

Full Length Research Paper

Sorption mechanisms of Chromium(III), Copper(II) and Lead(II) on two natural mixed clays from Burkina Faso as determined by extended X-ray absorption fine structure (EXAFS) spectroscopy

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Chromium(III), copper(II) and lead(II) are among the heavy metals produced and released in large amounts by anthropogenic sources worldwide, including Burkina Faso. Previous studies have demonstrated the successful application of domestic natural mixed clays for the removal of these metal ions as a cheap and environmentally friendly method. Qualitative mineralogical characterization of the clays revealed that they consist of kaolinite, illite, orthose and quartz, and minor quantities of albite and montmorillonite. pH_{PZC} for the clays, as determined by potentiometric titrations, are in the range 6.8 to 7.3. In this study, the interactions of chromium(III), copper(II) and lead(II) ions with these clay minerals were examined by the use of extended X-ray absorption fine structure (EXAFS) spectroscopy. Cr^{3+} forms tetrameric hydrolysis complexes on the mineral surface with a Cr–O bond distance of 1.98 Å, and two Cr...Cr distances at 3.02 and 3.62 Å. This is indicative of a tetrameric $[\text{Cr}_4(\text{OH})_6(\text{H}_2\text{O})_{12}]^{6+}$ entity bound to the clay mineral surface. A distance of 3.17 Å, regarded as a Cr...Fe distance, indicates that one Cr^{3+} ion in the hydrolyzed tetramer binds to two oxygens in the mineral surface which are bound to either one or two iron(III) ions in the surface. Pb^{2+} binds two oxygen atoms at an average bond distance of 2.31 Å, with a significant contribution of linear multiple scattering from the PbO_2 entity. The EXAFS results of Cr^{3+} sorption are consistent with the presence of a hydrolysis product of polymeric Cu^{2+} species with a surface complex or precipitate.

Key words: Sorption, extended X-ray absorption fine structure (EXAFS) spectroscopy, clay, precipitation, Burkina Faso.

INTRODUCTION

Water pollution, with high levels of particular heavy metals have been found in streams and soils mainly due

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to anthropogenic activities such as mining, agriculture, society's effluents and discharge from industrial and sewage plants in Burkina Faso (Etienne et al., 1997; Inoussa et al., 2009). Compounds of chromium(III), copper(II) and lead(II) are among the most common heavy metal pollutants found in Burkina Faso.

Efficient removal of toxic metal ions from drinking water as well as wastewater is an important research area and several technologies have been developed over the years (Deans and Dixon, 1992; Sajidu et al., 2008). The potential of natural or alkaline mixed clays to sorb heavy metals dissolved in aqueous systems and the possible sorption mechanism was investigated in order to find effective and inexpensive materials (Sajidu et al., 2006a, 2008; Sällström, 2008; Pare et al., 2012, 2013).

A large number of studies have investigated the adsorption of Cr^{3+} , Cu^{2+} and Pb^{2+} with different kind of materials. Cr^{3+} was found to: coordinate with phosphate ions and substitute calcium ions on bone char surfaces in aqueous solution (Jose et al., 2016); be physically adsorbed on the surface of chorfa silt material (Oudjenia-Marouf et al., 2013); be uptake on micaceous polymineral from Kenya (Attahirua et al., 2012); be adsorbed following pseudo-second-order kinetics on natural clay from Kono-Bowe in Nigeria (Ajemba, 2014). Pb^{2+} was adsorbed as an acetylacetonate complex by hydrophobic interaction on mesoporous silicate surface (Oshima et al., 2005) and with electrochemical ion-exchange between Pb^{2+} and clays surfaces (smectite and kaolin), and complexation reaction (Etoh et al., 2016). It was found to adsorb through ion exchange between metal cations and protons at the surface of activated carbon cloths, including precipitation (Kadirvelu et al., 2010). Copper(II) adsorption onto magnetite surface was found to be a fast process following pseudo-second order kinetics (Adewuyi and Pereira, 2016). It was successfully adsorbed on amino-functionalized magnetic nanoparticle surfaces with ion exchange-surface complexation being the main adsorption mechanism (Li et al., 2013) and also found to be adsorbed on the upper layer of the crystalline structure of activated carbon prepared from *Azadiracta indica* bark by means of physisorption (Balakrishnan et al., 2010).

An EXAFS study of chromium(III) sorbed on silica (Fendorf et al., 1994) indicated formation of monodentate Cr^{3+} surface complex on silica with a Cr...Si distance of 3.39 Å and formation of polynuclear chromium hydroxide octahedra. Sajidu et al. (2008) found that on a natural mixed alkaline clay from Malawi, Cr^{3+} forms polynuclear hydrolysis complexes on the mineral surface with Cr–O bond and Cr...Cr distances of 2.00 and 3.03 Å respectively. Copper(II) was found to bind to phosphate groups on the surface at low pH and had a first shell of coordinated oxygen atoms with Jahn–Teller distortion with Cu–O bonds of 1.96 Å for the equatorial ones, at 2.30 and 2.65 Å for the axial oxygens, and a Cu–P distance at 3.29 Å was distinguished as well. Studies

reported that Cu^{2+} coordinates with sulphur on the surface of pyrite with an average bond length of 2.27 Å, and precipitated as $\text{Cu}(\text{OH})_2$ with a Cu–O bond length of 2.00 Å at pH 8.5 (Weisener and Andreas, 2000). No precise chemical environment around the Pb^{2+} was observed by Sajidu et al. (2008).

Previous works by the author highlighted the potential of natural mixed clays in removing heavy metal from aqueous solution. This study investigates the local structural environment of Cr^{3+} , Cu^{2+} , Pb^{2+} ions sorbed on natural clay surfaces KOR and SIT without any pre-treatment as function of pH using EXAFS to deduce the mechanism of the sorption process.

MATERIALS AND METHODS

Samples

The clay samples were collected from two locations in Burkina Faso as indicated in previous works (Sorgho et al., 2011). Mineralogical characterization of the clays by XRD revealed that the KOR clay contains montmorillonite, quartz, albite, illite, kaolinite, goethite and orthose (Sorgho et al., 2011), and the SIT clay contains kaolinite, montmorillonite, quartz, illite/mica, albite and orthoclase (Kam et al., 2009). The pH_{pzc} values of the clays were 7.3 and 6.8, for KOR and SIT, respectively, and the cation exchange capacity was 42.4 ± 1.1 and 53.6 ± 1.1 (cmolc/kg) for KOR and SIT, respectively (Sorgho et al., 2011).

Metal sorption

20 $\text{mmol}\cdot\text{dm}^{-3}$ aqueous solutions of Cr^{3+} , Cu^{2+} and Pb^{2+} were prepared by dissolving weighed amounts of the nitrate salts $\text{Cr}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2\cdot 3\text{H}_2\text{O}$, and $\text{Pb}(\text{NO}_3)_2$ (analytical grade, and impurity of less than 0.5%), respectively, in deionized water. 25 mL of prepared metal solution was added to 1.0 g of the clay and the pH was adjusted using 1.0 $\text{mmol}\cdot\text{dm}^{-3}$ nitric acid or sodium hydroxide under vigorous stirring to maintain homogenous suspensions. After stirring at room temperature for 48 h, the clay suspensions were centrifuged to separate the clays from the aqueous phase. The remaining clays were dried in air before the EXAFS measurements. For each sample, pH was adjusted to slightly acidic and alkaline pH values as shown in Table 1.

EXAFS - Data collection

Chromium and copper K-edge and lead L_3 -edge X-ray absorption spectra were collected at the wiggler beam-line I811, MAX-lab, Lund University, Sweden, which was operated at 1.5 GeV and a maximum current of 200 mA. Data collection was performed in transmission and fluorescence mode simultaneously. The fluorescence detection was made with a passivated implanted planar silicon (PIPS) detector (Canberra, 2013). The EXAFS station was equipped with a Si[111] double crystal monochromator. In order to remove higher order harmonics, the beam intensity was detuned to 30, 50, and 50% for chromium, copper and lead, respectively, at the end of the scans. Internal energy calibration was made with corresponding metal foil with first inflection point on the absorption edge at 5989.0, 8980.3 and 13038 eV for chromium (K edge), copper (K) and lead(L_3), respectively (Thompson et al., 2001). The treatment of the EXAFS data was carried out by means of the EXAFSPAK program package (George and Pickering, 1993),

Table 1. pH of the treated samples.

Metal ion	Sample	pH
Cr ³⁺	KOR	3.4 and 11.0
	SIT	3.3 and 11.0
Cu ²⁺	KOR	6.0 and 10.17
	SIT	6.0
Pb ²⁺	KOR	6.0
	SIT	6.0

using standard procedures for pre-edge subtraction and spline removal.

EXAFS - Data analysis

The program package EXAFSPAK was used for data treatment and refinement of structure parameters as indicated elsewhere (Sajidu et al., 2008; George and Pickering, 1993). The EXAFS functions were obtained after performing standard procedures for pre-edge subtraction, and spline removal. The k^3 -weighted model functions were calculated using *ab initio* calculated phase and amplitude parameters using the FEFF7 program (Zabinsky et al., 1995). The standard deviations are obtained from k^3 -weighted least squares refinements of the EXAFS function $\chi(k)$, and do not include systematic errors of the measurements. These statistical error estimates provide a measure of the precision of the results and allow reasonable comparisons, e.g. of the significance of relative shifts in the distances. However, the variations in the refined parameters, including the shift in the E_0 value (for which $k = 0$), using different models and data ranges, indicate that the absolute accuracy of the distances given for the separate complexes is within ± 0.01 - 0.02 Å for well-defined interactions (Sajidu et al., 2008).

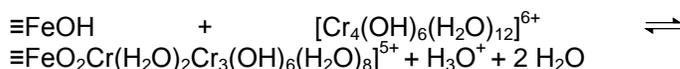
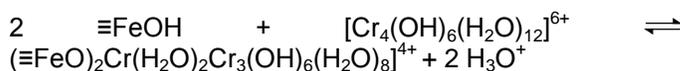
RESULTS AND DISCUSSION

Chromium(III) treated clay samples

Fits of the EXAFS spectra and FT of chromium(III) treated clay samples are shown in Figure 2a and b, with quantitative fitting results listed in Table 2. The EXAFS spectra and Fourier transforms (FTs) of the samples studied are similar for the two pH values studied, acidic (pH 3.3 and 3.4) and basic (pH 11.0) for the KOR and SIT samples. The FTs show that Cr³⁺ binds to six oxygens at mean bond distance of 1.98 Å, in octahedral configuration, and the corresponding CrO₆ core multiple scattering was observed at 3.93 Å (Table 2). In addition, three distances to relatively strong back-scatterers at 3.0, 3.2 and 3.6 Å are observed. The distances at 3.0 and 3.6 Å correspond most probably to the tetrameric [Cr₄(OH)₆(H₂O)₁₂]⁶⁺ complex, dominating in weakly acidic aqueous solution (Torapava et al., 2009), with Cr...Cr distances of 2.98 and 3.59 Å. This complex seems also to be the dominating one on the surfaces of both KOR and SIT clay with two oxygens binding to Fe(III) in the

surface with a Cr...Fe distance of 3.2 Å. This Cr...Fe distance corresponds to a tetrahedral Cr-O-Fe angle. These results are in close agreement with the adsorption of Cr³⁺ to the surfaces of alkaline clays from Malawi (Sajidu, 2008), showing formation of hydrolyzed Cr³⁺ complexes on the surfaces of basic clays. Fendorf et al. (1994) discerned formation of polynuclear chromium hydroxide octahedral on silica.

From our study, the following alternative reaction equilibria on the clays surface are expected:



The Cr...Cr bond distances in the hydrolyzed tetrameric Cr³⁺ indicate that one chromium in the hydrolyzed tetramer binds to the surface through two oxygens to one or two iron(III) ions in the mineral surface. Iron, present on the clay surface plays key role in the removal of Cr³⁺.

Lead(II) treated clay samples

The EXAFS data of lead(II) adsorbed to the surfaces of the KOR and SIT clays shows a very short Pb-O bond distance, 2.31 Å, with a relative small Debye-Waller coefficient being a Pb²⁺ complex (Persson et al., 2011). Furthermore, a weak contribution of multiple scattering within the PbO₂ entity at ca. 4.61 Å supports a linear complex. It has not been possible to detect any Pb...X distance making it impossible to estimate the angle this complex has *versus* the surface. The finding of linear O-Pb-O (possibility shown on Figure 1) with such a short Pb-O bond distance is unusual. The number of reported linear lead(II) complexes is very limited. Pb-O bond distance of 2.334 Å has been found in [Pb₂(H₂O)₂(ClO₄)₂]_n, (Persson et al., 2011), and a distance of 2.32 ± 0.03 Å has been reported in Pb²⁺ co-precipitated with Fe³⁺ oxyhydroxide (Kelly et al., 2008). Whether the formation of a surface complex with Pb(II) also results in hydrolysis of Pb²⁺ cannot be distinguished from the present study leaving both possibilities open.

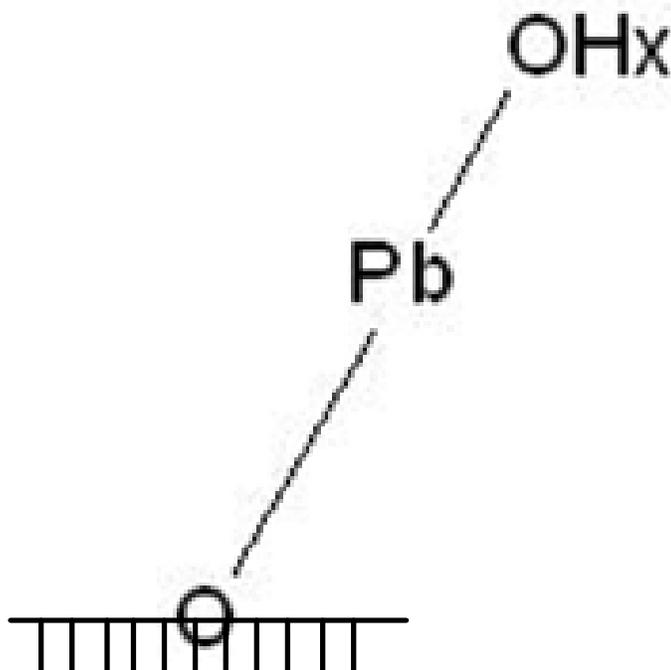


Figure 1. Scheme of the possible interaction of the lead(II) cations on the clay.

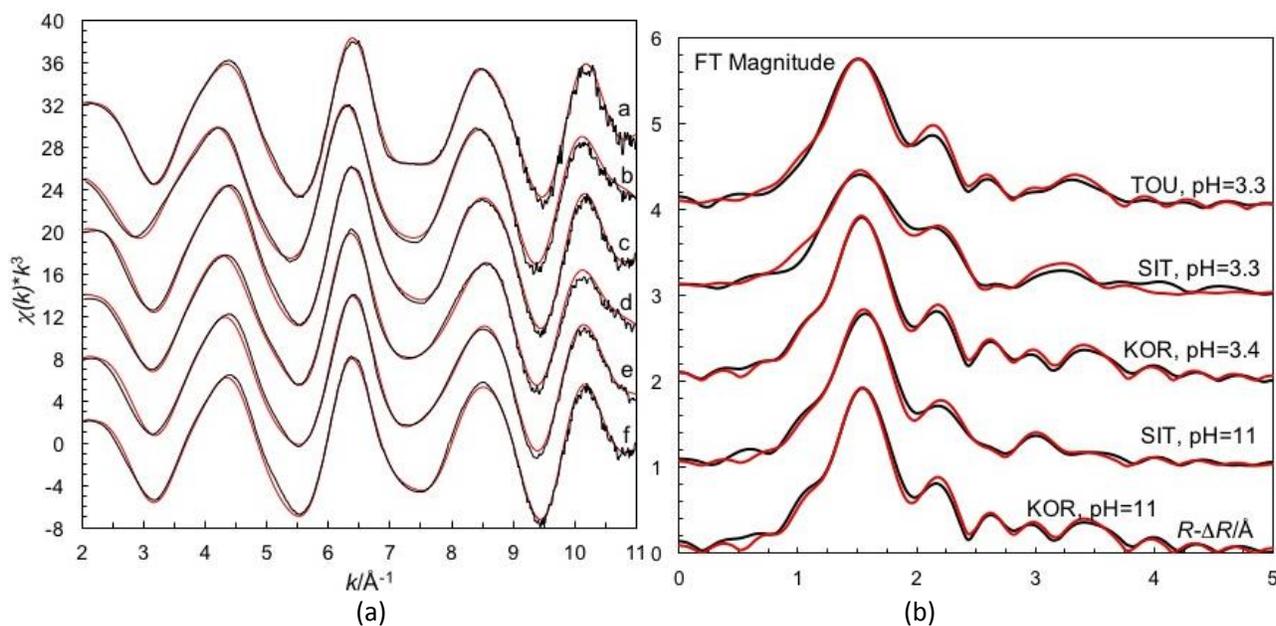
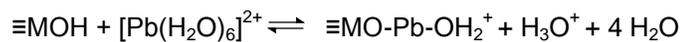
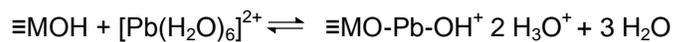


Figure 2. (a) Upper panel) Fit of k^3 -weighted Cr K-edge raw EXAFS spectra for Cr-clay samples treated at different pH (black lines) compared with the calculated EXAFS function using the parameter summarized in Table 2. (red lines); (b) Lower panel) Fit of the Fourier transforms of the EXAFS data (black lines) with the calculated Fourier transforms (red lines).



or



Experimental and fitted EXAFS data in k -space, and the

Table 2. Number of distances, N , mean bond distances, $R/\text{\AA}$, and Debye-Waller factor coefficients, $\Delta^2/\text{\AA}^2$ in the EXAFS studies of the KOR and SIT clays treated with chromium(III), lead(II) and copper(II) nitrate in aqueous suspension at ambient room temperature.

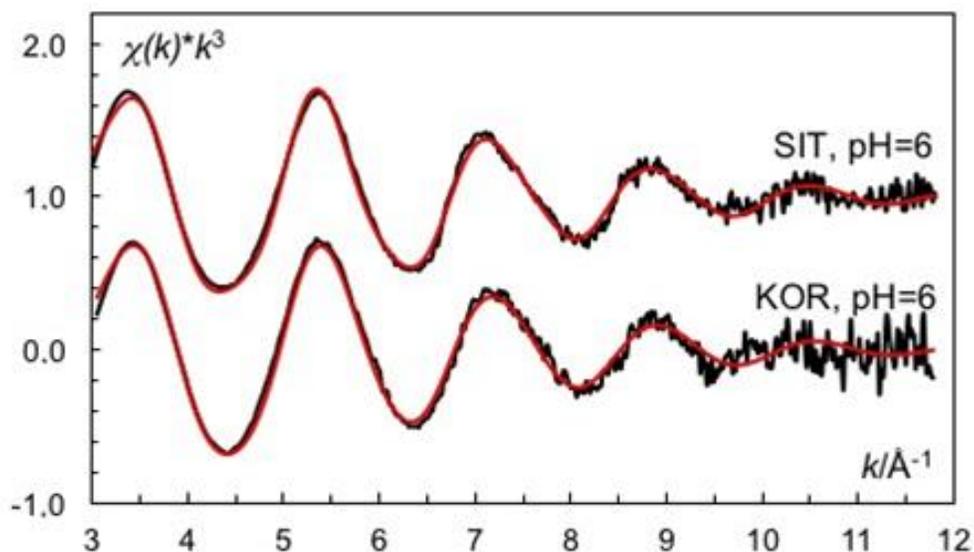
Species	Interaction		R	σ^2	N	R	σ^2
Samples	KOR, pH=3.4			KOR, pH=11.0			
$\equiv\text{O}_2\text{-Cr}_4(\text{OH})_6(\text{OH})_x^{(4-x)+}$	Cr-O	6	1.975(1)	0.0025(1)	6	1.975(1)	0.0023(1)
	MS(CrO ₆)	3x6	3.93(2)	0.0042(6)	3x6	3.94(2)	0.0050(6)
	Cr...Cr	1	3.012(4)	0.0036(5)	1	3.014(3)	0.0040(4)
	Cr...Cr	2	3.606(8)	0.011(1)	2	3.599(9)	0.012(1)
	Cr...Fe ^{III}	2	3.17(2)	0.011(2)	2	3.18(2)	0.011(2)
Samples	SIT, pH=3.3			SIT, pH=11.0			
$\equiv\text{O}_2\text{-Cr}_4(\text{OH})_6(\text{OH})_x^{(4-x)+}$	Cr-O	6	1.970(1)	0.0024(1)	6	1.986(1)	0.0023(1)
	MS(CrO ₆)	3x6	3.91(2)	0.0039(7)	3x6	3.95(2)	0.0076(11)
	Cr...Cr	1	3.019(4)	0.0035(6)	1	3.019(3)	0.0052(8)
	Cr...Cr	2	3.606(10)	0.009(1)	2	3.62(2)	0.017(2)
	Cr...Fe ^{III}	1	3.17(3)	0.018(3)	1	3.15(2)	0.017(3)
Samples	KOR, pH=6.0			SIT, pH=6.0			
$\equiv\text{O-PbOH}_x^{(1-x)+}$	Pb-O	2	2.305(4)	0.0162(4)	2	2.317(2)	0.0145(4)
	MS(PbO ₂)	3x2	4.60(3)	0.023(4)	3x2	4.62(2)	0.022(3)
Samples	KOR, pH=6.0			SIT, pH=9.0			
$\equiv\text{O-Cu}(\text{OH}_{1+x})_3(\text{OH}_2)_2^{(1-x)+}$	Cu-O	4	1.980(1)	0.0051(2)	4	1.971(1)	0.0035(2)
	Cu-O	2	2.301(4)	0.0077(7)	2	2.251(5)	0.0149(9)
	MS(CuO ₄)	3x4	3.925(6)	0.0080(7)	3x4	3.905(6)	0.0079(8)
	Cu...Cu	2	3.051(3)	0.0085(3)	2	3.045(3)	0.0117(3)
	Cu...Cu	2	3.259(3)	0.0075(3)	2	3.193(3)	0.0113(3)
	Cu...Cu	2	5.36(2)	0.020(2)	2	5.46(2)	0.019(3)
	Cu...Cu	4	5.78(2)	0.023(2)	4	5.79(1)	0.019(2)
Sample	KOR, pH=10.2						
$\equiv\text{O-Cu}_4(\text{OH})_5(\text{OH}_{1+x})^{(6-x)+}$	Cu-O	4	1.988(2)	0.0050(3)			
	Cu-O	2	2.333(5)	0.0111(8)			
	MS(CuO ₄)	3x4	3.932(6)	0.0078(9)			
	Cu...Cu	2	2.982(3)	0.0075(2)			
	Cu...Cu	2	3.177(6)	0.0135(7)			
	Cu...Cu	2	5.39(3)	0.025(5)			
	Cu...Cu	4	5.713(7)	0.0118(7)			

corresponding Fourier transforms are given in Figure 3a and 3b, respectively.

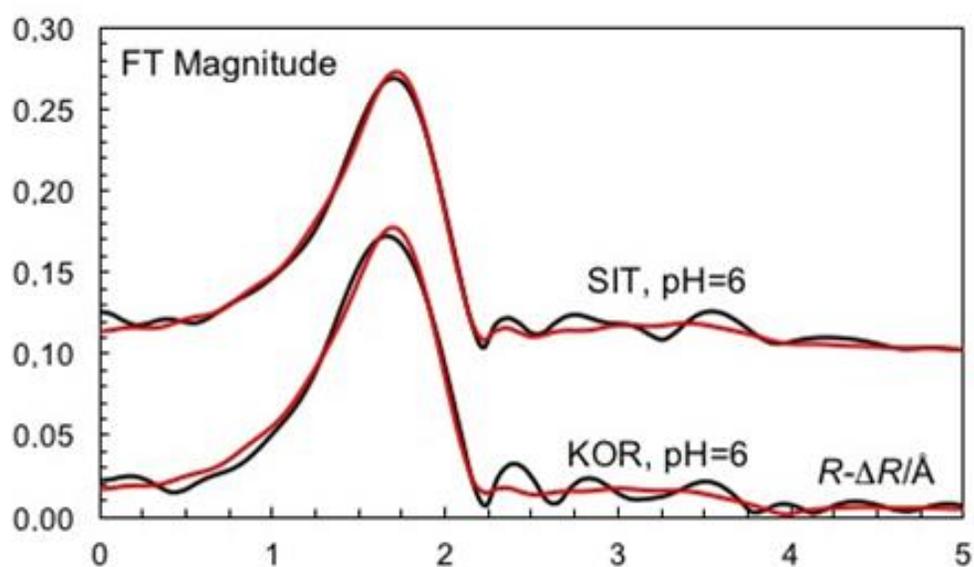
Copper(II) treated clay samples

The EXAFS spectra recorded at acidic pH 6 for the KOR sample and in basic medium with pH 9.0 for SIT and pH 10.2 sample are almost identical (Figure 4). The FT spectra as well as the fittings result (Table 2) show specific Cu...Cu distances clearly indicating that copper(II) has hydrolyzed. The pattern of Cu...Cu distances is fairly similar to that of crystalline

trihydroxidonitratodicopper(II), $\text{Cu}_2(\text{OH})_3\text{NO}_3$ (Effenberger, 1983). This is not surprising as Cu^{2+} nitrate was used as starting material, and Cu^{2+} is known to hydrolyze at the pH values applied (Paulson and Kester, 1980). It can furthermore be assumed that copper(II) adsorbed to a mineral or clay surface is more readily hydrolysed than the hydrated copper(II) ion in aqueous solution. This study can however not determine whether the copper(II) species on the surface is a polymeric surface complex or a crystalline or amorphous solid phase. The significantly longer Cu-O bond distances in these complexes on the clay surfaces, ca. 1.98 Å, than in the hydrated copper(II) ion, 1.95 Å, indicates that



(a)



(b)

Figure 3. (a) (Upper panel) Fit of k^3 -weighted Pb L_3 -edge raw EXAFS spectra for lead(II) treated samples treated at different pH (black lines) compared with the calculated EXAFS function using the parameter summarized in Table 2 (red lines); (b) (Lower panel) Fit of the Fourier transforms of the EXAFS data (black lines) with the calculated Fourier transforms (red lines).

copper(II) is mainly binding hydroxide groups as the atomic radius of the hydroxide oxygen is ca. 0.03 Å larger than of water oxygen (Shannon, 1976).

Conclusion

Chromium(III), copper(II) and lead(II) sorbed on some natural mixed clays from Burkina Faso were studied

using EXAFS spectroscopy. Chromium(III) is adsorbed as hydrolyzed tetrameric complexes at both acidic and basic pH values, one chromium in the hydrolyzed tetramer binds to the surface through two oxygens to one or two Fe^{3+} ions in the mineral surface. Linear coordination of Pb^{2+} is rare, but especially Pb^{2+} complexes with hydroxide ion display low coordination number, e.g. the trishydroxidoplumbate complex, $[\text{Pb}(\text{OH})_3]^-$, is the dominating species in hyper-alkaline

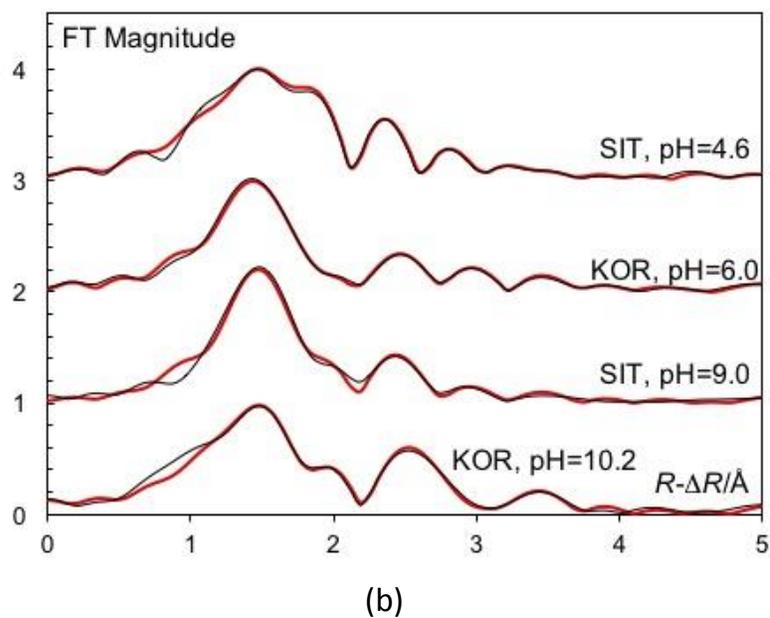
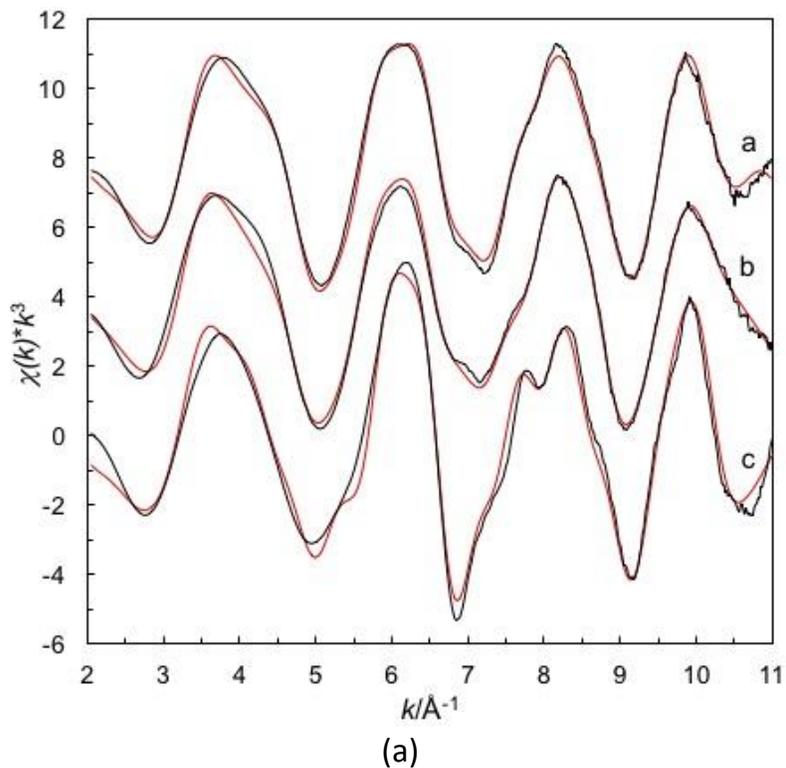


Figure 4. (a) (Upper panel) Fit of k^3 -weighted Cu K-edge raw EXAFS spectra for copper(II) treated samples treated at different pH (black lines) compared with the calculated EXAFS function using the parameters summarized in Table 2 (red lines); (b) (Lower panel) Fit of the Fourier transforms of the EXAFS data (black lines) with the calculated Fourier transforms (red lines).

aqueous solution (Bajnóczi et al., 2014). Copper(III) is hydrolyzed to a polymeric complex or precipitate adsorbed to the clay surface. Hydrolysis and

precipitation are seen as main mechanism governing heavy metal uptake by the two study natural clays from Burkina Faso.

CONFLICT OF INTERESTS

The authors have not declared any conflict of interests.

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