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Sorption of selenate on soils and pure phases: kinetic parameters and stabilisation

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ABSTRACT

This study was conducted to identify the principle selenate carrier phases for two selected soils, by comparing their reactivity with selenate to that of pure phases of the solids. Silica, calcium carbonate, aluminium hydroxide, goethite, bentonite and humic acid were selected as the main soil carrier phases. Comparisons were made first on the parameter values obtained with the best fit of a kinetic sorption model which can discriminate instantaneous sorption from kinetically limited sorption. Then comparisons were made of the ability for each solid to stabilise selenate by measuring the ratio of the partition coefficient for sorption ($Kd_{sorption}$) over that of the desorption ($Kd_{desorption}$). Kinetics and stabilisation were used to help elucidate the nature of interactions with the test solid phases for a large range of selenate concentrations. The experiments were conducted over 165 h in batch reactors, the solid being isolated from the solution by dialysis tubing, at two pH (5.4 and 8) and three selenate concentrations (1×10^{-3}, 1×10^{-6} and 1×10^{-8} mol L^{-1}). The results obtained showed that only aluminium hydroxide can sorb selenate throughout the studied pH range (pH 5.4 to 8.0). The sorption capacity on this mineral was high ($Kd_{sorption} > 100$ to 1×10^4 L kg^{-1}) and the selenate was mainly stabilized by the formation of inner sphere complexes. The sorption on goethite occurred at pH 5.4 ($Kd_{sorption}$ 52 L kg^{-1}), mainly as outer sphere complexes, and was null at pH 8. On silica, a weak sorption was observed only at pH 5.4 and at 165 h ($Kd_{sorption}$ 4 L kg^{-1}). On bentonite, calcium carbonate and humic acid no significant sorption was observed. Concerning the two soils studied, different behaviours were observed for selenate. For soil Ro (pH 5.4), $Kd_{sorption}$ was low (8 L kg^{-1}) compared to soil Bu (pH 8) (70 L kg^{-1}). The sorption behaviour of selenate on soil Ro was mainly due to outer sphere complexes, as for goethite, whereas for soil Bu the sorption was mainly attributed to inner sphere complexes followed by reduction mechanisms, probably initiated by microorganisms, in which no steady state was reached at the end of the 165 h experiments. The sorption of selenate decreased when concentrations reached 1×10^{-3} mol L^{-1}, due to solid saturation, except for aluminium hydroxide. Reduction of selenate seemed also to occur on goethite and soil Ro, for the same concentration, but without preventing a decrease in sorption. Thus, this work shows that the comparison of selenate behaviour between soil and pure phases helps to elucidate the main carrier phases and sorption mechanisms in soil.

1. Introduction

Selenium (Se) is an essential micronutrient for organisms, a characteristic of which is the narrow range of concentrations between deficiency and toxicity (Barceloux, 1999). It is present in the terrestrial crust and in soil at mean concentrations of 0.05 mg kg^{-1} and 0.39 mg kg^{-1}, respectively (Sposito, 1989). Natural concentrations vary and can result in levels that induce deficiency (e.g. in China) to spots of high concentrations where toxicity occurs (e.g. the San Joaquin Valley, USA or Yutangba, China). Furthermore, anthropogenic activities are also responsible for some Se polluted areas. In the nuclear industry, the isotope ^{79}Se is a long-lived fission product of ^{235}U, and is one of the most troubling of radionuclides in the context of risks from nuclear waste repository studies (Aguerre and Frechou, 2006). Selenium-79 was identified as an isotope which could potentially be released from nuclear waste repositories into the groundwater systems. The subsequent pumping of deep water for irrigation could then result in its potential transfer to the biosphere. In a worst case scenario

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prediction, the irrigated soil plays an important role in influencing the behaviour of ^{79}Se in the biosphere. Selenium is present in the soil under different oxidation states, namely selenate (+VI), selenite (+IV), elemental Se (0) and selenide (−II), which form different mineral and organic compounds with different behaviours (Ashworth and Shaw, 2006; Chabroullet, 2007; Scott et al., 1998). Speciation of Se is a key factor controlling its behaviour in soils and numerous factors, abiotic (e.g. pH and soil solution composition) and biotic, can influence speciation.

Currently, selenite and selenate, which are the most mobile forms, are considered to be the most probably oxidation states of theoretical Se contamination in the biosphere. Numerous studies have been carried out on the behaviour of selenite in soils and pure phases (e.g. Chabroullet, 2007; Coppin et al., 2006; Darcheville et al., 2008; Dynes and Huang, 1997; Haudin et al., 2007; Øgaard et al., 2006; Sposito et al., 1988). However, only a few studies have been conducted on selenate, even though it is potentially the most mobile form (Séby et al., 1998), probably because it is not the major form of Se for in situ measurements (Wang and Gao, 2001). The low levels of selenate in soils may be due to (i) selenate reduction to other Se forms in soils and/or (ii) the mobility of selenate is very high and so it rapidly migrates to the groundwater. The remaining selenate is usually found in association with specific soil phases (iron and aluminium oxides, clays (Hyun et al., 2006; Sharmasarkar and Vance, 2002; Singh et al., 1981; Vuori et al., 1994). These two hypotheses would have different consequences. The first would result in accumulation of Se in the subsurface soil, while the second would result in the migration of selenate to the groundwater. The different transport fates of Se have obvious implications in calculations of environmental and human risks.

In the last two decades, studies on selenate interactions with pure minerals have led to a better understanding of selenate sorption mechanisms. Selenate may preferentially form highly mobile complexes on the surface of numerous solids, outer sphere complexes (OSC) (apathite, goethite, magnetite, aluminium hydroxide (Duc et al., 2003; Kuan et al., 1998; Lo and Chen, 1997; Martinez et al., 2006; Rovira et al., 2008; Schulthess and Hu, 2001; Scott et al., 1998; Wijnja and Schulthess, 2002), but in some cases less mobile inner sphere complexes (ISC) (Peak, 2006; Wijnja and Schulthess, 2002). The formation of ISC depends on the nature of the solid material (Peak and Sparks, 2002), on pH (i.e. increase of ISC with pH decrease) (Peak and Sparks, 2002; Wijnja and Schulthess, 2000a) and on the drying of solid material which could generate a partial loss of the first hydration sphere of the selenate (Manceau and Charlet, 1994; Parfitt and Russell, 1977; Peak and Sparks, 2002; Wijnja and Schulthess, 2000a). Other than these direct interactions between selenate and solid material, reduction processes could transform selenate into lower oxidation state Se which generates stabilisation in soil. Some authors have observed that reduction could be biotic (Siddique et al., 2006) or abiotic (Johnson and Bullen, 2003; Olegario et al., 2010).

Although these earlier studies helped to establish the nature of selenate interactions with soils, the concentrations of selenate used in the experiments were high ($>1 \times 10^{-5}$ mol L^{-1}). It is therefore difficult to predict the interactions of trace levels of selenate with soil based on this data. Furthermore, these studies mainly considered sorption processes only and did not take into consideration their reversibility, an important step when modelling the behaviour of selenate in soil.

The first objective of this study was to identify the main potential selenate carrier phases for two selected soils by comparing their reactivity with selenate to that of pure phases of the solids. This approach differs from approaches that identify carrier phases based on correlations between soil elementary concentrations. The following phases, which are representative of the major soil components, were selected: silica, calcium carbonate, aluminium hydroxide, goethite, bentonite and humic acid. The comparison was made (1) by using the Lee et al. (2009) model, based on the two sites model proposed by Van Genuchten and Wagenet (1989), completed by taking account of the diffusion through the solid in the dialysis tubing, and (2) the ability of the solid to stabilise selenate by measuring the ratio of the partition coefficient for sorption (Kd_{sorption}) over that of the desorption ($Kd_{\mathrm{desorption}}$). These two factors (kinetic and stabilisation) were used to help elucidate the nature of interactions with the test solid phases for a large range of selenate concentrations (1×10^{-3}, 1×10^{-6} and 1×10^{-8} mol L^{-1}). The model of Lee et al. (2009) was chosen because it permits simultaneous simulation of equilibrium/kinetic sorption, which could correspond to OSC and ISC reactions with solid. To better identify the sorption mechanisms occurring in soils, pure phases (i.e. humic acid) were used in mixtures with soils to modify their reactivities with selenate. The use of an identical protocol for the selenate sorption on pure phases permited the construction of a coherent database, and the identification of the reactive phases, their kinetics of sorption, and their ability to stabilise selenate. This information could be of primary importance in chosing which mineral phases should be used to immobilise Se pollution in a contaminated area, as has already been done for other pollutants (e.g. Cui et al., 2010).

2. Materials and methods

2.1. Materials

2.1.1. Solid samples

The following commercially available pure phases were used in this study: silica (Quartz & Silice®), goethite (Fluka®), aluminium hydroxide (sigma–aldrich®), calcium carbonate (VWR®), humic acid (VWR®) and bentonite (Sigma®). The two soils used were a silty clay loam soil (soil Ro), collected at the Rothamsted (UK) experimental station in a grassland area known as Highfield (Coppin et al., 2006) and a silty clay soil, collected at Bure (soil Bu), in the north east of France. The main differences in soil characteristics were pH (5.4 and 8.0 respectively) and carbonate levels (<0.1 and 2.84 %, respectively). The soils were air dried and sieved (<2 mm) before use. The main physical and chemical properties of the solids are given in Table 1.

2.1.2. Sorption and desorption experiments

2.1.2.1. Solid suspension preparation. To prepare soil suspensions, 2, 4, 20 and 30 g of bentonite, humic acid, aluminium hydroxide and other solids, respectively, were placed in 200 mL polypropylene batch reactor. For the mixture experiments of humic acid with soils, 0.3 and 1.2 g of humic acid were added to 29.7 and 28.8 g of soils, respectively. Sixty mL of NaCl at 3×10^{-3} mol L^{-1} were then added to the solids. The weight of each solid was optimised to permit a good homogenisation of the suspensions with a magnetic stirrer. The batches were then placed in an incubation chamber at 25 °C for 6 days minimum with a daily agitation. The pH of the suspension was measured at the end of six days and then adjusted each day (for 5 more days), if necessary, to 5.4 or 8 until stabilisation at the chosen value.

2.1.2.2. Selenate solution preparation. Selenate solutions were prepared by dissolving Na_2SeO_4 salts (Sigma®) in NaCl 3×10^{-3} mol L^{-1} (prepared with ultra high quality water (UHQ)) to obtained the desired selenate concentrations. The selenate solution was then spiked with a solution of ^{75}Selenate to obtain 170 kBq mL^{-1}. The solution of ^{75}selenate was generated by oxidation of a solution of ^{75}selenite (Isotope product IPL 6075-1233-21).