

Full Length Research Paper

Heavy metal removal from aqueous solutions by sorption using natural clays from Burkina Faso

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The acid-base properties of two raw and purified mixed clays from Burkina Faso were studied, as well as their potential to remove copper(II), lead(II) and chromium(III), and thereby their ability to be used to purify water from heavy metals. The purification procedure of the clays involved removal of carbonates, iron oxides and organic matter. A determination of the elemental composition of the mixed clays revealed the presence of aluminum, iron and silicon as main constituents. The high alkaline pH in one of the samples is attributable to the presence of carbonate in the raw clay. The point of zero charge (pH_{pzc}) values of the clays, as determined by potentiometric titrations, were 6.79 and 9.52 for the raw clays, while after purification they were 6.87 and 6.76, respectively. Metal adsorption to the clay surfaces started at pH values below pH_{pzc}, strongly indicating formation of inner-sphere complexes. With contact time of 48 h, complete removal of copper(II) was achieved at pH 8 for all samples. More than 90% of the lead(II) removal was attributed to adsorption while for chromium(III), it was 85%. Adsorption to organic matter and iron oxides, and precipitation of metal hydroxides gave significant contributions to the removal of metal ions in aqueous systems.

Key words: Mixed clays, potentiometric titration, heavy metals, pH_{pzc}.

INTRODUCTION

Over the last few decades, a considerable population growth has taken place accompanied by a steep increase in urbanization, industrial and agricultural land use in many African countries (Saad et al., 1994; Ogbeibu and Ezeunara, 2002; Idodo-Umeh and Oronsaye, 2006). This has entailed a great increase in discharge of pollutants to receiving waters, causing undesirable effects on the aquatic environment. Heavy metal ions are the most toxic inorganic pollutants which occur in soils and can be of natural or anthropogenic origin. Studies conducted in Burkina Faso revealed high levels of particular heavy

metals in streams and soil, mainly due to anthropogenic activities such as mining society's effluents, agricultural activities, discharge from industrial plants and sewage works (Etienne et al., 1997; Inoussa et al., 2009). Water pollution by heavy metals is an area of major concern today in Burkina Faso and many other countries as well (UN, 1983; Etienne et al., 1997).

Clays are known for their ability to effectively remove heavy metals by specific adsorption and cation exchange (Bradl, 2004; Sajidu, 2008). Large quantities of clay are available in Burkina Faso, where the main use today is for traditional potter, ceramic and brick production. Some studies have been conducted on clay material in Burkina Faso where the study of the chemical and mineralogical characteristics has been in focus, the potential use

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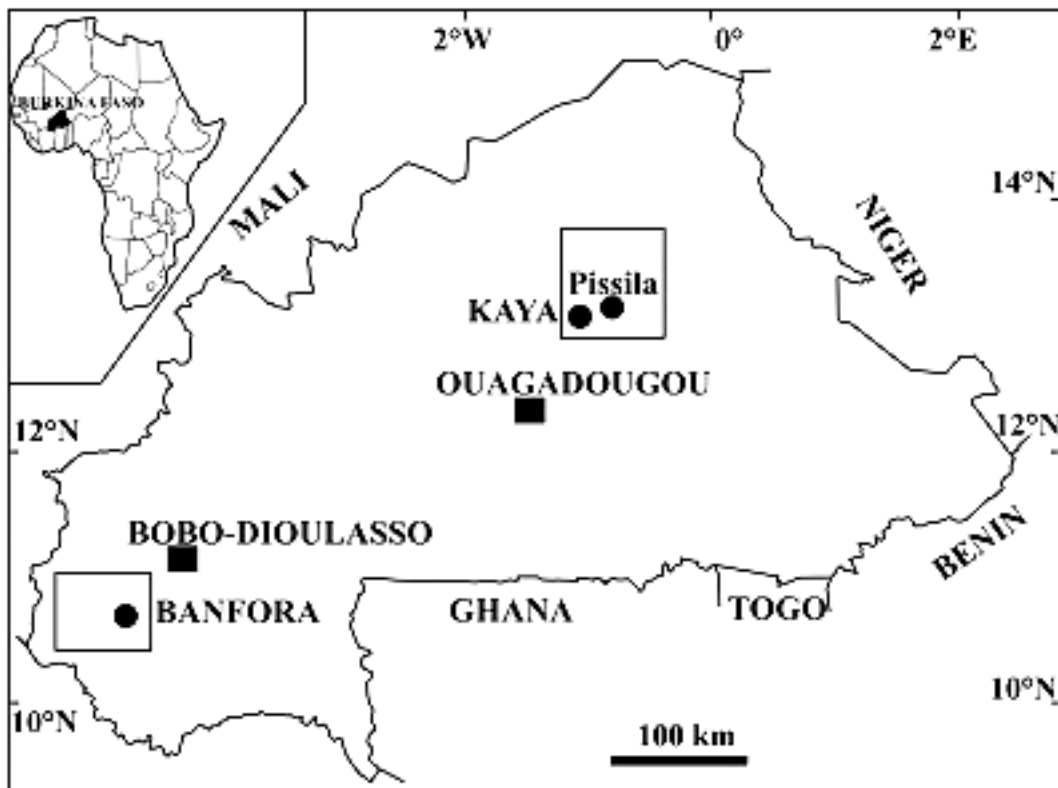


Figure 1. Burkina Faso map and samples' sites location (redrawn by Kam et al., 2009).

of clay in pottery and building materials, where traditional fabrication technique has been used (Kabre et al., 1998; Traoré et al., 2007; Traore and Blanchard, 2003; Kam et al., 2009). A recent study investigated the permeability to water of sintered clay ceramics (Kam et al., 2009). To the best of our knowledge, no study has been performed on the acid-base properties of clay from Burkina Faso, it is investigate the potential of such clays to be used in removal of heavy metals from contaminated water.

All over the world, many studies have been conducted on heavy metal sorption using clay mineral such as montmorillonite (Brigatti et al., 2005; Auloir et al., 1996; Zeng and Jiang, 2005;), allophane (Okada et al., 2005), sepiolite (Brigatti et al., 1996; Brigatti et al., 2000), smectites (Arpa et al., 2000), kaolinite (Srivastava et al., 2005), bentonite (Khan et al., 1995; Al-Qunaibit et al., 2005; Donat et al., 2005), illite (Elzinga and Sparks, 2001; Echeverria et al., 2005) and vermiculite (Brigatti et al., 2005). Recently, Sajidu et al. (2006) investigated the potential of natural mixed clays to be used for heavy metal removal from aqueous solutions. The most important parameters controlling heavy metal adsorption and their distribution between clay and water are clay type, metal speciation, metal concentration, soil pH, solid: solution mass ratio and contact time (Coles and Yong, 2000; Bradl, 2004; Maguire et al., 1981; Barrow et al., 1981; Barbier et al., 2000). Of all these factors, pH is

considered the 'master variable' controlling ion exchange, dissolution/precipitation, reduction/oxidation, adsorption and complex formation reactions (McBride, 1994).

In this study, two natural clays from Burkina Faso, SIT and ROU2 were on the focus. The study investigated the use of these natural mixed clays as low-cost adsorbent for heavy metal remediation. Acid-base properties of the clays were determined by potentiometric titrations. Elementary composition of elements of sodium or heavier of the clay samples were investigated using the energy dispersive spectrometer (EDS) detector of a scanning electron microscope (SEM) instrument, Hitachi TM-1000, and the removal of copper(II), lead(II) and chromium(III) as function of pH for these clays, with contact time of 48 h were studied using atomic absorption spectrophotometry.

MATERIALS AND METHODS

Clay samples

The clay samples used in this study were collected at two locations in Burkina Faso (Figure 1). SIT was from Sityena village, about 10 km from the city of Banfora in the south-western part of Burkina Faso. This clay is formed by weathering of the underlying granite (Kam et al., 2009). The ROU2 clay was from the Pissila village, located at about 3 km from the city of Kaya in the central part of the

Table 1. Chemical compositions of ROU2 and SIT clays (wt.%) according to Kam et al. (2009).

Clay	SiO ₂	TiO ₂	Al ₂ O ₂	Fe ₂ O ₃	MgO	CaO	Na ₂ O	K ₂ O	LOI
ROU2	56.51	0.66	23.24	4.11	0.54	1.46	0.10	1.77	11.64
SIT	55.91	0.63	20.15	6.82	1.23	1.21	2.70	2.15	8.97

country. It is formed by weathering of talc-alkaline intrusive granite dykes (Kam et al., 2009). The major phases detected by Kam et al. (2009) using X-ray diffraction in the two raw samples are kaolinite, illite, orthose and quartz, feeble quantities of albite and montmorillonite, with chemical composition as shown in Table 1 (Kam et al., 2009). Even both clay contain Fe₂O₃, no associated iron mineral were detected by these authors. Oxygen is assumed to be a dominant element of the clays samples.

Sorption experiments of copper(II), lead(II) and chromium(III) were performed on raw (SIT and ROU2) and purified (PSIT and PROU2) samples. The clay purification procedure was performed as described by Sajidu (2008) and reference therein (Sajidu et al., 2006). In order to remove carbonates, 100 g of raw clay was dispersed in 100 ml 1.0 mol·dm⁻³ acetic acid-sodium acetate buffer and stirred from time to time for a few days until there was no more evolution of bubbles of carbon dioxide (indicating presence of carbonates).

The slurry was then centrifuged and dispersed in 270 ml citrate buffer in order to remove iron oxides. pH was adjusted to 8.3 and 20 g of sodium dithionite was added. The slurry was stirred for 70 h, centrifuged and washed four times with a solution of 0.5 mol dm⁻³ sodium chloride and 0.025 mol·dm⁻³ hydrochloric acid. The entire procedure was performed twice. In order to remove organic matter, 500 ml of 0.1 mol·dm⁻³ sodium acetate solution and 170 ml of 30% (w/w) hydrogen peroxide solution were added to the slurry and the mixture was stirred for 10 h at 90°C and then for 20 h at room temperature. The clay was then washed three times with a 1.0 mol·dm⁻³ sodium chloride solution. Finally, it was washed with distilled water to remove excess salt, dried and ground to a fine powder.

The clay fractionation was made by sifting with an automatic sieve (Retsch Vibro) yielding five fraction sizes, f_i : $f_1 < 0.032$ mm, $0.032 < f_2 < 0.045$ mm, $0.045 < f_3 < 0.063$ mm, $0.063 < f_4 < 0.125$ mm and $0.125 < f_5$. The f_1 fraction was used when the quantity was sufficient, if not, f_1 and the f_2 were mixed. Cation exchange capacity (CEC) values was determined to be 53.6±1.1, 49.8±0.1, 47.2±1.1 and 37.8±0.6 cmol/kg for SIT, PSIT, ROU₂ and PROU₂, respectively, by adsorption of copper(II) ethylenediamine complex as previously described (Bergaya and Vayer, 1997). The CEC values of these mixed clays was strangely high but similar to CEC found in previous study on Burkina Faso mixed clay of 42.38 cmol/kg (Sorgho et al., 2011).

Raw samples had slightly higher values in comparison to purified samples. This is explained by iron oxides and organic material in the raw samples contributing to a higher capacity of exchanging cations.

Elementary analysis

Elementary composition of elements of sodium or heavier of the clay samples were determined using the EDS detector of a SEM, Hitachi TM-1000. A small amount of the sample (fraction f_1) was attached to a piece of carbon rich sticky tape, and placed in the instrument. The obtained data were interpreted by the software program SwiftED-TM. The acquisition conditions were as follows: time, 120.0 s; process time, 4; accelerating voltage, 15.0 kV; quantification method of all elements was normalised.

Potentiometric titration

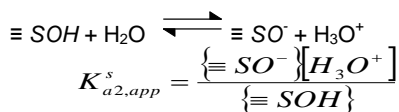
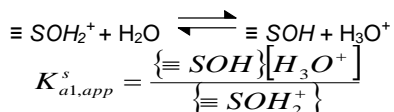
Potentiometric pH titrations were performed on suspensions containing 6.0 g sample/L as previously described (Sajidu et al., 2006). In brief, 50 ml of the clay suspension containing 0.1 mol·dm⁻³ NaNO₃ as supporting electrolyte, was titrated with 0.0218 mol·dm⁻³ nitric acid with increments of 0.1 ml to total of 20.0 ml using a Metrohm 665 Dosimat titrator.

The pH values were read after equilibration of each addition and recorded by a Ross Sure Flow combination electrode Orion No. 8172 using an Orion 940 pH meter. The suspensions were kept homogenous using magnetic stirring, and the titration vessel was covered with parafilm to avoid up-take of carbon dioxide, which is especially important at pH values > 6. A similar titration on a new suspension was made with an aqueous solution of 0.0200 mol·dm⁻³ NaOH.

In contact with water, the total concentration of binding positions in the surface of the clay, denoted $\equiv SOH_{tot}$, which can act as both acid and base giving negatively and positively charged surface sites, $\equiv SO^-$ or $\equiv SOH_2^+$, respectively. The acid-base processes are fast on these hydrated oxide surfaces and equilibrium is normally reached within minutes in acidic solution, and somewhat slower in alkaline solutions. The total concentration of active acid-base sites is expressed by:

$$\{\equiv SOH_{tot}\} = \{\equiv SOH_2^+\} + \{\equiv SOH\} + \{\equiv SO^-\}$$

$\equiv SOH_2^+$ is considered to be a two-protonic acid with the following dissociation steps:



$$[Q] = \{\equiv SOH_2^+\} - \{\equiv SO^-\}$$

$$Z = \frac{[Q]}{\{\equiv SOH\}_{tot}}$$

The volume, V_e , corresponds to the total volume of acid in the titration equivalent to the number of binding sites in the surface, $\{\equiv SOH_{tot}\}$ and was calculated from a pH vs. V_t plot, where V_t is the total volume of added acid. The concentration of surface charge, $[Q]$, which is the difference between positive and negative surface sites at every titration point and the mean number of protons per surface site (Z) can be calculated.

Plots of apparent, pK_a , pK_{app} , values vs. Z for both the base and acid titrations were made to determine the intrinsic, pK_a^e , pK_{a1intr}^e and pK_{a2intr}^e values, and the point of zero charge (pH_{pzc}) values

Table 2. Weight percentage of detectable elements in the samples at x500 magnification spot.

Element	SIT	PSIT	ROU2	PROU2
Aluminum	14.3	14.8	12.2	24.1
Silicon	28.1	17.9	11.2	39.8
Iron	40.1	47.0	56.0	20.5
Calcium	3.0	1.9	nd	nd
Chlorine	nd	nd	nd	2.5
Copper	nd	7.0	nd	nd
Germanium	nd	nd	0.8	nd
Magnesium	1.5	nd	nd	0.4
Manganese	0.5	nd	4.9	nd
Nickel	nd	nd	1.9	nd
Potassium	4.6	nd	1.4	6.2
Sodium	nd	10.0	nd	0.7
Zirconium	nd	1.4	nd	nd

nd, Not detected.

were calculated as:

$$pH_{pzc} = \frac{pK_{a1}^{s_{intr}} + pK_{a2}^{s_{intr}}}{2}$$

Preparation of solutions and adsorption experiments

Aqueous solutions of copper(II), lead(II) and chromium (III), 1.25, 1.00 and 2.00 mmol·dm⁻³, respectively, were prepared from their nitrate salts AR grade reagent Cu(NO₃)₂·3H₂O, Pb(NO₃)₂ and Cr(NO₃)₃·9H₂O (all with a declared impurity of less than 0.5%). Milli-Pore filtered deionized water was used at the preparation of all solutions. For each metal, a set of 12 solutions with pH 1 to 12 were prepared by pipetting into centrifuge tube 7.5 ml of 0.1 mol·dm⁻³ NaNO₃, 2.5 ml of clay suspension (6 g/L) and 0.5 ml of the metal stock solution.

The pH was adjusted to the predetermined values with appropriate amounts of acid (21.8 mmol·dm⁻³ nitric acid) or base (20.0 mmol·dm⁻³ NaOH). The mixture was shaken for 48 h followed by centrifugation for 15 min at 3 000 r/min using a KUBOTA KS-5200C centrifuge. Afterward, 3 to 4 ml of the supernatant was taken off, acidified with a drop of concentrated nitric acid, to avoid hydrolysis, and analyzed for metal concentration on an atomic absorption spectrophotometer (Perkin Elmer Analyst 100). The pH in the remaining supernatant in the centrifuge tubes was recorded as the equilibrium pH of the solution. Percentage metal uptake (%E) was calculated by use of following equation:

$$\%E = \frac{(C_0 - C) \times 100}{C_0}$$

Where C_0 and C are the initial and final concentrations of the metal ion in solution, respectively.

RESULTS AND DISCUSSION

Elementary composition and SEM of the clay

The EDS used in this study only detects sodium and

heavier elements. It was difficult to find clear evidence for clay mineralogy from the EDS results. Nevertheless, it gives an overview of the elementary composition of the clay and some general conclusions about the mineral composition of the clays soils⁽⁵⁾ can be drawn. However, this was not the intention of the investigation, but it aimed to give an approximate indication of elemental chemical composition of the SIT and ROU2 clays, and to account for heavy metal removal from it. As shown in Table 2, and depending on the random package of the sample, aluminum, silicon and iron are present in all samples. The method does not detect oxygen, and oxygen is assumed to be the dominating element of clay mineral.

In SIT, silicon is the most important element detected, since the measurement is done by weight percentage, and iron molecular weight is greater than silicon and aluminum molecular weight. The weight percentage of iron was similar in raw sample SIT (40.1%) and purified sample PSIT (47.0%). However, the small increase of iron wt% was astonishing, since iron oxides, at least Fe₂O₃ at 6.8% present in the raw sample (Kam et al., 2009), are removed during the clay purification. This may be attributable to the removal of some silicon component during the purification process as the weight percentage of silicon drop from 28.1 to 17.9%, or simply an unlucky choice of determination spot of sample. It can also indicate incomplete removal of iron oxide component during the purification process.

Iron was also present in ROU2 (56.0%), whose raw sample seem to contain large amount of iron oxides, as the weight percentage of iron decrease from 56.0 to 20.5% during the purification process (Table 2). ROU2 clay contain large amount of carbonates as revealed by a lot of carbon dioxide bubbles during the purification process. From the raw clay to the corresponding purify one (SIT → PSIT; ROU2 → PROU2), new chemical elements were detected by EDS. Chlorine is absent in

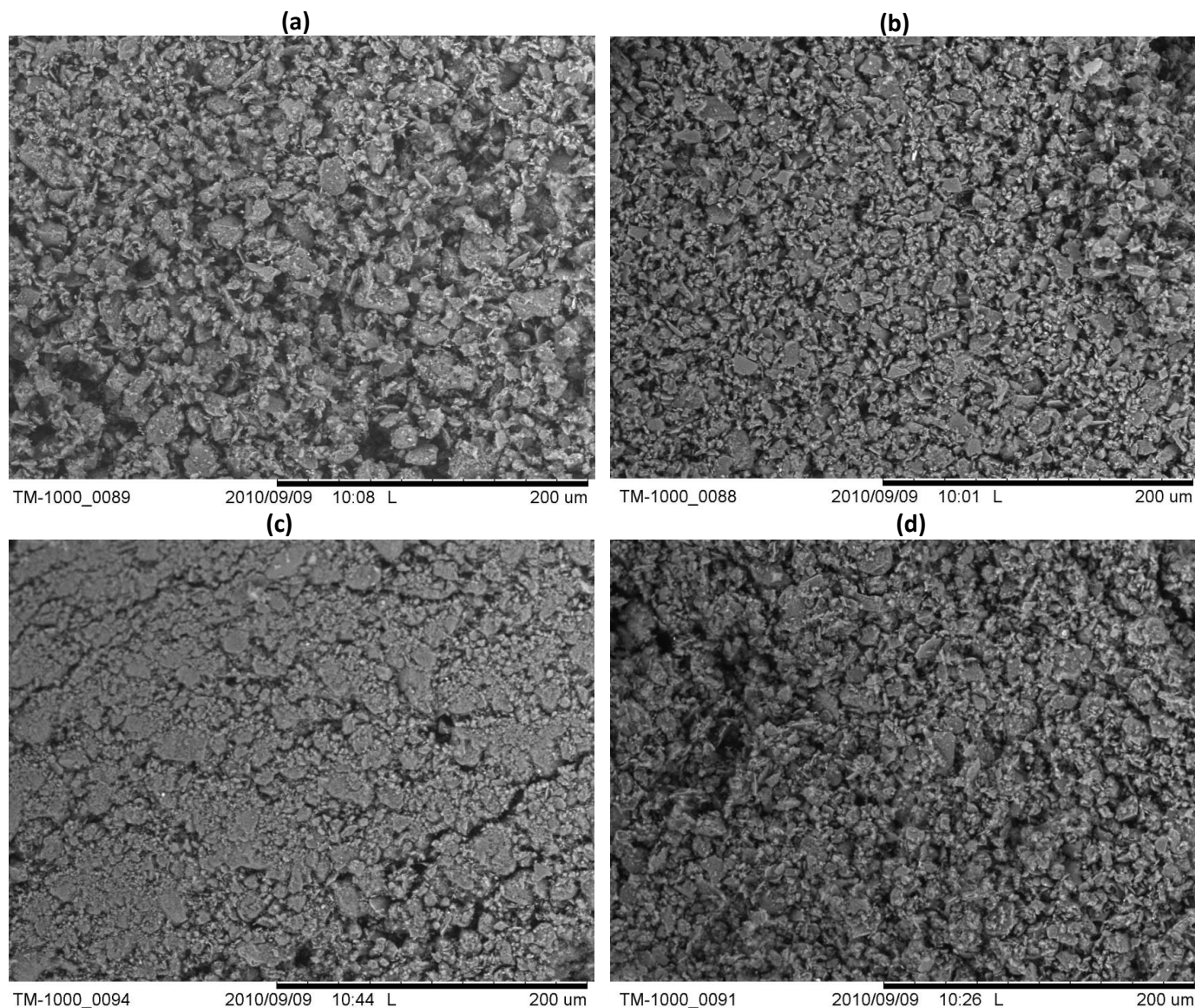


Figure 2. Scanning electron microscope (SEM) image of the sample at x1000 magnification for (a) SIT; (b) PSIT; (c) ROU2 and (d) PROU2.

ROU2, therefore, its presence (2.5%) in PROU2 is attributable to contamination during clay washing with sodium chloride solution in purification process. This may explain sodium detected in PSIT. Nevertheless, as found by Kam et al. (2009), wt% of Mg, Ca, Na and K in the raw sample are negligible.

The enlarged images produced by SEM at 1000 times magnification show that the studied material was not uniform, amorphous minerals were clearly visible in all samples (Figure 2), mainly in the raw clay (Figures 2a and c). Micrograph of the samples (Figures 2a to d), illustrate some tiny particles as well as particles of a somewhat larger size indicating crystallinity. When comparing the micrograph of the raw sample of SIT and

ROU2 (Figures 2a and c), respectively to the purified sample PSIT and PROU2 (Figures 2b and d), there is a little difference. SIT is more heterogeneous with more open porosity, 33.1% as detected by Kam et al. (2009), while PSIT, even heterogeneous with different particle size, is more compact. In ROU2 (Figure 2c), it is difficult to distinguish separate particles and the clump together mater is either amorphous or very small aggregated crystalline particles. There are loads of tiny particles as well as particles of a somewhat larger size in PROU2 as well, which is more compact than ROU2. In order to clearly settle on a crystalline structure, the samples have to be analyzed with X-ray diffraction. All samples are confirmed to consist of crystalline material as found by

Table 3. pK_{a1intr}^s , pK_{a2intr}^s , pH_{pzc} , V_e /mL, $\{\equiv SOH_{tot}\}$ /mol·dm⁻³ and $\{\equiv OH_{tot}\}$ /mol·g⁻¹, values for the different clays.

Parameter	SIT	PSIT	ROU2	PROU2
pK_{a1intr}^s	4.65	4.90	8.01	4.90
pK_{a2intr}^s	8.93	8.84	11.03	8.61
pH_{pzc}	6.79	6.87	9.52	6.76
V_e	1.60	1.20	3.20	1.48
$\{\equiv SOH_{tot}\} \times 10^4$	6.76	5.11	13.10	6.27
$\{\equiv OH_{tot}\} \times 10^4$	1.13	0.85	2.19	1.40

Kam et al. (2009) in the raw samples.

pH range.

Potentiometric titration

The ROU2 clay is highly alkaline due to the presence of carbonate with an initial pH of 9.5, whereas, SIT, PSIT and PROU2 have initial pH below 7, with $pH_{pzc} = 6.79$, 6.87 and 6.76, respectively (Table 3). The removal of the carbonates in ROU2 makes that the pH_{pzc} drop to a value very close to those observed for the SIT clay (Table 3). The pK_{a1intr}^s and pK_{a2intr}^s values as well as the pK_{app} value at Z (surface charge) = 0, are obtained in the titrations with strong acid and base, respectively [Figures 3a to d and Supplementary Figures 1a to h]. The CEC of the raw ROU2 (47 cmol_c/Kg), as well as its total surface (2.19 10⁻⁴ mole/g) are higher than the PROU2 (38 cmol_c/Kg and 1.4 10⁻⁴ mole/g, respectively) probably due to the contribution of some organic matter (OM) in the raw material. In addition, ROU2 showed high buffering capacity at pH 5 to 6, but small buffering capacity in the pH range of 4 to 5 (Figure S1e). The strong buffering capacity could be characteristic of carboxylate groups bound to organic material in the sample. The buffering capacity in the pH range of 4 to 6 could be attributed to small water-soluble organic acids such as oxalic, citric, formic and lactic acid and to carboxylic acid groups in the OM as suggested by Sajidu et al. (2006). These acidic constituents are removed during the purification process, and hence absent in the PROU2 sample (Figure S1g). SIT and PSIT curve (Figures S1a to S1d) are similar. Slightly lower pH values are noted in the raw SIT sample. This can be explained by the presence of acidifying factors such as humic acids in the unpurified samples.

Adsorption and removal of copper(II), lead(II) and chromium(III)

The sorption of copper(II), lead(II) and chromium(III) ions to the surfaces of the SIT, PSIT, ROU2 and PROU2 samples as a function of pH in aqueous suspensions are given in Figure 4. The adsorption patterns are similar, and the amount uptake metal increases from almost zero to complete adsorption within a specific and fairly narrow

Adsorption of copper(II)

Copper(II) is completely removed from the aqueous phase at pH 7.0 with SIT, and above pH 8 for the other clay samples (Figure 4a). At a total copper(II) concentration of 0.06 mmol·dm⁻³ (3.8 mg·L⁻¹) obtained after dilution as used in this study, precipitation of copper(II) hydroxide, Cu(OH)₂, is expected to start at pH 6.3 at the prevailing conditions, $C_{Cu} = 0.06$ mmol·dm⁻³ and $K_{sp}(Cu(OH)_2) = 2.2 \times 10^{-20}$ (mol·dm⁻³)⁻³. However, at this pH of 6.3, 50, 70 and 60% of the copper(II) was already adsorbed with SIT, PSIT, ROU2 and PROU2, respectively. This shows that adsorption is the almost completely dominating process at the removal of copper(II) under the conditions used in this experiment. The adsorption starts at pH < pH_{pzc} for all samples, hence formation of inner-sphere complexes are expected. Copper(II) is known to strongly adsorb on organic matter and iron oxides than on the clay minerals (Bradl, 2004). These particular adsorption may enhance the copper(II) removal from the aqueous solution in ROU2 sample. In addition, copper removal by raw samples, particularly ROU2, may be enhanced by precipitation of malachite (Cu₂(OH)₂CO₃).

Adsorption of lead(II)

The removal of lead(II) from the aqueous phase as a function of pH showed a similar behavior for all the samples studied (Figure 4b). Precipitation of Pb(OH)₂ at a total lead(II) concentration of 0.048 mmol·dm⁻³ (9.9 mg·dm⁻³) is expected to start at pH 8.7. At this pH, more than 90% of the lead(II) is already removed by all samples in this study. Lead(II) has been shown to exhibit the strongest affinity to clays as well as iron oxides (Sauve et al., 2000). This specific adsorption may enhance lead removal in raw samples. Previous study showed that formation of Pb(OH)⁺ is important between pH 6 and 10 (Bradl, 2004). Uptakes of lead(II) may be done through this hydrolyzed species. General results from our study implies that lead(II) is strongly bound to the clay surfaces.

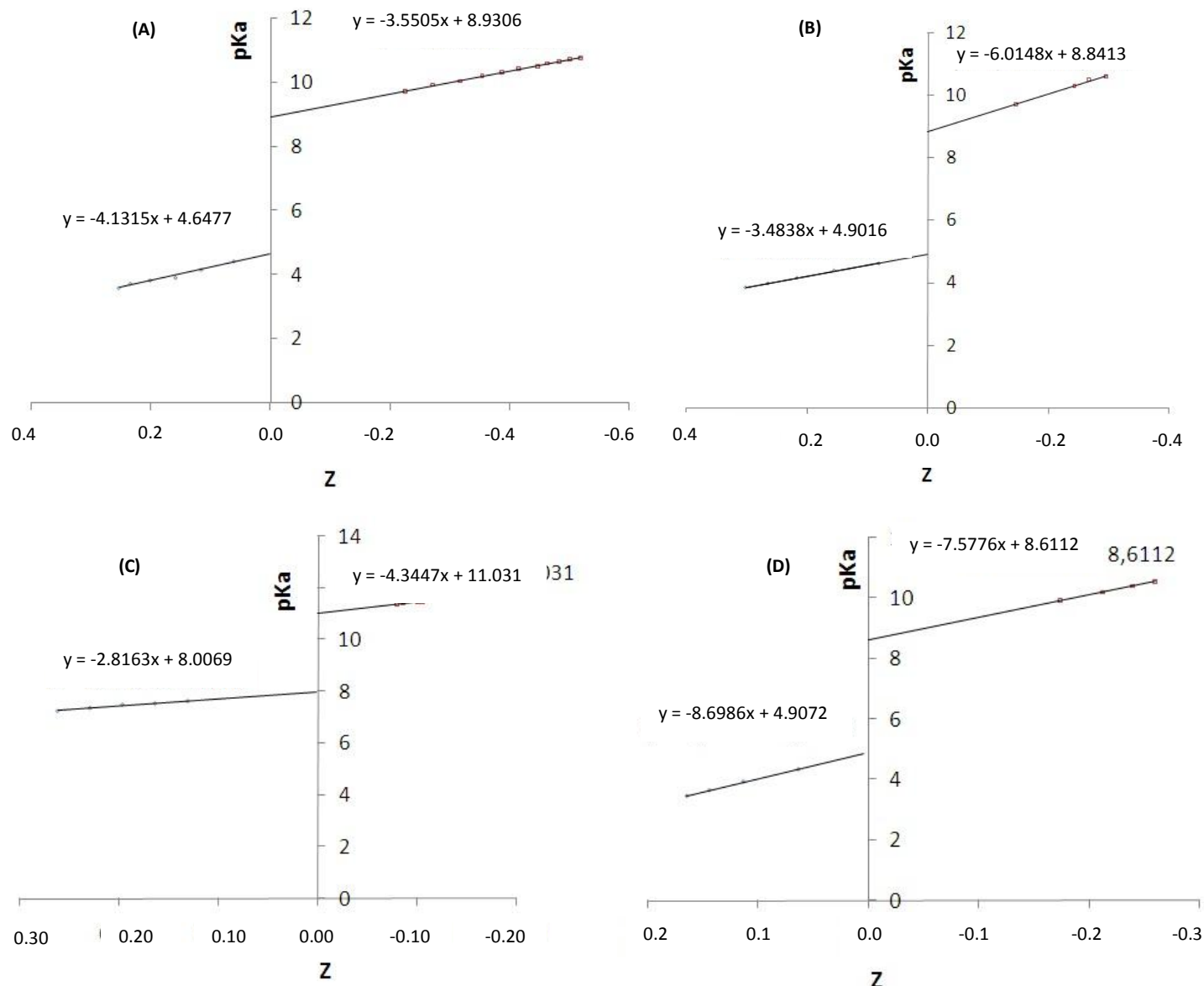


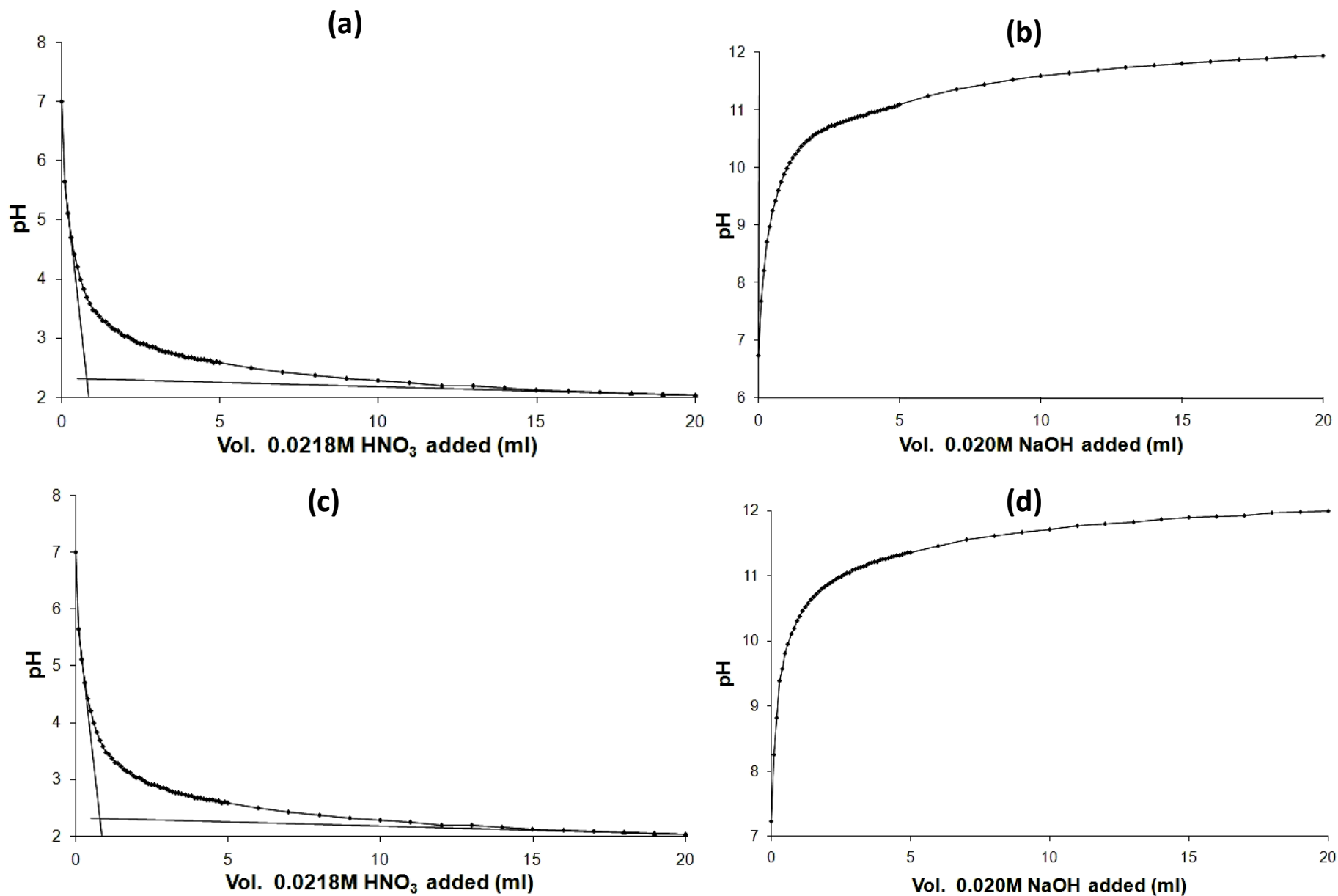
Figure 3. Apparent acidity constants (pK_{app}) plotted against charge density (Z) both calculated from the acidic and alkalimetric titration data for: (a) SIT, (b) PSIT, (c) ROU2 and (d) PROU2.

As for copper(II), these results strongly indicate that formation of inner-sphere complexes are expected as sorption started below pH_{pzc} of each sample. The extent of adsorption by SIT and PSIT is similar at given pH value; the absence of data for ROU2 between pH 4 to 6.5 do not allow comparison of the adsorption pattern with the purify sample PROU2.

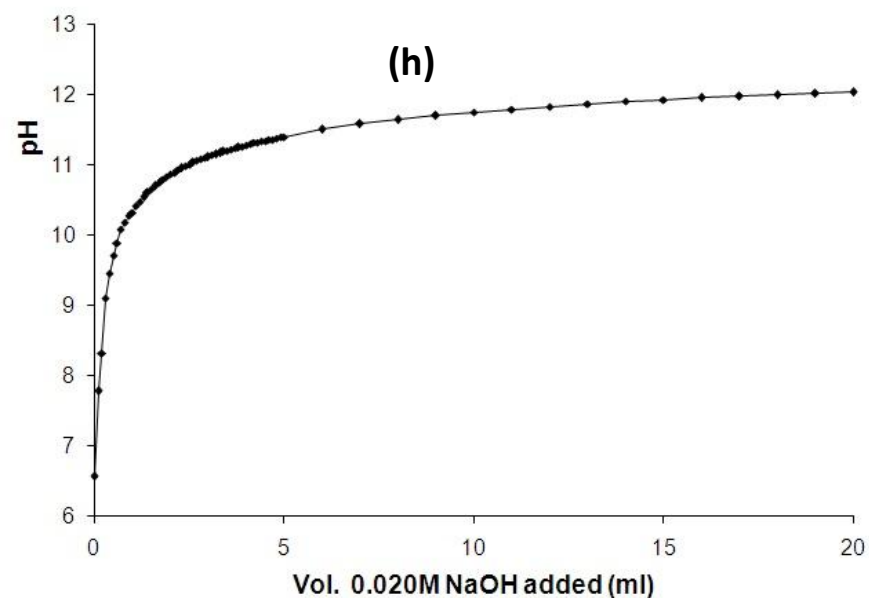
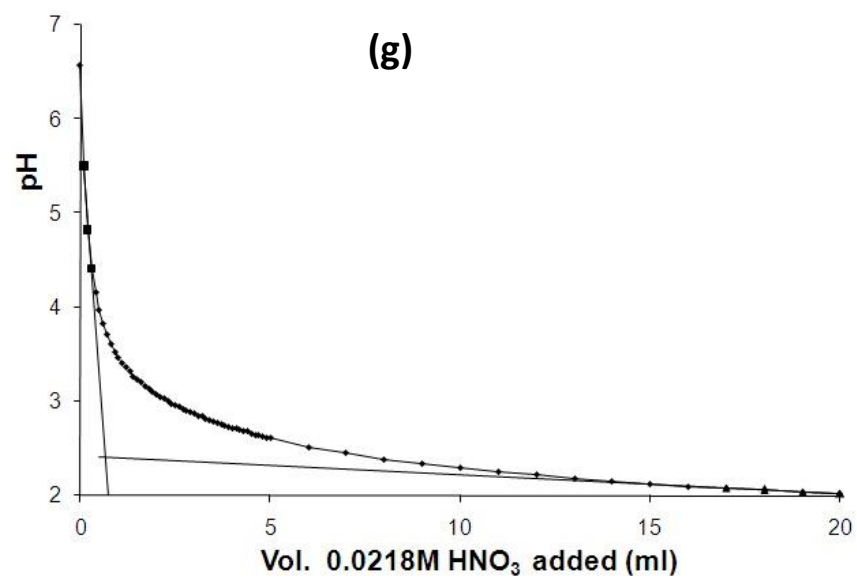
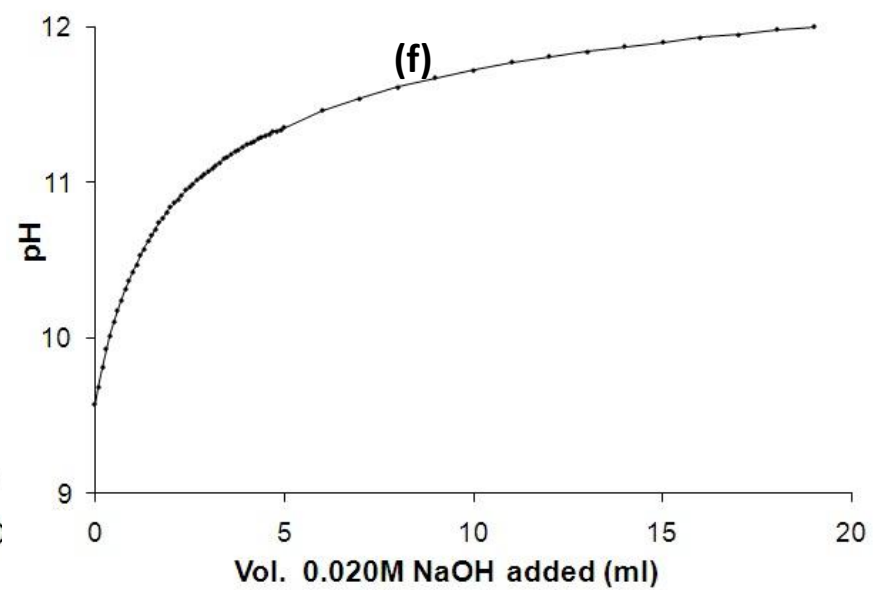
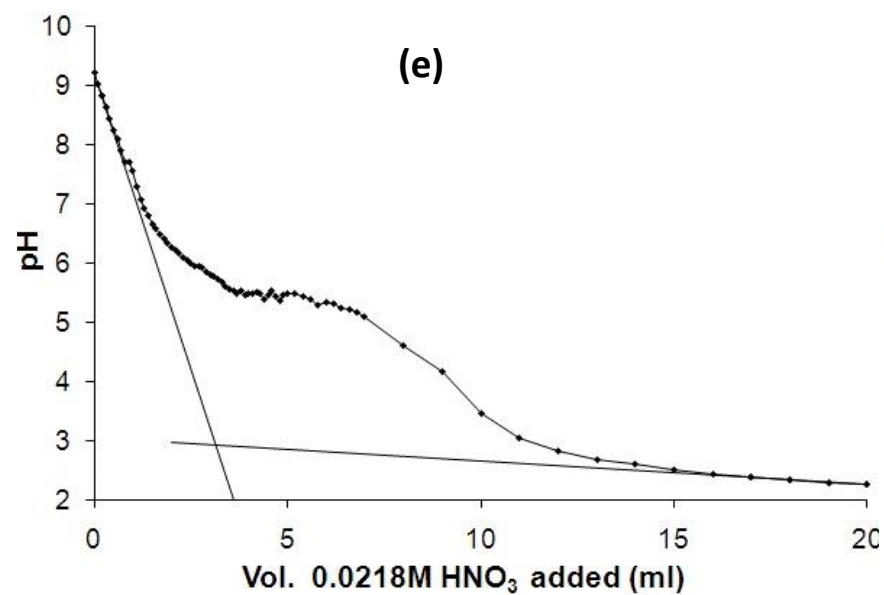
Adsorption of chromium (III)

The removal of chromium(III) by sorption to clay surfaces was even more effective than for copper(II) and lead(II) with complete removal by all clay samples studied at pH 7 (Figure 4c), showing that inner-sphere complexes are

likely formed. A substantial removal of chromium is observed at low pH values of 2 to 3. In a solution containing a total chromium(III) concentration of $0.096 \text{ mmol}\cdot\text{dm}^{-3}$ ($5.0 \text{ mg}\cdot\text{L}^{-1}$) precipitation of $\text{Cr}(\text{OH})_3$ is expected to start at pH 5.27. However, at this pH more than 85% of the chromium(III) was already removed, showing that adsorption to clay surfaces is a completely dominating form of removal of chromium(III) from the aqueous phase. Trivalent Cr is known to be extensively hydrolyzed in acid solutions to species such as $\text{Cr}(\text{OH})^{2+}$, $\text{Cr}_2(\text{OH})_4^{2+}$, or $\text{Cr}_6(\text{OH})_6^{6+}$. The increased adsorption of Cr(III) with increasing pH is caused by cation exchange reactions of the hydrolyzed species (Bradl, 2004), and may account for the cation removal in this experiment.



Supplementary Figure 1. Titration of the four clay samples with strong acid (nitric acid) and strong base (sodium hydroxide); (a) and (b) for SIT; (c) and (d) for PSIT; (e) and (f) for ROU2; (g) and (h) for PROU2.



Supplementary Figure 1. Continued.

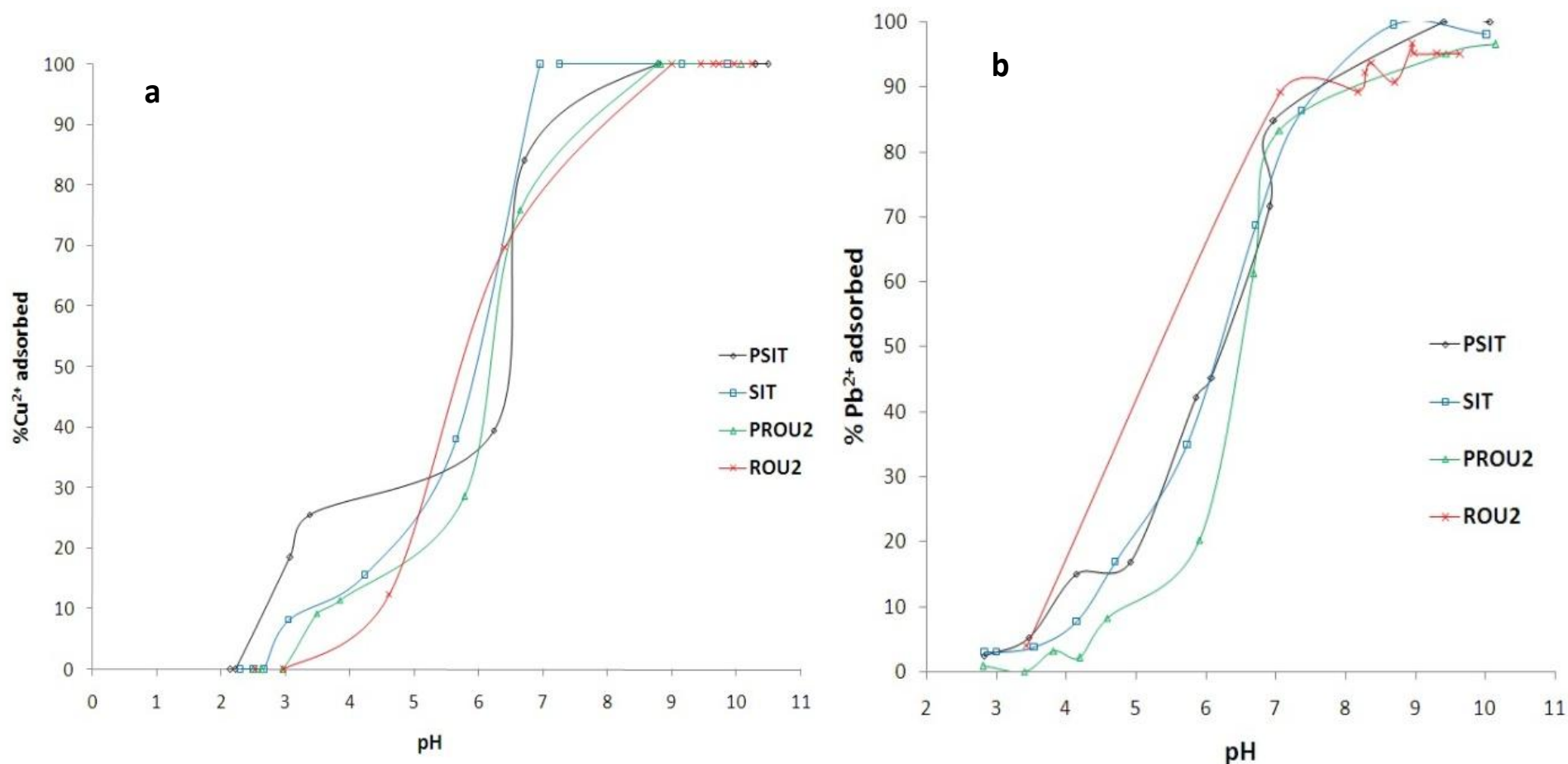


Figure 4. Removal of copper(II), lead(II) and chromium(III) in percent (%) as function pH for the four studied clays.

Chromium(III) is also strongly adsorbed on iron oxides as well as OM (Bradl, 2004). This specific adsorption may contribute to the removal of chromium(III) in the raw samples, even though there is no significant difference between raw and purified clay (Figure 4c).

Conclusion

The ROU2 clay has alkaline properties due to presence of carbonates giving a pH_{pzc} of 9.52, while the SIT clay has a pH_{pzc} of 6.79. The acid-base behavior of the natural mixed clays show

buffering capacity in ROU2 which could be attributed to carboxylate groups bound to organic material in the raw clay. This study shows that the raw ROU2 clay most efficiently removes metal ions as copper(II), lead(II) and chromium(III) from aqueous phases, mainly due to the high pH

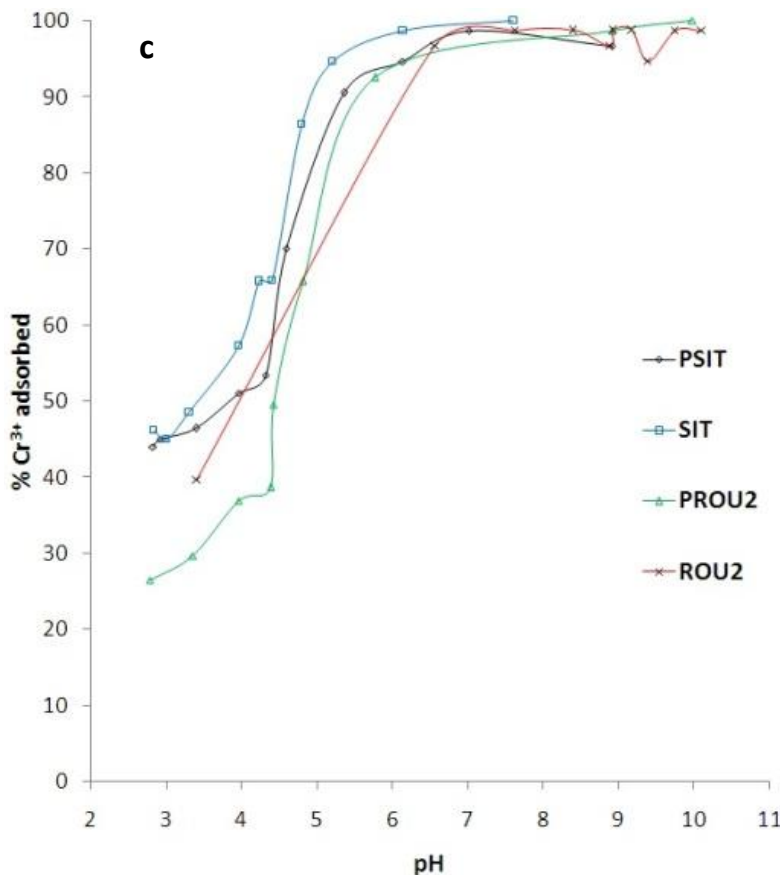


Figure 4. Continued.

values obtained by the presence of carbonates. The removal of cationic species on oxide mineral surfaces is favored by high pH values. Clays with pH_{pzc} values will be more effective for two reasons, absorption increases with increasing pH, and precipitation of metal hydroxides/oxides with low solubility takes easily place. Further work is being considered on the mechanisms of heavy metal sorption on the clays, as the work demonstrated the successful application of SIT and ROU2 clays as low-cost adsorbent for heavy metal remediation.

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