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The role of counter ions in nano-hematite synthesis: Implications for surface area and selenium adsorption capacity

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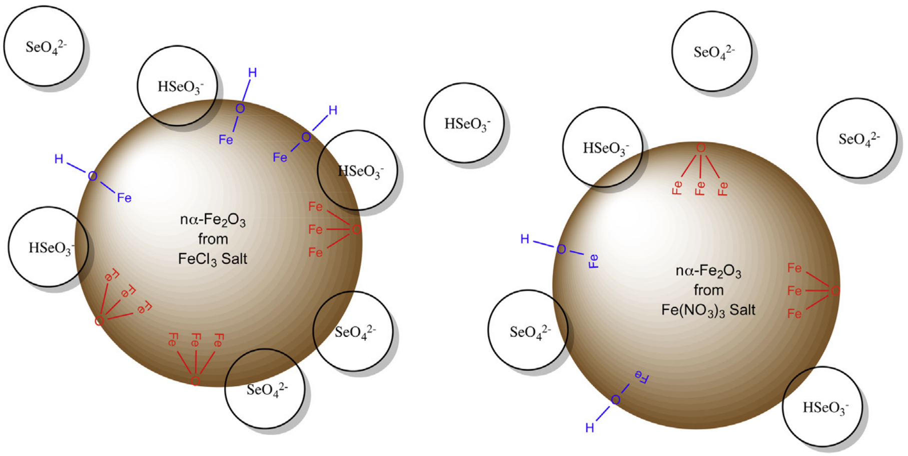
HIGHLIGHTS

- Macroscopic description Se(IV) and Se(VI) adsorption onto nα-Fe_2O_3.
- Evidence that a higher surface area does not translate to increased adsorption on the nano-scale.
- Evidence that synthesis materials impact adsorption ability of Se onto nα-Fe_2O_3.
- Spectroscopic evidence of the binding mechanism of Se(VI) onto nα-Fe_2O_3.

GRAPHICAL ABSTRACT



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ABSTRACT

Nano metal oxides are of interest for aqueous selenium (Se) remediation, and as such, nano-hematite (nα-Fe_2O_3) was examined for use as a Se adsorbent. The effect of surface area on adsorption was also studied. nα-Fe_2O_3 particles were synthesized from $Fe(NO_3)_3$ and $FeCl_3$ via forced hydrolysis. The resulting particles have similar sizes, morphologies, aggregate size, pore size, and PZC. The nα-Fe_2O_3 from $FeCl_3$ (nα-Fe_2O_3-C) differs from the nα-Fe_2O_3 from $Fe(NO_3)_3$ (nα-Fe_2O_3-N) with a $\sim 25 \pm 2\ m^2/g$ greater surface area. Selenite Se(IV) adsorption capacity on nα-Fe_2O_3 has a q_{max} ~17 mg/g for the freeze-dried and re-suspended nα-Fe_2O_3. The Δq_{max} for nα-Fe_2O_3 from $Fe(NO_3)_3$ and $FeCl_3$ that remained in suspension was 4.6 mg/g. For selenate Se(VI), the freeze-dried and re-suspended particles realize a Δq_{max} = 1.5 mg/g for nα-Fe_2O_3 from $Fe(NO_3)_3$ and $FeCl_3$. The nα-Fe_2O_3 from $Fe(NO_3)_3$ and $FeCl_3$ that remained in suspension demonstrated Se(VI) Δq_{max} = 5.4 mg/g.

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In situ ATR–FTIR isotherm measurements completed for Se(VI) at a pH 6 suggest that Se(VI) forms primarily outer–sphere complexes with nα-Fe_2O_3 synthesized from both salts.

1. Introduction

Selenium (Se) enters the environment predominately via anthropogenic sources such as industrial effluent, agricultural runoff and waste from power generation [1,2], and tends to persist [3]. While there is moderate human health concern associated with ingestion above 5 mg/kg-day, the primary concern is for aquatic life and wildlife, where Se contamination causes teratogenesis [4]. As a result of recent findings, the US EPA is in the process of reducing the aquatic life [4] for Se as well as increasing restrictions for power generation effluent containing Se [5].

Of the four main oxidation states of inorganic Se, selenite (Se(IV)) and selenate (Se(VI)) are of greatest significance because they are soluble, mobile and bioavailable [6]. At relevant aquatic pH and pE conditions, Se(IV) and Se(VI) exist primarily as the oxyanions $HSeO_3^-$ and SeO_4^{2-}, respectively [1,2]. Most natural mineral sorbents have a low affinity for Se(VI), which makes it more difficult to remove from solution and therefore more bioavailable compared to Se(IV) [1,2]. For this reason, many aqueous Se remediation technologies reduce Se(VI) to Se(IV) prior to removal [7]. However, currently there exists no full scale technology capable of removing Se to below the US EPA maximum contaminant drinking water limit of 5 μg/L in a cost-effective and widely applicable manor [7].

Due to these system constraints, adsorption is currently the favored remediation technology since most adsorbents are chemically benign, do not require toxic chemicals, and facilitate regeneration and reuse [7]. Metal oxides are ubiquitous, inexpensive, and effective anion adsorbents. This has led to increased interest for their applicability as sorbents for inorganic contaminants across a wide range of system conditions [8]. In nature, iron and aluminum (hydr) oxides (Fe-/Al-oxides) are predominant sinks for aqueous inorganic contaminants such as Se and play an important role in the fate and transport of these contaminants in soil [9,10]. Fe-/Al-oxides have also demonstrated some of the highest affinity for Se in laboratory-based studies [7,9,11] due to the high specific surface area (SSA) and desirable point of zero charge values (PZC) [10]. With the development of nanotechnology, the applicability of nano materials in engineered systems has also grown [8,12]. In general, nano metal oxides possess increased surface area per mass, suggesting a larger sorption capacity per mass than their micro- and macro-scale counterparts [6,8].

While the potential of nanoparticulate adsorbents has been attributed to high specific surface area (SSA), examination of the literature suggests certain nano-effects and characteristics beyond surface area may also be important for adsorption capacity and adsorption sites once in the nano-regime [13–16]. For example, Torrent et al. [13] have shown that an increase in SSA does not necessarily correlate to an increase in sorption ability of goethite for phosphate. Madden et al. [14], showed that size was a determining factor in adsorption of Cu^{2+} on different sized nα-Fe_2O_3, probably due to the increased presence of coordinatively undersaturated surface anions [14]. While it is suggested that shape and size [8,14,17] increase sorption ability and favorable adsorption sites of nanoparticles, the effects of these and other characteristics has not been well-studied [17].

There are few papers that examine the impact of different anions in particle synthesis on particle function. Gemeay et al., examined the use of HSO_4^-, $H_2PO_4^-$, Cl^-, and NO_3^- in the synthesis of polyaniline(PANI)/MnO_2 composites, and determined that the degree of crystallinity, thermal stability, and the doping level of the prepared composites are dependent on the type of acid used [18]. Zhang et al., synthesized ultrafine rutile TiO_2 by varying the hydrolytic conditions with HCl, NH_4Cl, NaCl, and $TiCl_4$ and found that the Cl^- concentration impacts the surface area and morphology of the resulting particles [19]. Moore et al., synthesized zero valent iron (ZVI) with phosphate, sulfate, Cl^-, and NO_3^- and found that ZVI synthesized in the presence of different ions has different reactions with respect to carbon tetrachloride [20]. Moore et al., suggested that differences in the crystal faces of the resulting ZVI outside the resolution of the HR-TEM could be responsible [20]. These papers suggest that anions may be a characteristic worth examining in synthesizing nanomaterials with favored crystal faces, which can directly impact adsorption and other behavior.

There has been extensive study on the ability of Se oxyanions to sorb onto various bulk and nano iron (hydr) oxides [12,15,16,21–25]. As a class of nanoparticles, Fe-oxides are ubiquitous in nature, easily synthesized, largely non-toxic, and have a high affinity for inorganic contaminants [15,26]. Of the 16 iron oxides and (oxy) hydroxides, hematite (α-Fe_2O_3) is one of the most thermodynamically stable, abundant, and well-characterized, and is also known to be an efficient anion sorbent [26]. However, there are no studies on the affinity or capacity of nano-hematite (nα-Fe_2O_3) to adsorb Se.

While the mechanism by which Se(IV) and Se(VI) complex to iron (hydr) oxides has long been a topic of interest, there are only a few studies that examine the binding of Se on α-Fe_2O_3 [12,27]. Binding mechanisms are important for both adsorption for remediation purposes and for understanding the fate and transport of oxyanions in natural environments. Catalano et al., characterized Se(IV) sorption onto the (100) face of bulk α-Fe_2O_3 with EXAFS as an inner-sphere bridging bidentate complex with the singly coordinated oxygen groups of the iron face [27]. Peak and Sparks examined Se(VI) adsorption onto bulk α-Fe_2O_3, goethite (α-FeOOH), and HFO with ATR–FTIR and XAS [12]. For HFO, inner- and outer–sphere complexes are seen. For α-FeOOH, there is a continuum of inner- and outer–sphere complexes and as pH and ionic strength increase so too do the inner-sphere complexes. Further, for α-Fe_2O_3, only inner-sphere monodentate complexes were reported [12]. However, the extent to which outer–sphere Se(VI) complexes form on nα-Fe_2O_3 at higher pH has yet to be determined. Since different iron (hydr) oxides bind Se differently, further work is necessary to understand the complexation of Se onto the α-Fe_2O_3 surface.

Since Al-oxides are nature's other predominant anion sink, nano-Al-oxides are a reasonable baseline comparison for Se adsorption onto Fe-oxides. Yamani et al. [29], Zelmanov and Semia [11], Duc et al. [15], Mitchell et al. [16] and Jegadeesan et al. [28] recently reported a higher sorption capacity of both Se(IV) an Se(VI) for (nγ-Al_2O_3) than previously reported for many other pure phase nano-metal oxides (NMO). Therefore, nγ-Al_2O_3 will be used as a comparative Se adsorbent.

The purpose of this study is two-fold. First, this study aims to examine the influence of anions in the synthesis process and the influence of surface area on nα-Fe_2O_3 adsorption of Se oxyanions. As such, nα-Fe_2O_3 was synthesized with two different source materials. Second, this study aims to examine the extent to which Se