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Kilogram-scale synthesis of iron oxy-hydroxides with improved arsenic removal capacity: Study of Fe(II) oxidation–precipitation parameters

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ABSTRACT

Various iron oxy-hydroxides were synthesized in a continuous flow kilogram-scale production reactor through the precipitation of $FeSO_4$ and $FeCl_2$ in the pH range 3–12 under intense oxidative conditions to serve as arsenic adsorbents. The selection of the optimum adsorbent and the corresponding conditions of the synthesis was based not only on its maximum As(III) and As(V) adsorption capacity but also on its potential efficiency to achieve the arsenic health regulation limit in NSF challenge water. As a result, the adsorbent prepared at pH 4, which consists of schwertmannite, was selected because it exhibited the highest adsorption capacity of 13 μg As(V)/mg, while maintaining a residual arsenic concentration of 10 μg/L at an equilibrium pH 7. The high surface charge and the activation of an ion-exchange mechanism between SO_4^{2-} adsorbed in the Stern layer and arsenate ions were found to significantly contribute to the increased adsorption capacity. Adsorption capacity values observed in rapid scale column experiments illustrate the improved efficiency of the qualified adsorbent compared to the common commercial arsenic adsorbents.

1. Introduction

Due to the establishment of the toxic effects imposed by the consumption of arsenic-containing drinking water and the reports of elevated arsenic concentrations in numerous water supplies around the world, arsenic removal is regarded as one of the most serious issues related to public health (Henke, 2009; Kaltreider et al., 2001). Depending on the daily dose, the long-term exposure to arsenic-contaminated water increases the risk for the development of skin, cardiovascular and hematological disorders, as well as many cancer forms. Because of that a variety of methods have been employed to address this problem. The most important are chemical coagulation using metal salts (Mitrakas et al., 2009; Lakshmanan et al., 2008; Chwirka et al., 2004; Zouboulis and Katsoyiannis, 2002), adsorption on activated alumina (Tripathy and Raichur, 2008; Chwirka et al., 2000; Jing et al., 2005), iron oxy-hydroxides (Mohan and Pittman, 2007; Badruzzaman et al., 2004), TiO_2 (Jing et al., 2005; Hristovski et al., 2007), ZrO_2 (Hristovski et al., 2007), or zero-valent iron

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(Katsoyiannis et al., 2008; Bang et al., 2005; Nikolaidis et al., 2003; Daus et al., 2004), ion exchange using organic resins (Ghurye et al., 1999) and membrane processes, such as nanofiltration (Sato et al., 2002) and reverse osmosis (Kang et al., 2002).

However, the existed removal techniques were re-evaluated regarding their efficiency to comply with the recently established arsenic limit of 10 μg/L and cost parameters. For instance, the coagulation/filtration using iron salts appears to be cost effective for large-scale water plants but the effort required for handling the wastes prevents its application when the treated volume of water corresponds to the one produced for a small town. On the other hand, adsorption offers many advantages including simple and stable operation, easy handling of waste, absence of continuously added reagents, compact facilities and generally lower labor cost. The major part of the total cost of an adsorption process (>80%) arises from adsorbent's price (Wang and Chen Abrahan, 2011). Therefore, the development of arsenic adsorbents either at reduced cost or improved adsorption capacity may drastically decrease treatment cost or in turn further increase the competitiveness of the adsorption process.

Many different materials appear efficient to adsorb arsenic from water (Mohan and Pittman, 2007) but iron oxides and oxy-hydroxides are the most widely studied and their commercial products already dominate a large part of the market. In water plants, iron oxy-hydroxides are applied as mechanically resistant granules in fixed-bed pressure columns. The use of iron oxy-hydroxides is promoted by their cheap and easy production, their amorphous structure which gives high specific surface area values and their strong affinity and relative high selectivity for the most frequently occurring arsenate species under natural pH-values of potable water. In this process, arsenate oxy-anions are retained onto the surface of the adsorbent through various physical or chemical mechanisms resulting in a stable and non-reversible linkage. Typically, arsenate is adsorbed onto iron oxy-hydroxides by the formation of monodentate and bidentate inner sphere complexes depending on water pH (Henke, 2009). Such strong binding provides to the iron oxy-hydroxides an additional advantage, which is the safety in environmental disposal of the saturated material.

Since arsenic adsorption is an association between arsenic species and adsorbent's surface, there are many parameters which define the adsorption efficiency. Particularly, the ability of a material in selective arsenic removal is mainly a property determined by the surface morphology and charge of the material. However, for a specific material, the aquatic environment may inhibit or favor the process. The effect of water pH at equilibrium on As(III) and As(V) adsorption from amorphous iron oxy-hydroxides is related to the speciation of arsenic and the surface charge of the adsorbents as well. As the equilibrium pH increases from 5 to 9, the transformation of the dominant monovalent $H_2AsO_4^-$ to the $H_2AsO_4^{2-}$ causes a decrease of As(V) adsorption, while As(III) uptake is less susceptible to pH changes below 9 where it appears in the neutral H_3AsO_3 form (See supporting information). The equilibrium pH-value may also indirectly affect arsenic adsorption through the serious interferences caused by the presence of common ions in natural water, such as phosphate (Xie et al., 2007) and silicate anions (Smith and Edwards, 2005). For each adsorbent, a reliable evaluation of these parameters should include the separate and most importantly the collective investigation of their influence on arsenic adsorption capacity.

Iron oxy-hydroxides can be directly obtained from natural sources (rocks, soils) or chemically synthesized by the precipitation either of Fe(III) or Fe(II) salts (Cornell and Schwertmann, 2003). The hydrolysis and oxidation rate of the Fe(II) salts mainly determine the obtained iron oxy-hydroxide structure and lead to a large variety of compounds (akaganeite, goethite, lepidocrocite, ferrihydrites, green rusts). In addition, the chemical environment and the reaction parameters may determine the critical factors regulating the adsorption efficiency, such as specific surface area and available adsorption sites. Practically, the common one-pot and batch preparation methods have problems in stabilizing constant conditions (redox and pH) throughout the synthesis procedure, resulting in lack of repeatability, low productivity as well as variations in product composition and properties. Thus, the scale-up of such processes and the high production yield are not always guaranteed.

This work describes a thorough research of the iron oxy-hydroxides' preparation using the most common low cost iron salts ($FeSO_4 \cdot H_2O$ and $FeCl_2 \cdot 4H_2O$) and their evaluation as As(III) and As(V) adsorbents. The first part deals with the optimization of a procedure for the kilogram-scale continuous flow synthesis considering a variety of pH-values while preserving maximum reaction yield and high redox values. According to the obtained efficiency of the products, the mechanisms that lead to maximum arsenic adsorption capacity are further analyzed in the second part. In addition, the discussion is focused on the implementation of realistic arsenic concentrations found in natural water and the achievement of residual arsenic levels conforming to the regulation limit. To the best of our knowledge, it is the first study that summarizes the role of synthesis parameters on the arsenic adsorption efficiency of iron oxy-hydroxides under the perspective of large-scale production and application in water treatment plants.

2. Experimental

2.1. Synthesis

Iron oxy-hydroxides used as arsenic adsorbents were prepared at a kilogram-scale in a laboratory two-stage continuous flow reactor (CSTR-1 and CSTR-2) working at 1 h retention time (Fig. 1). The chemical process included a sequence of oxidation, hydrolysis and precipitation of ferrous salts ($FeSO_4 \cdot H_2O$, $FeCl_2 \cdot 4H_2O$) in aqueous environment at high redox conditions and a wide range of pH-values. Preliminary experiments showed that the second reactor stage was critical to accurately control and tune the key parameters of the process, such as the pH and the redox potential. The inflow of 40 g/L $FeSO_4 \cdot H_2O$ solution was set to 10 L/h which resulted in the production of around 0.25 kg of dry product per hour. Drops of NaOH (30% w/w) were added to