An electrochemical sequential injection method to investigate the adsorption of selenite on Fe(III) polyhydroxy cations intercalated vermiculite

Fernando H. do Nascimento and Jorge Cesar Masini

ABSTRACT

A sequential injection – square wave anodic stripping voltammetry (SI-SWASV) method for determination of Se(IV) at a gold working electrode was developed to investigate the adsorption of Se(IV) onto vermiculite intercalated with Fe(III) polyhydroxy cations. The limits of detection and quantification were 0.060 and 0.20 μmol L⁻¹, respectively (4.7 and 15.7 μgL⁻¹ CO). The linearity was up to 1.0 μmol L⁻¹, and the sampling throughput was 18 analyses h⁻¹. The proposed approach is a low-cost alternative to more expensive spectrometric methods. Adsorption onto vermiculite intercalated with Fe(III) polyhydroxy cations removed 93% of Se(IV) from a 1.0 μmol L⁻¹ solution (250 mL) after 5 min of contact time with 625 mg of adsorbent. Adsorption isotherms (25.0 ± 0.5 °C) were fitted by the Freundlich equation resulting in 1/n = 0.51 ± 0.03 and Kf = (1.584 ± 0.002) × 10³ μmol⁻¹/mg g⁻¹ L¹/n (r² = 0.995). Fitting by the Langmuir equation resulted in an adsorption constant of 0.026 ± 0.008 L g⁻¹ and adsorption capacity of 47 ± 5 μmol g⁻¹ (3.7 ± 0.4 mg g⁻¹) (r² = 0.97). This capacity was higher than that found for several other iron oxides, but lower than that obtained for oxide/hydroxide-based Fe(III) nanoparticles.

Key words | adsorption, Fe(III) polyhydroxy cations, gold electrode, intercalated vermiculite, selenite, square wave voltammetry

INTRODUCTION

Among the environmental trace elements with beneficial and toxic effects to human and animal health, selenium is the one with the narrowest concentration range between dietary deficiency and toxicity (from 40 to 400 μg day⁻¹) (Howarth et al. 2015; Santos et al. 2015). Aquatic environments may be contaminated by natural and anthropogenic sources of Se. Natural contamination is caused by weathering of rocks and soils containing selenium, as well as by volcanic activities (Bailey 2017). Anthropogenic contamination may occur by agricultural runoff, mining, industrial activities, coal combustion, oil refining, flue gas desulfurization, etc. (Santos et al. 2015; Tan et al.; Bailey 2017). The maximum concentration of Se allowed in drinking waters has been established as 10, 40 and 50 μg L⁻¹ by the European Union (EU), World Health Organization (WHO) and US Environmental Protection Agency (US-EPA), respectively (Santos et al. 2015).

Atomic absorption methods based on hydride generation (HG-AAS) or electrothermal atomization on graphite furnace (GF-AAS) are currently the most used methods for determination of total concentration of Se (Chen et al. 2007; Mollo et al. 2013; Santos et al. 2015). Fluorescence and inductively coupled plasma atomic emission spectrometry (ICP-AES) have also been used for determination of Se (Pettine et al. 2015). Although these spectrometric methods are very sensitive and selective, they use high cost instrumentation with high cost of maintenance. Besides, the instruments are large and are not suitable to perform field measurements.

Electroanalytical methods are well known for the use of low-cost and portable instrumentation, especially if using battery-powered potentiostats and screen-printed electrodes (Pereira et al. 2006; Monteiro et al. 2016; Devi et al. 2017). To reach the detection limits suitable for trace analysis of Se in aquatic samples, either cathodic or anodic stripping voltammetry methods have been described with a variety of working electrodes such as mercury (drop or film), gold,
platinum, and iridium (Tan & Kounaves 1998; Saji & Lee 2013; Devi et al. 2017).

Automation of voltammetric measurements by sequential injection analyses (SIAs) improves the precision of the results because this technique confers excellent reproducibility of the sample zone dispersion and precise time control, thus providing a diffusion layer with well-defined and reproducible thickness (dos Santos et al. 2005; do Nascimento & Masini 2012, 2016). Therefore, SIA provides very reproducible mass transport of the analyte from bulk solution to the electrode surface (Ivaska & Kubiak 1997; Punrat et al. 2013). Although SIA has been used to automate GF-AAS and HG-AAS (Chen et al. 2007, 2009; Jitmanee et al. 2007; Yang et al. 2011; Mollo et al. 2015; Ezoe et al. 2016), only one article describes the automation of voltammetric determination of Se (Wang et al. 2009). In that article, Wang et al. (2009) developed an SIA method using a lab-on-valve system to miniaturize an electrochemical flow cell with an in situ platted thin film mercury electrode. Despite the excellent sensitivity and selectivity achieved, the in situ plating of Hg generates residues of toxic Hg. Gold electrodes provide well-defined anodic stripping peaks for oxidation of Se to Se(IV) (Tan & Kounaves 1998; Saji & Lee 2013). SIA methods using gold as the working electrode for Se determinations have not yet been published.

Additional to the need for efficient analytical monitoring, the potential toxicity of Se has motivated the development of strategies and materials for its removal from aqueous samples (Peak 2006; Missana et al. 2009; Saha & Huang 2010; Chen & An 2012; Santos et al. 2015; Vinicius Constantino et al. 2017; Zhang et al. 2017). Adsorption is a very efficient approach because of the inherent simple implementation and low cost of adsorbents. Vermiculite is an abundant 2:1 layered clay mineral affording large surface area and high cation exchange capacity, which has been used for adsorption of pollutants (McBride 1994). Isomorphic substitution of Si by Al in the crystalline structure confers to vermiculite a permanent negative charge which is balanced by exchangeable cations such as Mg$^{2+}$ in the interlayer (McBride 1994). Adsorption of oxy anions such as selenite on clay minerals is a slow process, taking several days to reach the equilibrium (Missana et al. 2009), but the intercalation of Al(III) polyhydroxy cations in the interlayer provides positively charged sites which enable strong and fast adsorption of anions (Saha & Huang 2010). Fe(III) poly cations are also used for pillarization of clay minerals, increasing the adsorption capacities of anions and providing larger surface areas than their Al(III) counterparts (Bouras et al. 2010; Yang et al. 2013).

Characterization of new adsorbents requires sensitive analytical methods with high sampling throughput to enable characterization of adsorption parameters such as adsorption kinetics, adsorbent dose, adsorption and desorption isotherms, and influence of the solution chemistry. The determination of these parameters requires a large number of analyses in a wide range of concentrations in order to investigate the adsorption phenomenon under both low and high degrees of site occupation. The present paper describes a new electrochemical sequential injection method to investigate the adsorption of selenite on vermiculite intercalated with Fe(III) polyhydroxy cation, an interesting low-cost and environmental-friendly adsorbent which has been underexplored for water purification.

**EXPERIMENTAL**

**Apparatus and reagents**

All reagents were of analytical grade from Merck (Darmstadt, Germany) and Sigma-Aldrich (St Louis, MO, USA). Solutions were prepared with deionized water (resistivity > 18 MΩ cm). Working solutions of Se were prepared by dilution of a 1,000 mg L$^{-1}$ atomic absorption standard stock solution from Merck (Rio de Janeiro, RJ, Brazil). Analytical grade NaNO$_3$ was used to adjust ionic strength in the adsorption experiments. NaOH or HNO$_3$ (0.10 mol L$^{-1}$) was used to adjust the pH in the adsorption studies.

Stripping voltammetry was carried out in a PalmSens potentiostat (Palm Instrument BV, Houten, The Netherlands) using the PTrace 2.4 software for instrument control and data acquisition. Detection was made in a thin layer cross-flow cell from Bioanalytical Systems (West Lafayette, IN, USA) using a dual crystalline gold electrode (3 mm diameter), settled as working and counter electrodes. An Ag/AgCl (3 mol L$^{-1}$ NaCl) RE-6 reference electrode from Bioanalytical Systems completed the flow cell. A 380 µm polytetrafluoroethylene (PTFE) gasket defined the internal volume of the flow cell as 22 µL. Prior to use, the dual electrode block was polished with a 0.25 µm alumina suspension over metallographic cloth until a mirror-like surface was observed. Next, the electrodes were sonicated for 5 min in deionized water. Solution handling was carried out using a homemade sequential injection instrument described by Ribeiro & Masini (2014) (Figure 1S, available with the online version of this paper).
Adsorption experiments were performed in a thermostatic orbital shaker from Marconi (Piracicaba, SP, Brazil), settled at 25.0 ± 0.5 °C. The experiments were done inside polypropylene centrifuge tubes from Corning® (capacity of 15 mL), accommodated horizontally inside the shaker.

Vermiculite

The crude vermiculite (VT) sample from the Massapê mine (Paulistana, PI, Brazil) was milled with a mortar and pestle, and sieved. A granulometric fraction between 212 and 300 μm was chosen for the adsorption studies. Prior to the modification with the Fe(III) polyhydroxy cations the Na⁺ exchanged (Na-VT) was obtained as previously described (Vieira dos Santos & Masini 2007; do Nascimento et al. 2016). Characterization of Na-VT and FeOH-VT (total surface area, basal spacing, scanning electronic microscopy) is described elsewhere (Abate & Masini 2005; do Nascimento et al. 2016) and some results are given in the Supplementary Material (available with the online version of this paper).

Modification of vermiculite with Fe(III) polyhydroxy cations

Intercalation of vermiculite with the polyhydroxy cations of Fe(III) was made as previously reported by Abate & Masini (2005). The intercalating Fe(III) suspension was obtained by adding 50 mL of 0.40 mol L⁻¹ NaOH to 50 mL of 0.40 mol L⁻¹ FeCl₃ at the flow rate of 1.0 mL min⁻¹ under vigorous stirring, providing a 1:1 molar ratio of OH⁻ to Fe(III). The intercalation suspension was maintained at 50 °C for 48 h. Next, the Na-VT suspension was heated at 50 °C, and the intercalating suspension was added under vigorous stirring at 1.0 mL min⁻¹ using a peristaltic pump. The material was obtained with a ratio of 10 mmol of Fe(III) per gram of Na-VT. Next, the suspensions were left to rest for 72 h (Abate & Masini 2005). The suspensions were centrifuged at 1,000 g for 10 min and the solid was washed five times with deionized water. The modified clay mineral was dried at 40 °C for 12 h under vacuum, crushed and stored in a desiccator, and is named as FeOH-VT.

Adsorption experiments

For construction of adsorption isotherms, 25.0 mg of the adsorbents were treated with Se(IV) concentrations varying from 1 to 400 μmol L⁻¹ in 0.05 mol L⁻¹ NaNO₃ at pH 6.0 (0.010 mol L⁻¹ MES buffer). The dispersions were stirred for 60 min (250 rpm, 25.0 ± 0.5 °C) and then filtered through 0.45 μm membranes. The resulting solutions were diluted and acidified to 0.10 mol L⁻¹ H₂SO₄ to enable the electrochemical quantification. To evaluate the desorption rates, the residues in the centrifuge tubes were sequentially extracted (60 min) with 10 mL of 0.050 mol L⁻¹ NaNO₃ and 10 mL of 0.10 mol L⁻¹ H₂SO₄ at 25.0 ± 0.5 °C. The dispersions were filtered through 0.45 μm membranes and the supernatant solutions were analyzed by the proposed sequential injection – square wave anodic stripping voltammetry (SI-SWASV) method after acidification of the solution to 0.10 mol L⁻¹ H₂SO₄.

Adsorption data treatment

The adsorbed quantity of Se(IV) was computed as:

\[
q = \frac{(c_{Se,T} - c_{Se})V}{m} \tag{1}
\]

where \( q \) is the quantity of Se(IV) adsorbed per unit mass of adsorbent (μmol g⁻¹), \( c_{Se,T} \) and \( c_{Se} \) are the initial and equilibrium concentrations of Se(IV) (in μmol L⁻¹), respectively. The value of \( c_{Se,T} \) is known from the dilution of the stock standard solution, whereas \( c_{Se} \) is determined by the proposed SI-SWASV following the procedure described in the Supplementary Material after conditioning/diluting the liquid phase in 0.10 mol L⁻¹ H₂SO₄. \( V \) is the volume of dispersion and \( m \) is the mass of adsorbent.

The values of \( q \) were plotted as a function of \( c_{Se} \) and the data were fitted to the Langmuir and Freundlich equations (Equations (2) and (3), respectively) by non-linear regression analysis using the software Origin 8.0 (OriginLab Corp., Northampton, MA, USA).

\[
q = \frac{q_{max}b c_{Se}}{1 + b c_{Se}} \tag{2}
\]

where \( q_{max} \) is the maximum amount of Se(IV) that can be adsorbed and \( b \) is the adsorption Gibbs free-energy related term.

\[
q = K_f c_{Se}^{1/n} \tag{3}
\]

where \( K_f \) is the Freundlich empirical constant related to adsorption capacity (μmol⁻¹/n g⁻¹ L¹/n) and \( 1/n \) is the term related to intensity of adsorption and energetic heterogeneity of the adsorption sites (Buffle 1988).
RESULTS AND DISCUSSION

Cyclic voltammetry of Se(IV)

Cyclic voltammetry of 0.50 mmol L\(^{-1}\) Se(IV) in 0.10 mol L\(^{-1}\) \(\text{H}_2\text{SO}_4\) was obtained at flow rate of 15 \(\mu\text{Ls}^{-1}\) (Figure 1), starting and finishing the voltamogram at 0.2 V vs Ag/AgCl (3 mol L\(^{-1}\) NaCl), setting –0.8 V as vertex 1 and 1.5 V as vertex 2. A cathodic process was observed at potential of 0.3 V (peak 1, Figure 1), probably related to the under potential deposition responsible for the formation of a monolayer of Se\(^0\) on the gold surface (Reaction (1)) (Beni et al. 2014; Saji & Lee 2013).

\[
\text{H}_2\text{SeO}_3 + 4\text{H}^+ + 4\bar{e} \rightarrow \text{Se}^0 + 3\text{H}_2\text{O} \tag{1}
\]

As the potential is scanned to more negative values a strong cathodic peak was observed at –0.50 V (peak 2, Figure 1) before the reduction of H\(^+\). This cathodic peak may be due to the formation of selenium hydride, as shown in Reactions (2) and (3):

\[
\text{H}_2\text{SeO}_3 + 6\text{H}^+ + 6\bar{e} \rightarrow \text{H}_2\text{Se} + 3\text{H}_2\text{O} \tag{2}
\]

\[
\text{Se}^0 + 2\text{H}^+ + 2\bar{e} \rightarrow \text{H}_2\text{Se} \tag{3}
\]

As the scanning is reversed to positive potentials, the oxidation of Se was observed as peak 3 (Figure 1) with a maximum at 1.07 V, and shoulders at 0.96 and 0.76 V. This peak is related to complex processes involving oxidation of Se deposited on the Se monolayer, and of Se deposited over the gold surface. Additionally, oxidation of the intermetallic Se-Au may occur at the potential close to 1 V (Pereira et al. 2006; Saji & Lee 2013). Peaks 4 and 5 (Figure 1) are related to redox processes of gold oxides.

Based on the cyclic voltammetry experiments under flowing conditions, as well as on other works describing stripping voltammetric determination of Se(IV) (Tan & Kounaves 1998; Pereira et al. 2006), the deposition potential was set at –0.2 V whereas stripping was made by scanning the potential from –0.2 to 1.2 V.

Composition of the supporting electrolyte and carrier solution

Diluted \(\text{H}_2\text{SO}_4\) has been demonstrated as a suitable supporting electrolyte for voltammetric determination of Se(IV) compared to other acids such as HCl, HNO\(_3\) and HClO\(_4\) (Gil & Ostapczuk 1994; Tan & Kounaves 1998). Increasing the concentration from 0.010 to 0.10 mol L\(^{-1}\) caused a five-fold increase in peak currents (Figure 2S(a)) (Figure 2S is available with the online version of this paper). This result is consistent with the role of H\(^+\) facilitating the reduction of Se(IV) to Se\(^0\), according to Reaction (1). As the increase of the \(\text{H}_2\text{SO}_4\) concentration from 0.10 to 0.20 mol L\(^{-1}\) caused an increase of only 11% in the peak current, the concentration of 0.10 mol L\(^{-1}\) was chosen for continuing the method development, thus reducing the consumption of reagent and generation of residues.

In SI-SWASV the stripping step is made in presence of the carrier solution (do Nascimento & Masini 2012), so the carrier composition plays an important role in the sensitivity of the method. \(\text{H}_2\text{SO}_4\), HCl, NaNO\(_3\) and NaCl (all 0.050 mol L\(^{-1}\)) were investigated. \(\text{H}_2\text{SO}_4\) was the carrier that produced the highest peak currents (Figure 2S(b)), and was chosen for the applications of the method.

Effect of flow rate, sample volume and square wave frequency

For a fixed sample volume of 1,000 \(\mu\text{L}\), the flow rate during the deposition time was studied between 15 and 100 \(\mu\text{Ls}^{-1}\) (Figure 3S). As the flow rate increased, less deposition time was used for the fixed sample volume, causing a systematic decrease in the peak currents. For the cross-flow thin layer cell used in the present work, the enhanced mass transport at high flow rate did not compensate for the shorter contact time between the sample solution and the electrode surface.
Thus, the flow rate of 15 μL s⁻¹ was chosen for continuing the method development.

Increasing the sample volume increased the peak currents as a consequence of the larger amount of matter that was exposed to the electrode surface (Figure 4S). At a constant flow rate of 15 μL s⁻¹, larger sample volume required longer deposition times. Thus, a sample volume of 1,500 μL was chosen for the method because it provided the highest value of peak current without compromising the sampling throughput.

A significant increase in the peak current occurred as the square wave frequency increased from 25 to 50 Hz (Figure 5S). For frequencies between 50 and 100 Hz the peak currents remained approximately constant. Tan & Kounaves (1998) found that the peak currents increased linearly with the frequencies from 15 to 600 Hz using an array of gold ultramicroelectrodes (UMEs). The differences between the results of Tan and Kounaves and those found in the present work may be related to the fact that UMEs are able to achieve steady state conditions even at very high scan rates, contrary to the millimeter scale electrodes used in the SI-SWASV method. (Figures 3S–5S are available with the online version of this paper.)

Validation parameters

A linear response was observed for Se(IV) concentrations between 0.25 and 1.0 μmol L⁻¹ (r = 0.999) (Figure 2). The linear range is narrow, so dilution of the samples from adsorption studies investigating the saturation of adsorbents may be necessary. Thus, manual dilutions were performed to accommodate the concentrations of the solutions within the linear dynamic range of the method, although it is well-known that SIA has the capability to perform in-line automated sample dilutions (dos Santos et al. 2005). The limits of detection and quantification (LOD and LOQ) were computed at 3 and 10 times the standard deviation of blank measurements (n = 10) divided by the slope of the calibration curve, resulting in LOD and LOQ of 0.06 and 0.20 μmol L⁻¹, respectively. The LOD (4.7 μg L⁻¹) is about two fold lower than the maximum concentration level established by the EU (10 μg L⁻¹), and about ten fold lower than the levels established by WHO (40 μg L⁻¹) and US-EPA (50 μg L⁻¹) (Tan et al. 2016). The repeatability was evaluated with Se(IV) solutions of concentrations 0.20, 0.60 and 1.0 μmol L⁻¹, resulting in relative standard deviations of 9.4, 4.2 and 1.5%.

Potential interference of As(III), Hg(II) and Cu(II), species that exhibit redox potentials near to that of Se on gold electrodes, was evaluated using a 1.0 μmol L⁻¹ Se(IV) solution. Variations of peak current <± 5% were observed for As(III), Hg(II) and Cu(II) at concentrations of 0.44, 0.01 and 20 μmol L⁻¹, respectively. Humic and fulvic acids at concentrations of 10 mg L⁻¹ (approximately 5 mg L⁻¹ C) depressed the peak current of the 1.0 μmol L⁻¹ Se(IV) by 31 and 40%, respectively. The interference of humic substances may be caused by electrode passivation or hydrogen binding of HSeO₃ with carboxylic and phenolic groups protonated in the measurement medium.

The method was applied to two river waters spiked with 50 μg L⁻¹ Se(IV), resulting in a mean recovery of 80.7 ± 0.4%. Thus, acceptable recoveries were found in complex matrices of natural waters. These results encouraged the application of the method to investigate the adsorption of Se(IV) onto natural and modified vermiculite, in well-controlled composition media, providing sensitive measurements of free Se(IV).

Characterization of FeOH-VT

The intercalation of Fe(III) polyhydroxy cations changed the gray color of Na-VT to a golden intercalated vermiculite (Figure 6S). The iron content in the FeOH-VT was 1.208 mmol g⁻¹, determined by inductively coupled plasma optical emission spectrometry (ICP-OES) after extraction with concentrated HNO₃ at 80 °C. This value is close to 1.154 ± 0.006 mmol g⁻¹, which was previously determined as the cation exchange capacity of Na-VT (do Nascimento...
As the homoionic Na-VT contained no detectable Fe(III) (Vieira dos Santos & Masini 2007), this result suggests the Na¹ was quantitatively exchanged by the polyhydroxy cations of Fe(III) during the intercalation.

X-ray diffractometry of Na-VT shows an intense peak at $2\theta = 6.24^\circ$ corresponding to basal spacing (d001) of 1.415 nm (Figure 7S), typical for hydrated vermiculites exchanged with Na⁺. The exchange of Na⁺ by the Fe(III) polyhydroxy cations did not promote any significant alteration in the basal space of the modified vermiculite (Figure 7S). Similarly, the total surface area determined by the ethylene glycol monoethyl ether method did not suffer significant alterations, being determined as $122 \pm 12 \text{ m}^2 \text{g}^{-1}$ for FeOH-VT and $112 \pm 3 \text{ m}^2 \text{g}^{-1}$ for Na-VT. These results are consistent with the scanning electron microscopy images of both Na-VT and FeOH-VT (Figure 8S), which show the typical lamellar structures of vermiculites, but without a significant morphological alteration after the intercalation of Fe(III) polyhydroxy cations. (Figures 6S–8S are available with the online version of this paper.)

**Adsorption experiments**

**Contact time**

To evaluate the contact time needed to determine the adsorption capacities of FeOH-VT, an aliquot of 250 mL of 1.0 $\mu$mol L⁻¹ Se(IV) in 0.05 mol L⁻¹ NaNO₃ at pH 6.0 (0.01 mol L⁻¹ MES) was treated with 625 mg of adsorbent for 5, 15, 30, 60 and 120 min. After 5 min of contact time, 93% of the initial Se(IV) was removed. For longer contact times the remaining concentrations were smaller than the LOD of the SI-SWASV method. A similar experiment made with Na-VT showed no adsorption on the unmodified clay mineral. The fast adsorption is consistent with the findings of other authors studying adsorption of Se(IV) onto Fe(III) oxide/hydroxide (Martínez et al. 2006; Rovira et al. 2008; Gonzalez et al. 2012; Sharrad et al. 2012; Zelmanov & Semiat 2013).

**Mass of adsorbent**

Adsorbent doses of 25, 50, 75 and 100 mg were dispersed in 20 $\mu$mol L⁻¹ Se(IV) in 0.05 mol L⁻¹ NaNO₃ at pH 6.0 (0.01 mol L⁻¹ MES). After the contact time (60 min) the supernatant was analyzed by the proposed SI-SWASV method revealing that adsorption percentage varied from 96.9 to 97.6% as the mass of adsorbent increased from 25 to 100 mg (Figure 3). Thus, the adsorption was independent of the adsorbent mass in the studied conditions. There is a clear decrease in the adsorbed amount of Se(IV) per unit mass of adsorbent, suggesting that there was no saturation of the adsorbent. For construction of the adsorption isotherms, a mass of 25 mg was used.

**Adsorption isotherms**

Common concentrations of Se in waters are between 0.1 and 6,000 $\mu$g L⁻¹ (0.0013 to 76 $\mu$mol L⁻¹) (Tan et al. 2016). To evaluate the adsorbent performance under low and high degrees of site occupation, adsorption isotherms were constructed using $c_{\text{Se,T}}$ varying from 1 to 400 $\mu$mol L⁻¹, thus covering a range of concentrations from those found in most natural freshwaters to those in highly polluted wastewaters. Besides, high $c_{\text{Se,T}}$ enables the experimental estimation of the maximum adsorption capacity of the adsorbent.

The adsorption isotherm was well fitted to the Freundlich equation (Figure 4), resulting in $1/n = 0.51 \pm 0.03$ and $K_r = (1.584 \pm 0.002) \times 10^1 \mu$mol⁻¹ g⁻¹ L⁻¹/n with $r^2 = 0.995$. The $1/n$ value between 0 and 1 suggests strong binding of Se(IV) and high energetic heterogeneity of adsorption, which may be explained by electrostatic interactions and formation of inner sphere complexes. The fitting to the Langmuir equation was acceptable ($r^2 = 0.97$), resulting in a Gibbs free-energy related parameter of 0.026 ± 0.008 L g⁻¹ and maximum adsorption capacity ($q_{\text{max}}$) of 47 ± 5 $\mu$mol g⁻¹ (3.7 ± 0.4 mg g⁻¹). The $q_{\text{max}}$ value found is higher than those reported for several sorbents such as goethite (0.52 mg g⁻¹), hematite (0.39 mg g⁻¹) (Rovira et al. 2008), magnetite (0.22 mg g⁻¹) (Martínez et al. 2006), aluminum oxide coated sand (1.08 mg g⁻¹) (Kuan et al. 1998) and...
Fe₃O₄ nanomaterials (2.38 mg g⁻¹/C₀₁) (Gonzalez et al. 2012). On the other hand, the qmax of FeOH-VT was significantly lower than those of FeOOH (26.3 mg g⁻¹/C₀₁) (Sharrad et al. 2014), binary oxides Al(III)/SiO₂ and Fe(III)/SiO₂ (32.7 and 20.4 mg g⁻¹, respectively) and oxide/hydroxide-based Fe(III) nanoparticles (95 mg g⁻¹) (Zelmanov & Semiat 2013).

Influence of pH and ionic strength

The pH of 5.0 μmol L⁻¹ Se(IV) solutions in 0.05 mol L⁻¹ NaNO₃ was adjusted to 4.0, 6.0, 8.0 and 10 using either diluted NaOH or HNO₃. After the contact time (60 min) the pH of the dispersions adjusted to 4.0, 6.0 and 8.0 decreased to 3.7, 5.1 and 6.2, respectively. The pH of the dispersion adjusted to pH 10 did not have significant variation after the contact time. The adsorption percentage decreased from 56 to 17% as the pH increased from 4.0 to 6.0. At pH 8.0 and 10, no adsorption was observed. This result is consistent with the electrostatic repulsion between negative charges on the adsorbent surface and the selenite anion, in agreement with the findings of several other works studying adsorption of Se(IV) onto oxides (Kuan et al. 1998; Martínez et al. 2006; Rovira et al. 2008; Sharrad et al. 2012; Zelmanov & Semiat 2013).

Martínez et al. (2006) found that adsorption of Se(IV) onto magnetite could be well fitted to the following equilibria, involving the formation of inner sphere complexes:

\[
\begin{align*}
S\text{-FeOH} + H\text{SeO}_3^- & \rightleftharpoons S\text{-FeOHSeO}_3^{2-} + H^+ \quad (4) \\
S\text{-FeOH} + H\text{SeO}_3^- + H^+ & \rightleftharpoons S\text{-FeHSeO}_3 + H_2O \quad (5)
\end{align*}
\]

where S- represents the mineral surface. The results obtained in the present work are consistent with these equilibria because they explain the acidification of the medium (Reaction (4)), as well as the enhanced adsorption at lower pH (Reaction (5)) (Duc et al. 2006).

Formation of inner sphere complexes is the main mechanism governing the adsorption of Se(IV) onto oxides, as described by the Reactions (4) and (5). However, electrostatic interactions also play a role, as demonstrated by the fact that the increase in the salt concentration (NaNO₃) from 0.050 to 1.0 mol L⁻¹ decreased the adsorption of a 5.0 μmol L⁻¹ Se(IV) onto FeOH-VT from 70 to 55% (Figure 5). This finding is consistent with the adsorption mechanism involving a first step of electrostatic interaction and outer sphere complexes, followed by formation of inner sphere complexes.

Adsorption selectivity

The presence of Cu(II), Pb(II), Mg(II) and Ca(II) all at concentration of 5.0 μmol L⁻¹ did not affect the adsorption of Se(IV) (5.0 μmol L⁻¹) on FeOH-VT. No significant effects were observed for Cl⁻, SO₄²⁻ (1.0 mmol L⁻¹) and AsO₃²⁻ (5.0 μmol L⁻¹) as well. The adsorption of Se(IV) decreased from 83.5% in the control experiment to 61 ± 2% in presence of 1.0 mmol L⁻¹ H₂PO₄. Thus, phosphate species compete with Se(IV) for the adsorption sites of FeOH-VT. Compared with other Fe(III) oxides, the results are consistent with those observed for iron oxide nanomaterial (Gonzalez et al. 2012), FeOOH (Sharrad et al. 2012) and

![Figure 4](https://iwaponline.com/wst/article-pdf/2017/1/134/216376/wst2017010134.pdf)

Figure 4 | Adsorption isotherm (25.0 ± 0.5 °C) of Se(IV) on FeOH-VT fitted by Freundlich and Langmuir equations at pH 6.0 (0.010 mol L⁻¹ MES buffer) in 0.050 mol L⁻¹ NaNO₃. The contact time was 60 min.

![Figure 5](https://iwaponline.com/wst/article-pdf/2017/1/134/216376/wst2017010134.pdf)

Figure 5 | Adsorbed amount and percentage of Se(IV) as a function of salt concentration (NaNO₃) at pH 6.0 ± 0.1 (0.010 mol L⁻¹ MES buffer), at 25.0 ± 0.5 °C. Initial Se(IV) concentration = 5.0 μmol L⁻¹; adsorbent mass = 25 mg; dispersion volume = 10 mL.

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tropical soil (Goh & Lim 2004); that is, phosphate is a potential competitor for adsorption sites on FeOH-VT. On the other hand, the results suggest the FeOH-VT has potential application in the removal of phosphate from contaminated waters.

### Desorption

The residues of the adsorption experiments made with initial concentrations of Se(IV) of 1.0, 25 and 200 μmol L⁻¹ were sequentially treated with 0.050 mol L⁻¹ NaNO₃ and 0.10 mol L⁻¹ H₂SO₄ for 60 min under stirring in the horizontal shaker at 180 rpm (25.0 ± 0.5 °C). As expected, desorption in 0.05 mol L⁻¹ NaNO₃ from the first point of the isotherm (initial C_Se,T = 1.0 μmol L⁻¹) was negligible, since at this condition of low site occupation, Se(IV) is adsorbed to the strongest adsorption sites. Desorption in the other conditions did not exceed 6.1%, denoting the low competition effect of NO₃⁻ by other oxyanions. Desorption in 0.10 mol L⁻¹ H₂SO₄ varied from 26 to 37% (Table 1). In this case, the explanation may be the protonation of both HSeO₃⁻ and polyhydroxy cations in the interlayer forming selenous acid or dissolving part of the Fe(III) hydroxides, thus releasing the Se(IV) species.

### Table 1 | Desorption of Se(IV) from FeOH-VT

<table>
<thead>
<tr>
<th>Adsorbed Se (μmol g⁻¹)</th>
<th>0.050 mol L⁻¹ NaNO₃</th>
<th>0.10 mol L⁻¹ H₂SO₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.40</td>
<td>undetectable</td>
<td>26 ± 3</td>
</tr>
<tr>
<td>7.70</td>
<td>3.4 ± 0.5</td>
<td>34 ± 2</td>
</tr>
<tr>
<td>22.0</td>
<td>6.1 ± 0.8</td>
<td>37 ± 3</td>
</tr>
</tbody>
</table>

### CONCLUSION

The proposed SI-SWASV method automated the determination of Se(IV) allowing 18 analyses per hour to be performed, with LOD and LOQ of 4.7 and 15.6 μg L⁻¹, respectively. The detectability and the sampling frequency, together with the low cost of instrumentation and reagents, make the method suitable for adsorption studies aiming to characterize new adsorbent materials (Devi et al. 2017).

Adsorption of SeO₃²⁻ by unmodified Na-VT was negligible, but intercalation of the clay mineral with Fe(III) polyhydroxy cations enabled strong adsorption of the oxyanion from aqueous medium. The modified clay mineral exhibited adsorption capacity larger than that of many other oxides. For an initial concentration of 1.0 μmol L⁻¹ Se(IV) (79 μg L⁻¹), the removal of Se(IV) approached 100%, leaving undetectable free Se(IV) in solution. Ongoing work is evaluating the potential of Fe(III) polyhydroxy cations modified clay minerals to remove other oxyanions such as phosphate, chromate and arsenite/arsenate.

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### REFERENCES


Tan, L. C., Nanchariah, Y. V., van Hullebusch, E. D. & Lens, P. N. L. 2016 Selenium: environmental significance,
pollution, and biological treatment technologies.


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