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

Authors: AMANDA W. LOUNSBURY^a, JAMILA S. YAMANI^a, CHAD P. JOHNSTON^{bl},
PHILIP LARESE-CASANOVA^c, JULIE B. ZIMMERMAN^{*a,d}

*Corresponding author: Julie B. Zimmerman, Tel.: +1.203.432.9703. Email address:

julie.zimmerman@yale.edu

^a Yale University Department of Chemical and Environmental Engineering

Mason Lab, 9 Hillhouse Ave

New Haven, CT 06511, United States of America

^b University of Connecticut Department of Civil and Environmental Engineering

Castleman Building, 261 Glenbrook Road,

Storrs, CT 06269, United States of America

^c Northeastern University Department of Civil and Environmental Engineering

Snell Engineering Center, 360 Huntington Avenue

Boston, MA 02115 United States of America

^c Yale University School of Forestry and Environmental Studies

Kroon Hall, 195 Prospect St.

New Haven, CT 06511, United States of America

^lPresent Address: Loyola University Chicago

Cuneo Hall, 6430 N. Kenmore Ave.

Chicago , IL 60660, United States of America

Abstract

Nano metal oxides are of interest for aqueous selenium (Se) remediation, as such nano-hematite (α -Fe₂O₃) was examined for use as a Se adsorbent. The effect of surface area on adsorption was also studied. α -Fe₂O₃ particles were synthesized from Fe(NO₃)₃ and FeCl₃ via forced hydrolysis. The resulting particles have similar sizes, morphologies, aggregate size, pore size, and PZC. The α -Fe₂O₃ from FeCl₃ (α -Fe₂O₃-C) differs from the α -Fe₂O₃ from Fe(NO₃)₃ (α -Fe₂O₃-N) with a $\sim 25 \pm 2$ m²/g greater surface area. Selenite Se(IV) adsorption capacity on α -Fe₂O₃ has a $q_{\max}$ ~ 17 mg/g for the freeze-dried and re-suspended α -Fe₂O₃. The $q_{\max}$ for α -Fe₂O₃ from Fe(NO₃)₃ and FeCl₃ that remained in suspension were 35.6 and 40.2 mg/g respectively. For selenate Se(VI), the freeze-dried and re-suspended particles realize a $q_{\max} = 6.01$ and 7.47 mg/g for α -Fe₂O₃ from Fe(NO₃)₃ and FeCl₃ respectively. The α -Fe₂O₃ from Fe(NO₃)₃ and FeCl₃ that remained in suspension demonstrated Se(VI) $q_{\max} = 10.2$ and 15.6 mg/g respectively. In situ ATR-FTIR isotherm measurements completed for Se(VI) at a pH6 suggest that Se(VI) forms primarily outer-sphere complexes with α -Fe₂O₃ synthesized from both salts.

Key Words: adsorption; selenium; iron oxide; hematite; nanoparticles

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 $\mu\text{g/L}$ in a cost-effective and widely applicable manner [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 counterpart [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. (1990) have shown that an increase in SSA does not necessarily correlate to an increase in sorption ability of goethite for phosphate. Madden et. al. (2006) showed that size was a determining factor in adsorption of Cu^{2+} on different sized $\alpha\text{-Fe}_2\text{O}_3$, 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. (2005) 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. (2002) 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. (2011) 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 ($\alpha\text{-Fe}_2\text{O}_3$) 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 ($n\alpha\text{-Fe}_2\text{O}_3$) 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 $\alpha\text{-Fe}_2\text{O}_3$ [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. (2006) characterized Se(IV) sorption onto the (100) face of bulk $\alpha\text{-Fe}_2\text{O}_3$ with EXAFS as an inner-sphere bridging bidentate complex with the singly coordinated oxygen groups of the iron face [27]. Peak and Sparks (2002) examined Se(VI) adsorption onto bulk $\alpha\text{-Fe}_2\text{O}_3$, goethite ($\alpha\text{-FeOOH}$), and HFO with ATR-FTIR and XAS [12]. For HFO inner- and outer-sphere complexes are seen. For $\alpha\text{-FeOOH}$, 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 $\alpha\text{-Fe}_2\text{O}_3$ only

inner-sphere monodentate complexes were reported [12]. However, the extent to which outer-sphere Se(VI) complexes form on α -Fe₂O₃ 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 -Fe₂O₃ 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. (2014) recently reported a higher sorption capacity of both Se(IV) and Se(VI) for (γ -Al₂O₃) than previously reported for many other pure phase nano-metal oxides (NMO) [11, 15, 16, 28, 29]. Therefore γ -Al₂O₃ 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 α -Fe₂O₃ adsorption of Se oxyanions. As such, α -Fe₂O₃ was synthesized with two different source materials. Second, this study aims to examine the extent to which Se oxyanions adsorb to α -Fe₂O₃ and through *in situ* ATR-FTIR techniques determine the mechanism of Se adsorption.

2. Materials and Methods

2.1 Nanoparticle Synthesis.

Hematite nanoparticles were synthesized by dripping 60mL of 1M ferric nitrate (99.99% trace metal basis, Sigma Aldrich) (scaled method 4) Schwertmann and Cornell [14, 30] or ferric chloride (ACS reagent, 97%, Sigma Aldrich) solutions (as specified) from a 60-mL syringe into 750 mL of boiling Millipore deionized (DI) water mixing on a hot plate. The resulting suspension was then removed from heat, allowed to cool for 24 hours, and put into dialysis (6000 to 8000 Dalton MWCO, Fisher Scientific) until the conductivity of the solution was below 5 μ S.

A portion of the nanoparticle suspensions were stored in Nalgene bottles and the remainder were frozen at -80°C overnight and freeze-dried for three days (VerTis Lyophilizer).

2.2 Nanoparticle Characterization.

Surface area. Surface area was determined using N₂-physisorption Branauer-Emmett-Teller (BET) isotherm fits (Particle Technology Laboratory). Micro and mesopore size distribution was determined with a density functional theory (DFT) fit from N₂ sorption with a Quantachrome Autosorb As-3B multistation, after degassing the powder at 200°C for at least three hours[31]. *Crystal Structure.* X-ray diffraction (XRD) analysis of freeze-dried powders was completed using a Rigaku R-Axis SPIDER equipped with sealed tube molybdenum radiation. Freeze-dried powder samples were loaded using 400 µm MiTeGen MicroMesh pins to mount the powders as oil emulsions. As there have been reports that freeze drying particles can cause a phase-change in iron particles, air-dried slurry samples were loaded using a dip coat method onto the mesh pins to ensure hematite phase [32, 33]. Analysis was completed on a MicroMax-007 HF Cu radiation with a Saturn 944+ detector. *Size and Morphology.* High-resolution transition electron micrographs (HR-TEM) were obtained using a FEI Tecnai Osiris 200kV transition electron microscope. Nanoparticle suspensions were placed on a lacy carbon grid supported with a 200 mesh copper holder (Ted Pella, Inc.) for TEM imaging. Dynamic Light Scattering (DLS) was completed using an ALV-GmbH instrument at an angle of 90°. The raw correlation functions were analyzed in MATLAB and Fortran, using the CONTIN Algorithm [34]. *Point of Zero Charge.* Point of zero charge (PZC) was determined by potentiometric titration of solutions of the (α -Fe₂O₃) starting at a pH of ~12.6 and titrating with 0.1M HNO₃ (TraceMetal Grade, Fisher Chemical).

2.3 Selenium Sorption Experiments.

Carbonate species can act as a competitor for adsorption sites [14]. Therefore, all adsorption experiments were carried out under an N₂ atmosphere (Coy vinyl anaerobic chamber) with autoclaved DI water to remove dissolved CO₂. Experiments were performed in 50 mL polypropylene Falcon tubes. Adsorbent was added to the system as 0.2 mL or 1 mL α -Fe₂O₃, stored as a suspension in oxic conditions, determined to be 4.79 mg/L and 4.53 mg/L for particles synthesized from FeCl₃ and Fe(NO₃)₃ respectively. Se was then introduced to the system as either Na₂SeO₃ or Na₂SeO₄ salt (>98%, Sigma Aldrich) within aliquots of stock solutions, as specified, to make a final batch reactor volume of 50 mL.

Batch experiments were used to characterize the sorption ability of the nano ferric oxide particles. Reactors were rotated for ca. 24 hours at 25°C and allowed to equilibrate without manual pH adjustment. This was tested by means of time-dependent adsorption experiments and the solution pH was determined to be within pH 5.5-6.5 (Figure A1) [12, 24]. For most experiments, unless otherwise noted, initial Se concentrations ([Se]₀) was 0.2 ppm as this concentration is the higher end of concentrations found in contaminated water sources and waste waters [2, 35]. At this concentration, for Se(VI), the pH ranged from 5.97-6.65, and the experiments were unbuffered. pH increased with increasing Se(IV) concentrations. Therefore with the exception of the experiments probing pH effects, all Se(IV) solutions were buffered to pH 6 with a 25 mM acetate buffer (acetic acid (ACS reagent grade, JT Baker) and sodium acetate (ACS reagent grade, Sigma-Adrich). Samples of each reactor were filtered through a 0.2 μ m syringe-driven filter unit (PVDF Millipore) for analysis. Controls were designed to ensure no nanoparticles passed through the filters and that all adsorption reported was due to the nanoparticles and not due to the experimental equipment. pH was subsequently measured for all

samples using a VWR pH probe and a standard 3-point calibration. Reactor pH was measured after aliquots were removed and prepared for analysis. Experiments were completed in duplicate based on standard procedures for similar experiments reported in the literature [29, 36]. Error is reported as standard error.

2.4 Analysis by ICP-OES and ICP-MS.

Concentrations of the initial nanoparticles suspensions were determined using inductively coupled plasma optical emission spectrometry (ICP-OES) (Perkin Elmer Optima 3000) with an AS90 autosampler and a scandium internal standard. Initial nanoparticle suspensions were diluted 1000 fold and dissolved in 10% HCl prior to ICP-OES analysis. All Se concentrations were analyzed using inductively coupled plasma mass spectrometry (ICP-MS) (Perkin Elmer DRC-e) with a Meinhardt nebulizer and argon plasma. Internal germanium and yttrium standards were utilized. Both ^{78}Se and ^{82}Se were measured; only ^{78}Se was used for data analysis though no significant difference was noted between the trends for each isotope. Quality control readings were periodically performed to ensure limited drift during analysis for both ICP-MS and ICP-OES readings [29].

2.5 In situ ATR-FTIR spectroscopy. Infrared spectra were collected to probe the bonding environment of Se(VI) adsorbed on $\alpha\text{-Fe}_2\text{O}_3$. Measurements were collected with a Bruker alpha-P Fourier transform infrared (FTIR) spectrometer equipped with a diamond attenuated total reflectance (ATR) accessory (Bruker Optics). Measurements were performed in situ with a flow-cell apparatus and thin-film deposition technique described elsewhere [37]. A peristaltic pump was used to react the film with a nitrogen-purged solution of known composition: pH (6.5), ionic strength (0.01M NaCl) and Se (10-500 μM). Following equilibration, a background spectrum was recorded such that any subsequent spectral changes were solely the result of Se

adsorption. Isotherm experiments were conducted by incrementally changing the Se concentration. Final spectra were taken as the result of 1200 averaged scans with a resolution of 4cm^{-1} .

3. Results and Discussion

To determine the impact of surface area on adsorption ability, $\alpha\text{-Fe}_2\text{O}_3$ was synthesized with different anions. $\alpha\text{-Fe}_2\text{O}_3$ synthesized from $\text{Fe}(\text{NO}_3)_3$ is referred to as $\alpha\text{-Fe}_2\text{O}_3\text{-N}$ and $\alpha\text{-Fe}_2\text{O}_3$ synthesized from FeCl_3 is referred to as $\alpha\text{-Fe}_2\text{O}_3\text{-C}$. $\alpha\text{-Fe}_2\text{O}_3\text{-N}$ and $\alpha\text{-Fe}_2\text{O}_3\text{-C}$ are similar in size, shape, and PZC, but have different surface area. $\alpha\text{-Fe}_2\text{O}_3$ synthesized from both methods demonstrated only reflections for $\alpha\text{-Fe}_2\text{O}_3$ within XRD patterns from the ICDD database (Figure A2a) [PDF Card No. 00-033-0664]. Pure hematite was confirmed with the ATR-FTIR (Figure A3a with reference spectrum A3b) All freeze-dried particles and suspensions were found by HR-TEM to be 5-7nm $\alpha\text{-Fe}_2\text{O}_3$ platelets, however the specific crystal faces formed are too small to be determined by this technique (Figure 1) [20].

Surface area results of the freeze-dried particles are shown in Table 1. $\alpha\text{-Fe}_2\text{O}_3\text{-C}$ have a larger surface area than $\alpha\text{-Fe}_2\text{O}_3\text{-N}$ particles by $\sim 25 \pm 2 \text{ m}^2\text{g}^{-1}$. It is important to note that the surface area reported in Table 1 only pertains to the freeze-dried particles. Agglomeration occurs during drying, causing changes in surface area between the suspended particles and the freeze-dried particles [14]. From Cornell and Schwertmann, $\alpha\text{-Fe}_2\text{O}_3$ nanoparticles prepared using the forced hydrolysis method used in these syntheses, and from $\alpha\text{-Fe}_2\text{O}_3$ nanoparticles synthesized at temperatures at or less than 100°C typically have BET surface area's ranging from $10\text{-}90 \text{ m}^2 \text{ g}^{-1}$ [26]. As such, the observed difference of $25 \text{ m}^2 \text{ g}^{-1}$ represents at least a 25% difference in the surface area of the particles, a seemingly significant difference between the two samples.

Negligible differences in crystal morphology, size, shape, aggregate size, and PZC were found between $\alpha\text{-Fe}_2\text{O}_3\text{-N}$ and $\alpha\text{-Fe}_2\text{O}_3\text{-C}$ (Figure 1, A2-A5).

3.1 Selenium Adsorption.

Isotherms for adsorption of Se(IV) and Se(VI) onto the nano metal oxides are shown in Figure 1a and b, respectively. All sorption data was fit using Langmuir, Freundlich and BET isotherm models, with the best-fit model presented. Se(IV) adsorption onto $\alpha\text{-Fe}_2\text{O}_3$ exhibits BET liquid to solid adsorption behavior [38], equation (1).

$$q = q_m \frac{k_s C_{eq}}{(1 - k_L C_{eq})(1 - k_L C_{eq} + k_s C_{eq})} \quad [1]$$

where q_m is the maximum amount of adsorbate on the surface and corresponds to complete coverage of monolayer adsorption, C_{eq} is the equilibrium concentration of adsorbate in solution after adsorption, k_s is the equilibrium constant of adsorption for the 1st layer of adsorption in the Langmuir model, and k_L is the equilibrium constant of adsorption for adsorption layers greater than the first layer of adsorption [38]. The Langmuir model was applied to Se(VI) adsorption onto $\alpha\text{-Fe}_2\text{O}_3$, equation (2), which can be achieved from BET theory by assuming $k_L = 0$.

$$q = q_m \frac{k_s C_{eq}}{1 + k_s C_{eq}} \quad [2]$$

The monolayer Langmuir assumption can be attributed to a single dominant anion binding site type [39]. The dominant binding site for iron oxides is often singly coordinated hydroxyl functional group [26, 39] with triply coordinated hydroxyl groups potentially acting as additional, although a less favorable, binding site type (Figure 2) [26, 27, 40, 41]. The lack of Langmuirian behavior in the Se(IV) sorption data for all $\alpha\text{-Fe}_2\text{O}_3$, and most prevalent in the $\alpha\text{-Fe}_2\text{O}_3$ suspensions, in Figure 3a, suggests that Langmuirian assumptions do not hold. This may be due

to one of two things: single site adsorption exists at low Se(IV) concentrations and at higher concentrations the increasing surface deposition results in a surface precipitation process [39]; or multi-site adsorption is occurring throughout the concentration range once the dominant binding site is saturated. Zelmanov and Smiat (2013) attributed similar behavior for Se adsorption onto nano iron hydroxide suspensions to more complex surface structure than indicated by the Langmuir assumptions, and preferred to use the empirical Freundlich isotherm to fit the data. Wei et al. (2012) characterized the sorption capacity of Se(IV) by nano-magnetite with the Freundlich isotherm as Langmuirian behavior was not exhibited, they suggested the existence of heterogeneous sorption sites. This contradicts the Langmuir adsorption behavior reported by Rovira et. al. (2008) and Martinez et. Al. (2006) for Se(IV) onto bulk α -FeOOH, α -Fe₂O₃, and magnetite (Fe₃O₄).

Unlike the Se(IV) adsorption isotherms, Se(VI) shows pseudo-Langmuirian behavior. Se(VI) has a lower affinity for α -Fe₂O₃ than Se(IV), which is in agreement with other reports [12]. The values reported for q_m (Figure 3a and b) are greater than that previously reported for other single-phase iron or aluminum oxide nano-sorbents [6, 11, 16, 29, 42]. Since the adsorption capacity of Se by α -Fe₂O₃ is higher than or similar to the γ -Al₂O₃, no other comparison was conducted.

3.2 Complexation Mechanism with *in situ* ATR-FTIR

In situ ATR-FTIR was used to determine the bonding environment of Se(VI) adsorbed on α -Fe₂O₃. From a qualitative standpoint, spectral intensity increases with increasing Se(VI) concentration, consistent with macroscopic isotherm behavior (Figure 4). Spectra corresponding to both α -Fe₂O₃ samples are nearly identical to one another. The lack of spectral differences is suggestive that the adsorption mechanism is independent of the ferric salt precursor used in the

synthesis. Insight into the complexation mechanism is obtained from group theory considerations. In aqueous solution, the free Se(VI) ion has tetrahedral symmetry (T_d) and produces a single peak at 872 cm^{-1} corresponding to the triply degenerate asymmetric Se–O stretch (ν_3). Coordination to the surface results in a decrease in Se(VI) symmetry and splitting of the ν_3 mode to split into two or three components for nonprotonated monodentate and bidentate complexes, respectively. Outer-sphere complexes retain their inner hydration shells, and thus produce spectra that closely resemble the ion in solution. The normally infrared-inactive Se–O symmetric stretch (ν_1) at 837 cm^{-1} may become active in all coordination states.

From the preceding discussion, the intact ν_3 at $871 - 875\text{ cm}^{-1}$ in all spectra indicates that Se(VI) primarily forms outer-sphere complexes at pH 6.5. There is some indication of a very weak shoulder at 900 cm^{-1} that likely corresponds to a small fraction of inner-sphere complexes. The broad peak around 820 cm^{-1} is assigned to the activated ν_1 mode. The spectra are similar to those previously reported for Se(VI) adsorbed on amorphous iron oxide and α -FeOOH [22, 43]. Overall, the pH 6.5 isotherm results are consistent with previous studies suggesting Se(VI) forms primarily outer-sphere complexes at above pH 6 on HFO and α -FeOOH [12, 43]. Although Peak and Sparks (2002) suggested that only monodentate complexes form on α -Fe₂O₃, it is likely that the lack of spectroscopic data for samples at pH greater than 3.5 for α -Fe₂O₃/ η -Fe₂O₃ preclude detection of outer-sphere complexes [12]. Thus, these findings are suggestive of a similar outer-to inner-sphere continuum exhibited by Se(VI) on other iron (hydr)oxides and contribute to the data set by adding spectroscopic data for samples at a higher pH at varying concentrations.

4. Discussion

For both Se(IV) and Se(VI), adsorption capacity is greater for the iron oxide suspensions than for the freeze-dried particles. This is likely due to the prevention of surface site access due

to the visible aggregation of freeze-dried particles. As surface binding sites are typically correlated with surface area, the specific surface area of the freeze-dried particles was measured. Powder α -Fe₂O₃-C and α -Fe₂O₃-N have similar sorption capacities for Se(IV) and the α -Fe₂O₃-C Se(VI) adsorption than the α -Fe₂O₃-N despite a 25 m²g⁻¹ larger surface area. This is in disagreement to the common hypothesis that an increase in surface area results in an increase in sorption capacity. The pore-size determined by a DFT distribution suggests that α -Fe₂O₃-C has similar pore sizes to α -Fe₂O₃-N particles (Figure A4), thereby indicating that the increased surface area and decreased adsorption is probably not due to pore sizes. Due to similar particle (Figure 1) and aggregate size (Figure A5), and morphology (Figure 1) of the nanoparticles, differences in surface area and adsorption due to size effects are unlikely. Instead, the surface area and adsorption differences are likely due to the role of the counter ion in the synthesis. Sugimoto et. al. (1998) previously reported that high concentrations of Cl⁻ ions in the synthesis of α -Fe₂O₃ disrupt nuclei fusion resulting in more “porous” or higher surface area particles [44]. Although there is not a report on the impact of NO₃⁻ on α -Fe₂O₃ structure during synthesis, it is possible that NO₃⁻ may further increase the surface area of the particles due to ionic properties. Based on previous literature and the observations reported here, it is possible that the differences in surface area can be attributed to the presence of the specific anions in solution during synthesis and should be examined subsequently.

A possible explanation for an increase adsorption by α -Fe₂O₃-C despite the lower surface area may be due to an increase in prevalence of active surface sites, resulting in the observations of increased sorption capacity, Figure 2. It has been suggested and shown that it is only the singly and triply coordinated hydroxyl groups that are active surface sites for α -Fe₂O₃ adsorption [13, 26, 27, 40, 41]. This is because the singly and triply coordinated hydroxyl groups

are undersaturated, and therefore more reactive than the saturated stable doubly coordinated hydroxyl group [41]. This explanation is further supported by particles in suspension. The α -Fe₂O₃-C has a higher sorption capacity than α -Fe₂O₃-N for both Se(IV) and Se(VI). Chloride and nitrate ions may promote or hinder the formation of active surface sites, namely the singly or triply coordinated hydroxyl groups by enhancing the growth of certain crystal faces or by otherwise altering the free energy of the nanoparticle surface, that like Moore et. al. (2011) are not visible on the TEM. This is in agreement with the general trend that typically α -Fe₂O₃ formed from FeCl₃ follows a phase transfer process through akaganeite [26], however in forced hydrolysis with fast nucleation some other amorphous iron phase is formed prior to α -Fe₂O₃ [45]. α -Fe₂O₃ formed from Fe(NO₃)₃ transforms from goethite to hematite [26, 45]. The growth process can be responsible for deformities which would allow for different proportion of singly, doubly, or triply coordinated surface hydroxyl groups than in the pure crystal face form. Alternatively, these transformation pathways could favor crystal faces that contain more of the favored binding sites [17, 41]. Furthermore, at small particle sizes, amorphous crystal forms tend to be more stable than the more crystalline polymorphs [17]. Therefore, the formation of α -Fe₂O₃-C may have amorphous iron phases isolated at the surface of the particles and thereby favor more of the reactive sites [17]. Additionally, according to Waychunas et al. (2005) a higher surface free energy could directly drive adsorption in order that the adsorbed species helps to relax the crystal surface [17].

For the freeze-dried particles, it is possible that the aggregation occurred on the most reactive faces during the drying process [41] leaving the lesser reactive faces, such that the re-suspended particles from different sources adsorbed Se to the same capacity. It is also possible

that the freeze-drying of the particles helped to relax the crystal surface leaving fewer reactive sites for adsorption after re-suspension [32].

The PZC results between the different sourced suspended particles, and the different sourced dried particles are similar (less than 2% difference). However, the PZC increases from the suspended particles to the dried particles. It has been suggested that the pH at which the binding sites of the iron oxide surface deprotonate are highest for the most stable complexes, namely deprotonation is highest for the doubly coordinated hydroxyl surface group, when the binding site deprotonates from $\#Fe_2OH^0$ to $\#Fe_2O^{-1}$ [41, 46, 47]. This change in PZC may suggest that there are more protonated sites (i.e. less reactive sites) on the dried particles than in the suspension, supporting the hypothesis that aggregation occurs along the more reactive (singly and triply coordinated) sites. Thus, this supports the observed reduction in sorption of selenium on the dried particles because the more reactive sites for sorption are involved in the aggregation and are not available to the Se. Further, the similarity in the PZC between the suspended particles and the dried particles does not counter the proposed hypothesis, as the singly and triply coordinated sites represent a variety of species that have different log K values for which they are reactive and non-reactive [46].

5. Conclusions

The results of this research suggest that specific surface area is not the key determinant of adsorption ability within the nano-range but rather available surface area based on the number of reactive sites is a more important characteristic. Anions in the synthesis process influence Se adsorption capacity onto $\alpha\text{-Fe}_2\text{O}_3$ and their impact should be examined in other systems as potential influences of sorption ability and available surface area. To further elucidate this point, other similar systems can be examined or quantum chemical modeling may be employed. This

research also demonstrated that the anions in synthesis did not impact the complexation of Se(VI) with α -Fe₂O₃ across different Se concentrations according to ATR-FTIR. ATR-FTIR showed predominantly outer-sphere complexes across these concentrations. Given the high sorption capacity for both Se(IV) and Se(VI) across a wide pH range, α -Fe₂O₃ could potentially be explored in relevant systems to serve as part of a more effective Se sorbent filter media than other currently proposed materials.

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8. Appendix A

Appendix A contains XRD, ATR-FTIR, DFT, DLS, XPS, α -Fe₂O₃-N effects of competing ions, and ionic strength on Se adsorption, as well as α -Fe₂O₃-C and α -Fe₂O₃-N effects of pH on Se adsorption data.

Captions:

Figure 1: TEM images of **a)** α -Fe₂O₃-C and **b)** α -Fe₂O₃-N. Particles from both salt sources formed individual platelets, roughly 5-7nm in size with larger aggregate sizes.

Table 1: PZC data was completed via potentiometric titration for α -Fe₂O₃ from both sources in suspension and powder. Specific surface area (SSA) was determined via BET N₂ physisorption for the α -Fe₂O₃ from both sources in powder form.

Figure 2: Schematic demonstrating the increased reactivity of the undersaturated singly and triply coordinated hydroxyl groups over the stable doubly coordinated hydroxyl groups.

Figure 3: Adsorption behavior of **a)** Se(IV) with the nano metal oxides. The nano iron oxides demonstrate multi-layer BET behavior using the isotherm constants provided, shown as lines. pH of the iron oxide system is buffered at 6.5 with acetate buffer and the η -Al₂O₃ system is buffered at pH 6.0; **b)** Se(VI) with the nanometal oxides. The nano iron oxides demonstrate pseudo-Langmuir behavior across all the Se concentration range, using the constants are provided, shown as lines. α -Fe₂O₃ suspensions from different ferric salt sources, freeze-dried α -Fe₂O₃ from the same ferric salt sources, and purchased η -Al₂O₃ as previously reported [29]. Markers represent data.

Figure 4: ATR-FTIR spectra (solid lines) and the negative of their second derivatives (dotted lines) corresponding to isotherm experiments of Se(VI) adsorption on **a)** α -Fe₂O₃-C and **b)** α -Fe₂O₃-N. [Se]₀=10-500 μ M as specified and pH=6.5, and I= 0.01M NaCl.

SAMPLE	PZC	SSA (m ² /g)
α -Fe ₂ O ₃ -C Suspension	8.73 ± 0.02	--
α -Fe ₂ O ₃ -N Suspension	8.95 ± 0.01	--
α -Fe ₂ O ₃ -C Powder	9.52 ± 0.04	74 ± 1
α -Fe ₂ O ₃ -N Powder	9.33 ± 0.03	99 ± 1

A

	$q_{\max}$ (mg/g)	k_s (mg/L) ⁻¹	k_L (mg/L) ⁻¹
α-Fe₂O₃-C Suspension	40.2 ± 0.60	13.7 ± 1.0	0.018 ± 0.001
α-Fe₂O₃-N Suspension	35.6 ± 0.62	15.2 ± 1.2	0.017 ± 0.001
Al₂O₃ (<i>Yamani et. al. 2013</i>)	10.88	14.92	--
α-Fe₂O₃-C Powder	17.9 ± 0.66	12.1 ± 2.0	0.017 ± 0.003
α-Fe₂O₃-N Powder	17.3 ± 0.59	13.4 ± 2.0	0.015 ± 0.003

B

	$q_{\max}$ (mg/g)	k_s (mg/L) ⁻¹	k_L (mg/L) ⁻¹
α-Fe₂O₃-C Suspension	15.6 ± 0.50	109 ± 27	--
α-Fe₂O₃-N Suspension	10.2 ± 0.625	73.5 ± 30	--
Al₂O₃ (<i>Yamani et. al. 2013</i>)	9.35	29.14	--
α-Fe₂O₃-C Powder	7.47 ± 0.473	799 ± 400	--
α-Fe₂O₃-N Powder	6.01 ± 0.64	82.3 ± 84	--