ELSEVIER

Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of Colloid and Interface Science 298 (2006) 556–563

Journal of
Colloid and
Interface Science

www.elsevier.com/locate/jcis

Sorption of selenite ions on hematite

M. Duc [1], G. Lefèvre *, M. Fédoroff

Laboratoire d'Electrochimie et de Chimie Analytique (ENSCP-CNRS UMR7575), 11, Rue Pierre et Marie Curie, F75231 Paris Cedex 05, France

Received 10 November 2005; accepted 14 January 2006

Abstract

The sorption of selenite from aqueous solutions onto hematite was investigated as a function of pH (2–12), ionic strength (0.01–0.1 M), and concentration of selenium (10^{-7}–10^{-2} M). The sorption may proceed according to two processes: surface complexation, followed by the precipitation of ferric selenite starting at approximate $[\mathrm{Se}] = 4 \times 10^{-4}$ M (surface coverage > ca. 2 at nm^{-2}). The sorption isotherms have been fitted by a Tempkin equation. A surface complexation model (2-pK/Constant Capacitance Model) was used to fit the sorption data. The nature of the surface species of selenite cannot be determined by modeling since monodentate $>\mathrm{FeO{-}Se(O)O^-}$ or $>\mathrm{FeO{-}Se(O)OH}$ and bidentate $(>\mathrm{FeO})_2\mathrm{SeO}$ surface complexes are both able to fit the experimental data. The reversibility and kinetics of sorption were also studied. The affinity of selenite ions toward hematite, expressed as the distribution coefficient with respect to the surface area (K_D in L m^{-2}), was compared with results published for other ferric oxides (goethite and amorphous ferric oxide). It was found that the reactivity toward selenite is similar, contrary to acid–base properties which depend on the nature of the oxide and its level of purity.

Keywords: Selenium; Iron oxide; Isotherm; Surface complex

1. Introduction

Selenium (Se) is present in radioactive wastes by several radionuclides (^{75}Se, ^{79}Se, ...). In the French underground depository concept, the long-lived radionuclide ^{79}Se (half-life: 6.5×10^4 y) could be released from underground waste depositories. It is important to know which solids present high retention properties toward selenium, so as to model the migration of selenium species in soils and geological media around waste depositories for the eventual determination of the risk of dispersion of the radioactivity.

Chemical forms of Se in natural waters are governed by various physicochemical factors including oxidation–reduction status, pH, and sorbing surfaces. Oxidation of the less soluble forms of Se such as selenides and elemental Se^0 leads to the more soluble anions. This study was focused on the selenite anion ($\mathrm{SeO_3^{2-}}$), since it is expected to be very mobile in rocks found around the underground depositories (clays or granite) whose major components present a very low affinity toward anions.

Iron oxy-hydroxides are present in numerous natural media in contact with water: soils, sedimentary rocks, cracks in igneous rocks. Thus, they will play an important role in the retention of radionuclides in underground water. Several crystallographic structures of iron oxy-hydroxides exist: goethite and hematite are the most stable oxides in aerobic conditions and are widespread in soils; ferrihydrite has the highest specific surface area but is poorly crystalline and its occurrence requires the presence of a crystallization inhibitor [1].

Both selenite and selenate ($\mathrm{SeO_4^{2-}}$) species adsorb onto ferric oxy-hydroxides, but the affinity for $\mathrm{Se^{VI}}$ is generally smaller than for $\mathrm{Se^{IV}}$ [2–7]. This behavior may be related to differences in the nature of the respective surface complexes. Several experimental results, from the ionic strength effect [4,6], sorption modeling [8], X-ray absorption spectroscopic studies (EXAFS) [3,9,10], and pressure-jump experiments [7], have led to the conclusion that selenite is sorbed by inner-sphere (IS) complexation, although the exact coordination (mono- or bi-dentate) and species protonated or deprotonated is not clear. Among the ferric oxy-hydroxides whose surface reactivity toward selenium species has been studied are goethite [2–4,6–13], HFO

---

* Corresponding author. Fax: +33 1 56 81 30 59.
E-mail address: gregory-lefevre@enscp.fr (G. Lefèvre).

[1] Present address: Laboratoire Central des Ponts et Chaussées (DMSRGI/SGMRGE) 8, Bd Lefebvre F75732 Paris Cedex 15, France.

doi:10.1016/j.jcis.2006.01.029

(hydrous ferric oxide) [4–6,9,10,12,14], other polymorphs of FeOOH [12], and hematite [10]. Most of the researchers who have compared the reactivity of goethite and HFO (calculation corrected for specific surface area) have found no difference [4,6,9,12] in the reactivity for selenium species.

The affinity of goethite toward selenium species has been thoroughly investigated. The results on the goethite/selenium system could be therefore applied in the modeling of radioactive selenium transport in soils whose retention would come mainly from iron minerals. However, the crystallographic iron phase mostly found in rocks and soils in the vicinity of underground depositories is hematite [15,16]. The affinity of selenium species toward this ferric oxide was scarcely studied. In a preliminary study on the comparison of the sorption behavior of apatites and iron oxides toward selenite and selenate, we have shown that the distribution coefficients (K_D) values for these Se species are very close for hematite and goethite where the values are defined with respect to the surface area of the solids [17].

In the present study, the sorption of selenite ions onto hematite surface was characterized by sorption kinetics and reaction reversibility. The effects of pH, ionic strength, and concentration of selenium in solution on the sorption were also investigated. Different sorption models (Tempkin, surface complexation 2-pK/Constant Capacitance Model) were used to interpret the selenium sorption. Finally, a comparison of the surface reactivity of hematite and goethite was done.

2. Materials and methods

2.1. Sorbents

Hematite and goethite are commercial powders and were used for the experiments as obtained from Alfa products and BASF. Characteristics of both solids are listed in Table 1. Carbon and sulfur, found as impurities, probably correspond to the presence of carbonate and sulfate, the latter species coming from the iron salt used for the synthesis.

2.2. Ferric selenite

To study the dissolution of ferric selenite, this compound was synthesized by addition of 25 ml of 0.2 M Na_2SeO_3 to 50 ml of 0.067 M $Fe(NO_3)_3$ (stoichiometric ratio corresponding to $Fe_2(SeO_3)_3$). The yellow-green suspension was stirred for 2 h at 25 °C, filtered, rinsed with water and dried. After drying at atmospheric pressure in a dessicator partly filled with silica gel, about 1 g of material was obtained. The analysis of the solution indicated that more than 99% of iron and selenium has been precipitated. Dissolution experiments were carried out with suspensions of ca. 50 mg ferric selenite in 25 ml of solutions whose pH was adjusted with HNO_3 and ionic strength with $NaNO_3$ (10^{-2} M). After stirring for 1 and 6 days, suspensions were centrifuged (30 min at 5000g) and pH was measured in the tubes. Aliquots of 5 ml were withdrawn and filtered using 0.025-μm membranes for analysis of Se and Fe.

2.3. General procedures

To study kinetics and reversibility, suspensions of hematite (16 $\mathrm{g\,L^{-1}}$ in 4.1×10^{-4} M Na_2SeO_3, 0.1 M $NaNO_3$ solutions, whose initial pH had been adjusted to 3.5 or 7 with HNO_3) were stirred at 25 and 50 °C. After shaking for various time intervals, the suspensions were filtered and the Se concentration measured by inductively coupled plasma optical emission spectrometry (ICPOES). The accuracy of this method is better than 5%. For desorption studies, the above-mentioned suspensions at various pH were stirred for 24 h, filtered and dried. The solids were then equilibrated with a solution of 0.1 M $NaNO_3$ at pH 12 (adjusted by NaOH) for various time intervals for desorption kinetics. The suspensions were then filtered, and analyzed for Se concentration.

For sorption studies, except for some samples detailed in the text (with different solid concentrations or ionic strengths), suspensions of hematite (16 $\mathrm{g\,L^{-1}}$) or goethite (6 $\mathrm{g\,L^{-1}}$ in 4.1×10^{-4} M Na_2SeO_3, 0.01 M $NaNO_3$ solutions) were used. The initial pH was adjusted with HNO_3 and NaOH. The suspensions were stirred for 24 h at 25 °C, and the pH measured thereafter. After filtration, Se and Fe concentrations in the solution were determined by ICPOES.

2.4. Surface complexation modeling

Acid-base properties of hematite used in sorption modeling were determined by titration. The fit of the titration curve by a surface complexation model 2-pK/Constant Capacitance electrostatic Model (CCM) using the software FITEQL [18] gave the following values for the acid-base constants and capacitance: $\mathrm{p}K_+ = 6.80$, $\mathrm{p}K_- = 7.80$ and $C = 1.5\ \mathrm{F\,m^{-2}}$. The site density was obtained by saturation curves [19]: $N_S = 1.1\ \mathrm{at\,nm^{-2}}$. The value of the point of zero charge (7.3) was found to range within previously published point of zero charge (pzc) values [20], but was lower than the pzc values of between 8.5 and 9.5 measured for compounds of high purity [21–24]. The presence of impurities in the commercial product may explain this difference.

Table 1
Characteristics of the iron oxides used in the present study

Mineral	Specific surface area ($\mathrm{m^2\,g^{-1}}$)			Impurities ($\mathrm{mg\,g^{-1}}$)		
	From N_2 adsorption, BET calculation	From SEM pictures, geometrical surface	From SEM pictures, shape	Calcium	Sulfur	Carbon
Goethite[a]	17.9	13	Needles	0.65	2.60	0.14
Hematite	8.4	7.6	Spheres	0.33	0.48	0.15

[a] From Prélot et al. [36].