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Adsorption of selenite and selenate by nanocrystalline aluminum oxide, neat and impregnated in chitosan beads

Jamila S. Yamani [a], *Amanda W. Lounsbury* [a], *Julie B. Zimmerman* [a,b,*]

[a] *Yale University, Department of Chemical and Environmental Engineering, 9 Hillhouse Ave., Mason Lab 301, New Haven, CT 06511, United States*

[b] *Yale University School of Forestry and Environmental Studies, 195 Prospect St., New Haven, CT 06511, United States*

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ABSTRACT

Nanocrystalline metal oxide impregnated chitosan beads (MICB) were successfully developed with nanocrystalline aluminum oxide (n-Al_2O_3) to form n-Al_2O_3 impregnated chitosan beads (AICB). AICB were able to simultaneously adsorb inorganic aqueous selenite and selenate more effectively than n-Al_2O_3 or chitosan alone. For completeness, adsorption performance was also compared to n-TiO_2, a widely studied adsorbent for selenium, and n-TiO_2 impregnated chitosan beads (TICB). For the selenite system, n-Al_2O_3 was the primary active adsorbent responsible for removal as chitosan has a low affinity for selenite. For selenate, however, chitosan was the primary active adsorbent. The association constants for the adsorbent/adsorbate complexes and the relative amounts in which they are present supported this hypothesis. The association constants for selenate binding on n-Al_2O_3 and chitosan were 1.215×10^{-2} and 3.048×10^{-3}, respectively, and the association constants for selenite binding on n-Al_2O_3 and chitosan were 1.349×10^{-2} and 1.990×10^{-4}, respectively. For systems with coexisting selenite and selenate, AICB is potentially the most robust option as it maintained the most consistent performance regardless of fractionation of the selenium species. Kinetic studies and equilibrium isotherms were completed and effectively modeled using pseudo-second order kinetics and Langmuir adsorption theory, making it the first comprehensive systematic study of neat n-Al_2O_3 and AICB for selenium adsorption. pH significantly impacted adsorption due to changes in the adsorbent surface charge; increasing pH corresponded with decreasing adsorbent performance, beginning at approximately pH 6.5–7 for AICB. The trend in performance due to the effect of pH indicated that selenate binds to the amine group in chitosan, as suggested by other studies. In addition, increasing background sulfate concentration was found to negatively impact adsorption efficacy for both selenite, and more significantly, selenate, as sulfate is known to compete with selenium oxyanions due to their similar structures. The results indicate that, in order to maintain consistent removal in more realistic systems, a pre-treatment process to manage sulfate will be necessary as indicated for other adsorbents implemented for selenium adsorption in aqueous systems.

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* *Corresponding author*. Yale University, Department of Chemical and Environmental Engineering, United States. Tel.: +1 203 432 9703.
E-mail address: julie.zimmerman@yale.edu (J.B. Zimmerman).

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1. Introduction

Selenium occurs naturally in the environment and is an essential micronutrient for mammals within a narrow low concentration range. Above this range, selenium can be toxic, including potentially carcinogenic, depending on dose and speciation (US EPA). Chronic ingestion by humans at levels above 5 μg/kg-day, the US EPA reference dose for selenium, can result in gastrointestinal, cardiac, skin and neurological disorders (Goldhaber, 2003). As such, the US EPA has mandated the maximum contaminant level for selenium in drinking water at 50 ppb (Goldhaber, 2003). Anthropogenic activities such as smelting, mining, industrial production, and agricultural runoff have greatly increased the amount of selenium found in natural aquatic systems. In California, concentrations as high as 1400 ppb have been observed (Min and Hering, 1999). Selenium occurs in both organic and inorganic forms, but due to the high solubility, and therefore bioavailability, of inorganic selenium in water, most remediation techniques focus on the predominant inorganic species at environmentally relevant conditions, selenite (SeO_3^{2-}, Se(IV)) and selenate (SeO_4^{2-}, Se(VI)) (Plant et al., 2003). Although both oxyanions are toxic, selenate is reported to be more difficult to remove due to the predominance of electrostatic dependent outer-sphere complexes it forms with many adsorbents and the high solubility of selenate salts which makes adsorption thermodynamically unfavorable (Mondal et al., 2004; Sheoran and Sheoran, 2006).

Multiple technologies have been explored for the remediation of selenium. Coagulation, ion exchange, membrane filtration, and biological and chemical reduction are several of the methods that are currently used, but high operating and maintenance costs, sludge generation, and use of toxic chemicals severely limit their wide application (Tan et al., 2003; Hu et al., 2006; Sharma et al., 2009; Bleiman and Mishael, 2010). Recently, remediation through adsorption has been widely investigated as a cost effective alternative because of the possibility of sustainable implementation including the regeneration and reuse of the adsorbing media (Wang and Lo, 2009). Activated materials, such as carbon and alumina, are commonly used for the removal of inorganics from aqueous solutions. While activated carbon has a poor affinity for selenium (Sharma et al., 2009), remediation of selenium by activated alumina (AA) is highly pH dependent, and AA is not easily regenerated. Furthermore, the activation process is highly energy intensive (Hu et al., 2006).

As such, there is a need to identify and evaluate additional potential adsorbent materials for the removal of selenium from aqueous systems. In the last twenty years, metal oxides have gained interest for their applicability across a wide range of system conditions. In general, these materials are inexpensive, widely manufactured, and in most cases, benign (Miller and Zimmerman, 2010). Their use has grown even more with the advent of nanotechnology and the development of nanocrystalline metal oxides (Sharma et al., 2009). Nanocrystalline metal oxides (NMO) have a high surface area leading to an increased number of available sites for adsorption. Many NMO are well characterized with their highly ordered structure being well defined, making these materials ideal for predictive performance in use. There is a potential trade-off that should be carefully evaluated for this system in terms of the efficiency benefits in the use phase versus additional environmental or monetary costs associated with producing these nanomaterials.

Nanocrystalline forms of titanium dioxide (n-TiO_2), iron oxide (n-Fe_2O_3), and aluminum oxide (n-Al_2O_3) have all shown promise as effective adsorbents for a variety of inorganics, including selenium (Peak, 2006; Elzinga et al., 2009; Shi et al., 2009; Zhang et al., 2009; Jordan et al., 2011). A significant amount of research has been dedicated to understanding the potential of n-TiO_2 as a possible adsorbent for both selenite and selenate (Shi et al., 2009; Zhang et al., 2009; Jordan et al., 2011). n-TiO_2 moderately removes selenite, but is far less effective for selenate remediation (Zhang et al., 2009). For this reason, some treatment options that utilize n-TiO_2 include a reduction step where, in the presence of UV light and a hole scavenger like formic acid, selenate is reduced to selenite (Nguyen et al., 2005). In this system, the degree of reduction is difficult to control, and a portion of the selenate can be reduced beyond selenite to either elemental selenium (Se(0)) or hydrogen selenide gas (H_2Se) (Nguyen et al., 2005). Additional steps are required to separate the precipitated elemental selenium from the solution mixture or to scrub the toxic gas product.

Recently, due to the potential to harvest it from waste streams for use as an adsorbent, considerable research has been dedicated to bulk and n-Fe_2O_3, including for selenium remediation (Wei and Viadero, 2007). There are two main forms of Fe_2O_3, hematite and maghemite, which differ in crystalline structure, photocatalytic activity, and selenium affinity. Few studies have investigated bulk Fe_2O_3 for selenium removal (Peak and Sparks, 2002; Sheha and El-Shazly, 2010), but focus has recently shifted to n-Fe_2O_3 due to the higher surface area and concentration of adsorption sites. The main drawback to n-Fe_2O_3 is difficulty in synthesizing a uniform material for which performance can be accurately predicted as the crystalline and morphological characteristics of each synthesis are highly dependent on the method used (Carbajal-Franco et al., 2013). Furthermore, the limited data that is available is inconsistent, and a comprehensive study for selenium and the various forms of n-Fe_2O_3 has yet to be completed as the field is in its infancy (Jordan et al., 2012).

Due to the inconsistency and the complexity of adsorption on to n-Fe_2O_3, and as an alternative to a potentially complex system comprised of n-TiO_2 and a hole scavenger, Al_2O_3 has been explored. The ability to remediate both selenite and selenate without the need to carry out a reduction reaction has made bulk Al_2O_3 an interesting alternative adsorbent (Wu et al., 2000; Jegadeesan et al., 2003; Peak, 2006). Peak investigated the binding structures of selenite and selenate on bulk Al_2O_3 (Peak, 2006) while Elzinga et al. characterized selenite and selenate binding at the n-Al_2O_3/water interface (Elzinga et al., 2009). In both studies, selenite was found to form predominantly inner-sphere complexes with Al_2O_3, while selenate formed mostly outer-sphere complexes. Furthermore, the binding structure for each selenium–Al_2O_3 complex was found to be very pH dependent (Peak, 2006; Elzinga et al., 2009). Jegadeesan et al. performed a comparative study to evaluate bulk Al_2O_3, n-Al_2O_3, and chitin as potential adsorbents for selenite, but the applicability of the adsorbents for