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# Transport of selenium oxyanions through $TiO_2$porous media: Column experiments and multi-scale modeling

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## ABSTRACT

The present work deals with the modeling of selenium oxyanion (selenite/selenate) retention in $TiO_2$ rutile porous media. A set of chemical interactions was elaborated from spectroscopic measurements and adsorption experiments in batch and column reactors, and a model of transient transport of the selenium species through laboratory column was developed. The adsorption model considered that both forms of selenium (Se) compete for the same sorption sites, hydroxyl groups, allowing taking into account a competitive adsorption. Stoichiometry and equilibrium constants of adsorption reactions were determined on the basis of spectrometric measurement and adsorption isotherm curve fitting. This approach led to a model of Sips type isotherm including a pH-dependence. It offers an excellent fitting compared to the classical Langmuir equation and provides a unique set of parameters for both oxyanions. IMPACT code and associated modeling method were then used to couple transport and chemical reactions. The obtained numerical results showed a reasonable prediction of the shape and the time location of selenium oxyanions and pH breakthrough curves.

## 1. Introduction

Selenium (Se) pollution of the environment comes mainly from combustion of fossil fuels and its widespread use in agriculture, electronics and glass industry (Lemly, 2004). Furthermore, radioactive isotopes of selenium especially Se-79 are long half-life fission products of uranium ranging from $10^5$ to $11 \times 10^5$ years (Bienvenu et al., 2007). Their fate and behavior in the environment are important issues in nuclear waste management (Aguerre and Frechou, 2006). Attention is particularly given to its transport properties through porous media (Beauwens et al., 2005). This behavior strongly depends on speciation. In a geochemical context, selenium can exist as soluble selenium oxyanions, selenate, Se(VI), and selenite, Se(IV), as sparingly soluble Se(0), as selenides Se(-II) or Se(-I) that commonly form highly insoluble compounds such as FeSe. Under reducing conditions, selenium main aqueous species is Se(-II) whereas Se(IV) is the dominant aqueous species under mildly reducing conditions and presents as its protonated form $HSeO_3^-$ at acidic to neutral pH, or as selenite anion $SeO_3^{2-}$ at alkaline pH. Under oxidizing conditions, Se(VI) is the main species, either as selenate anion $HSeO_4^-$ or $SeO_4^{2-}$, depending on pH conditions (Beauwens et al., 2005).

The sorption of selenium oxyanions onto different types of minerals has been investigated to explain the mobility of selenium species in the environment. For instance, adsorbing materials such as iron oxides and hydroxides (Catalano et al., 2006; Duc et al., 2003; Peak et al., 2006; Rovira et al., 2008; Wijnja and Schulthess, 2000), manganese oxides (Foster et al., 2004), titanium dioxide (Svecova et al., 2011), cements and clays (Charlet et al., 2007), biomass filters (Alvarado-Rodriguez

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et al., 2013) or soils (Collins et al., 2006; Nakamaru et al., 2005) have been considered in the literature. In most cases, Se(IV) appeared to be more retained by solid surfaces than Se(VI). Sorption onto either oxide or hydroxide minerals was found to be pH dependent, which suggested a surface complexation mechanism. Most of these works showed that the optimum adsorption pH was generally met in the acidic area.

Due to its low solubility and its value of the point of zero charge near to the neutrality, $TiO_2$ has been regarded as a model mineral in sorption studies. In a previous investigation, Svecova et al. (2011) reported a detailed experimental study on the sorption of selenite and selenate anions onto $TiO_2$ rutile surface at acidic pH. A combined approach was chosen and the crystallographic properties were linked to the sorption behavior in batch reactor and through $TiO_2$ porous media in column experiment. EXAFS spectra confirmed that for selenite anions, an inner-sphere mechanism was the most probable process observed. Dynamic sorption experiments using a column filled with rutile powder not only substantiated that a part of the surface complexes follows the inner-sphere mechanism, but also evidenced that an outer-sphere mechanism cannot be excluded, especially for selenate anions. This finding represent very useful information to predict the Se susceptible to migrate under specific conditions, but a satisfactory modeling and mathematical parameterization of obtained experimental data is still necessary for applications in the field of contaminant migration.

The adsorption process of many inorganic oxyanions onto mineral surfaces has been commonly described by chemical Surface Complexation Models (SCMs) (Gunneriusson et al., 1994; Lackovic et al., 2004; Hizal and Apak, 2006). Unlike empirical models (e.g. Langmuir and Freundlich models), chemical models (SCM) have the advantage to explicitly define surface species, chemical reactions and equilibrium constant expressions. The SCM approach can also be readily incorporated within solute transport models (Kent et al., 2000; Kohler et al., 1996).

Despite the numerous contributions, to our knowledge, there is no consistent modeling approach able to link $TiO_2$ mineral surface properties to a same set of experiments performed in batch or column. Thus, there is a real need to develop modeling approaches including transport mechanisms to predict quantitatively the reactions occurring at the solid surface and the fate of contaminant in contact with these surfaces that can have practical environment implications.

The present study is essentially methodological and carried out with the aim to develop a model able to describe the interactions of selenium oxyanions with $TiO_2$ rutile that accounted for competitive adsorption, and that can be applicable in various experimental conditions around pH 3. A step-by-step modeling process from the spectroscopic determination of interactions to the transient transport of Se-oxyanions in a laboratory column was developed. A set of adsorption reactions, so-called "phenomenological mechanism", was built to describe batch and column sorption experiments of selenite and selenate. Transport simulations were then performed with the IMPACT code (Baranger et al., 2002; Jauzein et al., 1989; Lefèvre et al., 1993; Scholtus et al., 2009; Simonnot and Ouvrard, 2005) and the calculated and experimental breakthrough curves of selenium oxyanions and pH behavior were compared.

## 2. Materials and methods

### 2.1. Adsorbent

The adsorbent used in laboratory experiments was a very fine powder of titanium dioxide in rutile allotropic form (CERAC Inc., Milwaukee, USA). Pre-treatment and physico-chemical parameters of this rutile powder have been reported in detail (Svecova et al., 2008, 2011). The particle size was between 200 nm and 1 μm, the specific surface area was 5 $m^2\ g^{-1}$ and the point of zero charge was around 4.5 to 5.0. For column experiments, the powder was compacted under the effect of a certain compaction pressure of 20, 30, and 40 kN using an instron 5569 traction machine. The size of the formed aggregates varied from 112 to 200 μm. The physico-chemical parameters of the aggregates were close to those of the initial powder (Svecova et al., 2008) except the BET surface area that reached 7 $m^2\ g^{-1}$. This increase was assigned to surface activation by compacting and grinding.

### 2.2. Batch sorption experiments

Adsorption isotherms of Se(IV) and Se(VI) onto rutile powder were previously determined by batch reactor experiments at constant temperature, ionic strength and pH. In the first step, the rutile powder (0.2 g) was contacted with 10 mL of sodium perchlorate solution at the selected ionic strength for 12 h at 22 °C; pH was adjusted to 3 by addition of 1 mol $L^{-1}$ $HClO_4$ stock solution (Svecova et al., 2011). Then, a given volume of a stock solution of selenium oxyanions was added to the suspensions in order to obtain concentrations ranging from $5 \times 10^{-5}$ to $5 \times 10^{-3}$ mol $L^{-1}$ at pH 3 and sorption time was set at 100 h (Svecova et al., 2011). The supernatant was further filtered at 0.22 μm before being analyzed by ion chromatography. Empirical fittings of experimental points by Langmuir or Freundlich isotherms were available in annexes jointed to a previous paper (Svecova et al., 2011).

### 2.3. Column experiments

Column experiments were performed at 22 °C in a set-up composed of: two reservoirs of solutions degassed by nitrogen bubbling, a pump feeding the packed column at constant flow rate in the up-flow direction, two continuous detectors (pH and conductivity) and a fraction collector (Svecova et al., 2011). The collected samples were analyzed by ion chromatography (ICS 3000 by Dionex, Sunnyvale, USA). The transient measurements of pH during column experiments were considered as qualitative.

In a typical experiment, the column was filled with 7.88 g $TiO_2$ aggregates corresponding to a total volume of 5.5 mL (length, 7.0 cm; diameter: 1.0 cm). The flow rate was 0.2 mL $min^{-1}$, which corresponded to a mean residence time of 17.5 min. The accessible pore volume was determined by residence time distribution measurements performed with $NaClO_4$ solutions: its value was 3.47 mL. Total accessible porosity of column bed was 63.5% including external (about 0.4) porosity of packing and internal (about 0.39) porosity of agglomerated grains. Pressure drop was negligible.