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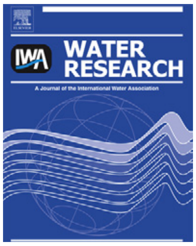

Individual and combined effects of water quality and empty bed contact time on As(V) removal by a fixed-bed iron oxide adsorber: Implication for silicate precoating

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ABSTRACT

The individual and combined effects of changes in water quality (i.e. pH, initial concentrations of arsenate (As(V)) and competing ions) and empty bed contact time (EBCT) on As(V) removal performance of a fixed-bed adsorber (FBA) packed with a nanostructured goethite-based granular porous adsorbent were systematically studied under environmentally relevant conditions. Rapid small scale column tests (RSSCTs) were extensively conducted at different EBCTs with synthetic waters in which pH and the concentrations of competing ions (phosphate, silicate, and vanadate) were controlled. In the absence of the competing ions, the effects of initial As(V) concentration, pH, and EBCT on As(V) breakthrough curves were successfully predicted by the homogeneous surface diffusion model (HSDM) with adsorption isotherms predicted by the extended triple layer model (ETLM). The interference effects of silicate and phosphate on As(V) removal were strongly influenced by pH, their concentrations, and EBCT. In the presence of silicate ($\leq$21 mg/L as Si), a longer EBCT surprisingly resulted in worse As(V) removal performance. We suggest this is because silicate, which normally exists at much higher concentration and moves more quickly through the bed than As(V), occupies or blocks adsorption sites on the media and interferes with later As(V) adsorption. Here, an alternative operating scheme of a FBA for As(V) removal is proposed to mitigate the silicate preloading. Silicate showed a strong competing effect to As(V) under the tested conditions. However, as the phosphate concentration increased, its interference effect dominated that of silicate. High phosphate concentration ($>$100 μg/L as P), as experienced in some regions, resulted in immediate As(V) breakthrough. In contrast to the observation in the presence of silicate, longer EBCT resulted in improved As(V) removal performance in the presence of phosphate. Vanadate was found to compete with As(V) as strongly as phosphate. This study reveals the competitive interactions of As(V) with the competing ions in actual adsorptive treatment systems and the dependence of optimal operation scheme and EBCT on water quality in seeking improved As(V) removal in a FBA.

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1. Introduction

Potable water supplies drawn from groundwater with high levels of arsenic are a serious public health concern all over the world (Nordstrom, 2002). The prolonged drinking of such water can cause various adverse health effects including cancer (Chowdhury et al., 2000). The USEPA has set the maximum contaminant level (MCL) for arsenic in drinking water at 10 μg/L as As.

Adsorption has been widely applied for arsenic removal, and various types of nanostructured metal oxide adsorbents have been developed (Amy et al., 2005; Mohan and Pittman, 2007; Seigel et al., 2007). These adsorbents are usually packed in a column, called a fixed-bed adsorber (FBA). FBAs packed with metal oxide adsorbents are particularly suitable for water systems without on-site operators, such as those in small communities or remote locations, because of their high performance and easy maintenance. In some developing countries, fixed-bed adsorption systems containing alumina and iron oxides, such as the SONO filter (Hussam and Munir, 2007), have been used to remove arsenic. Prior to adsorption, arsenite (As(III)) is usually oxidized by a disinfectant to As(V) (Dodd et al., 2006), which is less toxic and binds more strongly on oxides than arsenite (As(III)).

Continuous usage of FBAs packed with metal oxide adsorbents results in increasing As(V) concentration in the effluent. Adsorbents must be replaced to maintain As(V) concentrations below the maximum contaminant limit (MCL). Accurate prediction of As(V) breakthrough curves from FBAs is important to determine and plan for future operating and maintenance costs. Water quality and empty bed contact time (EBCT), defined as bed volume over volumetric flow rate, significantly affect As(V) breakthrough curves (Nguyen et al., 2011; Seigel et al., 2007; Vaughan et al., 2007; Zeng et al., 2008b). Although several studies have been conducted to investigate the effects of these factor for iron oxide coated materials (Katsoyiannis and Zouboulis, 2002; Vaughan et al., 2007), these materials can be exhausted very quickly. Few studies has been conducted to investigate their individual and combined effects with nanostructured granular porous metal oxide adsorbents with high performance that are actually used in real water treatment systems under environmentally relevant conditions. This is because those metal oxide adsorbents generally last much longer than coated materials. The values of bed volume treated (BV), which is defined as the volume of treated water divided by the reactor volume, for those adsorbents usually reach to several tens of thousands before replacement is required (Nguyen et al., 2011; Seigal et al., 2007; Zeng et al., 2008a). Such a high adsorptive capacity results in the requirement of large volume of water or extremely high initial As(V) concentration in column studies to obtain experimental results. Therefore, it has been difficult to conduct a number of column studies under environmentally relevant conditions to study the competitive interactions of As(V) with competing ions in an FBA during the prolonged operation.

Rapid small-scale column tests (RSSCTs), originally designed to simulate breakthrough curves of organic compounds from FBAs packed with granular activated carbon (GAC) (Crittenden et al., 1987), have been successfully applied to FBAs packed with nano-structured granular porous metal oxide-based adsorbents to simulate As(V) breakthrough curves from full-scale columns (Seigel et al., 2007; Westerhoff et al., 2005). RSSCTs, however, are site-specific, and the results reflect mixed effects of water quality and EBCT (Westerhoff et al., 2005). A recent systematic investigation of the effect of key interferences on arsenic breakthrough conducted in our laboratory compared the sensitivity of three commercially available adsorbents to changes in water quality, including changes in pH and in the concentrations of arsenic, phosphate, silicate, and vanadate (Nguyen et al., 2011). The levels of interferences employed in that study were selected specifically to address conditions found in California where the interferences were jointly varied following a factorial experimental design. Since fixed-bed adsorbers are among the most frequently used treatment technologies for As(V) removal worldwide, it is necessary to conduct a study that expands on the previous work by examining a broader range of concentrations of potentially interfering constituents and exploring the both individual and combined effects of water quality and EBCT.

Here, we report the results of extensive RSSCTs with synthetic waters in which water quality was controlled within the globally relevant range at different EBCT to quantitatively investigate their individual and combined effects on As(V) breakthrough curves from fixed-bed adsorbers packed with a nanostructured goethite-based granular iron oxide adsorbent. Silicate, phosphate, and vanadate were selected as competing ions. It has been reported that silicate and phosphate are the most significant competing ions to As(V) adsorption on mineral surfaces (Badruzzaman, 2005; Dixit and Hering, 2003; Hug et al., 2008; Roberts et al., 2004; Speitel et al., 2010; Su and Puls, 2003; Westerhoff et al., 2006; Zeng et al., 2008b). Vanadate is also known to strongly bind to iron oxides and has been identified as a possible competing ions with As(V) (Badruzzaman, 2005; Speitel et al., 2010). Peacock and Sherman (Peacock and Sherman, 2004) reported that vanadate can form inner-sphere complexes on goethite surfaces. In this study, a commercial goethite-based granular porous adsorbent, Bayoxide E33® (E33), was used for column tests. This adsorbent is frequently used for As(V) removal in water systems in the U.S.(Amy et al., 2005; Seigel et al., 2007), and the adsorbent typically lasts several tens of thousands of BV until the MCL. In previous studies, we systematically characterized this material and determined the protonation constants, electrolyte adsorption constants, and adsorption equilibrium constants of As(V), phosphate, and carbonate for the adsorbent (Kanematsu et al., 2010, 2011) to apply the extended triple layer surface complexation model (ETLM) to this system. The RSSCT results reported here are analyzed with reference to the previous ETLM results.

The objectives of this study were 1) to quantitatively elucidate the influence of globally relevant water quality parameters (pH, initial As(V) concentration, absence and presence of the competing ions) and EBCT on As(V) breakthrough curves from fixed-bed iron oxide adsorbers and 2) to examine the ability of adsorption parameters derived from the ETLM to simulate and interpret the effect of pH, initial As(V) concentration, and EBCT on As(V) removal.