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Ionically modified magnetic nanomaterials for arsenic and chromium removal from water

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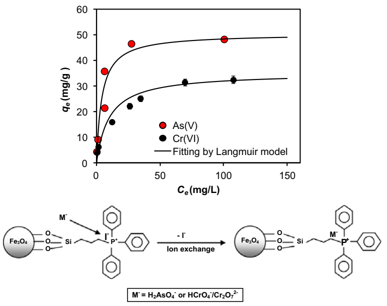
HIGHLIGHTS

- Ionically modified magnetic adsorbent was synthesized for As(V) and Cr(VI) removal.
- Maximum uptakes for As(V) and Cr(VI) were 50.5 mg/g and 35.2 mg/g, respectively.
- Adsorption occurred via electrostatic interaction and ion exchange mechanism.
- Adsorption is dependent on pH and independent of coexisting ions except phosphate.
- It can be magnetically separable, reusable and promising for anionic metal removal.

GRAPHICAL ABSTRACT



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ABSTRACT

We describe a method for the removal of arsenic and chromium contaminants from water by using ionically modified magnetic nanoparticles (PPhSi-MNPs). We synthesized and covalently attached a cationic ligand: phosphonium-silane (PPhSi), onto iron oxide magnetic nanoparticles. We exploit the ion-exchange capability of the phosphonium ligand for the removal of the metal ions from water and superparamagnetic nature of iron oxide for physical separation of the sorbent materials for recovery and regeneration. Chemical and physical properties of the phosphonium-coated MNPs are investigated by FTIR, TEM, XPS, EDX, XRD and zeta potential. The highest As(V) and Cr(VI) adsorption efficiency is observed at pH 3. The adsorption of As(V) and Cr(VI) on PPhSi-MNPs is not affected to any considerable extent by the presence of coexisting anions such as chloride, nitrate, and sulfate except phosphate. The adsorption data are best fitted with the Langmuir isotherm model and a pseudo-second-order kinetic model is proposed. Based on the zeta-potential and chemical analyses of the adsorbent surface, we propose that a synergy of electrostatic interaction and ion-exchange between anionic metals and the cation-modified magnetic nanoparticles allow highly efficient removal of the pollutants. A simple pH-triggered desorption and regeneration of the adsorbent is also presented. With adsorption capacities for arsenic (50.5 mg/g) and chromium (35.2 mg/g), coupled with facile magnetic separation, this nanoadsorbent can be an attractive material for the removal of several anionic metal species from water.

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1. Introduction

The presence of toxic heavy metals in water poses serious health and environmental hazard. Hence, significant research activities are aimed for analysis, minimization, containment and mitigation of such pollution. Arsenic stands as one of the most toxic and carcinogenic chemical element, which is a common naturally occurring material found in the surface and ground water as a result of weathering of rocks, industrial waste discharges, agricultural use of arsenical herbicides, pesticides, crop desiccants, etc [1–3]. It is generally mobilized through natural processes and results in severe environmental hazards and chronic poisoning [4,5]. Like arsenic, chromium is another highly toxic heavy metal and a common element of earth's crust [6]. Chromium acts as carcinogens, mutagens, and teratogens in biological systems [7]. It enters the aquatic systems through discharge of concentrated effluents mainly from leather tanning, smelting, electroplating, paint, textile and paper industries. Both of these toxic metals gradually accumulate in the living organisms and thereby cause disorders and life threatening diseases [7,8]. World Health Organization (WHO) has set a maximum limit of 10 μg/L arsenic in the drinking water, whereas US Environmental Protection Agency (EPA) has set the maximum contaminate level for chromium at 0.1 mg/L [2,7,9]. Due to their toxic, carcinogenicity and harmful nature, and also legislative bindings, the removal of arsenic and chromium pollutants from various water sources is very crucial and critical.

Several treatment technologies have been developed for the removal of arsenic and chromium from water: chemical precipitation, ion exchange, membrane separation, filtration/ultrafiltration, electrocoagulation, extraction, sedimentation, reduction, reverse osmosis, dialysis/electrodialysis, adsorption, etc [3,10]. Among these techniques adsorption is most popular because of its simplicity, easy handling and sludge-free operation, regeneration capacity and cost effectiveness [11,12]. For removal of arsenic and chromium from water several adsorbents such as, oxides and hydroxides of metals, activated carbon, polymeric resins, clay minerals and zeolites have been reported [3,8,13–21]. Recently, the exploitation of nanomaterials for removal of metallic pollutants from water or wastewater has emerged as an intriguing research direction. Because, compared to the bulk counterparts, nanomaterials-based adsorbents have a much larger surface area to accommodate far greater number of active sites for interaction/adsorption. Different types of nanomaterials such as, carbon nanotube, iron oxide, aluminum oxide, and titanium oxide were employed in many studies as nanoadsorbents and showed excellent adsorption capacities for various heavy metals including arsenic and chromium [22–29]. Recently, iron oxide nanoparticles attracted great interest in the field of environmental remediation because these superparamagnetic materials can be easily dispersed in, and quickly retrieved from water simply by switching off and on an external magnetic field. Hence, retrieval in most cases nearly 100% and reuse is facile. To avoid the oxidation of magnetic nanoparticles and also to increase the stability and adsorption capacities of nanoparticles, different coating materials or ligands have been employed to modify the surface. Over the past few years several magnetic nanoadsorbents are developed, e.g., magnetite (Fe_3O_4), diatomite supported/unsupported magnetite nanoparticles, flower like Fe_2O_3 nanoparticles, magnetite-reduced graphene oxides composites, CTAB modified magnetic nanoparticles, polypyrrole/Fe_3O_4 magnetic nanocomposite, surface modified jecobosite nanoparticles and calix[4]arene-grafted magnetite nanoparticles [22,29–35]. In this work, we utilize an ionic liquid analogue (phosphonium based silane, PPhSi) as an ion-exchange coating material to modify the Fe_3O_4 nanoparticles to accomplish high adsorption capacity for anionic pollutants and easy magnetic separation.

Ionic liquids (ILs) are of particular interest in recent years, since these unique materials have shown potentials as extracting agents for elimination of heavy metals from wastewater [36–38]. ILs are generally defined as organic salts that are liquid below 100 °C and consist entirely of ions. ILs can absorb contaminants by electrostatic interaction, and preferential solubilization of polar molecules and ions. ILs show extraordinary properties such as an extremely low vapor pressure, high thermal stability and their physico-chemical properties can be tuned by modifying their chemical structure. ILs have been also widely used as solvents in organic and inorganic syntheses, catalysis, and chromatography [39–41]. Several types of ionic liquids based on imidazolium-, pyridinium-, pyrrolidinium- or phosphonium cations have been investigated for the extraction and separation of inorganic substances from aqueous media [42–44]. Although bulk ionic liquid has been recognized as an efficient fluidic sorbent for removal of heavy metals from water and wastewater solutions, grafting ionic liquid molecules on the nanoparticles as a coating layer for metal ion removal has been rarely exploited. Compared to the use of bulk ionic liquid, covalent grafting of IL ligands onto nanoadsorbents would be operationally simpler, because (i) most ionic liquids are highly viscous materials: biphasic mixing and separation is energy-intensive due to mass transfer, (ii) ionic liquid recovery can be an issue as many IL have finite solubility in water, and most importantly (iii) typically, ILs are expensive materials. In our case IL molecules are chemically grafted on the inexpensive iron oxide nanoparticles, which would increase the surface area and the active surface sites for metal ion adsorption, and facile magnetic separation would allow fast and complete separation of the sorbent phase for regeneration and recycling.

We ionically modified the iron oxide nanoparticles with an ionic liquid ligand which is designed to possess a trimethoxysilane pendant group for attaching onto the iron oxide surface and a phosphonium iodide head group for chemically interacting with the metal ions. These easily separable and recyclable nanoadsorbents were characterized by FTIR, TEM, XPS and zeta potential. Influence of external parameter such as, pH, competitive anions, contact time on the extent of adsorption of As(V) and Cr(VI) were investigated. Adsorption equilibrium and kinetic properties of this adsorption process were also studied. The As(V) and Cr(VI)-sorbed PPhSi-MNPs were analyzed with XPS and EDX for elucidating the adsorption mechanism.

2. Materials and methods

2.1. Chemicals

Iron (II) chloride tetrahydrate, iron (III) chloride hexahydrate and sodium hydrogen arsenate were purchased from Alfa Aesar (Singapore). Ammonium hydroxide (25%) and toluene were purchased from Merck (Germany). Triphenylphosphine and 3-iodopropyl (trimethoxy)silane were purchased from Sigma–Aldrich (Singapore). For As(V) and Cr(VI) adsorption/desorption studies, potassium dichromate ($K_2Cr_2O_7$) and disodium hydrogen arsenate (Na_2HAsO_4) salts were used. The water used in this entire work was Milli-Q ultrapure water.

2.2. Synthesis of phosphonium silane

Phosphonium silane was synthesized by the condensation reaction between triphenylphosphine and 3-iodopropyl(trimethoxy)silane. 1 mL of 3-iodopropyl (trimethoxy)silane and 1.34 gm triphenylphosphine (1:1 molar ratio) was taken in a schlenk tube. 5 mL of toluene was added into the tube and the components were dissolved completely by magnetic stirrer. Meanwhile, the air was