

Sorption of selenium(IV) and selenium(VI) onto natural iron oxides: Goethite and hematite

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Abstract

Selenium is a toxic element with a relatively high mobility in the natural waters. Iron oxy-hydroxides might play an important role in the migration of this element as well as on its removal from contaminated water. In this work we study the interaction of Se(IV), and Se(VI) with natural iron oxides hematite and goethite through two series of batch experiments at room temperature. In the first series, sorption as a function of initial selenium concentration is studied and the results have been fitted with Langmuir isotherms. In a second series of experiments, sorption is studied as a function of pH, being the main trend an increase of the sorption at acidic pH. The variation of the sorption with pH has been modelled with a triple layer surface complexation model and using the FITEQL program. The experimental data have been modelled considering for the Se(IV) the formation of the FeOSe(O)O^- complex onto the hematite surface, and a mixture of FeOSe(O)O^- , and FeOSe(O)OH onto the goethite surface. For Se(VI) the surface complex considered is $\text{FeOH}_2^+ - \text{SeO}_4^{2-}$ on both goethite and hematite.

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1. Introduction

Selenium is a relevant element due to its important role in life processes, being recognized as an essential nutrient [1,2]. On the other hand, selenium is toxic at concentrations above the range of that considered a health level in human diet, 1 mg of selenium per kg of body weight [3]. Selenium is introduced in the environment from different sources, both natural and anthropogenic, in the last case mainly from activities related to the agriculture and combustion of fossil fuels [3–6].

In particular, selenium is an element of special concern in the nuclear fuel cycle and it is one of the main radionuclides considered in the safety analysis of a high level nuclear waste repository (HLNWR), because of the long half-life ^{79}Se isotope, which is chemically and radiologically toxic [7,8]. In addition to the toxicity of the ^{79}Se isotope, selenium is a highly mobile

element in oxidizing geochemical environments and may have a high impact on the cumulative radioactive dose if there is not a mechanism that might retard its transport through the geosphere [9].

Iron oxy-hydroxides such as magnetite, hematite, and goethite might represent a main role in the retardation of the transport of different contaminants because they are present in many natural media in contact with water and they have well known high sorption capacities for a number of trace elements. In particular, in the case of a HLNWR, selenium might be incorporated onto iron oxy-hydroxides. In this case selenium could interact not only with the iron solid phases of the geological environment but also (and before) with the iron oxy-hydroxides formed as a consequence of the failure or defect of the iron container and its anoxic corrosion [10–12]. For these reasons, it is important to study the selenium retention/sorption capacity of the iron solid phases and to evaluate the potential capacity of these solid phases to retard the migration of selenium through the environment. In this sense, in a previous work we have studied the sorption of Se(IV) and Se(VI) onto magnetite [13] because

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magnetite is believed to have a passivating role in the repository environment [14].

In addition, some works can be found in the literature concerning the sorption of selenium on synthetic goethite. Hayes et al. [15] studied the sorption of selenium on goethite by using EXAFS and observed the formation of an inner-sphere bidentate surface complex in the case of Se(IV) and outer-sphere hydrated complex for Se(VI). Zhang and Sparks [16] studied the kinetics of sorption of Se(IV) on a synthetic goethite (surface area $70.1 \text{ m}^2 \text{ g}^{-1}$) and observed that the first step of the sorption mechanism implied the formation of outer-sphere complexes which, in a subsequent step, transformed into inner-sphere complexes. In addition, they determined the variation of selenite and selenate sorption with the pH, obtaining in both cases a decrease of the sorption with increasing pH. Duc et al. [17] also studied the variation of the sorption of selenite and selenate on commercial goethite and magnetite with pH, obtaining a similar trend than the one observed by Zhang and Sparks.

Peak and Sparks [18] and Wijnja and Schulthess [28] studied the mechanism of selenate sorption on different iron oxides such as synthetic goethite and hematite by using different spectroscopic techniques. The main finding was that selenate forms outer-sphere complexes at alkaline pH on goethite and inner-sphere complexes at acidic pH. Recently, Fukushi and Sverjensky [31] successfully modelled data on selenate adsorption on iron oxides using a new approach of the triple layer surface (TLM) complexation model. Recently, the sorption geometry of selenite onto a hematite single crystal has been determined by Catalano et al. [19] while the sorption of selenite ions on commercial hematite has been studied by Duc et al. [20].

Since most studies reported in the literature have been performed using synthetic materials, the objective of this work is to study the sorption of Se(IV) and Se(VI) onto natural goethite and hematite. In addition, the information obtained in the literature on the mechanisms of selenium sorption to synthetic goethite and hematite will be used to model the variation of experimental sorption data with solution pH in the natural solids used in our work.

2. Experimental

Both natural hematite and goethite from Cerro del Hierro (Spain) were used in the experiments, crushed and sieved to a particle size of 0.25 mm. X-ray diffraction analysis (Fig. 1) revealed the presence of the pure iron oxi-hydroxides and traces of quartz. The specific surface area was determined by the BET methodology, the values obtained were 2.01 ± 0.01 and $0.38 \pm 0.01 \text{ m}^2 \text{ g}^{-1}$ for goethite and hematite, respectively.

Selenium solutions used in the experiments were prepared dissolving either $\text{Na}_2\text{SeO}_4 \cdot 10\text{H}_2\text{O}$ or Na_2SeO_3 (both from Aldrich) in Milli-Q water.

The study has been undertaken by conducting sorption batch experiments at room temperature and using the same methodology reported in Martínez et al. [13]: 0.1 g of the minerals were put in contact with 20 cm^3 of metal solution in stoppered polystyrene tubes. The tubes were continuously stirred until equilibrium was reached, which occurred always in less than 50 h (see below).

Once the equilibrium was reached, samples were taken and filtered through $0.22\text{-}\mu\text{m}$ pore size filters. Selenium concentration in solution was determined by ICP. The concentration of selenium attached to the solid in units of moles of selenium per metre square of dry solid, $\{\text{Se}\}_s$ was calculated by subtracting the final selenium concentration, $[\text{Se}]$ in mol dm^{-3} , to the initial selenium concentration, $[\text{Se}]_0$ in mol dm^{-3} , and normalising with the surface area (SA) to volume (V) ratio:

$$\{\text{Se}\}_s = ([\text{Se}]_0 - [\text{Se}]) \frac{V}{\text{SA}}$$

The pH of the solutions was varied by adding either HCl or NaOH. The ionic medium was 0.1 mol dm^{-3} NaCl.

Three different series of experiments were carried out:

1. To study the sorption kinetics, different experiments were prepared with the same weight of solid (0.1 g) and the same initial selenium concentration ($2 \times 10^{-5} \text{ mol dm}^{-3}$) at pH 7.5 (the variation of pH during the experiments was less than 0.3 units). The selenium concentration in solution was determined in each tube at a different contact time.
2. The second series of experiments consisted on solutions with different initial selenium concentrations and 0.1 g of solid (the pH values at equilibrium were 7.6 ± 0.1 for Se(IV)-goethite; 7.2 ± 0.1 for Se(IV)-hematite; 7.3 ± 0.1 for Se(IV)-goethite; and 6.9 ± 0.2 for Se(VI)-hematite). Selenium concentrations in solution were measured after 50 h.
3. In the last series, the sorption of selenium was determined as a function of solution pH (between 2 and 11) by means of different experiments with a constant amount of solid and an initial selenium concentration of $2 \times 10^{-5} \text{ mol dm}^{-3}$.

3. Results and discussion

3.1. Sorption kinetics

The variation of the selenium sorption with the contact time for goethite and hematite is shown in Fig. 2. As it can be seen, equilibrium is always reached in less than 50 h, in concordance with the sorption of selenium on magnetite [13].

The modelling of the kinetic data has been carried out using a pseudo-second order rate equation [21], which has been widely used to describe trace element sorption as well as organic compounds sorption on different sorbents [21,22]. The pseudo-second order kinetic rate equation is:

$$\frac{t}{\{\text{Se}\}_s} = \frac{1}{k \cdot \{\text{Se}\}_{s,\text{eq}}^2} + \frac{1}{\{\text{Se}\}_{s,\text{eq}}} t$$

where $\{\text{Se}\}_{s,\text{eq}}$ is the amount of metal sorbed at equilibrium (in mol m^{-2}), k is the rate constant of sorption (in $\text{m}^2 \text{ mol}^{-1} \text{ h}^{-1}$) and $\{\text{Se}\}_s$ is the amount of metal sorbed on the surface of the solid (in mol m^{-2}) at any contact time, t (in hours).

The plotting of $t/\{\text{Se}\}_s$ against t from the data shown in Fig. 2 resulted in straight lines, indicating that the sorption process follows a pseudo-second order kinetics. The values of the parameters obtained from the fitting are shown in Table 1 and the fitting of the model to the experimental data is also shown in Fig. 2.

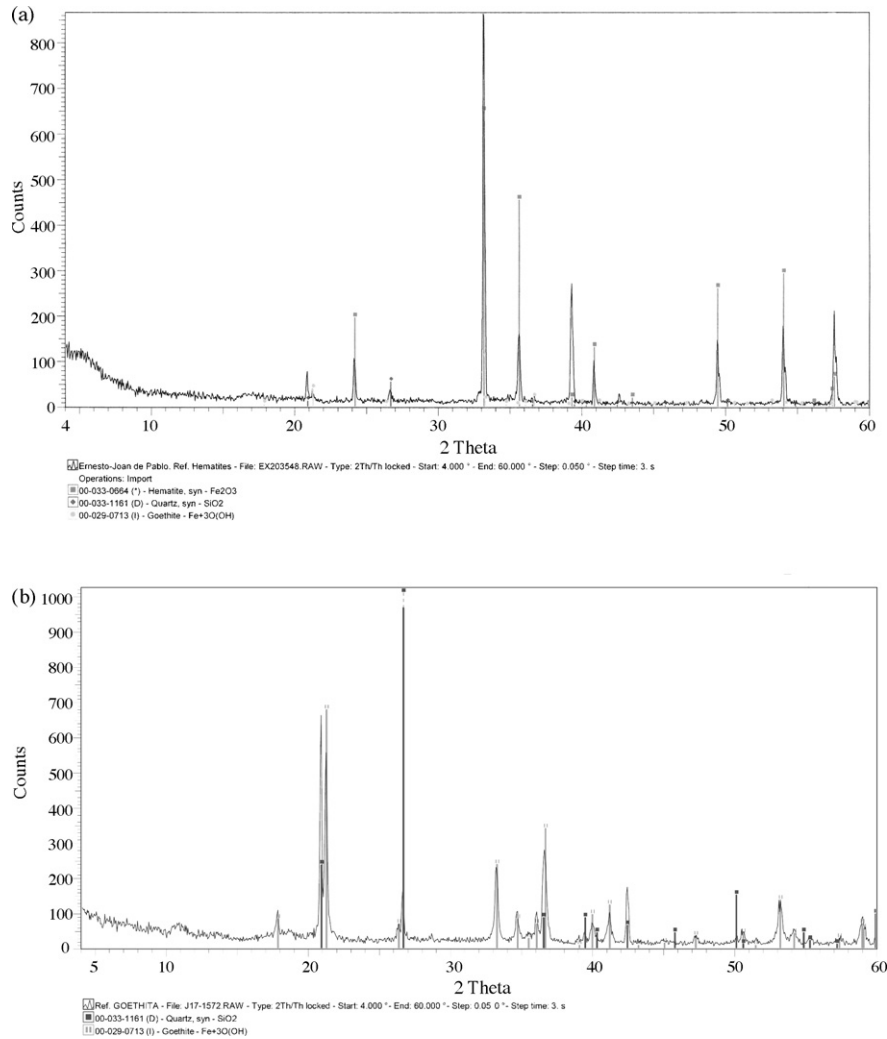


Fig. 1. XRD patterns of the (a) hematite, and (b) goethite samples.

As it can be seen in Table 1, there are not big differences in the sorption rate constants for both solids, but they are higher for Se(IV) than for Se(VI).

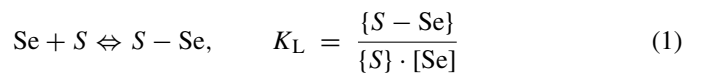
3.2. Sorption isotherms

In this series of experiments, solutions with different initial selenium concentrations (between 3×10^{-6} and 5×10^{-4} mol dm⁻³) were put in contact with the minerals. The results obtained can be seen in Fig. 3.

Table 1
Kinetic data for the Se(IV) and Se(VI) sorption onto goethite and hematite obtained through the fitting of a pseudo-second order rate equation to the experimental data

	Rate constant, k (m ² mol ⁻¹ h ⁻¹)	{Se} _{s,eq} (mol m ⁻²)	R ²
Se(IV)-goethite	0.95 ± 0.03	(4.2 ± 0.1) × 10 ⁻⁷	0.9990
Se(IV)-hematite	1.12 ± 0.02	(3.0 ± 0.1) × 10 ⁻⁶	0.9997
Se(VI)-goethite	0.60 ± 0.02	(2.8 ± 0.1) × 10 ⁻⁷	0.9990
Se(VI)-hematite	0.64 ± 0.02	(1.5 ± 0.2) × 10 ⁻⁶	0.9990

The data have been fitted with a non-competitive Langmuir isotherm, based on the following sorption equilibrium:



where K_L is the Langmuir constant (dm³ mol⁻¹), {S–Se} stands for the concentration of occupied surface sites and {S} for the free surface sites.

The parameter gamma, Γ , in mole per metre square, is defined as the selenium concentration sorbed on the solid:

$$\Gamma = \frac{\{S - \text{Se}\}}{\text{surface area}} \quad (2)$$

and, therefore:

$$\Gamma_{\text{max}} = \frac{\{S\}_{\text{tot}}}{\text{surface area}} \quad (3)$$

where Γ_{max} is the maximum metal sorption (mol m⁻²) and {S}_{tot} stands for the total concentration of surface sites:

$$\{S\}_{\text{tot}} = \{S\} + \{S - \text{Se}\} \quad (4)$$

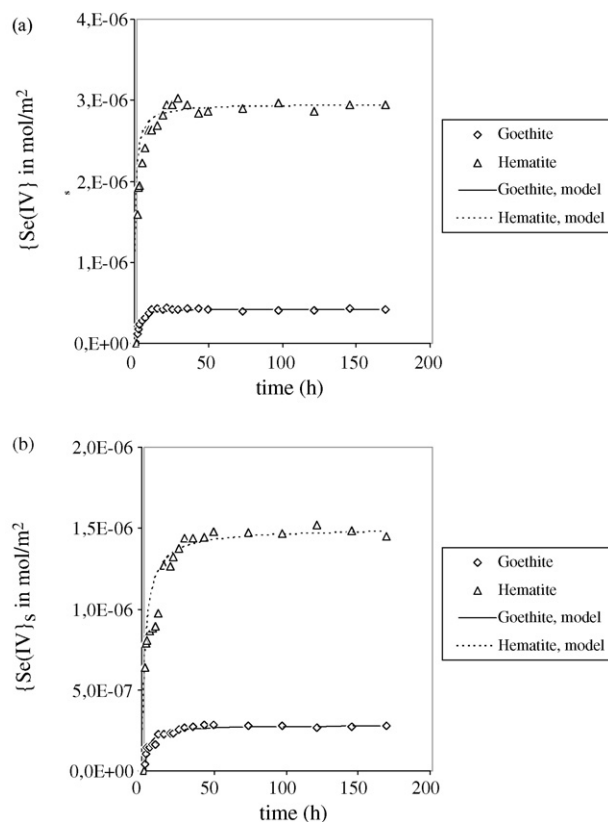


Fig. 2. Kinetics of selenium sorption onto magnetite and hematite: (a) Se(IV), and (b) Se(VI). The experiments were carried out with an initial selenium concentration of 2×10^{-5} M in NaCl 0.1 M at pH 7.5. The lines represent the fitting of the pseudo-second order rate equation to the experimental data.

From Eqs. (1)–(4) it is possible to derive the following expression:

$$\Gamma = \Gamma_{\max} \frac{K_L \cdot [\text{Se}]}{1 + K_L \cdot [\text{Se}]} \quad (5)$$

To obtain the values of the parameters Γ_{\max} , and K_L , we have used the linearized form of the equation:

$$\frac{[\text{Se}]}{\Gamma} = \frac{[\text{Se}]}{\Gamma_{\max}} + \frac{1}{\Gamma_{\max} \cdot K_L} \quad (6)$$

The linear plot of $[\text{Se}]/\Gamma$ against $[\text{Se}]$ gave us the values of the parameters K_L and Γ_{\max} shown in Table 2 while the fitting of the Langmuir isotherm to the experimental data is shown in Fig. 3. In spite of the fact that in the case of hematite, a maximum sorption is not reached in the range of selenium concentrations in solution, the main conclusion is that sorption of selenium (in both oxidation states) is higher in natural hematite than in natural goethite.

Table 2
Parameters of the Langmuir isotherm obtained for Se(VI) and Se(IV) sorption on hematite and goethite at pH 4

	Γ_{\max} (mol m ⁻²)	K_L (dm ³ mol ⁻¹)	R^2
Se(IV)-goethite	$(3.3 \pm 0.1) \times 10^{-6}$	$(1.5 \pm 0.1) \times 10^4$	0.994
Se(IV)-hematite	$(1.3 \pm 0.8) \times 10^{-5}$	$(9 \pm 1) \times 10^3$	0.96
Se(VI)-goethite	$(1.1 \pm 0.4) \times 10^{-6}$	$(1.1 \pm 0.3) \times 10^4$	0.96
Se(VI)-hematite	$(8.0 \pm 0.5) \times 10^{-6}$	$(6 \pm 2) \times 10^3$	0.91

3.3. Influence of pH on the sorption of selenium on hematite and goethite

The results obtained for Se(IV) and Se(VI) sorption as a function of equilibrium pH are shown in Fig. 4. As it can be seen, in all the cases the sorption of selenium decreases at alkaline pH, as it was expected considering surface charge and the predominant selenium species in solution. For both solids, maximum sorption is observed when surface charge is positive and for Se(VI), the sorption decreases at alkaline pH due to the decrease of the fraction of the aqueous species HSeO_4^- while for Se(IV) the maximum sorption coincides with the predominance of HSeO_3^- . The calculations of the predominance of the different aqueous species have been made with the MEDUSA code [23].

Although available data is insufficient to model the sorption behaviour, lines continuous drawn in Fig. 4 represent a surface complexation model fitted to the experimental data using the triple-layer model (TLM).

Experiments including batch sorption studies [16,20,22,24] and x-ray absorption and infrared spectroscopy studies [15,25] had brought enough evidences to conclude that sorption of selenite on ferric oxy-hydroxides occurs by inner-sphere complexation. However, the mechanism is not so clear for selenate sorption on goethite and hematite. Although Zhang and Sparks [16] successfully modelled experimental data of selenate adsorption on goethite with an outer-sphere complex, and Hayes et al. [24] brought similar spectroscopic evidences, early studies

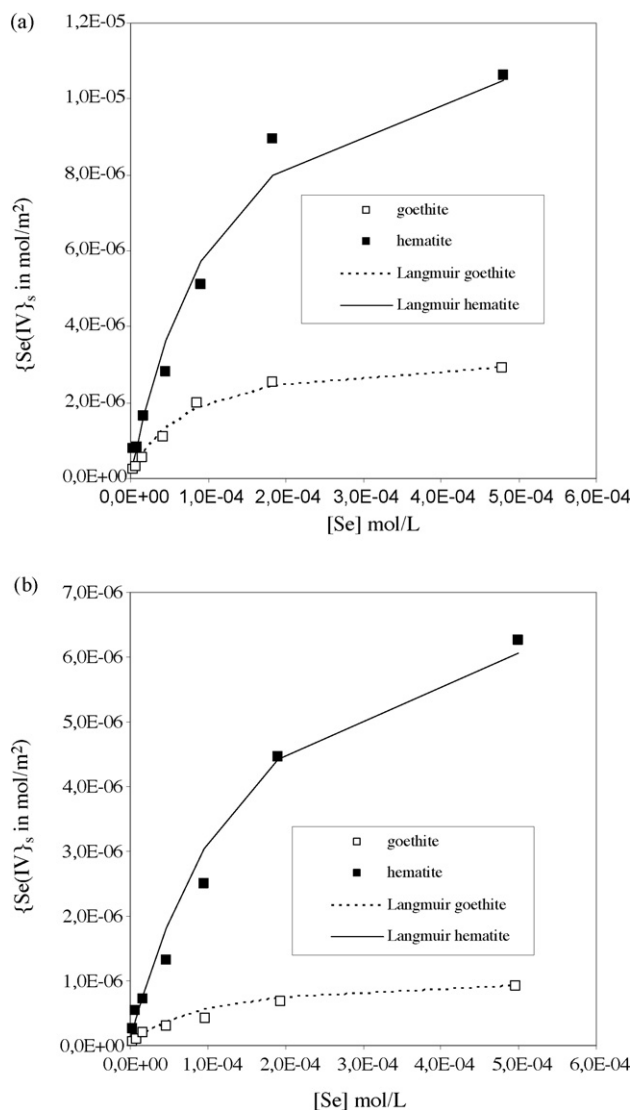


Fig. 3. Sorption isotherms for goethite and hematite for (a) Se(IV) and (b) Se(VI). 0.1 g of solid and pH 4. The lines correspond to the fitting by using a Langmuir isotherm.

involving spectroscopic techniques postulated the formation of inner-sphere complex [25–27] or a mixture of both inner- and outer-sphere complexes depending on pH, ionic strength, surface loading and pre-treatment of the sample [18,28].

The FITEQL 4.0 code [29] was used to compute and evaluate the fits to experimental data. Reactions listed in Table 3 were used to describe protonation and deprotonation of surface

Table 3
Reactions and constants of protonation, deprotonation, and background electrolyte complexation used for the fitting of the model to the experimental data

Reaction	log <i>K</i> (Hematite)	log <i>K</i> (Goethite)
Fe–OH + H ⁺ ⇌ Fe–OH ₂ ⁺	9.05	7.99
Fe–OH ⇌ Fe–O [−] + H ⁺	−10.05	−10.41
Fe–OH + H ⁺ + Cl [−] ⇌ Fe–OH ₂ ⁺ –Cl [−]	−6.85	11.18
Fe–OH + Na ⁺ ⇌ Fe–O [−] –Na ⁺ + H ⁺	11.84	−7.01

Equilibrium constants are computed from (Sverjensky, 2005) and referred to the hypothetical 1.0 M standard state.

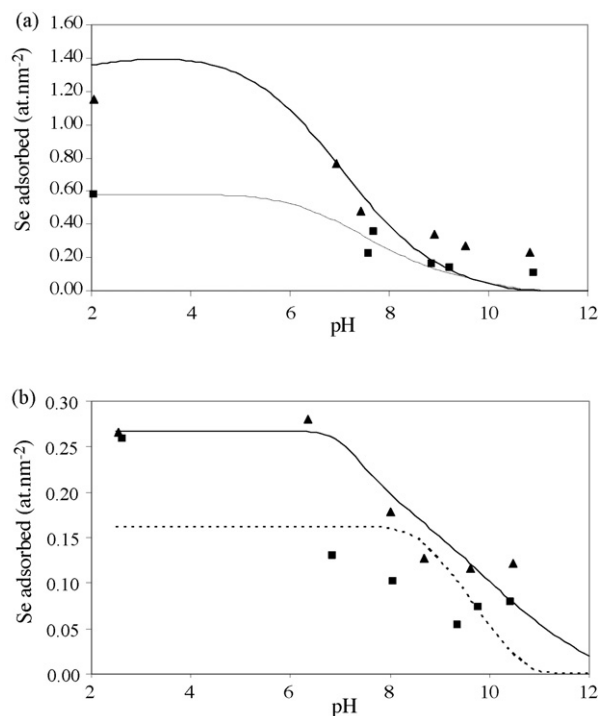


Fig. 4. Sorption of selenium on (■) goethite, and (▲) hematite as a function of equilibrium pH with 5 g dm^{−3} of solid and [Se]₀ = 10^{−5} mol dm^{−3}. (a) Se(IV); (b) Se(VI). The lines represent the model fitted to the experimental data.

sites and complexation of background electrolyte. Values were computed using the experimental values of site density (*N_s*) and superficial area (*A_s*) (Table 4) and the procedure described in Sverjensky [30]. The number of coordination sites was estimated from the experimental isotherm (Fig. 3) for modelling selenite adsorption behaviour and set to a fitting parameter in case of selenate. Inner capacitance of hematite was also obtained from Sverjensky [30] (Table 4). Due to the low superficial area of the goethite sample, inner capacitance was set to 0.6 [32]. Although CO₂ was not excluded from the experiments, carbonate and bicarbonate sorption was not included in the model. Quartz impurities have not been taken into account in the models, because selenate retention by quartz may be considered negligible in the pH range studied [32]. Previous studies concerning selenite sorption onto quartz could not be found in the literature but a significant influence of this mineral in selenite retention is not expected as confirmed by the good agreement between the experimental data and the models proposed.

Experimental data for selenite sorption on hematite and goethite was modelled assuming the surface species proposed by Duc et al. [20] (Table 4). Selenate sorption data on hematite was modelled assuming the species proposed by Fukushi and Sverjensky based on previous spectroscopy studies.

Natural and synthetic hematite and goethite exhibit a similar Se sorption behaviour. In the present study, similar models to those proposed for selenate and selenite sorption into synthetic hematite and goethite were successfully applied to describe selenium sorption into natural minerals. Selenite experimental data on natural hematite can be explained by a monodentate inner-sphere deprotonated surface complex while a mixture of a

Table 4
Results of the modelling of the experimental data by a surface complexation model by using the FITEQL code

	Mineral	Surface complexes	log <i>K</i>	<i>C</i> ₁ (μF cm ⁻²)	<i>A</i> _s (m ² g ⁻¹)	<i>N</i> _s (sites nm ⁻²)	WSOS/DF
Se(IV)	Hematite	>FeOSeO ₂ ⁻	5.49	0.88	0.38	7.83	1.39
	Goethite	>FeOSeO ₂ ⁻	16.03	0.6	2	1.99	1.61
Se(VI)		>FeOHSeO ₂	34.59				
	Hematite	(>FeOH ₂ ⁺) ₂ -SeO ₄ ²⁻	33.42	0.88	0.38	1.49	1.42
		>FeOSeO ₃ ⁻	12.92				
	Goethite	FeOH ₂ ⁺ -SeO ₄ ²⁻	11.7	0.6	2	7.43	0.06

monodentate inner-sphere deprotonated and protonated surface complex was needed to explain surface complexation of selenite on natural goethite. Selenate sorption data was modelled using a mixture of a monodentate inner-sphere complex and a bidentate outer-sphere complex in agreement with Fukushi and Sverjensky [31].

Finally, the modelling of sorption isotherms was attempted using surface species and parameters summarized in Table 4. Unfortunately, maximum sorption capacities were underestimated by the surface complexation model (as it can be seen from the isotherms data, sorption sites seem not to be all of them occupied even at the higher selenium concentrations) and the sorption modelled resulted to be always lower than the experimental at high selenium concentrations in solution at equilibrium.

4. Conclusions

The sorption of Se(IV) and Se(VI) onto natural hematite and goethite has been studied as a function of different parameters. The sorption follows in all the cases a pseudo-second order kinetics. And the variation of the sorption onto goethite with the selenium concentration in solution has been modelled considering a Langmuir isotherm.

The main trend of the variation of the selenium sorption with pH is an increase at acidic pH due to the predominance of the selenium species HSeO₃⁻, and HSeO₄⁻ for Se(IV) and Se(VI), respectively, as well as solid charge variation with pH.

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