Interfaces Against Pollution 2014

Effect of the presence of pyrite traces on silver behavior in natural porous media

Delphine Charrière [a,b], Manuel de A. Hernández Cortázar [c], Philippe Behra [a,b,*]

[a] Université de Toulouse; INPT, LCA (Laboratoire de Chimie AgroIndustrielle), UMR 1010, ENSIACET, 4, Allée Emile Monso, CS 44362, F-31030 Toulouse Cedex, France
[b] INRA, LCA (Laboratoire de Chimie AgroIndustrielle), F-31030 Toulouse, France
[c] CMP+L (Centro Mexicano para la Producción más Limpia Instituto Politecnico Nacional), Av. Acueducto S/N, col. Barrio la Laguna. Ticoman, 07340 México, D. F., Mexico

ARTICLE INFO

ABSTRACT

In order to better understand the fate of the toxic element Ag(I), sorption of Ag(I) was studied from batch experiments, at different pHs (2–8) and at 298 K. A pure quartz sand (99.999% SiO_2) and "natural" quartz sand (99% SiO_2, and traces of Fe, Al, Mn (hydr)oxides, of clays and of pyrite) were used as sorbents. The Ag(I) sorption behavior depends strongly on pH with isotherm shapes characteristic of Langmuir-type relationship for initial Ag concentration [Ag(I)], range between 5.0×10^{-7} and 1.0×10^{-3} M. Even if the Ag (I) sorption capacity on pure quartz sand is very low compared to the natural quartz sands, its affinity is rather high. From speciation calculations, several sites were proposed: at pH_i 4, 6 and 8, the first surface site is assumed to be due to iron (hydr)oxides while the second surface site is attributed to silanols. At pH_i 2, sorption of Ag(I) was assumed to be on two surface sites of iron (hydr)oxides and a third surface site on silanol groups. Even if the sand is mainly composed of silica, the trace minerals play an important role in sorption capacity compared to silica. The conditional surface complexation constants of Ag(I) depend on pH. On the other hand, it is shown that the Ag speciation depends strongly on the history of "natural" quartz sand due to initial applied treatment, little rinsing or longer washing. In the presence of low amount of pyrite, strong complexes between Ag(I) and sulfur compounds such as thiosulfates due to oxidative dissolution of pyrite are formed what decreases Ag sorption capability. SEM–EDS analyses highlighted the surface complexation–precipitation of Ag_2S and Ag(0) colloids which confirmed the important role of pyrite on Ag(I) speciation.

1. Introduction

Interactions of heavy metals at liquid–liquid and liquid–solid interfaces have been largely studying by the scientific community due to their role in the understanding of environmental pollution owing to the various human activities: metallurgy, dentistry, chemistry, nuclear industry, paint and batteries, and agricultural habits such as the use of fertilizers, fungicides and other pesticides. To prevent migration of heavy metal pollutants in wastewater, contaminated soil and solid waste, knowledge of mechanisms controlling transport and transfer of metals which occurs at the solid–liquid interface is thus a prerequisite. The possible mechanisms are numerous: precipitation, dissolution, sorption, complexation, oxidoreduction, etc. Silver is considered as a toxic metal either if present in cationic form, Ag(I), or as nanoparticles, mainly Ag(0) [1–3]. Anthropogenic activities (mining, steel mills, cement plants, burning fossil fuel, nuclear, biocides, etc.) have been among the main sources of Ag(I) in natural systems [1–5]. Nowadays its biocide effects when used as nanoparticles are considered as very strong and explained why Ag is very often present in its colloidal forms in the environment [1]. The maximum silver concentration in drinking water is recommended at $50 \, \mu g \, L^{-1}$ by the World Health Organization (1975) and limited at $10 \, \mu g \, L^{-1}$ in the European Union (98/83/CE). Silver is also included in the US EPA list of priority toxic pollutants. Thus, to avoid pollution, understanding the phenomena of sorption is essential to predict the speciation of Ag(I) and Ag nanoparticles in environmental system and matrix [1].
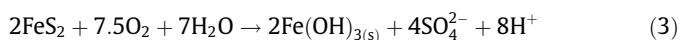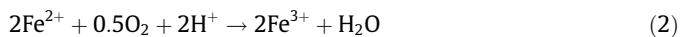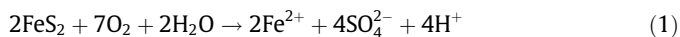
Ag(I) can form complexes with ligands present in the environment. It may, in the case of Ag(I), form stable complexes with ammonia, cyanide, thiosulfate, and halide. Silver sulfide, Ag_2S, is one of the most insoluble silver salts. However, the solubility of

* Corresponding author at: INPT, INRA, LCA (Laboratoire de Chimie AgroIndustrielle), F-31030 Toulouse, France.
E-mail address: philippe.behra@ensiacet.fr (P. Behra).

the salt can change with the presence of organic or inorganic ligands which form complexes depending on pH, ionic strength, redox conditions, etc. Few studies have reported on Ag(I) sorption on different natural minerals [6–9].

For example, the surface of pyrite is known for its properties of adsorption and retention of precious metals such as gold, silver, platinum and also mercury [10]. Moreover, the oxidative dissolution of pyrite releases aqueous SO_4^{2-}, Fe(II) and Fe(III) in acidic medium and SO_4^{2-} and iron (hydr)oxides $FeOOH_{(s)}$ in basic medium [11,12]:

$$2FeS_2 + 7O_2 + 2H_2O \rightarrow 2Fe^{2+} + 4SO_4^{2-} + 4H^+ \tag{1}$$

$$2Fe^{2+} + 0.5O_2 + 2H^+ \rightarrow 2Fe^{3+} + H_2O \tag{2}$$

$$2FeS_2 + 7.5O_2 + 7H_2O \rightarrow 2Fe(OH)_{3(s)} + 4SO_4^{2-} + 8H^+ \tag{3}$$

Rate law of pyrite oxidation has been reported by Williamson and Rimstidt [13], taking into account the O_2 and H^+ molalities. Recently, Gartman and Luther III [14] have shown that the oxidation rate of sub-micron pyrite in seawater is first order with respect to both O_2 and pyrite concentration.

Scaini et al. [6] have worked on the interaction of Ag(I) ([Ag(I)] = 10^{-4} M) with pyrite, at pH 3. Analyses of the solution after reaction have displayed measurable amounts of Fe^{2+}. According to their results, the presence of Ag_2S and the deposition of metallic silver (XPS and SEM analysis) have been detected on the surface of pyrite. In conclusion they have proposed the following mechanism [6]:

$$FeS_2 + 8Ag^+ + 4H_2O \rightarrow Fe^{2+} + Ag_2S + 6Ag(0) + SO_4^{2-} + 8H^+ \tag{4}$$
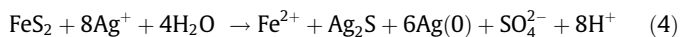
Ravikumar and Fuerstenau [7] have studied the Ag(I) sorption on cryptomelane, a manganese oxide. Sorption depends on surface chemistry of oxide and chemical composition of solution (e.g. pH). They have proposed an ion exchange reaction mechanism between Ag(I) and potassium [7]. In addition, Dzombak and Morel [8] have estimated many surface complexation constants of several metals with hydrous ferric oxide (HFO). They have concluded that the adsorption capacity of Ag(I) is higher at basic pH and that sorption is controlled by formation of monodentate surface complex. For the strong surface sites (s), Ag sorption is described by the following surface complexation reaction:

$$Ag^+ + \equiv Fe_s - OH \leftrightarrows \equiv Fe_s - OAg + H^+ \tag{5}$$
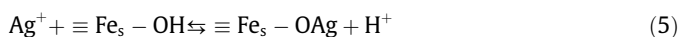
the surface complexation constant being estimated at $10^{-1.72}$, for 0.1 mM [Ag(I)] (for the weak surface site, the surface complexation constant is $10^{-5.3}$).

Moreover they have concluded that the behavior of Ag(I) could be controlled by a mechanism of complexation–precipitation at high pH and at Ag(I) concentration below 600 µM [8]. Jacobson et al. [9] have studied the Ag(I) sorption on various soils with different organic matter content and composition. In their conclusion they have stated that even if Ag(I) sorption is dominated by organic matter, illitic clays play an important role in retaining Ag(I).

The present work focused on the sorption of Ag(I) on three materials: a pure quartz sand, a washed and rinsed natural quartz sands. The raw natural quartz sand was shown to have small amounts of pyrite, clays and (hydr)oxides of Fe, Mn and Al. The objective was to understand the behavior of Ag(I) in the presence of different sands by identifying possible sorption mechanisms and estimating surface parameters. The sorption isotherm experiments of Ag(I) performed at 4 initial pHs (2–8) were analyzed by XPS and modeled according to Langmuir-type isotherms with 1, 2 or 3 sites. In addition, to highlight an area of precipitation, experiments with higher concentrations of Ag(I) (10^{-2} M) at pH 6 were performed. The products of reactions between sand minerals and Ag(I) were confirmed by SEM–EDS analysis.

2. Theories

2.1. Langmuir-type relationship

The Langmuir model [15] has been developed to study the equilibrium at gas–solid interface. Owing to similar shaped isotherms, this model has been extended for probing the sorption phenomenon at liquid–solid interface [16]. Some mathematic relationships have been adopted for fitting the experimental data. In this case the solution species, A, can be adsorbed on surface sites of a solid adsorbent $\equiv S$, with a 1:1 stoichiometry and $\equiv SA$, the adsorbat, present at the surface [17]:

$$\equiv S + A \rightleftarrows \equiv SA \tag{6}$$

The concentrations of $\equiv S$ and $\equiv SA$ are in mol m^{-2}. The equivalent of maximum surface site concentration in experimental conditions (mol m^{-2}) is:

$$\Gamma_{max} = \Gamma_{\equiv S} + \Gamma_{\equiv SA} \tag{7}$$

For two or more surface sites, Γ_1, Γ_2,...,Γ_n, which correspond to different site affinities, the relationship between the adsorbed and the aqueous concentrations of A can be calculated at equilibrium according to the Langmuir-type model [17]:

$$\Gamma = \sum_{i=1}^{n} \Gamma_{max,i} \frac{K_{ads,i}[A]_{aq}}{1 + K_{ads,i}[A]_{aq}} \tag{8}$$

where $K_{ads,i}$ is the Langmuir-type constant (L mol^{-1}), $[A]_{aq}$ is the total aqueous concentration of A (mol L^{-1}), Γ is the total sorbed concentration of Ag(I) (mol m^{-2}), and $\Gamma_{max,i}$ is the equivalent of maximum surface site concentration in experimental conditions (mol m^{-2}). The parameters, $\Gamma_{max,i}$ and $K_{ads,i}$, can be directly estimated, from experimental data with specific software, such as Origin spreadsheet.

The relationship between Langmuir-type model and surface complexation is described in more details in the Supporting information.

2.2. Speciation software: MICROQL

The software MICROQL [18,19] was used for speciation calculation of the adsorption of a given solute on mineral surfaces. The reactions and mass balances which are necessary for calculation are reported as a Tableau in Table S1 [20] (see the Supporting information for more detail about surface acidity and aqueous speciation theories).

3. Materials and methods

3.1. Sorbent materials

Three sorbent materials were used: (i) a pure quartz sand, (ii) a natural quartz sand washed in a column (treatment I) and (iii) the same natural quartz sand rinsed with pure water (treatment II).

3.1.1. Pure quartz sand

This material was purchased from the "Quartz & Silica Company" in Nemours (Seine-et-Marne, France). It was produced by heating silica at 1000 °C and treating with hydrofluoric acid and recrystallizing for purification. According to the company, and to XPS surface analyses, the pure quartz sand is composed of 99.999 % SiO_2 at its surface [21]. The specific surface area is rather low,