Research article

Overview of As(V) adsorption on Zr-functionalized activated carbon for aqueous streams remediation

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ABSTRACT

The present work introduces a simple methodology of carbon modification with zirconium, using an organic complexing ligand, as efficient media for selective As(V) removal. It is hypothesized that the incorporation of Zr-nanoparticles improves the attraction of anionic species such as arsenates ($HAsO_4^{2-}$/$H_2AsO_4^-$) making the material highly selective. The effects of pH (3–11) and temperature (15, 25 and 35 °C) were studied. Furthermore, potentiometric titrations, the effect of competing anions, thermodynamics, and adsorption kinetics were evaluated in order to clarify the rate-controlling process and the adsorption mechanism for arsenic removal. Results demonstrated that −OH and −COOH groups play an important role during the arsenic adsorption process; a small amount of Zr(IV) species (0.77%) increased the adsorption capacity of activated carbon in about a 43%. Thermodynamic analysis showed the spontaneous exothermic nature of the adsorption process was favored at lower temperatures. The presence of anions, such as chloride, sulfate, carbonate, nitrate and phosphate, did not affect the adsorption capacity, while kinetic studies demonstrated that the arsenic adsorption process in Zr-modified activated carbon is not exclusively controlled by intraparticle diffusion.

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1. Introduction

Arsenic is a highly toxic inorganic element that can be found in water supplies as a consequence of natural geochemical processes due to its dissolution and mobilization under normal conditions. Anthropogenic activities, including mining, use of pesticides, herbicides, additives, and crop desiccants, create additional environmental impacts. The maximum acceptable levels of inorganic elements in drinking water depend on each country's regulation, the World Health Organization (WHO) and the United States Environmental Protection Agency (US EPA) have set an arsenic maximum limit concentration of 0.01 mg L^{-1} (EPA, 2002; WHO, 2011).

Arsenic occurs in both organic and inorganic forms, but the inorganic form is more prevalent. Inorganic arsenic can be present in aqueous solution as (V) or (III) oxidation states, depending on their redox potential environment in natural conditions. At the normal conditions of natural water, arsenic species can be found as arsenate ($H_2AsO_4^-$ from pH of 2–7 and as $HAsO_4^{2-}$ from pH 5.5 to 12) or arsenite (AsO_3^{3-} up to pH 10), corresponding to As(V) and As(III), respectively. These ionic species are of great concern in drinking water sources because they are found in major proportions in fresh and groundwater, and are more toxic than their organic forms (Ng et al., 2003). Among the health problems that have been associated with arsenic ingestion include keratosis, hyperkeratosis, cancer, cardiovascular diseases, neuropathies, fetal loss and premature delivery, among others (Kapaj et al., 2006).

Several technologies have been applied to the removal of arsenic from water, including electrochemical and chemical precipitation, evaporation, ion-exchange, nanofiltration, reverse osmosis, membrane processes, or two or more of these techniques used in combination (Hafeznezami et al., 2017; Kurniawan et al., 2006). However, limitations associated with these technologies include high investment and maintenance costs, as well as the generation

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of toxic sludge. Therefore, adsorption processes have been found to be superior to the techniques mentioned above in terms of simplicity of design and operational costs (Ungureanu et al., 2015; Verma et al., 2014). Previous studies have used several materials as adsorbents for the removal of arsenic from aqueous streams, and include algae, activated carbon, alumina, synthetic resins, chars, fly ash, clay, moss, agro-waste materials, mud, etc. (Bailey et al., 1999; Bhatnagar and Sillanpää, 2010; Khan et al., 2008; Ungureanu et al., 2015). Nevertheless, the development of specific and selective adsorbents is still under study and is the subject of the current research.

The use of activated carbon or charcoal in water treatment is one of the oldest water purification technologies and is the most widely used adsorbent for the removal of pollutants from water (Ayranci and Duman, 2010; Duman and Ayranci, 2010; Radovic et al., 2000). This is due to its high mechanical strength, elevated specific surface area ($800-2000 \, m^2 \, g^{-1}$) and good permeability in flow-through systems (Bansal and Goyal, 2005). The adsorption capacity of a certain activated carbon depends on several factors including those of the adsorbent (e.g. the presence of functional groups, pore volume and specific surface area), those of the adsorbate (e.g. polarity, hydrophobicity, molecular weight, hydrated radius, pK_a, etc.), and the solution characteristics (such as pH, temperature, target concentration, presence of interferences, etc.) (Duman and Ayranci, 2006).

Despite these advantages, activated carbon has a poor capacity and affinity for the selective removal of arsenic from aqueous solutions. This is due to the lack of selectively-specific surface functionalities on activated carbon capable of adsorbing the arsenic species. In order to overcome the high cost of extensive use of AC, research is carried out to increase its adsorption capacity (Duman et al., 2015a, 2015b). Studies have demonstrated that the introduction of an insoluble foreign element, like a metal oxide, creates a positively charged surface capable of attracting anions (Jolivet et al., 2000; Puttamraju and SenGupta, 2006). Such metal oxides are rich in terminal hydroxyl groups that once in solution, release or adsorb protons developing a surface charge. They also provide coordination sites for the adsorption of anions like arsenates. For this reason, the addition of a metal oxide (heavy- or transition-) on the surface of activated carbon substrates improve their arsenic(V) adsorption capacity.

Of particular importance has been the introduction of iron (hydr)oxide particles on activated carbon. Studies have demonstrated the efficiency of these kinds of materials for arsenic adsorption, depending on the particular crystal structure, particle size, density of groups and porosity (Arcibar-Orozco et al., 2012; Chen et al., 2007; Fierro et al., 2009; Zhang et al., 2007). The vital importance of the incorporation of nanoparticles, with the objective of avoiding pore blockage and promoting the dispersion of adsorption centers, has been demonstrated in several articles (Arcibar-Orozco et al., 2012, 2013; Yean et al., 2005). Our research group has explored the use of complexing (or chelating) ligands, like phosphate anions, to control the growth and final particle size distribution of iron(III) loaded onto the activated carbon matrix for As(V) removal from water (Arcibar-Orozco et al., 2012, 2014; Vitela-Rodriguez and Rangel-Mendez, 2013).

However, iron nanoparticles are not the only metal oxides that can improve arsenic uptake. Other metals including, zirconium, silver and copper have also demonstrated efficiency for arsenic removal as well (Rajaković, 1992; Sandoval et al., 2011). Zirconium oxide has garnered recent attention by its capability to selectively remove arsenic(V) from aqueous solutions (Cui et al., 2012; Luo et al., 2013). On the other hand, organic acids have demonstrated a positive effect on the decrease in size of metal oxide particles (Ketabi et al., 2011; Muruganandham et al., 2010; Pettibone et al.,

2008), therefore enabling them to be loaded onto the carbonaceous surfaces of such activated carbon. Oxalic acid was employed in one of the group's adsorption studies to load Zr-containing nanoparticles onto activated carbon surfaces with a simple impregnation methodology (Velazquez-Jimenez et al., 2014). That material was efficient for the removal of fluoride from water, where the oxalic acid acted like a capping agent (Ketabi et al., 2011; Tanaka et al., 2002) to decrease the particle size of the anchored Zr particles, enhancing the adsorption capacity.

In the present study this material was selected for the removal of arsenic(V) from aqueous solution. The success of the adsorbent's performance depends on the experimental procedures, which most of the time do not account for the possible effect of pH, ionic strength, the presence of complexing agents, or temperature change. These experimental factors should be taken into account since they could affect the aggregation and organization of metal-loading particles onto the carbon matrix.

For that reason, the objective of the present research was to study a commercial activated carbon loaded with Zr(IV)-containing nanoparticles, mediated with oxalic acid as a complexing ligand, as an adsorbent for As(V) from aqueous solutions. To the best of our knowledge this kind of material, has never been employed as an arsenic(V) adsorption media. Effects of pH, temperature and presence of competitive anions, naturally present in water, were studied. The experimental conditions studied enabled the determination of the thermodynamic parameters underlying the adsorption process, the time necessary to reach equilibrium, as well as demonstrating the effect on the adsorption capacity of the co-anions naturally present in the contaminated water.

2. Experimental section

2.1. Materials and characterization

Zirconium impregnated activated carbon was prepared according to an experimental design that was previously described (Velazquez-Jimenez et al., 2014). Briefly, 0.1 g of commercial activated carbon (AC, F400) was added to 10 mL of $ZrOClO_2 \cdot 8H_2O$ at a 7% (w/v) solution of Zr^{4+} and continuously stirred for two days. Subsequently, the impregnated carbon was rinsed with deionized water and then mixed with 10 mL of a 7% (w/v) oxalic acid (OA) solution, stirring for 24 h. After, the modified material then was filtered, rinsed, and dried at 60 °C for 12 h. The impregnated adsorbent obtained was designated: ZrAO. Moisture of materials was obtained by weight difference after heating the materials for 3 h at 150 °C (according to ASTM-D2867). Potentiometric titrations were performed to determine the surface charge distribution (pH_{PZC}) of each adsorbent with an automatic titrator (Mettler-Toledo T70). A sample of 0.1 g was dispersed in 50 mL of 0.1 M of NaCl as background electrolyte. Titration was carried out by stepwise addition of 0.01 mL of 0.1 M NaOH to the flask while the solution was stirred under N_2 atmosphere to exclude CO_2. After each addition of titrant, the system was allowed to equilibrate until a stable pH value was obtained. The pK_a distribution was obtained with the SAEIUS-pK-Dist© (1994) program. FT-IR analyses were performed to verify changes in vibrational frequencies of functional groups in all samples with a Thermo Nicolet 6700 ATR-FT-IR spectrometer. The influence of atmospheric water and CO_2 was always subtracted. The spectra were collected 32 times at and corrected for background noise. The surface morphology of ZrOA was observed in a scanning electron microscope (SEM, LEO 1530 VP), the procedure for sample preparation was as follows: the sample was ground to a powder, then placed onto a double-sided carbon tape on a SEM pin holder. Samples were observed at an acceleration voltage of 20 KeV. Energy dispersive X-Ray