



## Trivalent Chromium removal from Aqueous solution using Raw Natural Mixed Clay from BURKINA FASO

Pare Samuel<sup>1</sup>, Persson Ingmar<sup>2</sup>, Guel Boubié<sup>3</sup>, and Lundberg Daniel<sup>2</sup>

<sup>1</sup>Laboratoire de Chimie organique, Structure et réactivité, U.F.R.-S.E.A–Université de Ouagadougou, Ouagadougou 03, BURKINA FASO

<sup>2</sup>Department of Chemistry, Swedish University of Agricultural Sciences, Uppsala, SWEDEN

<sup>3</sup>Laboratoire de Chimie Physique et d'Electrochimie, U.F.R.-S.E.A–Université de Ouagadougou, Ouagadougou 03, BURKINA FASO

Available online at: [www.isca.in](http://www.isca.in)

Received 10<sup>th</sup> January 2013, revised 20<sup>th</sup> January 2013, accepted 10<sup>th</sup> February 2013

### Abstract

Acid-Base properties of the raw mixed clay TOU from Burkina Faso, were study as well as the potential of the sample, in removing of chromium(III). The interactions of chromium(III) cation with the natural mixed clay minerals were examined using extended X-ray absorption fine structure (EXAFS) spectroscopy. Chemical elementary composition study of the mixed clay revealed presence of Silicon, Aluminum and Iron as mains elements. Qualitative mineralogical characterization of the clay by X-Ray diffraction, point out quartz and 7Å Halloysite as the dominating component in the sample.  $pH_{pzc}$  of the clays, as determined by potentiometric titrations, was 8.21.  $Cr^{3+}$  adsorption on clay started at pH below  $pH_{pzc}$  indicating inner-sphere complexes formation. More than 95% of chromium(III) is achieved at pH greater than 7. Chromium(III) forms a tetramer hydrolysis complex on the mineral surface with Cr–O bond and Cr · · Cr distances of 2.487, 3.087 and 3.636 Å, respectively, which is indicative of a chain structure with edge sharing  $CrO_6$  octahedra.

**Keywords:** Chromium (III), Natural mixed clays, Potentiometric titration,  $pH_{pzc}$ , EXAFS

### Introduction

Studies conducted in Burkina Faso reveal high level of particular heavy metal in streams and soil, mainly due to anthropogenic activities such as mining society's effluents, agricultural activities, discharge from industrial plants and sewage works<sup>1,2,3</sup>. Chromium(III) is among the most common heavy metal pollutants found in Burkina Faso<sup>2, 4</sup>, mainly from tannery effluent<sup>3</sup>.

Investigations have been made worldwide on available and environmental friendly material as adsorbent such as Chitosan<sup>5, 6</sup>, Activated *P. Lentiscus* Leaf<sup>7</sup>, Acid Acrylic Resin<sup>8</sup>, clays<sup>9</sup>.

Clays are known for their ability to effectively removed heavy metal by specific adsorption and cation exchange<sup>9</sup>. Large quantities of clay are available and are extracted and used in Burkina Faso for traditional potters, ceramic and individual brick<sup>10-13</sup>.

Recently, some studies<sup>11,14,15</sup>, investigated on the potential of natural mixed clays 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, contact time<sup>9,16,17,18,19</sup>. Of all these factors, pH is considered the 'master variable' controlling ion exchange, dissolution/precipitation, reduction/oxidation, adsorption and complexation reactions<sup>20</sup>. Cations adsorption, are more effective at high pH.

In this study, natural clay from Burkina Faso, TOU, acidic and basic properties were determined by potentiometric titration. Elementary composition of elements of sodium or heavier of the clay samples were investigated using the energy dispersive spectrometer (EDS) detector of scanning electron microscopy (SEM) instrument, Hitachi TM-1000, as well as qualitatively characterization of the clay mineralogical composition by powder X-ray diffraction. Dependence of chromium(III) uptake on pH by the clay were study.

Investigations on the local structural environment of chromium(III) sorbed on silica using EXAFS have been reported<sup>21</sup>. Their results showed formation of monodentate chromium (III) surface complex on silica with Cr–Si distance of 3.39Å for the sorbed chromium while formation of polynuclear chromium hydroxide octahedra was discerned on the surface. It has been found that on the natural mixed alkaline clay, chromium(III) forms a polynuclear hydrolysis complex on the mineral surface with Cr–O bond and Cr · · Cr distances of 2.00 and 3.03 Å respectively<sup>22</sup>.

In this work, EXAFS (extended X-ray absorption fine structure) spectroscopy was applied to characterize sorbed chromium (III) on the clay surfaces without any pre-treatment, at pH 3.3. The main advantages of EXAFS are that the nearest neighbour distances around the absorbing element are observed and all states of aggregation can be studied with high precision in the distances even in very dilute samples with metals sorbed on mineral or clay surfaces<sup>22</sup>.

## Material and Methods

**Clay's samples:** Clay's sample used in this study was collected from Tougan village, located in the North-Western part of Burkina Faso. Chromium(III) sorption was performed on the raw sample. The clay was grounded in pounder and fractionated by sifting with an automatic sieve (Retsch Vibro) yielding five fraction sizes,  $f_n$ :  $f_1 < 0.032$  mm,  $0.032 < f_2 < 0.045$  mm,  $0.045 < f_3 < 0.063$  mm,  $0.063 < f_4 < 0.125$  mm, and  $0.125$  mm  $< f_5$ . The  $f_1$  fraction was used in this investigation. Cation exchange capacity (CEC) values were determined by adsorption of copper ethylenediamine complex as describe by Bergaya and Vayer. The CEC values were  $33.33 \pm 1.11$  cmol/kg for TOU. These natural mixed clays have high CEC values, but similar to CEC found in previous study on Burkina Faso mixed clay of 42.38 cmol/kg<sup>11 15</sup>.

**Mineralogical analyses:** Two different techniques were used in order to investigate the mineralogical composition of the clays: scanning electron microscopy and X-ray powder diffraction. The intention of this investigation was to obtain an approximate indication of the mineralogical composition of the clay sample and to account for the clay's heavy metal cation adsorption properties based on this knowledge.

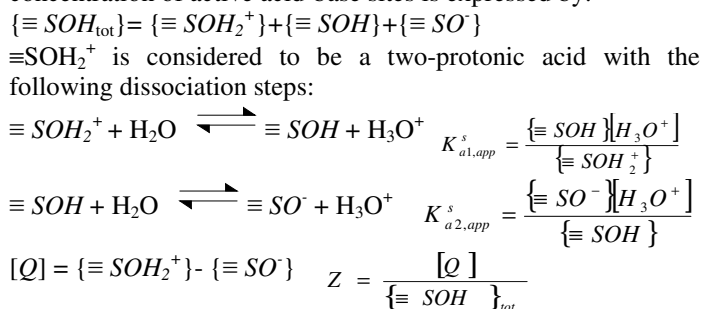
**Scanning electron microscopy:** Elementary composition of elements of sodium or heavier of the clay samples were determined using the EDS detector of a SEM, Hitachi TM-1000. A small amount of the sample (fraction  $f_1$ ) was attached to a piece of carbon rich sticky tape, and placed in the instrument. 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 normalized.

**Powder X-ray diffraction:** X-ray powder diffraction (XRD) analysis was performed on the two samples. Samples was packed into 1 mm glass capillary tubes and analyzed in a Bruker SMART CCD 1 K diffractometer at the Department of Chemistry, SLU-Uppsala SWEDEN with monochromatic MoK $\alpha$  ( $\lambda = 0.7093$  Å) radiation. The XRD patterns were integrated and converted to a 2D diffraction pattern with peaks to be identified. The software program EVA was used to identify the "fingerprint" and give suggestions on possible minerals together with diffraction profiles obtained from standards of clay minerals as reported in literature<sup>10, 23, 24, 25, 26</sup>. The final plot of the powder pattern was created using Microsoft Excel software on raw data text files.

**Potentiometric titration:** Potentiometric pH titrations were performed on suspensions containing 6.0 g sample/L as previously described<sup>14,15</sup>. In brief, 50 mL of the clay suspension, containing 0.1 mol·dm<sup>-3</sup> NaNO<sub>3</sub> as supporting electrolyte, was titrated with 0.0218 mol·dm<sup>-3</sup> 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<sup>-3</sup> 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:



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.  $V_i$  plot, where  $V_i$  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  $pK_{a1}^s$ ,  $pK_{a2}^s$  and  $pK_{a2}^{intr}$  values, and the point of zero charge,  $pH_{pzc}$ , values were calculated as:

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

**Preparation of solutions and adsorption experiments:** Aqueous solutions of 2.00 mmol·dm<sup>-3</sup> of chromium(III), were prepared from the nitrate salt Cr(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, analytical grade reagents, with a declared elemental impurity of less than 0.5%. Milli-Pore filtered deionized water was used at the preparation of all solutions. A set of 10 solutions of chromium(III) with pH 2-11 were prepared by pipetting into centrifuge tube 7.5 cm<sup>-3</sup> of 0.1 mol·dm<sup>-3</sup> NaNO<sub>3</sub>, 2.5 cm<sup>-3</sup> of clay suspension (6 g/dm<sup>-3</sup>) and 0.5 cm<sup>-3</sup> of the metal stock solution. The pH was adjusted to the predetermined values with appropriate amounts of acid, 0.0218 mol·dm<sup>-3</sup> nitric acid, or base, 0.0200 mol·dm<sup>-3</sup>

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. 3-4 cm<sup>3</sup> 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 AAnalyst 800). 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.

**Metal sorption and EXAFS - data collection:** A 20 mmol dm<sup>-3</sup> of chromium (III) solutions were obtained from dissolution of the nitrate salts AR grade reagent Cr (NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (with a declared impurity of less than 0.5%) in deionized water. 25 cm<sup>3</sup> of the 20 mmol dm<sup>-3</sup> of the metal solution was added to 1.0 g of the clay and the pH was adjusted by dropwise addition of 1.0 mmol dm<sup>-3</sup> NaOH for the suspensions. The clay suspensions were stirred for 48 h at room temperature and then centrifuged to separate the rich adsorbed clay samples which were dried in air before the EXAFS measurements. pH values were adjusted to 3.3.

Chromium K-edge spectra were collected at 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 measurements were performed with a PIPS (passivated implanted planar silicon) detector (Canberra, [http://hasylab.desy.de/e70/e207/e674/e6092/e30091/-detectors/pips\\_detector/index\\_eng.html?preview=preview](http://hasylab.desy.de/e70/e207/e674/e6092/e30091/-detectors/pips_detector/index_eng.html?preview=preview)). 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% at the end of the scans. Internal energy calibration was made with chromium metal foil. The treatment of the EXAFS data was carried out by means of the EXAFSPAK program package, 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. 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<sup>23</sup>. 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  $\pm 0.01$ – $0.02$  Å for well-defined interactions.

## Results and Discussion

**Clay's Mineralogy:** The intention of this investigation aimed to give an approximate indication of mineralogical composition of two clays samples, and to account for heavy metal removal from it.

The elemental analyses of the raw clay TOU shows that the dominating element in the samples is silicon (table 1), with total among of 52.8%, follow by aluminum (25.3%) and iron. The EDS used in this study only detects sodium and heavier elements. Hence, the method does not detect oxygen, even oxygen is assumed to be the dominating element of Burkina Faso clay mineral<sup>11</sup>. With wt% of 17.6%, iron content is much lower than silicon and aluminum since the measurement is done by weight percentage, and iron molecular weight is greater than silicon and aluminum molecular weight. There is also small fraction of calcium and potassium in the sample.

The enlarged images produced by SEM at 1000 times magnification shows that the studied material are not uniform (figure. 1). Most particles have sharp edges typical for a crystalline structure in the raw sample. There is a few bigger "clumps" sized that can either be small aggregated particles that are crystalline or one big amorphous "clump". Some particles have a rough surface that most likely is even smaller particles attached to the surface. The particle sizes are bigger and not compact.

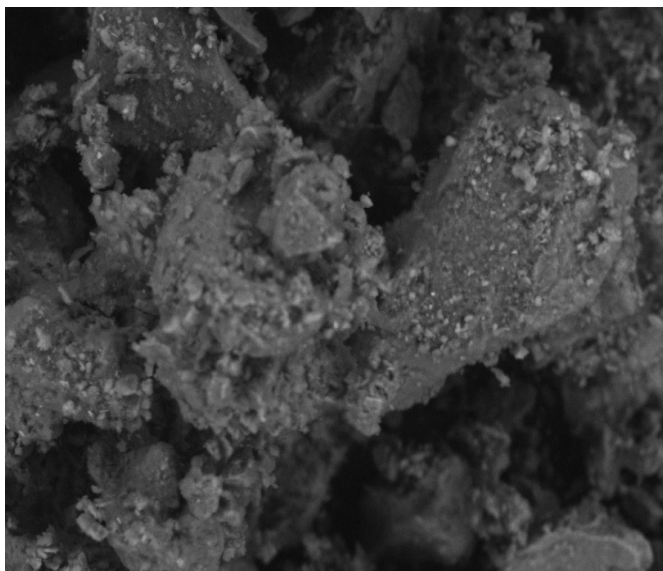
**Table-1**  
Weight percentage of detectable elements in the samples at 1000 time magnification spot

| Element  | Silicon | Aluminum | Iron | Calcium | Potassium |
|----------|---------|----------|------|---------|-----------|
| Weight % | 52.8    | 25.3     | 17.6 | 1.1     | 3.2       |

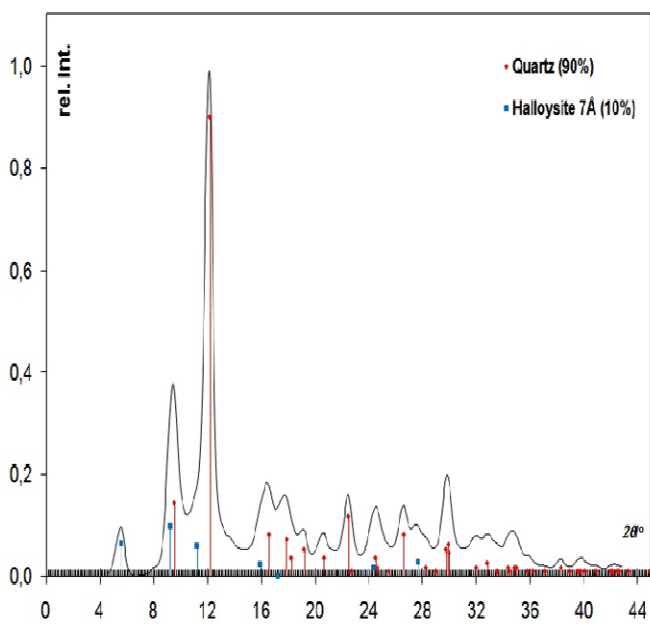
The diffraction patterns from the analyses with the X-ray powder diffractometer prove that the studied material is at least partly crystalline. Still, the broad peaks (Fig. 2) show that the crystallinity is low, and that some of the material doubtless is amorphous. When comparing the patterns with reference patterns, the clay sample shows different profiles, but consists of some type of quartz and the 7Å Halloysite.

The intention of this investigation, aimed to give an approximate indication of mineralogical of the TOU clay. Hence, the percentage list in the legend is that of the pure reference and not necessarily the sample as whole, but gives at

least an indication of the ratio between the different constituents. In summary, the mineral characterization point out quartz and 7Å Halloysite as the dominating component in the sample, and probably some amorphous iron compounds, as iron could not be detected through the X-Ray diffraction.



**Figure-1**  
 SEM image of the sample at 1000 times magnification



**Figure-2**  
 X-ray powder diffraction pattern of the raw clay sample

**Potentiometric titration:** The TOU natural mixed clay is alkaline as indicated by initial pH values of greater than 8 in Figs. 3. The  $\{ \equiv SOH_{tot} \}$  (Table 2) calculated from the equilibrium volume obtained in Figs. 3 is  $5.11 \times 10^{-4}$  M ( $8.52 \times 10^{-5}$  mole/g). The initial alkaline pH value of TOU could be

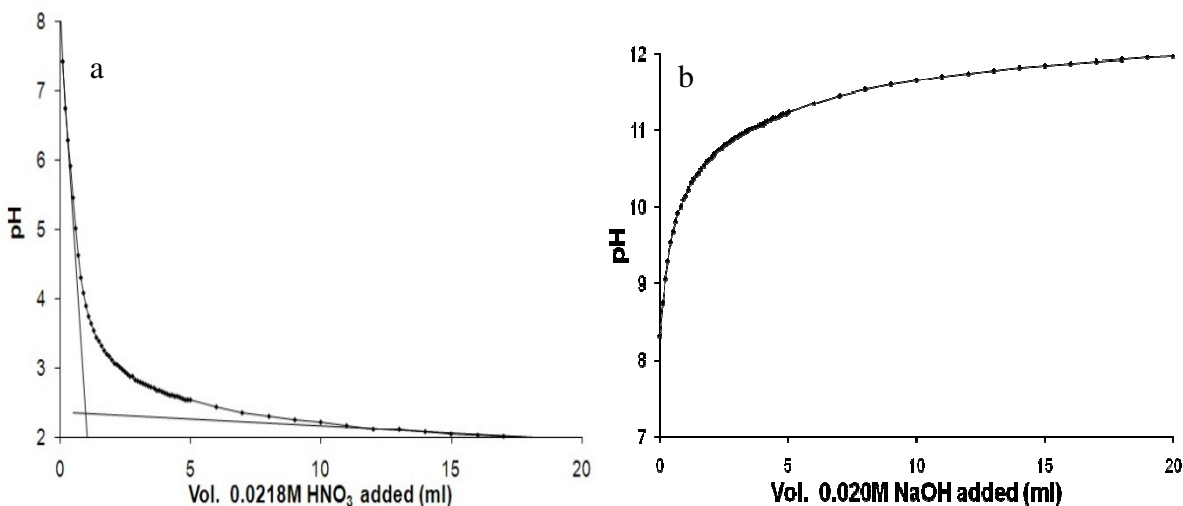
attributable to some carbonate contribution in the raw sample. This initial pH drops rapidly while adding concentrated acid. No evidence buffering properties is visible in the titration curve. However, the clay titration curve is not as smooth as it would have been in the case of the absolute absence of any water-soluble acids. The  $pK_{a1int r}^s$  and  $pK_{a2int r}^s$  values (Table 2), the  $pK_{app}$   $pK_{app}$  value at Z (surface charge) = 0, are obtained in the titrations with strong acid and base, respectively, Figs. 3 and 4.  $pHpzc$ , which is an average of  $pK_{a1intr}^s$  and  $pK_{a2intr}^s$  and is found to be 8.21 for TOU clay (Fig. 4).

**Adsorption of chromium(III):** Figure 5 shows per cent chromium adsorbed at varying suspension pH. The solubility product constant (Ks) for  $Cr(OH)_3$  at 25°C is  $6.3 \times 10^{-31}$ . This implies that precipitation of  $Cr(OH)_3$  is expected to start at pH 5.27 at the prevailing conditions, total chromium(III) concentration of  $0.096 \text{ mmol} \cdot \text{dm}^{-3}$  ( $5.0 \text{ mg} \cdot \text{L}^{-1}$ ). At this pH, more than 85% of the chromium(III) is already removed. This removal is attributable to adsorption on the clay. Chromium(III) is also strongly adsorbed on iron oxides as well as OM<sup>5</sup>. These specific surface complexation to iron oxides, organic complexation as well as adsorption to carbonates may also occur and contribute to the removal of chromium(III) in the raw sample. The removal of the remaining 15% at higher pH could thus be due to combination of adsorption on clay minerals and precipitation of  $Cr(OH)_3$ . The adsorption starts at  $pH < pH_{pzc}$  for all samples, hence formation of inner-sphere complexes are expected. In order to understand the mechanism governing the adsorption at low pH, EXAFS was used.

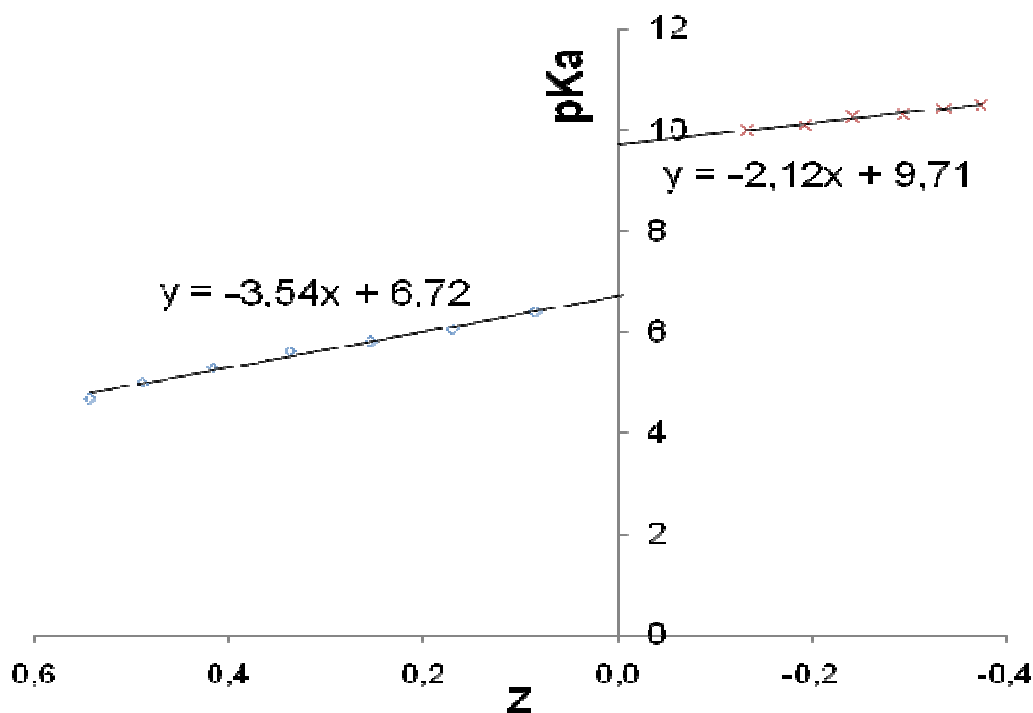
Fits of the EXAFS spectra and FT of  $Cr^{3+}$  clay samples are shown in figure 6 with quantitative fitting results listed in table 3. The FT shows that the Cr(III) has a nearest neighboring atom, certainly oxygen, at mean bond distance of 1.988 Å, with a coordination number of 6 (table 3). Three Cr...Cr bonds have been refined from the FT: The light back-scatterer with bond distance of 2.487 Å, and two heavier back-scatterers, with bond distance of 3.087 Å and 3.636 Å, respectively. Very weak contribution from multiple scattering within the  $CrO_6$  core were also detected at 3.986 Å. One indefinite hydrolysis complexes have been identified in aqueous solution  $\equiv O-Cr_4(OH)_5(OH_{1+x})^{(6-x)+}$  present in aqueous chromium(III) solution in acidic condition. From the identified indefinite form, Cr(III) is present at tetramer form in the complex. The Cr...Cr bond distance found are different to previous finding in the structure of tetramer hydrolysed chromium(III) complexes  $[Cr_4(OH)_6(H_2O)_{12}]^{12+}$  in aqueous solution of 3.585 and 3.599 Å<sup>28</sup>. Authors<sup>29</sup> have suggested tetramer  $[Cr_4O(OH)_5]^{5+}$  resulting from intermolecular deprotonation and condensation of  $[Cr_4(OH)_6]^{6+}$ . This deprotonation creates an oxo bond, reducing the angle and thereafter some Cr...Cr distance in the octahedral structure. Hence, one suggestion of Cr(III) in the solution could be the binding of Cr(III) to an oxygen on the clay surface, and five oxygen from hydroxyl/water group.

**Table-2**  
 $pK_{a1\text{int } r}^s$ ,  $pK_{a2\text{int } r}^s$ ,  $pH_{pzc}$ ,  $V_e$  and  $\{\equiv SOH_{Tot}\}$  value for the TOU clays

| $pK_{a1\text{int } r}^s$ | $pK_{a2\text{int } r}^s$ | $pH_{pzc}$ | $V_e$ (ml) | $\{\equiv SOH_{Tot}\} \times 10^4$ (mol·dm <sup>-3</sup> ) | $\{\equiv SOH_{Tot}\} \times 10^5$ (mole/g) |
|--------------------------|--------------------------|------------|------------|--|---|
| 6.72                     | 9.71                     | 8.21       | 1.2        | 5.11   | 8.52  |



**Figure-3**  
 Titration of the clay sample with strong acid (a) and strong base (b)



**Figure 4**  
 Apparent acidity constants ( $pK_{app}$ ) plotted against charge density ( $Z$ ) both calculated from the acidic and alkalimetric titration data (Figures 3) for the clay sample

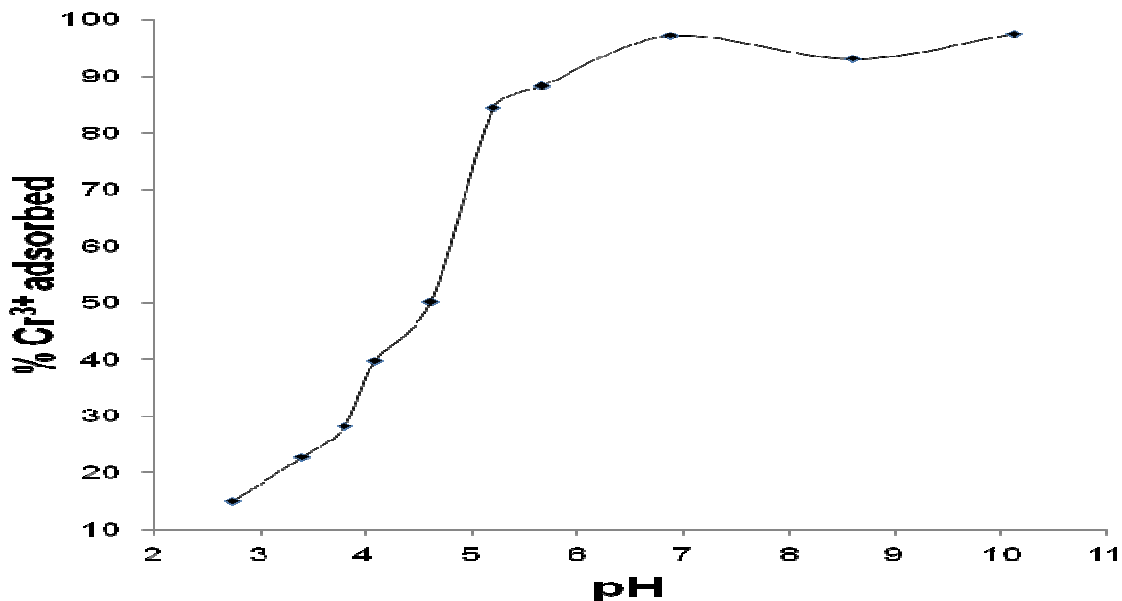


Figure-5  
 Removal of chromium(III) in percent (%) as function pH for the studied clay

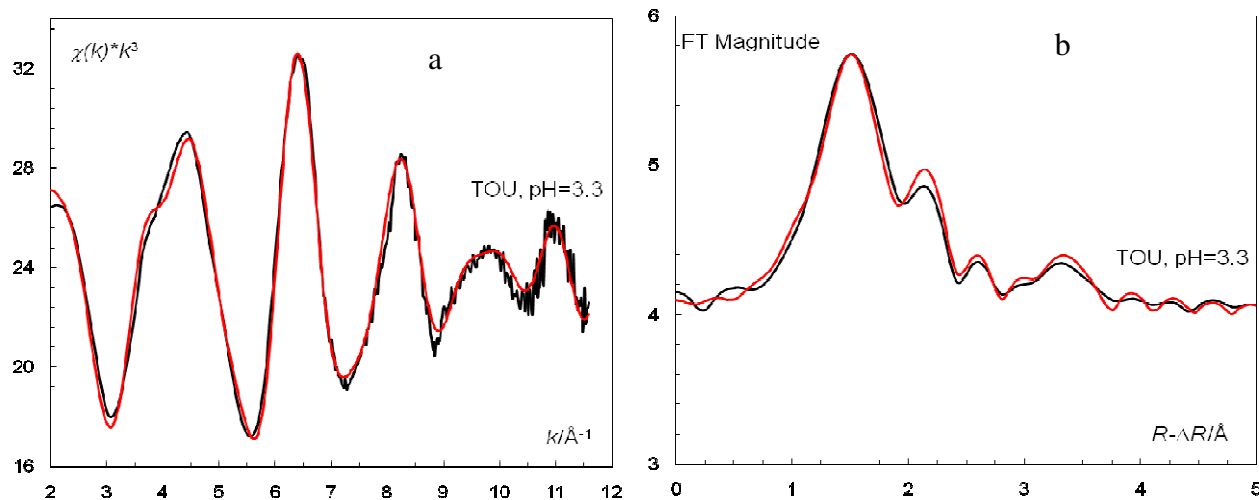


Figure-6

(a)  $k^3$ -weighted Cr K-edge EXAFS  $\chi$  spectra for Cr-clay samples treated at different pH compared with the theoretical signals (bold lines); (b) phase shifted Fourier transforms of the EXAFS data

Table-3

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

| Species   | Interaction           | N   | R(Å)     | $\Delta^2(\text{Å}^2)$ |
|---|-----------------------|-----|----------|------------------------|
| TOU treated at pH=3.3   |                       |     |          |                        |
| $\equiv\text{O}-\text{Cr}_4(\text{OH})_5(\text{OH}_{1+x})^{(6-x)+}$ | Cr-O                  | 6   | 1.988(2) | 0.0119(2)              |
|   | MS ( $\text{CrO}_6$ ) | 3x6 | 3.986(6) | 0.012(1)               |
|   | Cr...Cr               | 2   | 2.487(2) | 0.0104(3)              |
|   | Cr...Cr               | 1   | 3.087(3) | 0.0070(3)              |
|   | Cr...Cr               | 2   | 3.636(7) | 0.0073(4)              |

## Conclusion

The work has demonstrated the successful application of Tougan natural mixed clays for chromium(III) removal from aqueous solution as a cheap and environmentally friendly method. The TOU clay is alkaline with pH<sub>pzc</sub> value of 8.21. Chromium(III) sorbed on the natural mixed clay were studied using EXAFS spectroscopy at low pH (3.3), are showed to be sorbed as hydrolysed tetrahedral polynuclear complexes.

## Acknowledgment

Financial support of the BUF:02/ISP/IPICS/ project from the International Science Program (ISP) Uppsala-Sweden, through the International Program in Chemical Sciences (IPICS) is gratefully acknowledged. Portions of the research were carried out at beam-line I811, MAX-lab synchrotron radiation source, Lund University, Sweden. Funding for the beam-line I811 project was kindly provided by the Swedish Research Council and the "Knut och Alice Wallenbergs Stiftelse".

## References

1. UN, Ground Water in West Africa, *Natural Resources/Water Series*, **18**, 53-65 (1983)
2. Zongo I., Jean-Pierre L., Hama A. M., Joseph W. and Francois L. Removal of hexavalent chromium from industrial wastewater by electrocoagulation: a comprehensive comparison of aluminium and iron electrodes, *Separation and Purification Technol.*, **66**, 159-166 (2009)
3. Zongo I., Joseph W., Belkacem M., Amadou H.M., Lapique F. and Jean-Pierre L., Traitement de deux effluents textiles et d'un effluent simulé de tannerie par électrocoagulation: Etude énergétique et effet des paramètres opératoires sur le traitement des polluants, *European Journal of Scientific Research*, **62(2)**, 216 -235 (2011)
4. Etienne B., Bouda S. and Ouedraogo L., Physical, Chemical and biological characteristics of reservoirs in Burkina Faso. Tech. Center for Agric. and Rural Co-operation, ACP-EU, 28-42 (1997)
5. Singh D. and Singh A., Chitosan for the Removal of Chromium from Waste Water, *I. Res. J. Environment Sci.*, **1(3)**, 55-57 (2012)
6. Singh D. and Singh A., Chitosan for the Removal of Cadmium Rich Water, *I. Res. J. Environment Sci.*, **1(5)**, 81-83 (2012)
7. Abeer F.A., and Ghadir A. El-C., Adsorption of Citric Acid from Aqueous Solution onto Activated *P. Lentiscus* Leaves, *I. Res. J. Environment Sci.*, **1(4)**, 7-13 (2012)
8. Karthika C. and Sekar M., Removal of Hg (II) ions from aqueous solution by Acid Acrylic Resin: A Study through Adsorption isotherms Analysis, **1(1)**, 34-41 (2012)
9. Bradl H. B., Adsorption of heavy metal ions on soils and soils constituents, *J. Colloid Interface Sci.*, **277**, 1-18 (2004)
10. Kabre T.S., Traore K. and Blanchart P., Mineralogy of clay raw material from Burkina Faso and Niger used for ceramic wares, *Appl. Clay Sci.*, **12**, 463-477 (1998)
11. Sorgho B., Pare S., Guel B., Zerbo L., Traoré K. and Persson I., Study of locale mixed clay from Burkina Faso for the removal of Cu<sup>2+</sup>, Pb<sup>2+</sup> and Cr<sup>3+</sup>, *J. Soc. Ouest-Afr. Chim.*, **031**, 49-59 (2011)
12. Traoré K., Blanchart P., Structural transformation of a kaolinite and calcite mixture to gehlenite and anorthite. *J. of Materials Res.*, **18(2)**, 475-481 (2003)
13. Kam S., Zerbo L., Bathiebo J., Soro J., Naba S., Wenmenga U., Traoré K., Gomina M. and Blanchart P., Permeability to water of sintered clay ceramics, *Appl. Clay Sci.*, **46**, 351-357 (2009)
14. Sajidu S.M.I., Persson I., Masamba W.R.L., Henry E.M.T. and Kayambazinthu D., Removal of Cd<sup>2+</sup>, Cr<sup>3+</sup>, Cu<sup>2+</sup>, Hg<sup>2+</sup>, Pb<sup>2+</sup> and Zn<sup>2+</sup> cations and AsO<sub>4</sub><sup>3-</sup> anions from aqueous solutions by mixed clay from Tundulu in Malawi and characterisation of the clay, *Water SA*, **32(4)**, 519-526 (2006)
15. Pare S., Persson I., Guel B., Lundberg D., Zerbo L., Kam S. and Traoré K., Heavy metal removal from aqueous solutions by sorption using natural clays from Burkina Faso, *Afr. J. Biotechnol.*, **11(45)**, 10395-10406 (2012)
16. Barrow N.J., Bowden J.W., Posner A.M. and Quirk J.P., Describing the adsorption of Copper, Zinc and Lead on a Variable Charge Mineral Surface, *Aust. J. Soil Res.*, **19**, 309-321 (1981)
17. Maguire M., Slaveck J., Vimpany I., Higginson F. R. and Pickering W. F., Influence of pH on Copper and Zinc uptake by soil clays, *Aust. J. Soil Res.*, **19**, 217-229 (1981)
18. Barbier F. Duc G. and Petit-Ramel M., Adsorption of lead and cadmium ions from aqueous solution to the montmorillonite/water interface. Colloids and surfaces, *A Physicochem. Eng. Aspects*, **166**, 153-159 (2000)
19. Coles C.A. Yong R.N., Aspects of kaolinite characterization and retention of Pb and Cd, *Appl. Clay Sci.*, **22**, 39-45 (2000)
20. McBride M.B., Environmental Chemistry of Soils. Oxford University Press, New York (1994)
21. Fendorf S.E., Lamble G.M., Stepleton M.G., Kelly M.J. and Sparks D.L., Mechanisms of chromium(III) sorption on silica. 1. Cr(III) surface structure derived by extended

- X-ray absorption fine spectroscopy, *Environ. Sci. Technol.*, **28**, 284–289 (1994)
22. Sajidu S.M.I., Characterisation and interaction of mixed alkaline clays and moringa seeds with heavy metals in contaminated water, Doctoral dissertation, University of Malawi, Zomba, Malawi (2008)
23. Shannon R.D., Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides, *Acta. Cryst.*, **A32**, 751 – 767 (1976)
24. Brinatti A.M., Mascarenhas Y.P., Pereira V.P., Partiti C.S. de M., and Macedo A., Mineralogical characterization of a highly-weathered soil by the Rietveld Method, *Sci. Agric.* **67** (4), 454-464 (2010)
25. Marisa T.G. de O., Sandra M.A.F., Milton L.L.F., Richard A.E. and Norberto D., Coexistence of halloysite and kaolinite – a study on the genesis of kaolin clays of Campo Alegre Basin, Santa Catarina State, Brazil, *Annals of the Brazilian Academy of Sciences*, **79** (4), 665– 681 (2007)
26. Brindley G.W. and Brown G., Crystal structures of clay minerals and their x-ray identification, Mineralogical Society: London. (1980)
27. Zabinsky S.I., Rehr J.J., Ankudinov A., Albers R. C. and Eller M.J., Multiple-scattering calculations of x-ray-absorption spectra, *Physical Review B - PHYS REV B*, **52** (4), 2995–3009 (1995)
28. Drljaca A., Michael J., Hardie, Colin L., Raston and Leone S., Self-Assembled Superanions: Ionic capsules stabilized by polynuclear chromium(III) aqua cation, *Chem. Eur. J.*, **5**(8), 2295–2299 (1999)
29. Hans S. and Werner M., Early stages of the hydrolysis of chromium (III) in aqueous solution. 1. Characterization of the Tetrameric Species, *Inorg. Chem.*, **22**, 2155–2150 (1983)