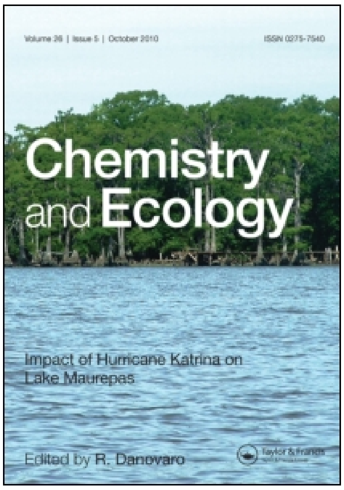
This article was downloaded by:
On: *15 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Chemistry and Ecology

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455114

Experimental study of chromium adsorption on minerals in the presence of phthalic and humic acids

L. Bois[a]; A. Ribes[a]; M. Petit-Ramel[b]; M. F. Grenier-Loustalot[a]
[a] Service Central d'Analyse, C.N.R.S., Echangeur de Solaize, BP 22, Vernaison, France [b] Laboratoire des Sciences et Stratégies Analytiques, CNRS FRE 2394, Université Claude Bernard, Villeurbanne, France

Online publication date: 12 May 2010

To cite this Article Bois, L. , Ribes, A. , Petit-Ramel, M. and Grenier-Loustalot, M. F.(2003) 'Experimental study of chromium adsorption on minerals in the presence of phthalic and humic acids', Chemistry and Ecology, 19: 4, 263 — 273
To link to this Article: DOI: 10.1080/0275754031000154844
URL: http://dx.doi.org/10.1080/0275754031000154844

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Chemistry and Ecology, Vol. 19(4), August 2003, pp. 263–273

EXPERIMENTAL STUDY OF CHROMIUM ADSORPTION ON MINERALS IN THE PRESENCE OF PHTHALIC AND HUMIC ACIDS

L. BOIS[a,]*, A. RIBES[a], M. PETIT-RAMEL[b], M. F. GRENIER-LOUSTALOT[a]

[a]*Service Central d'Analyse, C.N.R.S., Echangeur de Solaize, BP 22, 69390 Vernaison, France;*
[b]*Laboratoire des Sciences et Stratégies Analytiques, CNRS FRE 2394,*
Université Claude Bernard, 69616 Villeurbanne, France

(Received 29 January 2003; In final form 15 April 2003)

The effect of phthalic acid (benzene 1,2 dicarboxylic acid), a surrogate compound for natural organic matter, and of humic acid, on the adsorption of chromium to the surface of minerals was observed. In ternary systems involving phthalic acid, chromium(III) adsorption decreases on clays, probably because of aqueous Cr(III)-phthalate complexation, preventing ionic-exchange. Phthalic acid was also found to reduce chromium(VI) adsorption onto alumina, because of a competitive effect. In ternary systems involving humic acid, Cr(III) adsorption is increased in the low pH range because of the formation of surface ternary complex S-L-Cr(III) and is decreased in the high pH range because of aqueous Cr(III)-humate complexation.

Keywords: Chromium; Sorption; Natural organic matter; Ternary surface complexation

1 INTRODUCTION

Mobility of heavy metals in soils is governed by different parameters such as pH, the content of clay and organic matter (Schindler, 1990; Stumm, 1992). The adsorption of metal ions at the oxide/water interface can be significantly modified by organic substances present in solution and forming complexes with metal ions (Boily and Fein, 1996). The co-occurrence of dissolved metals and organic compounds is widespread in both natural waters and in contaminated groundwaters. Aqueous organic ligands can either promote or inhibit metal adsorption on mineral surfaces (Boily and Fein, 1996).

As a result of its widespread industrial use (metal finishing, corrosion control, leather tanning, textile dyeing, wood preserving . . .), chromium has led to serious water and soil contamination (Wittbrodt and Palmer, 1995). Chromium occurs in two major oxidation states, Cr(III) and Cr(VI). Hexavalent Cr(VI) is a toxic soluble anion (CrO_4^{2-}). Trivalent chromium is a much less toxic cation (Cr^{3+}) that has a strong affinity for particles surfaces (Peterson *et al.* 1997). For Cr(VI), tetrahedral oxo compounds, CrO_4^{2-} is the major species at pH higher than 6.5 and $HCrO_4^-$ is the major species at pH lower than 6.5. In the case

---

*Corresponding author. Laboratoire des Multimatériaux et Interfaces, Bat Berthollet, 43 Bd du 11 novembre 1918, 69622, Villeurbanne, France; E-mail: laurence.bois@univ-lyon1.fr

ISSN 0275-7540 print; ISSN 1029-0370 online
DOI: 10.1080/0275754031000154844

of Cr(III), octahedral compounds are found and the main species are $[Cr(H_2O)_6]^{3+}$, $[Cr(H_2O)_5(OH)]^{2+}$, $[Cr(H_2O)_4(OH)_2]^{+}$, $[Cr(H_2O)_3(OH)_3]^{(0)}$, $[Cr(H_2O)_2(OH)_4]^{-}$ at pH about 3, 5, 6 and 10 respectively (Deng et al., 1999).

Goethite is a common constituent of groundwater systems and is often present as coatings on mineral surface. Silica, alumina and anatase were also chosen as models of minerals. Montmorillonite was chosen to represent a 2:1 layer clay mineral carrying a high permanent negative charge (Strawn and Sparks, 1999). Montmorillonite is a dioctahedral smectite mineral. Substitution of Fe^{2+} and Mg^{2+} for Al^{3+} in the octahedral layer creates a positive charge deficit, giving the overall structure a net negative charge. The OH and O sites on the broken edges of montmorillonite hydrolyze and form functional groups which are the source of the pH dependent charge. The gibbsite sheets are not available for acid-base reactions (Kraepiel *et al.*, 1998). Therefore, cations can sorb by either electrostatic attraction on the basal plane or formation of covalent bonds with the functional groups at the broken edge. Clay minerals such as montmorillonite can form both inner sphere and outer sphere complexes with cations (Bradbury and Baeyens, 1999).

Kaolinite, $Si_2O_3Al_2O_6H_4$, a 1:1 layer type with only poor isomorphic substitution, is nearly uncharged and includes tetrahedral silica sheet bonded to an octahedral alumina sheet. Successive 1:1 layers are held by hydrogen bonding. The silica sheet has a small negative permanent charge because of isomorphous substitution between Si^{4+} by Al^{3+}. The alumina face and the broken edges have surface hydroxyl group, creating a pH dependent variable charge. Therefore, adsorption of cations occurs via an ionic-exchange mechanism in the lower pH range and then via an inner-sphere coordination mechanism (Ikhsan *et al.*, 1999; Angove *et al.*, 1998). The main difference between montmorillonite and kaolinite is the much higher cation exchange capacity for the montmorillonite (870 meq/kg) compared to the kaolinite (between 20 and 100 meq/kg).

Organic acids with low molecular weight are common in soil solution. Acetic, fumaric, lactic, malonic, oxalic, phthalic acids were detected in unpolluted stream waters (Deng and Stone, 1996). Organic compounds readily identifiable represent only a small portion of the total organic carbon contained in most environmental media. For this reason, the contribution of humic substances must also be evaluated.

Humic substances is a very complex organic material possessing various functional groups (carboxylic, amino, phenolic groups, groups involving sulfur atoms) and moieties (aliphatic chains and aromatic rings) which characterizes its composition and properties (Evanko and Dzombak, 1999; Marx and Heumann, 1999; Boily and Fein, 2000). They can significantly alter the characteristics of mineral surfaces. Organic acids sorbed onto mineral particles produce a net negative charge on the surface.

The purpose of this study is to determine the influence of phthalic acid (benzene 1,2 dicarboxylic acid) and humic acid on the Cr(III) and Cr(VI) adsorption on representative surface minerals.

2 EXPERIMENTAL SECTION

2.1 Materials

Amorphous silica with specific surface area of 360 m^2/g was obtained from SdS. Alumina, Al_2O_3 (acid) with a specific surface area 130 m^2/g (SdS, Peypin, France), anatase, TiO_2 (Hombikat) with a specific surface area of 300 m^2/g, goethite, FeOOH with a specific surface area of 200 m^2/g, and kaolinite with a specific surface area of 15 m^2/g were obtained from Fluka. Montmorillonite of Wyoming (SWy-2) with specific surface area of 30 m^2/g was

TABLE I Characterization of Oxides and Clay Minerals.

Minerals	*Surface area* m^2/g	*PZNC (Stumm, 1992)*
Silica	360	2
Alumina	130	9.1
Anatase	300	6.2
Goethite	200	7.3
Kaolinite	15	4.6
Montmorillonite	30	2.5

purchased from the Source Clay Mineral Repository, Columbia, Missouri. Point of zero charge and BET surface area of the minerals are listed (Tab. I). Chromium nitrate, potassium dichromate and phthalic acid (99%) were obtained from Fluka. Humic acid stock solutions were made from a commercial Na-humic salt (Aldrich Chemicals) which allows the preparation of concentrated solutions.

2.2 Adsorption

The adsorption of chromium onto minerals in the presence of phthalic and humic acids was studied as a function of pH. Mineral suspension with 1 g/L of 0.05 M $NaNO_3$ was prepared. A fixed amount of mineral (30 mg) was weighed into a 50 mL tube. Organic compound (phthalic and humic acids) and sodium nitrate solutions were added to a total volume of 30 mL and then solutions chromium were added (using a 10^{-2} mol L^{-1} concentration solution). pH was adjusted by adding small volumes of NaOH or HNO_3. The pH varied from 2 to 9. Considering the complexity of the chemical equilibriums involved, the use of a buffer to stabilize the pH value would have been preferable. The reaction bottles were then placed in a shaker at 30 rpm for 24 h. Unless otherwise stated, reaction suspensions contained Cr(III) 10^{-4} mol L^{-1} and Cr(VI) 2×10^{-4} mol L^{-1}, $NaNO_3$ 0.05 mol L^{-1}, phthalic acid (10^{-3} mol L^{-1}, 2×10^{-3} mol L^{-1}) and humic acid (50 and 100 mg/L). Then the mineral was separated by centrifugation (3000 rpm, 10 min). The concentrations of metal in the supernatants solutions were measured, after a 0.45 μm filtration, with an Inductively Coupled-Atomic Emission Spectrometer (ICP-AES, MAXIM III, Fisons), using emission lines at 205.552 nm and 267.716 nm. Minerals shaken in water releases amount of major elements which can produce interference during the ICP-AES measurement. For this reason, two emission lines of Cr were used in order to detect any interference.

3 RESULTS AND DISCUSSION

3.1 Binary Systems: Metal/Mineral

Cr(III) Sorption: The sorption of Cr(III) 10^{-4} mol L^{-1} versus pH on merals is represented on the Figure 1. In the case of silica and goethite, adsorption edge is in the pH range 5–6. For anatase, adsorption edge is at pH 2 and for alumina at pH 4. On silica and alumina, no change in the adsorption with the chromium concentration was noted. On goethite, a Cr(III) adsorption increase was observed in the lower pH range, when chromium concentration was decreased to 10^{-5} mol L^{-1}.

The sorption of Cr(III) 10^{-4} mol L^{-1} versus pH on clays shows an adsorption edge in the pH range 5–6. In the case of the montmorillonite, the adsorption is very high (90%) in the low pH range, probably because of an outer-sphere adsorption mechanism. While for

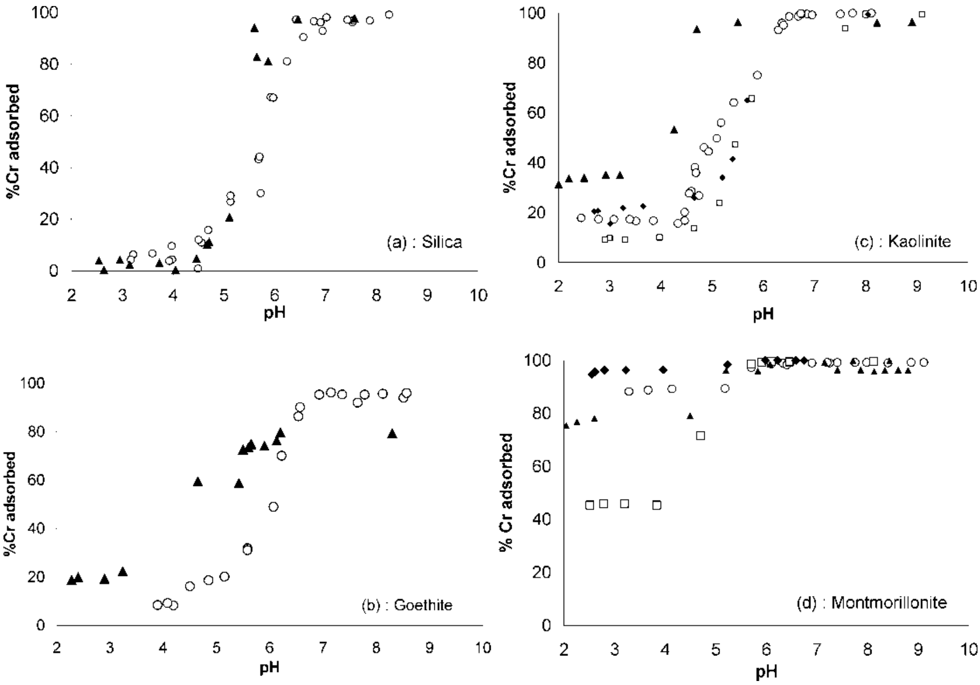


FIGURE 1 Adsorption edge for Cr(III) on minerals (a) silica, (b) goethite, (c) kaolinite, (d) montmorillonite. $I = 0.05\,\text{M}$, $[\text{Cr(III)}] = 10^{-4}\,\text{mol}\,\text{L}^{-1}$ (○); $I = 0.05\,\text{M}$, $[\text{Cr(III)}] = 10^{-5}\,\text{mol}\,\text{L}^{-1}$ (▲); $I = 0.01\,\text{M}$, $[\text{Cr(III)}] = 10^{-4}\,\text{mol}\,\text{L}^{-1}$ (◆); $I = 0.1\,\text{M}$, $[\text{Cr(III)}] = 10^{-4}\,\text{mol}\,\text{L}^{-1}$ (□).

kaolinite, Cr(III) adsorption in the low pH range is about 20%. On kaolinite, a Cr(III) adsorption increase was also observed, when chromium concentration was decreased to $10^{-5}\,\text{mol}\,\text{L}^{-1}$, as noted for goethite. On montmorillonite, a weak Cr(III) adsorption decrease was noted, when the chromium concentration is decreasing to $10^{-5}\,\text{mol}\,\text{L}^{-1}$.

At $I = 0.001\,\text{M}$, the montmorillonite removed nearly all the chromium from solution, regardless of pH. At $I = 0.1\,\text{M}$, uptake of metal was strongly pH-dependent; only about 40% of chromium is removed from the solution in the low pH range, whereas 100% of metal is removed from the solution in the high pH range. For montmorillonite, chromium adsorption decreases as ionic strength increases, which confirms an ionic exchange mechanism. There is also a slight dependency in the case of kaolinite. At $I = 0.1\,\text{M}$, only about 10% of chromium is removed from the solution in the low pH range. As pH and ionic strength increase, inner-sphere adsorption becomes more important.

Cr(III) adsorption has been investigated for a variety of soils minerals and soils (Koppelman *et al.*, 1980). On silica and alumina, the percentage uptake increases from about 0 to 100% over a narrow pH range (Csoban and Joo, 1999; Fitts *et al.*, 2000; Fendorf *et al.*, 1994a Fendorf and Sparks, 1994b; Charlet and Manceau, 1992). It is associated to the formation of Cr(III) hydrolysis products which appear at a pH as low as 4.

Adsorption of divalent transition metals on kaolinite, at low pH, occurs through ion exchange on the permanent negatively charged siloxanol sites (Spark *et al.*, 1995; Ikshan *et al.*, 1999; Angove *et al.*, 1998). Adsorption decreased as ionic strength is increased. Then adsorption occurs on the variable-charged aluminol sites on the edges and alumina faces of the kaolinite crystals. The same mechanism is probably observed in the case of Cr(III) adsorption on kaolinite.

Sorption edges of divalent cations (Ni, Zn, Mn) on montmorillonite suggested that two mechanisms were also involved: the first one, where the sorption was pH-independent is a cation-exchange mechanism and the second one, with a strong pH dependency is interpreted in terms of surface complexation reactions (Bradbury and Baeyens, 1997). Sorption edge of Cr(III) on montmorillonite is very similar to that of others divalent cations observed.

The Cr(III) adsorption decrease on kaolinite and montmorillonite as I is increased confirms the outer-sphere mechanism in the lower pH range.

Cr(VI) Sorption: Adsorption of chromate solutions $2 \times 10^{-4}\,\mathrm{mol\,L^{-1}}$ on oxides is represented on the Figure 2. Almost no adsorption could be observed in the case of silica, goethite and the two clays (not represented). A very strong adsorption was observed in the case of alumina and anatase. Cr(VI) adsorption on alumina exhibited a maximum at pH 6. Cr(VI) adsorption on anatase decreases as the pH increases as expected for an anionic adsorption process. Adsorption strongly increases when the chromate concentration is decreased to $2 \times 10^{-5}\,\mathrm{mol\,L^{-1}}$.

Like other oxyanions, CrO_4^{2-} adsorption is pH dependent with greater adsorption in the lower pH range (Aide and Cummings, 1997; Zachara *et al.*, 1987; Zachara *et al.*, 1988; Zachara *et al.*, 1989). These features were observed in our study, for anatase and for alumina.

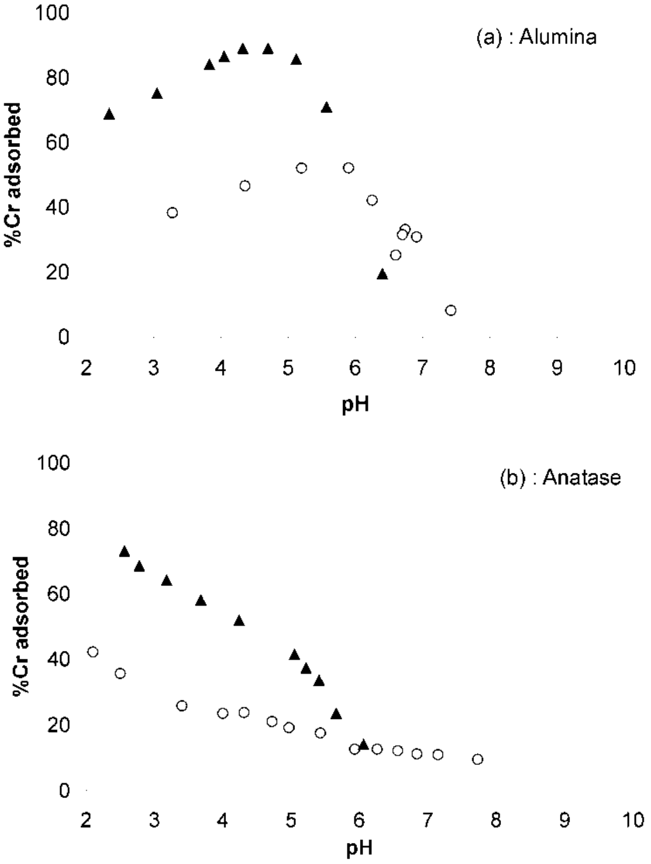


FIGURE 2 Adsorption edge for Cr(VI) on oxides $I = 0.05\,\mathrm{M}$, (a) alumina, (b) anatase. $[\mathrm{Cr(VI)}] = 2 \times 10^{-4}\,\mathrm{mol\,L^{-1}}$ (○) and $2 \times 10^{-5}\,\mathrm{mol\,L^{-1}}$ (▲).

At low solutions concentrations ($5 \times 10^{-7}\,\mathrm{mol\,L^{-1}}$), chromate adsorption on goethite increases sharply from 0 to 100% as pH decreased from 10 to 7 (Ainsworth *et al.*, 1989). Fractional adsorption decreased as the chromate concentration is increased at $5 \times 10^{-5}\,\mathrm{mol\,L^{-1}}$, as noted in our study. Chromate adsorption was not evidenced on silica, goethite and on the two clays, probably because of the high chromate concentration used (Buerge and Hug, 1999). Ward and Bassett (1990) studied the adsorption of Cr(VI) on kaolinite and illite. Adsorption was observed in the lower pH range for chromate concentration as low as $2 \times 10^{-6}\,\mathrm{mol\,L^{-1}}$. Reduction of Cr(VI) by Fe(II) containing minerals have been extensively studied; reduction of Cr(VI) was found not to be effective on montmorillonite (Brigatti *et al.*, 2000; Eary and Rai, 1998).

3.2 Ternary Systems: Metal/Mineral/Phthalic Acid

Cr(III) Sorption: The adsorption of Cr(III) ($10^{-4}\,\mathrm{mol\,L^{-1}}$) on oxides with phthalic acid ($10^{-3}\,\mathrm{mol\,L^{-1}}$ and $2 \times 10^{-3}\,\mathrm{mol\,L^{-1}}$) is almost unchanged. The Cr(III) adsorption ($10^{-4}\,\mathrm{mol\,L^{-1}}$) on clays with phthalic acid ($10^{-3}\,\mathrm{mol\,L^{-1}}$ and $2 \times 10^{-3}\,\mathrm{mol\,L^{-1}}$) is represented on the Figure 3. In the kaolinite system, there is a high shift of the adsorption

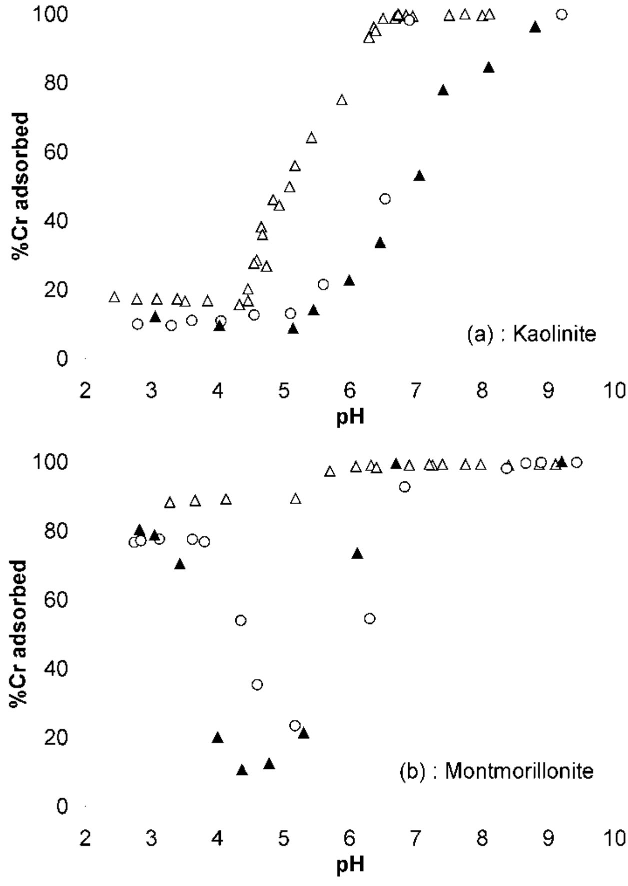


FIGURE 3 Adsorption edge for Cr(III) ([Cr(III)] = $10^{-4}\,\mathrm{mol\,L^{-1}}$) on clays in the absence (△) and in the presence of phthalic acid: [AP] = $10^{-3}\,\mathrm{mol\,L^{-1}}$ (○) and $2 \times 10^{-3}\,\mathrm{mol\,L^{-1}}$ (▲), (a) kaolinite, (b) montmorillonite.

edge. As phthalic acid concentration increases, chromium partition is shifted to the solution phase. In montmorillonite system, there is a different behavior since the decrease of chromium(III) adsorption occurs in the pH range 4–6. In the more basic and the more acidic regions, no change in the chromium adsorption was observed.

The Cr(III) adsorption edge shift at higher pH, observed on kaolinite, likely results from strong complexation between chromium and phthalate ion which acts as a chelating ligand and stabilizes metal cation in solution. The adsorption decrease may be explained by complexation between phthalate and chromium (Barbier *et al.*, 2000; Benyahya and Garniew, 1999; Puls *et al.*, 1991).

On montmorillonite, the decrease of the adsorption in the middle range pH may be explained by the formation of Cr(III)-phthalate species as $CrPht_2^-$, unadsorbed on the montmorillonite. In the higher pH range (pH > 6), these species disappeared as $Cr(OH)_3$ become the predominant chromium species, which could not form any complex with phthalate ligand. The decrease of Cr(III) adsorption is very high in the case of the two clays, probably because ionic-exchange mechanism may be prevented by the formation of anionic chromium species.

Cr(VI) Sorption: The adsorption of (Cr(VI) $2 \times 10^{-5}\,\mathrm{mol\,L^{-1}}$) on alumina and anatase, with phthalic acid is represented on the Figure 4. An important decrease of the Cr(VI) sorption onto alumina is noted in the presence of phthalic acid. The same effect is observed on anatase.

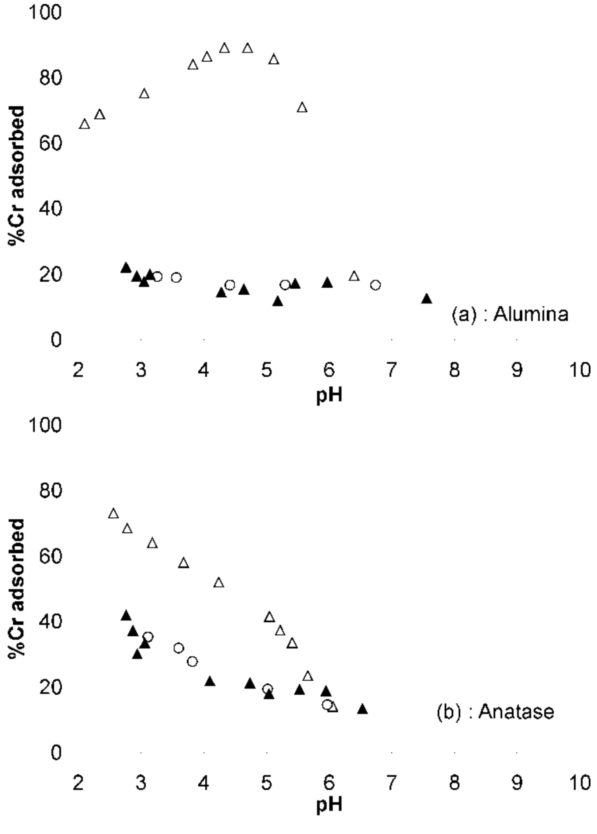


FIGURE 4 Adsorption edge for Cr(VI) ([Cr(VI)] = $2 \times 10^{-5}\,\mathrm{mol\,L^{-1}}$) on oxides in the absence (△) and in the presence of phthalic acid: [AP] = $10^{-3}\,\mathrm{mol\,L^{-1}}$ (○) and $2 \times 10^{-3}\,\mathrm{mol\,L^{-1}}$ (▲), (a) alumina, (b) anatase.

Phthalate adsorption on alumina and anatase may explain that less numerous sites are available for chromate adsorption. A competitive effect between chromate and phthalate adsorption certainly explain the lower adsorption of chromate.

The organic acid adsorption was found to enhance the mobility of chromate in acidic environment (Mesuere and Fish, 1992): oxalate diminished the adsorption of chromate most effectively at low pH. A significant reduction of chromate adsorption edge on goethite to lower pH values in the presence of CO_2 was noted and explained via site competition (Villalobos *et al.*, 2001). A reverse effect has also been observed for numerous low molecular weight organic compounds, which were found to reduce Cr(VI) and an appreciable catalytic effect of goethite and aluminum oxide was observed (Deng and Stone, 1996). Therefore, in this study, organic acids, such as phthalic acid, may contribute to the lower adsorption of inorganic contaminants such as chromate.

3.3 Ternary Systems: Metal/Mineral/Humic Acid

Cr(III) Sorption: Adsorption of chromium(III) with humic acid (50 and 100 mg/L) on clays is represented on the Figure 5. In the case of kaolinite, a shift of the Cr(III) adsorption edge is also observed and then an high adsorption reduction, as noted for silica, alumina and goethite

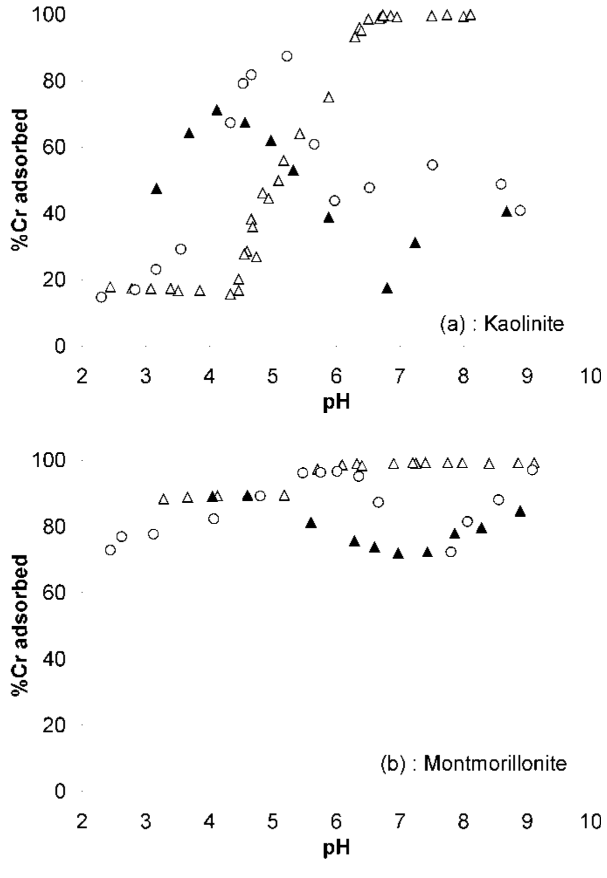


FIGURE 5 Adsorption edge for Cr(III) ([Cr(III)] = 10^{-4} mol L^{-1}) on clays in the absence (△) and in the presence of humic acid: [HA] = 50 mg/L (○) and 100 mg/L (▲), (a) kaolinite, (b) montmorillonite.

(not shown). Onto montmorillonite, a small decrease of chromium(III) adsorption is observed between pH 6 and 8. On anatase, no change in the Cr(III) adsorption process was noted.

Humate ions enhance Cr(III) adsorption in the low pH range, except in the case of anatase and montmorillonite where the adsorption was already very high. This enhancement may be explained by the formation of a surface ternary complex of the type SOH_2^+-L^{z-}-M^{n+}. This mechanism of metal-organic co-adsorption has been suggested for in a number of studies involving low molecular weight organic acids (Boily and Fein, 1996; Boily and Fein, 2000; Ali and Dzombak, 1996) or fulvic acid and humic acid (Schroth and Sposito, 1998; Takahashi *et al.*, 1999).

At high pH ($pH > 6$), chromium(III) adsorption is decreased. This is the result of aqueous Cr(III)-humate complexation which competes with Cr surface complexes and the ternary surface complexes. This was observed in the case of Pb^{2+}/aluminum hydroxide/humic acid (Boily *et al.*, 2000) and in the case of Cd^{2+}/corundum/citrate or polyacrylic acid (Boily *et al.*, 1996; Floroiu and Fein, 2001).

Cr(VI) Sorption: On alumina and anatase, almost no change in the chromate adsorption was induced by the presence of humic acid (not represented).

4 CONCLUSIONS

The aim of this study is to improve the understanding of adsorption properties within a multicomponent system which contains a complexing agent, a solid phase and a metal.

Phthalic acid was found to significantly affect adsorption of chromium(III) on minerals surfaces. It appears that Cr(III)-phthalate complexation reduces chromium(III) adsorption on kaolinite and montmorillonite. The impact of phthalate ion can modify the mobility of metals in an aqueous environment. At pH below 6, there is an increase in metal-phthalate complexes in solution, which suggests a greater mobilization of metal as metal-organic complexes.

Phthalic acid was also found to affect chromate adsorption on minerals. Chromate adsorption was decreased by the presence of phthalic acid, probably because of a competitive effect in the adsorption.

Cr(III) adsorption may be strongly influenced by the presence of large concentrations of humate. At low pH, Cr(III) adsorption may be enhanced through the formation of a Cr-humate ternary complex. At high pH, Cr-humate complexation competes with Cr surface complexes and may significantly solubilises Cr(III).

Acknowledgement

We acknowledge F. Barbier (SCA, Vernaison) for helpful discussions.

References

Aide, M. T. and Cummings, M. F. (1997). The Influence of pH and phosphorus on the adsorption of Cr(VI) on boehmite. *Soil Science*, **162**(8), 599.

Ainsworth, C. C., Girvin, D. C., Zachara, J. M. and Smith, S. C. (1989). Chromate adsorption on goethite : Effects of aluminum substitution. *Soil Science Society of America Journal*, **53**, 411–418.

Ali, M. A. and Dzombak. (1996).D.A. Effects of simple organic acids on sorption of Cu^{2+} and Ca^{2+} on goethite. *Geochimica and Cosmochima Acta*, **60**, 291–304.

Angove, M. J., Johnson, B. B. and Wells, J. D. (1998). The influence of temperature on the adsorption of Cd(II) and Co(II) on kaolinite. *Journal of Colloids and Interface Science*, **204**, 93–103.

Barbier, F., Duc, G. and Petit-Ramel, M. (2000). Adsorption of lead and cadmium ions from solution to the montmorillonite / water interface. *Colloids and Surfaces*, **166**, 153–159.

Benyahya, L. and Garnier, M. (1999). Effect of salicylic acid upon trace-metal sorption (CdII, ZnII, CoII and MnII) onto alumina, silica and kaolinite as a function of pH. *Environmental Science and Technology*, **33**, 1398–1407.

Boily, J.-F. and Fein, J. B. (1996). Experimental study of cadmium–citrate adsorption co-adsorption onto a-Al_2O_3. *Geochimica and Cosmochima Acta*, **60**, 2929–2938.

Boily, J.-F. and Fein, J. B. (1998). Adsorption of Pb(II) and benzenecarboxylates onto corundum. *Chemical Geology*, **148**, 157–175.

Boily, J.-F. and Fein, J. B. (2000). Proton binding to humic acids and sorption of Pb(II) and humic acid to the corundum surface. *Chemical Geology*, **168**, 239–253.

Bradbury, M. H. and Baeyens, B. (1997). A mechanistic description of Ni and Zn sorption on Na-montmorillonite. *Journal of Contaminant Hydrology*, **27**, 199–222.

Bradbury, M. H. and Baeyens, B. (1999). Modelling the sorption of Zn and Ni on Ca-montmorillonite. *Geochimica and Cosmochimica Acta*, **63**, 325–336.

Brigatti, M. F., Franchini, G. and Lugli, C. (2000). Interaction between aqueous chromium solutions and layer silicates. *Applied Geochemistry*, **15**, 1307–1316.

Buerge, I. J. and Hug, S. J. (1999). Influence of Mineral surfaces on chromium(VI) reduction by iron(II)., *Environmental Science Technology*, **33**, 4285–4291.

Charlet, L. and Manceau, A. (1992). X-ray absorption spectroscopic study of the sorption of Cr(III) at the oxide–water interface. *Journal of Colloids and Interface Science*, **148**, 443.

Csoban, K., Parkanyi-berka, M. and Joo, P. (1998). Sorption experiments of Cr(III) onto silica. *Colloids & Surfaces*, **141**, 347–364.

Csoban, K. and Joo, P. (1999). Sorption of Cr(III) onto silica and aluminum oxide. *Colloids & Surfaces*, **151**, 97–112.

Deng, B., Li, Z. and Brady, P. V. (1999). Catalysis of soils minerals on Cr(VI) reduction by organic compounds and its applications for contaminated site remediation. Technical completion report, U.S. Department of Energy.

Deng, B. and Stone, A. (1996). Surface-catalyzed chromium (VI) reduction: Reactivity comparisons of different organic reductants and different oxide surfaces. *Environmental Science and Technology*, **30**, 2484–2494.

Eary, L. E. and Rai, D. (1988). Chromate removal from aqueous waters by reduction with ferrous ion. *Environmental Science and Technology*, **22**, 972–977.

Evanko, C. R. and Dzombak, D. A. (1999). Surface complexation modeling of organic acid sorption to Goethite. *Journal of Colloids & Interface Science*, **214**, 189–206.

Fendorf, S. E., Lamble, G. M. and Stapleton, M. G. (1994a). Mechanisms of chromium (III) sorption on silica. *Environmental Science Technology*, **28**, 284–289.

Fendorf, S. E. and Sparks, D. L. (1994b). Mechanisms of chromium (III) sorption on silica. *Environmental Science Technology*, **28**, 290–297.

Fitts, J. P., Brown, G. E. and Parks, G. A. (2000). Structural evolution of Cr(III) polymeric species at the γ-Al_2O_3 water interface. *Environmental Science and Technology*, **34**, 5122–5128.

Floroiu, R. M., Davis, A. P. and Torrents, A. (2001). Cadmium adsorption on aluminium oxide in the presence of polyacrylic acid. *Environmental Science and Technology*, **35**, 348–353.

Fukushima, M., Nakayasu, K. and Tanaka, S. (1995). Chromium (III) binding abilities of humic acids. *Analytica Chimica Acta*, **317**, 195–206.

Ikhsan, J., Johnson, B. B. and Wells, J. D. (1999). A comparative study of the adsorption of transition metals on kaolinite. *Journal of Colloids and Interface Science*, **217**, 403–410.

Koppelman, M. H., Emerson, A. B. and Dillard, J. G. (1980). Adsorbed Cr(III) on chlorite, illite and kaolinite: an x-ray photoelectron spectroscopic study. *Clays and Clay Minerals*, **28**(2), 119–124.

Kraepiel, A., Keller, K. and Morel, F. (1998). On the acid-base chemistry of permanently charged minerals. *Environmental Science and Technology*, **32**, 2829–2838.

Marx, G. and Heumann, K. G. (1999). Mass spectrometric investigations of the kinetic stability of chromium and copper complexes with humic substances by isotope labelling. *Fresenius Journal of Analytical Chemistry*, **364**, 489–494.

Mesuere, K. and Fish, W. (1992). Chromate and oxalate adsorption on goethite, 1, Calibration of surface complexation models. *Environmental Science and Technology*, **26**, 2357.

Nordin, J., Persson, P., Laiti, E. and Sjoberg, S. (1997). Adsorption of o-phthalate at the water-boehmite interface: Evidence for two coordination modes. *Langmuir*, **13**, 4085–4093.

Peterson, M. L., Brown, G. E., Parks, G. A. and Stein, C. L. (1997). Differential redox and sorption of Cr(III/VI) on natural silicate and oxide minerals. *Geochimica and Cosmochima Acta*, **61**, 3399–3412.

Puls, R. W., Powell, R. M., Clark, D. and Eldred, C. J. (1991). Effetcs of pH, solid/solution ratio, ionic strength and organic acids on Pb and Cd sorption on kaolinite. *Water, Air and Soil Pollution*, **57–58**, 423–430.

Schindler, P. W. (1990). Co-adsorption of metal ions and organic ligands: Formation of ternary surface complexes. *Mineral–water Interface Geochemistry*, Chap. 7; M. Hochella *Reviews in mineralogy*, **23.**

Schroth, B. K. and Sposito, G. (1998). Effect of landfill leachate organic acids on trace metal adsorption by kaolinite. *Environmental Science Technology*, **32**(10), 1404–1408.

Spark, K. M., Wells, J. D. and Johnson, B. B. (1995). Characterizing trace metal adsorption on kaolinite. *European Journal of Soil Science*, **46**, 633–640.

Strawn, D. G. and Sparks, D. L. (1999). The use of XAFS to distinguish between inner and outer sphere lead adsorption complexes on montmorillonite. *Journal of Colloid and Interface Science*, **216**, 257–269.

Stumm, W. (1992). *Chemistry of the Solid–Water Interface*, John Wiley.

Takahashi, Y., Minai, Y., Ambe, S. and Makide, Y. (1999). Comparison of adsorption behavior of multiple inorganic ions on kaolinite and silica in the presence of humic acid using the multitracer technique. *Geochimica and Cosmochimica Acta*, **63**(6), 815–836.

Villalobos, M., Trotz, M. A. and Leckie, J. O. (2001). Surface complexation modeling of carbonate effects on the adsorption of Cr(VI), Pb(II) and U(VI) on goethite, *Environmental Science Technology*, **35**, 3849–3856.

Ward, N. E. and Bassett, R. L. (1990). Adsorption of hexavalent chromium on kaolinite and illite. *Trace Substances in Environmental Health*, **XXIV**, 193–206.

Wittbrodt, P. R. and Palmer, C. D.(1995) Reduction of Cr(VI) in the presence of excess of soil fulvic acid. *Environmental Science and Technology*, **29**, 255–263.

Zachara, J. M., Girvin, D. C. and Schmidt. R. L. (1987). Chromate adsorption on amorphous iron oxyhydroxides in the presence of major groundwater ions. *Environmental Science and Technology*, **21**, 598.

Zachara, J. M., Cowan, C. E., Schmidt, R. L. and Ainsworth, C. C. (1988). Chromate adsorption by kaolinite. *Clays and Clay Mineral*, **36**, 317–326.

Zachara, J. M., Ainsworth, C. C. and Cowan, C. E. (1989). Adsorption of chromate by subsurface soil horizons. *Soil Science Society of America Journal*, **53**, 418.