (i.e., initial arsenic concentration, kinetics, and selectivity). The hybrids with a higher hydrous zirconium oxide content exhibited greater sorption of arsenite, and the sorbents with the lowest content exhibited greater sorption of arsenate.

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## 1. Introduction

Diverse organic and inorganic pollutants are present in water sources for human consumption, and arsenic (organic and inorganic) exhibits one of the highest toxicities. The most popular

methods on a larger scale involve adsorption and ion exchange (IEX). In general, these approaches are highly efficient, easy to operate and handle, inexpensive, and the process is sludge-free. Despite the advantages of adsorption processes, a high removal efficiency is only achieved when the predominant species in the effluent is pentavalent arsenic ( $H_3AsO_4$ :  $pK_{a1} = 2.3$ ;  $pK_{a2} = 6.8$ ;  $pK_{a3} = 11.6$ ) because at the natural pH of water, the arsenate is in its anionic form, which allows for removal by ion exchange or

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electrostatic interactions with an adsorbent. However, in natural effluents, arsenic is primarily found in two oxidation states (III and V), and natural pH trivalent arsenic species are non-charged ( $\text{H}_3\text{AsO}_3$ ;  $\text{pK}_{\text{a}1} = 9.2$ ;  $\text{pK}_{\text{a}2} = 12.1$ ;  $\text{pK}_{\text{a}3} = 12.7$ ), which decreases the efficiency of sorption [1]. This situation is predominant when the effluent comes from groundwater. To improve the efficiency, an oxidation step is performed prior to the adsorption processes to increase the concentration of arsenates [2]. Therefore, more variables are introduced into the process (e.g., by-product waste oxidation and additional infrastructure). In addition, an increase in the cost of installation and operation occurs. Although ion exchange (IEX) resins are the primary materials for industrial use, metal oxides, such as zero-valent iron (ZVI) [3], activated alumina (AA) [4], iron oxide [5], titanium oxide [6], cerium oxide [7], have been extensively studied in both academic and industrial fields, and some of these metal oxides possess the ability to remove arsenic species with high selectivity due to the formation of inner or outer sphere complexes [8]. It is important to note that these processes do not use large amounts of additional chemicals, are easy to install [9] and do not produce polluting by-products [10].

These advantageous properties of metal oxides have been combined with cross-linked polymers through the incorporation of metal oxide nanoparticles into IEX resins, resulting in the production of a novel sorbent composite that exhibits the beneficial properties of IEX resins (i.e., hydraulic, porosity, and kinetics) and the selectivity provided by the metal oxide [11–15]. Susuki et al. prepared a porous resin loaded with monoclinic or cubic hydrous zirconium oxide (HZO) by incorporation of  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$  into porous spherical polymer beads followed by hydrolysis and hydrothermal treatment of the zirconium salt. The sorbent composite exhibited strong adsorption for As(V) in a slightly acidic to neutral pH region. In addition, As(III) was favorably adsorbed at a pH of 9–10 [16]. Recently, Pan et al. prepared a sorbent nanocomposite by encapsulating nano-sized HZO particles inside a polystyrene anion exchanger D201. The arsenate sorption reached  $88.7 \text{ mg g}^{-1}$  using the nanocomposite compared to  $70.0 \text{ mg g}^{-1}$  using the D201 resin [17]. In a similar way, the D201-HZO nanocomposite was used for fluoride uptake achieving an enhanced performance of the nanocomposite compared with the D201 polystyrene-based resin [18].

Based on the characteristics and properties of adsorbents, the aim of this study was to develop an interpenetrated hybrid network consisting of a polymer phase (organic) and a metal oxide (inorganic), and this material will be applied to the direct and selective removal of arsenic.

Interpenetrated network (IPN) hybrids are typically composed of two phases (i.e., organic and inorganic) that are mixed on the molecular level. The synthesis of interpenetrated hybrids occurs either by a sequential two-stage process where a secondary network is formed in the interior of a primary network or by simultaneous formation of both networks. The material obtained is microscopically composed of separated phases but macroscopically homogeneous [19]. These materials can be classified into two categories: (i) Class I corresponds to the hybrids where the phases are interacting by intermolecular forces, such as Van der Waals and hydrogen bonds and (ii) Class II consists of phases that are strongly linked by covalent bonds [20]. In the current present system, the organic phase will consist of a cationic polymer (i.e., poly(4-vinylbenzyl)trimethylammonium chloride), the same function can be found in strong anion exchange resins. For the inorganic phase, hydrous zirconium oxide will be employed because zirconium oxide has a high capacity for removal of arsenate [21–24], and few studies have been focused on the removal of arsenite [22,25,26] indicating that this compound has a high affinity for forming an inner sphere complex with the hydroxyl groups on the surface [8,27]. Unlike, those composite materials were

nanoparticles are embedded into a polystyrene matrix, these hybrids both inorganic and organic phases are intimately combined. We expect that the resulting material possesses a combination of properties that are specific to each independent phase: the polymer phase retains arsenate ions mainly through ion exchange process, while the inorganic phase through complexation process.

## 2. Materials and methods

### 2.1. Materials

The interpenetrated hybrids were obtained using zirconium tetrabutoxide (TBZr, 80%, Aldrich) as the starting material, the [3-(methacryloyloxy)propyl]trimethoxysilane (MPS, 95%, Aldrich) coupling reagent, and the 4-(vinylbenzyl)trimethylammonium chloride (CIVBTA, 99%, Aldrich) monomer. Acetylacetone (acac, 99%, Merck) and benzoyl peroxide (BPO, 99%, Aldrich) were used as a retardant compound and initiator, respectively. The other reagent used in the synthesis and sorption experiments included 2-butanol (anhydrous, >99.5%, Merck) as a synthesis solvent,  $\text{NaAsO}_2$  ( $0.05 \text{ mol L}^{-1}$ , Merck),  $\text{Na}_3\text{AsO}_4$  ( $1000 \text{ mg L}^{-1}$ , Merck), potassium chloride (Merck, 99%), hydrochloric acid (Merck, 37%) and sodium hydroxide (Merck, 99%).

### 2.2. Synthesis of hybrid materials

The syntheses were according to a two-stage procedure involving radical polymerization and a sol-gel process [28,29]. TBZr was dissolved in 2-butanol (10 mL) and heated at  $80^\circ\text{C}$ . Then, acetyl acetone, CIVBTA, MPS and BPO (2 mol-% based to CIVBTA) were added to the reaction mixture. TBZr/CIVBTA + TBZr mole ratios ( $\phi$ ) of 0.8, 0.6, 0.4, and 0.2 were used, and 0.01 mol of CIVBTA was used. The MPS was fixed to 1:1 respect to TBZr and acac. Once all of the reagents were dissolved, the mixture was degassed with  $\text{N}_2$  and polymerized at  $80^\circ\text{C}$  for 24 h. Next, the solution was transferred to a Teflon beaker and cooled to room temperature, and deionized water was added over the gel followed by mechanical mixing. The mixture was maintained at room temperature for 8 h followed by drying at  $80^\circ\text{C}$  in an oven until a fine white powder was obtained. All of the composites were washed with deionized water under magnetic stirring for 12 h and dried at  $70^\circ\text{C}$  to remove the unreacted reagents. It is important to note that control samples were prepared for comparison. In particular, HZO were obtained using the same procedure but without the addition of monomers. The (P[CIVBTA-co-MPS]) copolymer was obtained by radical polymerization of CIVBTA and MPS in the presence of a protic solvent, which favored hydrolysis and condensation of the methoxysilane groups, leading to the formation of a cross-linked polymer. The sorbents were ground and sieved to obtain a particle size of 100–180  $\mu\text{m}$  for the sorption experiments. The hybrids are referred to as HC( $\phi$ ), where  $\phi$  represents the (TBZr/CIVBTA + TBZr) mole ratio.

### 2.3. Physicochemical characterization

The morphology and structure of the hybrids were elucidated by infrared spectroscopy (FTIR, Perkin Elmer 1760-X spectrometer using a range of  $4000\text{--}400 \text{ cm}^{-1}$  and KBr pellets) and scanning electron microscopy, (SEM, SEM-PROBE CAMECA model SU-30 equipped with an energy dispersive X-ray device, EDX). Nuclear magnetic resonance (Bruker Ascend™ 400 MHz CP-MAS solid state NMR), FTIR microspectroscopy (Perkin Elmer, Spotlight 400 FTIR Imaging System model Spectrum Frontier mid-IR spectral range, reflectance mode) and the obtained images were analyzed using the Spectrum (version 10.03.06.0100) and SpectrumIMAGE

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