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Influence of humic acid on sorption of Co(II), Sr(II), and Se(IV) on goethite

Sonia MASSET, Fanny MONTEIL-RIVERA*, Laurent DUPONT,
Jacques DUMONCEAU*, Michel APLINCOURT

Université de Reims Champagne-Ardenne, GRECI, BP 1039, 51687 Reims Cedex 2, France

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Abstract – This work examined the influence of a leonardite humic acid on the sorption of Co(II), Sr(II), and Se(IV) onto goethite as a function of pH. The sorption of humic acid and ions alone was first studied. The humic acid sorbs appreciably to the goethite surface according to a reversible process, with a maximum sorption of 19 mg of total organic carbon per g of goethite reached at lower pH values (≈ 5). Cobalt and selenium are significantly sorbed on goethite while strontium is only weakly sorbed. In the presence of humic acid, the cobalt sorption is enhanced in acidic media due to the humic acid sorption on goethite, which modified the surface properties by making it more negative. However, it decreases in alkaline media due to the complexation of Co(II) by soluble humic acid. The sorption of Sr(II) is significantly increased in the presence of humic acid even in alkaline media. The sorption of selenite ions (SeO_3^{2-}) decreases in the presence of humic acid because a competition with humate ions occurs at the surface sites of the goethite. The results presented here constitute a good set of data for modelling the effect of humic acid on the sorption of ions on goethite.

sorption / humic acid / goethite / cobalt / strontium / selenium

Résumé – Influence de l'acide humique sur la sorption de Co(II), Sr(II) et Se(IV) sur une goethite. Dans ce travail est examinée l'influence de l'acide humique leonardite sur la sorption de Co(II), Sr(II) et Se(IV) sur une goethite en fonction du pH. La sorption de l'acide humique et de chaque ion a été étudiée séparément en premier lieu. L'acide humique est sorbé de façon non négligeable sur la goethite, selon un mécanisme réversible, avec un maximum sorbé de 19 mg de carbone organique total par g de goethite observé aux valeurs de pH les plus faibles ($\text{pH} \approx 5$). Le cobalt et le sélénium présentent une bonne aptitude à se sorber sur la goethite tandis que le strontium n'est que faiblement retenu. En présence d'acide humique, la sorption de Co(II) est favorisée en milieu acide car la sorption de l'acide humique sur la goethite rend la surface du minéral plus négative. En milieu basique, au contraire, la sorption est diminuée en raison de la complexation des ions cobalt par l'acide humique soluble. La sorption de Sr(II) augmente en présence d'acide humique,

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* Correspondence and reprints
fanny.monteil@univ-reims.fr
jacques.dumonceau@univ-reims.fr

même en milieu basique. La sorption des ions sélénite (SeO_3^{2-}) diminue en présence d'acide humique puisque l'humate est un anion compétiteur susceptible de se fixer sur les mêmes sites de surface. Les résultats présentés ici constituent une base de données importante afin de modéliser l'effet de l'acide humique sur la sorption d'ions sur la goéthite.

sorption / acide humique / goéthite / cobalt / strontium / sélénium

1. Introduction

Soil contamination by pollutant ions can have different origins: regular irrigation by contaminated water or waste burial. The gradual change of this contamination depends strongly on the speciation of pollutant ions in soil. The elements present in soluble form will migrate rapidly to the ground water and reach the biosphere whereas the elements associated with solid will remain immobilised in the soil. Uptake by plants of the most mobile species can lead to animal and human diseases. Association with solids is greatly influenced by the presence of natural organic matter. Indeed, when adsorbed on the surface of minerals, natural organic matter modifies the physicochemical (e.g., electrophoretic mobility, colloidal stability, and transport) and surface properties of these solids, while in solution it forms complexes with the pollutant metal ions thereby decreasing their adsorption [2, 6, 19, 22].

Much of the dissolved organic matter in natural water consists of humic substances, which are formed during the microbial degradation of biomass in the soil and water. In this paper, we investigate the effect of a leonardite humic acid on the adsorption of Co^{2+} , Sr^{2+} and SeO_3^{2-} onto goethite ($\alpha\text{-FeOOH}$). The latter has been selected because of its natural abundance in soils as well as its strong adsorptive properties toward a wide range of ions. The three ions are susceptible to being present in radioactive waste depositories. ^{90}Sr is a radionuclide of the fission products and ^{60}Co is an activation product observed in nuclear reactor circuits. ^{79}Se is a long-lived radionuclide present in high level radioactive waste. Moreover, selenium is also a nutritional element, the concentration of which has to be very well regulated since it can induce toxic effects for plants and animals if assimilated in excess and have severe consequences if deficient [13].

The behaviour of selenium in the environment strongly depends on its oxidation state. In nature it exists in different oxidation states: selenide (Se^{2-}), elemental selenium (Se^0), selenite (SeO_3^{2-}), and selenate (SeO_4^{2-}). The more mobile species are selenate and selenite, with SeO_3^{2-} being more strongly bound to sorbents.

To understand the effect of humic substances on the sorption of Co^{2+} , Sr^{2+} and SeO_3^{2-} onto goethite in aquatic systems, we first studied several binary systems (goethite/humic acid, goethite/ion). We then investigated ternary systems (goethite/humic acid/ion) and compared the latter results to those obtained in the simpler systems. In all experiments, the sorption to goethite was studied as a function of pH. Three different concentrations of humic acid were considered reflecting conditions of sub-saturation, saturation and excess.

2. Materials and methods

2.1. Materials

The goethite used in this study was synthesised by BASF. Its purity was verified by powdered X-ray diffraction (XRD) and its morphology was observed by electronic microscopy analysis. The mineral appeared as constituted of individual needles (mean diameter 100 nm; length 0.5 to 1 mm). A specific surface area of $20.0 \text{ m}^2\cdot\text{g}^{-1}$ was measured by multiple point B.E.T. N_2 adsorption [18]. A pH of zero charge and a site density of 7.2 and 1.8 sites per nm^2 , respectively, were determined by potentiometric titrations of suspensions of $10 \text{ g}\cdot\text{L}^{-1}$.

Leonardite Humic Acid standard (LHA) was purchased from the International Humic Substances Society (IHSS). It was extensively characterised by elemental analysis, acid-base titration curves, baryta

Table I. Analytical characteristics of LHA.

Elemental analyses (wt %)					wt %	
C	H	O	N	S	H ₂ O	Ash
57.74	4.17	33.90	1.16	0.69	7.4	2.35
Oxygen-containing functional groups						
Total acidity (baryta exchange) [17]					7.1 ± 0.2	mmol·g ⁻¹ _{LHA}
Carboxyl (Ca-acetate exchange) [17]					4.2 ± 0.1	mmol·g ⁻¹ _{LHA}
Phenolic hydroxyl					2.9 ± 0.3	mmol·g ⁻¹ _{LHA}

and Ca-acetate titrations [17], FT-IR, CPMAS ¹³C NMR and XPS. Some of its characteristics are gathered in Table I. Stock solutions of 300 mg·L⁻¹ were prepared as follows: the suspensions were stirred for 6 days at pH 7 after adding a small aliquot of KOH and then centrifuged at 26300 g for 30 minutes to eliminate the insoluble fraction which was composed of both humin and ash. The Total Organic Carbon (TOC) concentration determined for the resulting solution with a Shimadzu TOC-5050 Analyser was 167 mg_C·L⁻¹.

Stock solutions of ions were prepared from the nitrate salts for Sr(II) and Co(II) and from the sodium salt for Se(IV).

2.2. General sorption experiments

Deionized distilled water was used to prepare all solutions and suspensions. Sorption experiments were performed in 60 mL-polystyrene-disposable flasks according to the batch method. The suspensions of goethite were agitated with a thermostated swaying shaker at 25 °C for three hours to attain the hydration equilibrium of the surface of the solid. The ion or the LHA was then added to the suspensions for the binary systems. For the ternary systems, the LHA was first added to fix LHA on goethite before allowing the contact with the ion. All additions were settled to obtain 25 mL of solution containing 50 mg of goethite, 0.1 M KNO₃, HNO₃ or KOH for pH adjustment and the desired ion and/or LHA. After measuring the pH, the suspensions were centrifuged twice at 2400 g for 20 minutes and the supernatant was analysed for ion and/or LHA. The quantity of species sorbed was

deduced from the initial concentration. Blank experiments were also performed without goethite. No significant sorption was observed (< 2%).

Three different concentrations of LHA were used, i.e. 5.6, 16.7 and 33.4 mg_C·g⁻¹_{goethite} (11.2, 33.4, 66.8 mg_C·L⁻¹), corresponding to conditions below saturation, close to saturation and above saturation, respectively. The concentration of ion was equal to 1 × 10⁻⁵ mol·L⁻¹ in all experiments.

Preliminary kinetics experiments were conducted to determine the minimum time span required to reach the adsorption equilibrium for each species. Sorption kinetics were rapid for all species since less than 10 min, 2 hours, 2 hours and less than 1 hour were necessary for Se(IV), Sr(II), Co(II), and LHA, respectively. Whatever the species, suspensions were shaken for 24 hours.

2.3. Reversibility experiments

After performing 24-hour sorption experiments at pH 5, micro-litres of HNO₃ 0.1 M or KOH 0.1 M were added to the suspensions to obtain a final pH value ranging from 4 to 11. The suspensions were shaken again for 24 hours and centrifuged twice at 2400 g after measuring the pH. The species concentration was measured in the supernatant and the amount of species remaining in solid form was calculated from the initial concentration.

2.4. Analytical techniques

Co(II) and Sr(II) concentrations were estimated by ICP-AES (Varian Liberty Series II) while a flame atomic absorption spectrophotometer (Varian Spectra AA-250 Plus) equipped with a Varian Vapor Generation Accessory (VGA 77) was used to determine the concentration of Se(IV). LHA concentration was estimated by spectrophotometry at 465 nm in alkaline medium (Spectronic GENESYS 5 Spectrophotometer Milton Roy) after establishing the relationship between UV-Visible absorbance and Total Organic Concentration (TOC) (TOC (ppm) = 58.7 A_{465, pH12}).

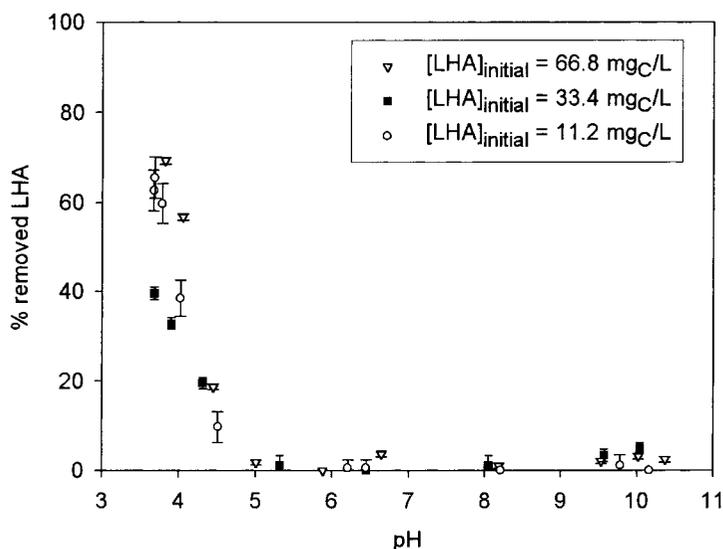


Figure 1. Effect of pH on the solubility of LHA in KNO_3 $0.1 \text{ mol}\cdot\text{L}^{-1}$.

3. Results and discussion

3.1. Sorption of LHA on goethite

3.1.1. Solubility of LHA

Due to the expected precipitation of LHA at lower pH, we investigated the precipitation of LHA, in absence of mineral, prior to studying its sorption on goethite. Figure 1 shows the solubility of LHA in KNO_3 0.1 M as a function of pH for the three different concentrations of LHA used. Whatever the concentration, LHA is completely dissolved at a pH above 5, and begins to precipitate out below 5.

3.1.2. Sorption of LHA on goethite

Sorption of LHA on goethite is presented in Figure 2 as a function of pH. Results are given in percents of removed LHA (Fig. 2a) to facilitate comparison with further results and in $\text{mg}_\text{C}\cdot\text{g}^{-1}_{\text{goethite}}$ (Fig. 2b) to clearly illustrate the saturation of the mineral surface.

For the lowest concentration of LHA ($5.6 \text{ mg}_\text{C}\cdot\text{g}^{-1}_{\text{goethite}}$), the humic acid is totally sorbed at any pH below 8 and only a small portion is soluble between pH 8 and pH 10. This point should be underlined since for this concentration of LHA, complexation

of metals by LHA in solution will not have to be taken into account below pH 8. This outcome simplifies the ternary system and facilitates its interpretation.

For the highest concentration of humic acid ($33.4 \text{ mg}_\text{C}\cdot\text{g}^{-1}_{\text{goethite}}$), the amount of LHA immobilised decreases with increasing pH in two steps. At $\text{pH} < 5$ the amount of solid LHA decreases dramatically according to the precipitation curve of LHA. It is most likely that below pH 5 a large part of LHA is precipitated rather than adsorbed at the surface of the goethite. At $\text{pH} > 5$, the amount of removed LHA decreases slightly. It is worth noting that for the two most concentrated systems (16.7 and $33.4 \text{ mg}_\text{C}\cdot\text{g}^{-1}_{\text{goethite}}$) the sorption curves are superimposed above pH 5.3, reflecting the saturation of the goethite surface. The maximum capacity decreases from 19 to $8 \text{ mg}_\text{C}\cdot\text{g}^{-1}_{\text{goethite}}$ as the pH increases from 5 to 10.

The gradual decrease of LHA sorption observed as the pH increases from 5 to 11 can be explained by both electrostatic interactions between the surface and the functional groups of the macromolecule and intramolecular interactions between the functional groups of the macromolecule itself.

For lower pH values, the surface of goethite is positively charged while the LHA is partially

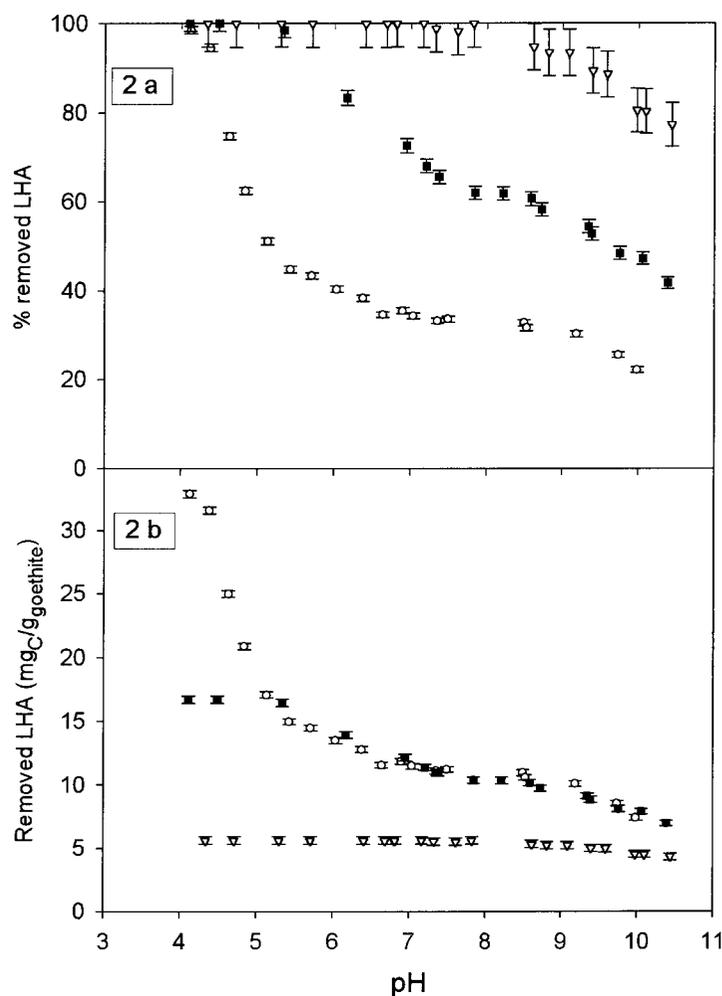


Figure 2. Sorption of LHA on goethite as a function of pH for three different concentrations ($[\text{KNO}_3] = 0.1 \text{ mol}\cdot\text{L}^{-1}$; $[\text{goethite}] = 2 \text{ g}\cdot\text{L}^{-1}$); (V: $[\text{LHA}]_{\text{initial}} (5.6 \text{ mg}_C\cdot\text{g}^{-1}_{\text{goethite}})$; ■: $[\text{LHA}]_{\text{initial}} (16.7 \text{ mg}_C\cdot\text{g}^{-1}_{\text{goethite}})$; O: $[\text{LHA}]_{\text{initial}} (33.4 \text{ mg}_C\cdot\text{g}^{-1}_{\text{goethite}})$).

dissociated. Therefore the sorption of LHA on the goethite is favoured by electrostatic attractions. For pH values higher than the point of zero charge ($\text{pH}_{\text{pzc}} = 7.2$), the goethite surface is negatively charged while the LHA is strongly dissociated. Thus sorption of LHA on goethite is hampered by electrostatic repulsions.

The pH-dependent behaviour as well as the consumption of protons observed when sorbing humic acids on goethite have prompted several authors to explain the sorption by a ligand exchange mechanism where anionic groups of the humic acid replace surface-coordinated H_2O or OH^- groups on the goethite [6, 7, 14, 21a]. Tipping showed that not all of the anionic groups of organic matter are involved in the surface interactions, giving rise to an

excess of negative charges that are expected to repel each other [21a–21b]. It is thus predictable that when increasing the pH, the degree of dissociation of the non-coordinated acidic groups of LHA and therefore the concentration of negative charge at the surface of the mineral will increase. We calculated the number of adsorbed carboxylic and phenolic groups and compared it to the number of surface sites on the goethite. Results are presented in Table II. By considering that all the available surface sites are involved in the exchange, all the carboxylic groups could be complexed with the surface in the most dilute medium while there is clearly an excess of carboxylic functions for the two higher concentrations. These acidic groups in excess will deprotonate and therefore repel each other as the pH

Table II. Content of carboxylic and phenolic groups in the adsorbed layer of LHA at pH 5.3.

$[C]_{\text{initial}}$ ($\text{mg}_C \cdot \text{g}^{-1}_{\text{goethite}}$)	$[C]_{\text{sorbed at pH 5.3}}$ ($\text{mg}_C \cdot \text{g}^{-1}_{\text{goethite}}$)	a) $[\text{COOH}]_{\text{sorbed at pH 5.3}}$ ($\text{mol} \cdot \text{g}^{-1}_{\text{goethite}}$)	b) $[\text{ArOH}]_{\text{sorbed at pH 5.3}}$ ($\text{mol} \cdot \text{g}^{-1}_{\text{goethite}}$)
5.6	c) 5.6	$4.2 \cdot 10^{-5}$	$2.9 \cdot 10^{-5}$
16.7	c) 16.5	$1.24 \cdot 10^{-4}$	$8.6 \cdot 10^{-5}$
33.4	c) 16.0	$1.20 \cdot 10^{-4}$	$8.3 \cdot 10^{-5}$

$[\text{surface sites}] = [\text{SOH}] = 1.8 \text{ sites} \cdot \text{nm}^{-2} \equiv 5.98 \times 10^{-5} \text{ mol} \cdot \text{g}^{-1}_{\text{goethite}}$

a) Calculated from the concentration of carboxylic sites in LHA ($4.2 \text{ mmol} \cdot \text{g}^{-1}_{\text{LHA}}$), the relation between solid LHA and soluble carbon ($0.557 \text{ g}_C \cdot \text{g}^{-1}_{\text{LHA}}$) and measured loss of LHA from solution.

b) Calculated from the concentration of phenolic sites in LHA ($2.9 \text{ mmol} \cdot \text{g}^{-1}_{\text{LHA}}$), the relation between solid LHA and soluble carbon ($0.557 \text{ g}_C \cdot \text{g}^{-1}_{\text{LHA}}$) and measured loss of LHA from solution.

c) Interpolation between experimental points.

increases. This outcome explains well the decrease observed with increasing pH and is in good agreement with the results of Spark et al. who measured the zeta potential of goethite sorbed with humic acid as a function of pH [19]. Between pH 6.5 and pH 10, they found a small and continuous increase of negative charge for the higher concentrations of humic acid.

Due to their polyelectrolyte feature, humic substances are able to take different conformations. In alkali media they adopt a “chain” conformation resulting from electrostatic repulsions between the negative charges of the dissociated functions and give rise to a high proportion of “trains” when sorbed on goethite [5]. In acidic media they adopt a “coil” conformation due to attractive intramolecular

strengths (hydrogen binding) between the different functions. The resulting adsorbed layer is constituted by a high proportion of “loops” and “tails” [5]. The more the humic substance withdraws into itself, the less space it takes on the surface of the goethite. This steric contribution acts in favour of a higher adsorption in acidic media.

3.1.3. Reversibility

Results of a desorption experiment are shown in Figure 3. The superposition of the curves obtained for sorption and desorption indicates that sorption of LHA on goethite is a fully reversible process. Murphy et al. reported a no-detectable desorption of humic acid from kaolinite and hematite but did not give any indication of the pH in the desorption

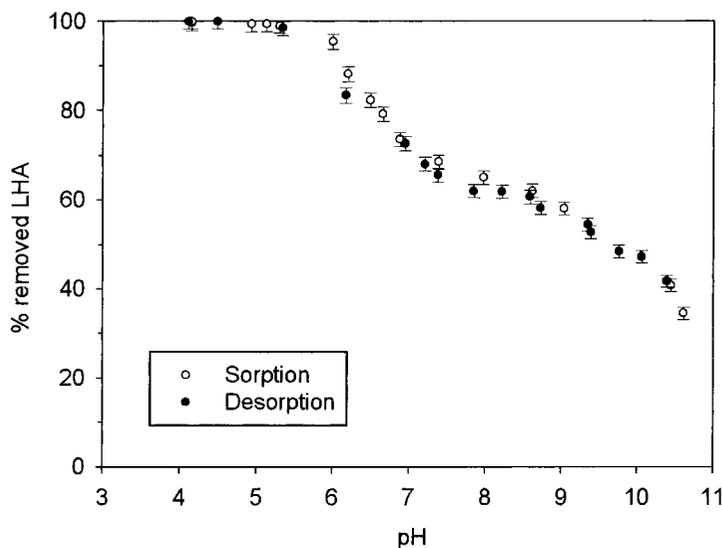


Figure 3. Desorption of LHA from goethite ($[\text{LHA}]_{\text{initial}} = 16.7 \text{ mg}_C \cdot \text{g}^{-1}_{\text{goethite}}$; $[\text{KNO}_3] = 0.1 \text{ mol} \cdot \text{L}^{-1}$; $[\text{goethite}] = 2 \text{ g} \cdot \text{L}^{-1}$).

experiments [12]. Spark et al. found that sorption of coal humic acid on kaolinite and alumina was fully reversible whereas it was not reversible for goethite [19]. However, in order to establish the reversibility of the sorption on goethite, the authors based their conclusion on the fact that the humic substance was not fully desorbed from goethite by pH 11. As it can be seen in Figure 3, LHA (which is also a coal humic acid) is not completely desorbed from the surface at pH 10.5 but the amount remaining on the solid is equal to the amount sorbed at this pH. Special attention should thus be given to the experimental conditions (especially to the pH values)

when assessing the reversibility of a sorbing process. Indeed the use of different experimental procedures may lead to different conclusions.

3.2. Sorption of Co(II), Sr(II), or Se(IV) on goethite in presence of LHA

Sorption experiments have been performed for each ion in systems containing goethite, 0.1 M KNO_3 , and LHA at the three concentrations of 5.6, 16.7 and 33.4 $\text{mg}_C \cdot \text{g}^{-1}_{\text{goethite}}$. Results, are shown in Figure 4 with the fraction of removed ion plotted as

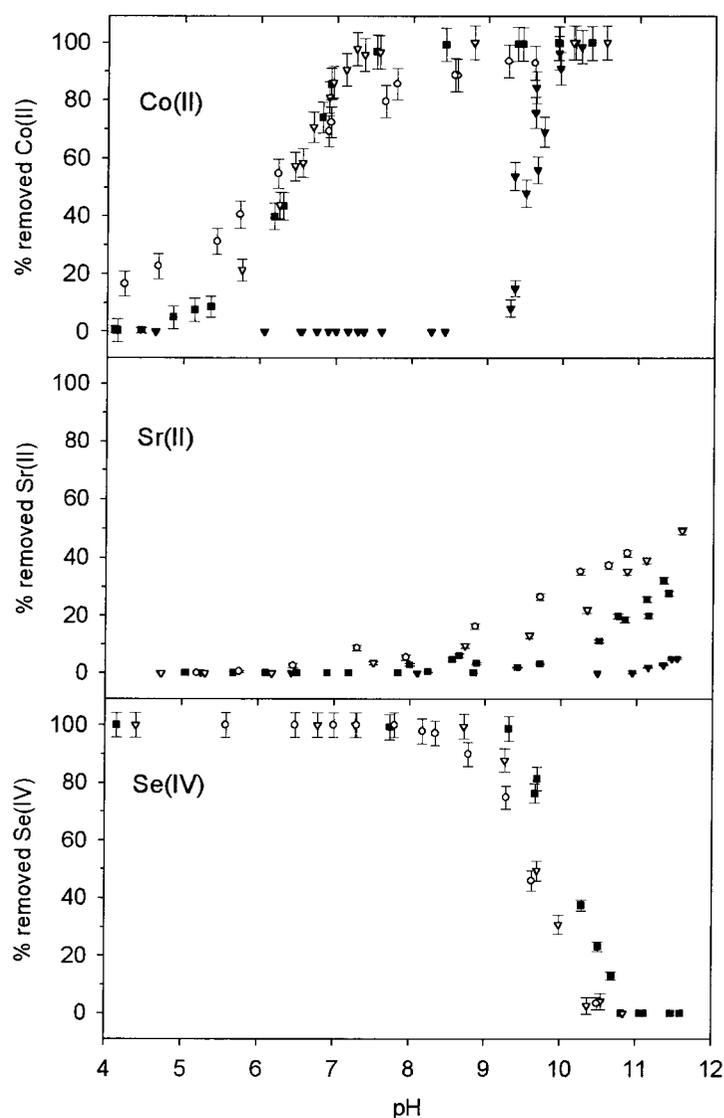


Figure 4. Fraction of sorbed ion (Co(II), Sr(II), or Se(IV)) as a function of pH in presence of three different concentrations of LHA ($[\text{ion}]_{\text{initial}} = 10^{-5} \text{ mol} \cdot \text{L}^{-1}$; $[\text{KNO}_3] = 0.1 \text{ mol} \cdot \text{L}^{-1}$; $[\text{goethite}] = 2 \text{ g} \cdot \text{L}^{-1}$) (▼: precipitation; ■: sorption on goethite without LHA; ▽: sorption on goethite in presence of LHA ($5.6 \text{ mg}_C \cdot \text{g}^{-1}_{\text{goethite}}$); ○: sorption on goethite in presence of LHA ($33.4 \text{ mg}_C \cdot \text{g}^{-1}_{\text{goethite}}$).

a function of pH. For reasons of clearness, results obtained in the presence of the intermediate concentration of LHA ($16.7 \text{ mg}_C \cdot \text{g}^{-1}_{\text{goethite}}$) are not shown. The results for the sorption of the ions on goethite in the absence of LHA and the precipitation of the cations alone are also presented.

3.2.1. Effect of LHA on sorption of Co(II) on goethite

At the considered concentration, Co(II) hydroxide starts to precipitate at pH 9 and is completely precipitated by pH 10. In the presence of goethite without LHA, the sorption of Co(II) begins at pH 5 and is total at pH 7, showing that the precipitation of $\text{Co}(\text{OH})_2$ cannot explain the data for Co(II) sorption on goethite. The strong dependence of sorption on pH is typical of a cationic species with the highest fraction sorbed at high pH [4].

Addition of a low concentration of LHA ($5.6 \text{ mg}_C \cdot \text{g}^{-1}_{\text{goethite}}$) has no effect on the sorption experimental data, which is in favour of a small amount of negative charges on the sorbed LHA. This result tends to show that for this concentration most of the deprotonated groups of LHA are coordinated to the goethite surface.

When higher concentrations are introduced, the presence of LHA increases the Co(II) sorption for pH values below 7 and decreases it for pH values higher than 7. Below pH 7, the results can be interpreted in terms of surface considerations. In the presence of LHA, the surface charge of goethite is reversed and becomes negative thus favouring the sorption of cations [2, 19, 22]. Above pH 7, the soluble LHA forms non-sorbing complexes with Co(II) so that a competition exists for cobalt ions between sorption and complexation by LHA in solution.

The complexation of Co(II) by LHA in solution was demonstrated by comparing the solubility of LHA or Co(II) alone to their respective solubility in the presence of each other (Fig. 5). The presence of LHA prevents the cobalt from precipitating at $\text{pH} > 9$. Moreover, the precipitation of LHA at acidic pH is shifted to lower pH in the presence of Co(II). Zachara et al. estimated by dialysis the binding capacity of a leonardite humic acid towards Co(II) and showed that a significant complexation was occurring above pH 5 [23]. In our study, the decrease in alkali media is much less pronounced at the LHA concentration of $16.7 \text{ mg}_C \cdot \text{g}^{-1}_{\text{goethite}}$

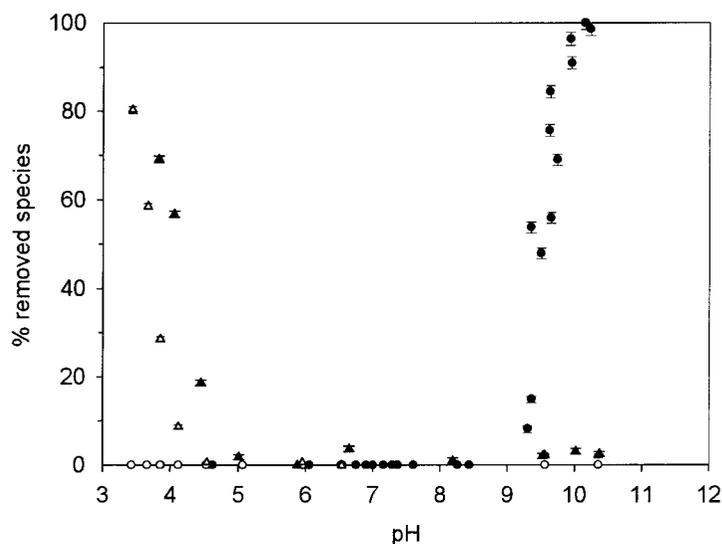


Figure 5. Solubility of LHA and Co(II) ($[\text{LHA}]_{\text{initial}} = 66.8 \text{ mg}_C \cdot \text{L}^{-1}$; $[\text{Co}(\text{II})]_{\text{initial}} = 10^{-5} \text{ mol} \cdot \text{L}^{-1}$; $[\text{KNO}_3] = 0.1 \text{ mol} \cdot \text{L}^{-1}$ (circles: % Co(II), triangles: % LHA; filled symbols: Co(II) and LHA shaken together; hollow symbols: LHA or Co(II) precipitated alone).

(results not shown here) when compared to the highest concentration, which is due to the smaller amount of humic acid in solution at this concentration.

3.2.2. Effect of LHA on sorption of Sr(II) on goethite

In absence of goethite, Sr(II) is completely soluble up to pH 10 and is only slightly precipitated above this pH value (5% at pH 10.5) (Fig. 4). The sorption of Sr(II) on goethite begins at pH 9 and reaches 30% at pH 10.5 in absence of LHA, which shows again that the precipitation of Sr(II) is not responsible for the results observed. The sorption “pH edges” obtained with Sr are less pH dependent than for Co. Similar gradual edges have also been obtained by Kinniburgh and Jackson when sorbing Ca(II) on hydrous ferric oxide [10]. The fact that sorption occurs at a higher pH for Sr(II) than for Co(II) with an identical sorbate/sorbent ratio demonstrates the weaker affinity of the former for goethite. Cations on the left side of the periodic table are known to form weaker surface complexes than those on the right. Several studies reported a good correlation between the surface complexation constants and the constant of first hydrolysis for different metals [1, 4]. Since constants of $10^{0.82}$ and $10^{4.3}$ [11] have been measured at $\mu = 0$ and $T = 25$ °C for the first hydrolysis of Sr^{2+} and Co^{2+} , respectively, the sorption of Sr(II) on goethite is expected to be weaker than the Co(II) one.

Adding LHA to the systems containing Sr(II) and goethite enhances significantly the strontium sorption with a maximum of 50% of sorbed Sr being reached at pH 10.5, when only 30% was attained under the same conditions without LHA (Fig. 4). If LHA was acting in a similar way for both Co(II) and Sr(II), at the pH at which sorption of Sr(II) occurs, the complexation with soluble LHA should be predominant and one should observe a decreasing of the sorption rather than its enhancement. Moreover, addition of 16.7 (not shown here) and $33.4 \text{ mg}_C \cdot \text{g}^{-1}_{\text{goethite}}$ led to comparable sorption curves thus reinforcing the negligible effect of soluble LHA. The results observed show that, conversely to Co, complexation of Sr(II) by soluble LHA is too weak to affect unfavourably the

sorption process. This outcome is in agreement with the stability constants given in the literature for the monodentate Sr/humic acid and Co/humic acid complexes ($\log\beta_{\text{Sr}} = 3.21$, $T = 25$ °C, pH 5, [16]; $\log\beta_{\text{Co}} = 4.1$, $T = 25$ °C, pH 5, [20]), which confirm the weaker binding of Sr by soluble humic acid.

Addition of the lowest concentration of LHA enhances Sr(II) sorption whereas it had no effect on Co(II) sorption. At the pH values at which Co(II) retention is observed (pH 5–6), only part of the carboxylic functions of LHA are expected to be dissociated so that the adsorbed LHA should present hardly any excess of negative charges (see Tab. I). On the opposite, at the pH involved for Sr(II) sorption (pH 9–10) significant dissociation of carboxylic as well as phenolic functional groups should occur and lead to an excess of negative charge on the goethite surface. Sr sorption can thus be increased by electrostatic interactions even at lower concentrations of LHA.

3.2.3. Effect of LHA on sorption of Se(IV) on goethite

Analysis of selenium by coupling hydride generation to atomic absorption allows Se(IV) to be differentiated from Se(VI) [3]. The samples were analysed both with and without a prereduction step conducted in 4.7 M HCl at 80 °C for 50 min. No Se(VI) was detected when the prereduction step was applied showing that there was no oxidation of Se(IV) to Se(VI) during the experiments.

In the absence of LHA, the sorption of Se(IV) on goethite is total at $\text{pH} < 9$ and decreases to reach zero at pH 11, in accord with the typical pH dependence expected for an anionic species [4]. Adding LHA decreases slightly the sorption of Se(IV) on goethite (Fig. 4) but the shift of the pH sorption edge towards lower values is independent of the concentration of LHA introduced.

It is generally held that sorption of the selenite ion (SeO_3^{2-}) at oxide surfaces involves ligand exchange with the hydroxide surface groups because of the weak influence of ionic strength on sorption [4, 9, 15]. The formation of strongly bonded inner-sphere complexes between selenite ion and goethite has also been evidenced by X-ray

Absorption Fine Structure (EXAFS) [8]. Since the concentration of KNO_3 in these systems was much larger than the LHA one, sorption of selenite should remain unaffected by the small introduction of LHA if only electrostatic interactions were to be considered between humate and goethite. The small but significant effect observed suggests that the humate ion forms inner-sphere coordination complexes with oxide surface oxygen. The decrease of SeO_3^{2-} sorption in the presence of LHA is then due to the competition between humate and selenite ions for the surface sites of the goethite. A similar competition has been shown by Tipping with inorganic phosphate and silicate which influence the sorption of humic acid on goethite [21a].

3.2.4. Effect of Co(II), Sr(II), and Se(IV) on the sorption of LHA on goethite

As pointed out earlier, the sorption of ions onto goethite is affected by the presence of LHA. In order to evaluate the effect of Co(II), Sr(II) and Se(IV) on the sorption of LHA on goethite, the amount of soluble LHA was measured in each ternary sorption experiment (ion/LHA/goethite) and compared to the sorption of LHA on goethite in the binary system.

The presence of selenite at the initial concentration of $10^{-5} \text{ mol}\cdot\text{L}^{-1}$ had no effect on the sorption of LHA at the considered concentrations. Indeed, the competitive effect of selenite ions on the sorption of LHA is negligible due to the much lower concentration of selenite ions.

As for Sr(II) and Co(II), two different trends were observed according to the concentration of LHA. For the two higher concentrations, the effect of the cation is negligible and the amount of sorbed LHA in the presence of Sr or Co is identical to the one measured without cation. For the lowest concentration ($5.6 \text{ mg}_\text{C}\cdot\text{g}^{-1}_{\text{goethite}}$), the sorption of organic matter is slightly inferior in the presence of Sr or Co. This outcome gives information on the sorption process of LHA. Indeed, if the immobilisation of LHA at the surface of the goethite was due only to electrostatic interactions, the negative surface should fix more Co-complexed-LHA, which is less negative than the free humic acid. In addition, less repulsions would take place between the sorbed

molecules so that a higher amount of LHA should be fixed. The slight decrease observed for the small addition of LHA thus demonstrates that the ligand exchange plays a major role when considering interactions of iron oxides with humic substances.

4. Conclusion

Leonardite humic acid sorbs appreciably to the surface of goethite with a maximum capacity of $19 \text{ mg}_\text{C}\cdot\text{g}^{-1}_{\text{goethite}}$. The sorbing process is fully reversible and the effect of Co(II) and Sr(II) on the sorption of LHA is in favour of a ligand exchange. The sorption of Co(II), Sr(II) and Se(IV) on goethite is significantly influenced by the presence of LHA in the system. If humic acid and selenite ions are simultaneously present in a medium, a competition occurs between both anions, which implies a lower sorption of selenite and thus a higher mobility of the ion in the soil. In contrast, the presence of humic acid enhances the sorption of Sr(II) on goethite by making the surface of the mineral more negative. As for Co(II), the effect of humic acid is more complex since at acidic pH, metal sorption is increased probably by electrostatic interactions, while at alkaline pH the sorption is decreased by competing with Co complexation by soluble humate.

The set of data presented here allowed a good qualitative understanding to be reached of the effect of humic acid on the sorption of cations and anions on goethite. A modelling of these results is currently in progress in order to obtain the different complexation constants and to verify whether the additivity theory can be applied to extrapolate the results of the ternary systems from the binary systems data.

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