

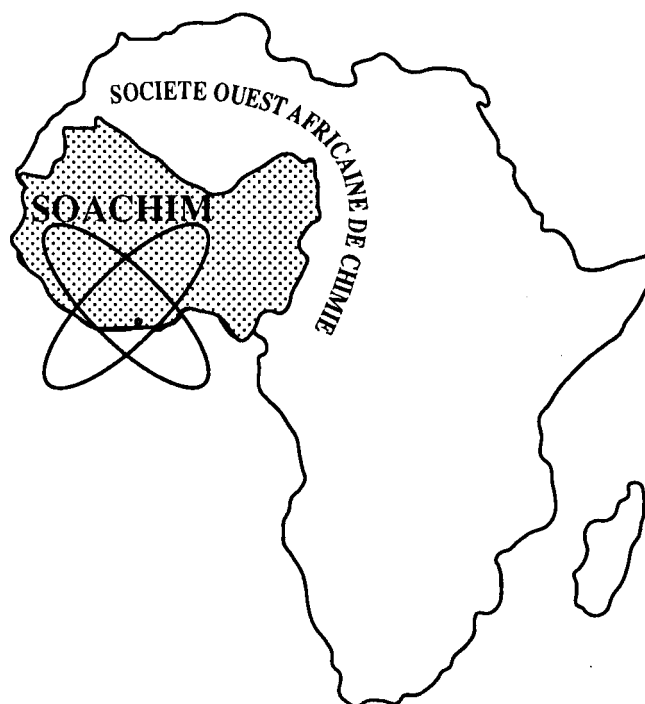
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Natural nano-kaolinite from Niono (Mali) II: Adsorption of chromium in tannery waste water in presence of organic compounds

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Abstract : The aim of this study is to explain how organic compounds, like acetate and propionate, affect the adsorption of chromium (III) in the clay surface according to the pH and to model heavy metal adsorption. Adsorption has been modelled by computer program PHREEQC using single and double site binding models. The modelling of binary and ternary surface complexation was deliberately done at high ionic strength (0,1 M NaNO₃) for eliminating adsorption onto the permanent negatively charged sites of MB clay. The bulk clay (MB) used in this study comes from Niono (Mali). Physicochemical characteristics of this clay were determined in the preliminary work ^[1]. Isotherm adsorption shows that adsorption increases with pH. Adsorption reaches 99% in pH 5 and become constant after this value of pH. These data are modelled using a computer program PHREEQC. The main study was carried out with chromium, but impurity organic compounds present in the system: sodium acetate and sodium propionate. The program shows that the weak concentrations of organic compounds (lower than 1 mmol/L) do not have an effect on chromium adsorption; but with high concentrations one has significant reductions in adsorption.

Keywords : clay, chromium (III), adsorption, Isotherm, model, PHREEQC

Nano - kaolinite Naturelle de Niono (Mali)

II. Adsorption du chrome dans les eaux usées de tannerie en présence de composés organiques

Résumé : Le but de cette étude est d'expliquer comment les composés organiques, tels que l'acétate et le propionate de potassium, affectent l'adsorption du chrome (III) sur la surface de l'argile en fonction du pH et de modéliser adsorption des métaux lourds. L'adsorption a été modélisée par un programme informatique PHREEQC utilisant des modèles site de liaisons simples et doubles. La modélisation sur les surface de complexation binaires et tertiaires a été délibérément fait à force ionique élevée (0,1 M de NaNO₃) pour éliminer l'adsorption sur les sites permanents de l'argile (MB), chargés négativement. L'argile brute (MB) utilisée dans cette étude provient de Niono (Mali). Les caractéristiques physico-chimiques de cette argile ont été déterminées dans un travail préliminaire ^[1]. L'isotherme d'adsorption montre que l'adsorption augmente avec le pH. L'adsorption atteint 99% à pH 5 et devient constante après cette valeur de pH. Ces données sont modélisées en utilisant le logiciel PHREEQC. L'étude a été effectuée sur une solution de chrome (III), en présence de composés organiques considérés comme impuretés présentes dans le système: l'acétate et le propionate de sodium. Le programme montre qu'à faibles concentrations les composés organiques (inférieur à 1 mmol / L) n'ont pas d'effet sur l'adsorption du chrome; mais à concentrations élevées on a une réduction significative de l'adsorption.

Mots clés : Argile ; chrome (III) ; adsorption, Isotherme, modèle, PHREEQC

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1. Introduction

Chromium contamination in soils and water poses a serious threat to humans, plants and animals. Chromium exists mainly in the III and VI oxidation state in soil and groundwater systems. Cr (VI) rarely occurs naturally and is acutely toxic, and is recognized as a human respiratory carcinogen [2]. Although trivalent chromium is less toxic than hexavalent chromium, long-term exposure to Cr (III) is known to cause allergic skin reactions and cancer [3].

Kaolinite is a well-defined naturally occurring 1:1 aluminosilicate mineral composed of one tetrahedral and one dioctahedral sheet. Kaolinite is very common in soils, especially in tropical and sub-tropical areas. The potential adsorption sites on kaolinite include the silanol, $\equiv\text{SiOH}$, and aluminol, $\equiv\text{AlOH}$, hydroxyl groups on the mineral edges and the permanently charged sites, $\equiv\text{X}^-$, on the basal surfaces [4]. Although some studies have concluded that there is no net permanent charge in kaolinite [5], most researchers now accept that there is a small pH independent cation exchange capacity of approximately $1-8 \text{ cmol}_c \text{ kg}^{-1}$ [6] [7] [8] estimated that aluminium substitution in tetrahedral sheets to be up to 0.012 per unit cell to give a negative charge of about $2 \text{ cmol}_c \text{ kg}^{-1}$. Protonation and deprotonation reactions on the edges of kaolinite result in positively or negatively charged edge sites. Permanent negatively charged sites on kaolinite surfaces arise from isomorphous substitution, although these sites are generally much less abundant than the edge sites. These permanent charges are neutralized by the adsorption of cations from the background electrolyte to form outer-sphere complexes.

Although both proton and metal binding onto kaolinite have been studied previously, there is no universal consensus as to which surface sites control pH-dependent adsorption from aqueous solutions. Motta et al. used a one-site model, $\equiv\text{SOH}_2^+$, to investigate the surface charges on

kaolinite [9]. Alberga et al. and Brady et al. used silanol and aluminol to represent the adsorption sites on kaolinite [10] [11]. Brady divided aluminol sites into those located at both the edge and basal plane of the dioctahedral sheet and also included the permanent charged site, $\equiv\text{X}^-$, on the siloxane face to represent sites where cation exchange reactions occur [12]. Huertas suggested another three-site model: external hydroxo-aluminum sites in the dioctahedral sheets with weak Al acidic sites and silanol groups at the mineral edges [13].

Although aluminol and silanol groups at the mineral edges exhibit different affinities for protons and metal cations, their differences normally show up at very acidic or alkaline conditions ($\text{pH} < 3$ or $\text{pH} > 9$) [13]. Spark et al. suggested that two main processes were involved in trace metal adsorption by kaolinite: the first occurred on the permanent charged sites and the second has characteristics similar to the adsorption on oxide minerals, indicating that this process occurred on the variable charged aluminol sites [14]. Schindler et al., and more recently Lackovic et al. have proposed a two-site model: permanently charged sites ($\equiv\text{X}^-$) on the basal faces accounting for cation exchange reactions and amphoteric edge hydroxyl groups ($\equiv\text{SOH}$), accounting for specific adsorption of cations (Fig. 1) [15] [16]. Results from previous studies have shown that the two-site model could successfully predict the adsorption of metallic cations onto kaolinite in the pH range 3–9. Because of its smaller number of input, parameters compared to the three-site model, the two-site model was used in this study.

Most previous studies on the adsorption of metallic cations onto kaolinite have been carried out at fixed ionic strengths and the adsorption behaviour of metal cations has not been fully investigated. In this study the adsorption of chromium in the presence of organics compounds onto kaolinite as a function of pH was investigated and a two-site surface complexation model was used to describe the adsorption behaviour of these metals onto kaolinite.

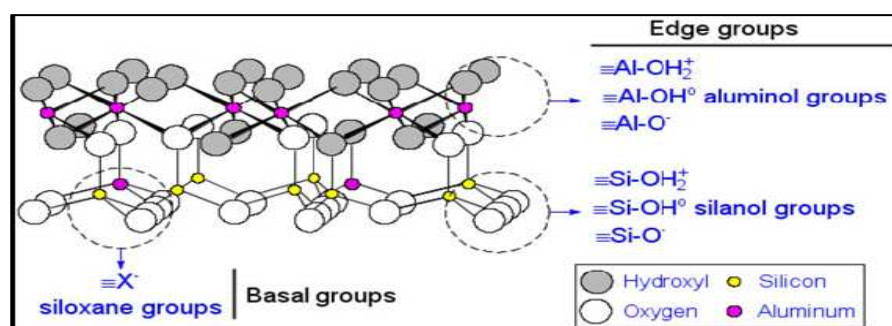


Figure 1: Proposed charged sites on kaolinite used in the two site adsorption model (from Xueyuan G. et al., 2005).

This work is justified by considering that chromium (III) is well adsorbed on clay in distilled water (more than 99%), without the presence of organic compounds (figure 5). On the contrary in the effluents of tannery this adsorption is very weak, less than 11% (figure 3). The objective of this work is to see the influence of some organic compounds like acetate, propionate and citrate of sodium on the adsorption of chromium (III) on clay in distilled water, and to simulate the adsorption process by the PHREEQC software [17].

2. Field sites

2.1. Kaolin

The kaolin used in this study comes from Marakabassi (MB), a small town close to Niono located at 300 km North from Bamako (Mali). The sampling area is in the south of the so called "lower Kala "(12 degrees North), near Niono, at 115 km - north of Segou and at 350 km north-east of Bamako (Figure 4). These areas included irrigated perimeters of Office du Niger and out of these perimeters (not irrigated zone).

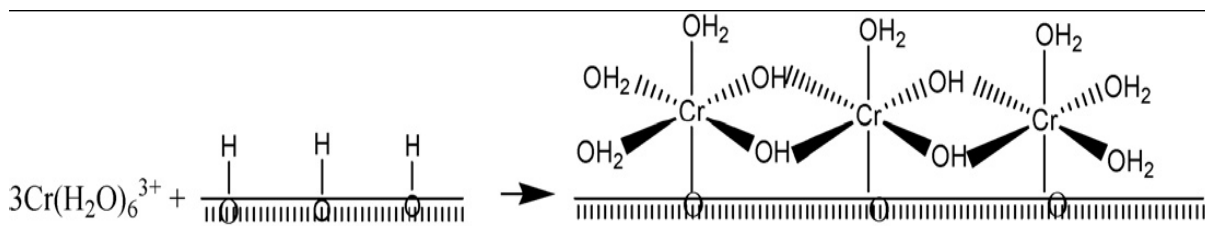


Figure 2: Interaction of the chromium (III) cations on the clay in the trimeric (from Sajidu, S.M.I. et al., 2008).

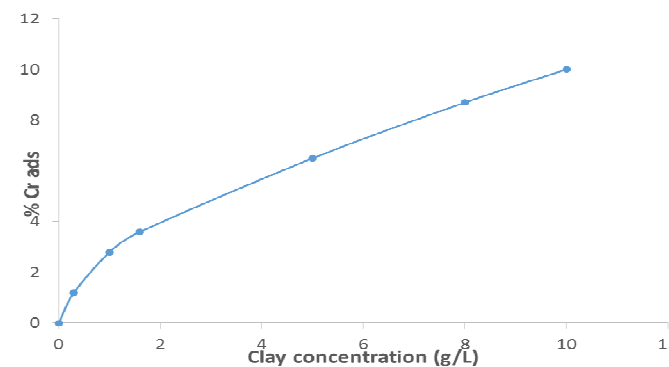


Figure 3: Chromium adsorption in tannery waste water. Experimental conditions: Solid/liquid ratio 1/100, speed agitator 200 tr/min; contact time 30 min.



Figure 4: Map of Niger inland Delta in Mali

Geological and pedological context

Geology the underground structure consists in three geological units of very different thickness depending upon the zones ^[18]: the infra Cambrian substratum (roof of horizon located at a 30 m average depth), the Continental Terminal (thickness varying from 10 to 60 meters) and the alluvial coverage (between 5 and 10 meters).

Pedology - Three morphological units can be distinguished in the Office of Niger's dead delta ^[19]: high sandy lifting, depressions between the sandy heights and basins of decantation.

The high sandy lifting comprises the different types of Seno soils. They consist in sands and silts and are located on both the two sides of the old outflows; they were often used as a background for the irrigation channels installation.

The decantation basins were submitted to a long period of flood when the dead delta was still functional. They are composed of clayey soils having a structure of two types: a coarse prismatic structure (soils of *Dian* type) or a structure of grained or polyhedral fine surface (soils of *Moursi* type). The clayey fraction amount is increasing as followed: *Seno*, *Danga*, *Dian* and *Moursi* soils respectively. Those clays are of illite, kaolinite and smectite types.

2.2. Tannery

The waste water concerned by this study come from a tannery factory named TAMALI – SA. It is located in the industrial park (Southern side) at the edge of the Niger River in Bamako city. Created in 1970 as a national production unit, TAMALI – SA was managed jointly since 1985 by Mali and China. From 1992 TAMALI – SA was privatised ^[1].

The following parameters were analyzed in situ with portable multiparameter Sension 156 from HACH. Temperature and pH with platinum electrode were calibrated using pH buffers 4.00 and 7.00; conductivity, dissolved salt rate were measured with Hach sunder type 51975-00; calibrated using NaCl solution 1000µS/cm standard, dissolved oxygen with electrode Clark calibrated with water saturated air (table I). Chromium concentration is measured using ICP. AES Perkin Elmer Optima 3300 DV and organic compounds using gas chromatograph coupled mass spectrometer Auto system -Turbomass of Perkin-Elmer.

Table I: Physicochemical characteristics of waste water from TAMALI

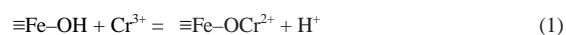
	T° C	pH	Cond. (mS/cm)	DO (mg/L)	TDS (g/L)	Cr conc (mg/L)
Water sample	22.4	3.53	74.54	48.55	5.32	5.3

DO – dissolve oxygen; TDS- rate dissolved salt.

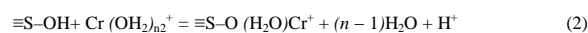
2.3. Simulation of surface complexation

PHREEQC is a computer program for speciation, batch reaction, and one dimensional transport calculations, distributed free of charge by the U.S. Geological Survey ^[20]. The thermodynamic database accompanying the code includes cation exchange equilibrium according to the Gaines-Thomas convention, but the flexible input format enables the application of other exchange equations used in soil science. Gapon, Vanselow, and Rothmund-Kornfeld showed that the formulas can be implemented in PHREEQC calculations to obtain the composition of (1) an exchangeable cation in equilibrium with a given solution composition, (2) a solution in equilibrium with a given exchangeable cation, and (3) a solution and exchangeable(s) cation(s) following the reaction after mixing. With the interface PHREEQC for Windows, an isotherm plot can be quickly obtained ^[17].

In aqueous solutions, metals can act as a Lewis acid (i.e., an electron acceptor). An electron-pair donating surface functional group (such as –OH, –SH, and –COOH) and an electron-pair acceptor metal ion (such as Me³⁺) form Lewis salt-type compounds. For an oxide (e.g., ferric oxide) the functional surface hydroxo group ≡Fe–OH may act as Lewis basis in deprotonated form (≡Fe–O[–]) to bind a Lewis acid metal ion Cr³⁺:



Where, ≡S–OH represents a surface functional group. As there are no molecules of the aqueous solvent (i.e., water) interposed between the surface functional group and the metal ion bound to it these surface complexes are called “innersphere complexes”.



Inner-sphere complexes are in general more stable than outer-sphere complexes as the primary bonding force in inner-sphere complexes is coordinate-covalent bonding in contrast to electrostatic bonding in outer-sphere complexes. Spectroscopic studies of surface complexes showed that the spectra of these complexes are often reminiscent to those of analogous aqueous complexes.

Investigations on the local structural environment of chromium (III) sorbed on silica using EXAFS have been reported by ^[20]. Their results showed formation of monodentate chromium (III) surface complex on silica with Cr–Si distance of 3.39 Å for the sorbed chromium while formation of

polynuclear chromium hydroxide octahedra was discerned on the surface.

^[21] identified two hydrolysis complexes in aqueous solution $[\text{Cr}_3(\text{OH})_4(\text{H}_2\text{O})_{10}]^{5+}$ present in aqueous chromium(III) solution with $\text{pH} \approx 3.5$, and indefinite $[\text{Cr}(\text{OH})_2(\text{OH})_2]_n^{n(2x-3)+}$ chains with double hydroxo bridges (figure 2) and each chromium also binds additionally two hydroxide ions/water molecules full-filling an octahedral configuration present in very alkaline aqueous solutions, $\text{pH} > 14$ ^[22]. It seems that both types of chromium(III) hydrolysis complexes are present on the clay surfaces with predominance of the indefinite chains as the contribution at 3.6 Å, typical of the trimer, is present but suppressed in comparison with the pure $[\text{Cr}_3(\text{OH})_4(\text{H}_2\text{O})_{10}]^{5+}$ complex (Figure 2).

Any presence of solid chromium(III) oxide on the clay surfaces can be ruled out as the Cr–O bond and Cr · · · Cr distance in Cr_2O_3 are significantly shorter than the distances observed of the chromium(III) species in this study ^[21]. A possible interaction of the chromium (III) cations on the clays in the trimeric form is shown in figure 3. Long-range distances expected in well-defined precipitations were not observed and the metals in most cases were in hydrolysed form.

$[\text{Cr}_3(\text{OH})_4(\text{H}_2\text{O})_{10}]^{5+}$ compared with the theoretical signals (bold lines). Lower panel: phase shifted Fourier transforms of the EXAFS data.

Table II : Surface complexation model parameters for Cr (III) adsorption onto kaolinite.

The acid-base constants are taken from the literature ^[15]

	logK
Surface acidity reactions	
$\equiv\text{SOH}^\circ + \text{H}^+ = \equiv\text{SOH}_2^+$	4.37
$\equiv\text{SOH}^\circ = \equiv\text{SO}^- + \text{H}^+$	-9.18
$\equiv\text{X} \cdot \text{H}^+ + \text{Na}^+ = \equiv\text{X} \cdot \text{Na}^+ + \text{H}^+$	-2.9
Surface cation adsorption reaction	
$\equiv\text{SOH}^\circ + \text{Cr}^{3+} = \equiv\text{SOCr}^{2+} + \text{H}^+$	0.9
$2\equiv\text{SOH}^\circ + \text{Cr}^{3+} = \equiv(\text{SO})_2\text{Cr}^+ + 2\text{H}^+$	-2
$2\equiv\text{SOH}^\circ + \text{Cr}^{3+} + \text{H}_2\text{O} = \equiv\text{SOCrOH} + 2\text{H}^+$	3.15
$2\equiv\text{X} \cdot \text{H}^+ + \text{Cr}^{3+} = \equiv\text{X}_2 \cdot \text{Cr}^+ + 2\text{H}^+$	3
$\equiv\text{SOH}^\circ + \text{H}^+ + \text{L}^{2-} = \equiv\text{SOH}_2\text{L}^-$	-6.25
Model	CCM
Site density $[\equiv\text{X}]_T$ (cmol.kg ⁻¹)	1.56
Site density $[\equiv\text{SOH}]_T$ (cmol.kg ⁻¹)	3.99
Specific capacitance, κ (Fm ⁻²)	2.2
Electrolyte (NaNO ₃)	
Specific surface (m ² .g ⁻¹)	0.1 M
Suspension density (g.L ⁻¹)	64
	10

Environmental relevance

The mineral tanning, based on chromium, is the most widespread process for the tanning on a large

scale because it acts quickly and produces leather with good physical and chemical properties. In many countries, the tannery effluents are poured in sewers in surface water or mixed with irrigation water. The strong inorganic salt (chromium) and organics concentrations affect the water quality and make it unsuitable to consumption. Particules in suspension (lime, hairs, fleshing waste, etc.) lead to turbid surface water and sometimes settle at the bottom of sewer pipes. These two processes lead to adverse conditions for wild life. Mineral tannery contaminated waters poured on the ground will have perverse effects on soil productivity and can make it sterile. The infiltration also has perverse effects on quality of subsoil ground waters. The discharges of untreated tannery effluents in sewerage water systems cause a calcium carbonate deposit and a clogging of the sewers. It is possible to effectively treat the industrial water used before pouring it in surface water. After this purification, the levels of chromium and DBO (biochemical demand for oxygen) are relatively low. Clay particles may enhance this coagulation / flocculation process and enhance chromium removal via, as we have seen, ternary complex formation. Muds produced in this treatment process must be stored in special discharges because of their chromium content.

3. Materials and methods.

3.1. Materials

The (MB) clay has a large specific surface area (64 m².g⁻¹) and a large cation exchange capacity (0.34 Meq. Kg⁻¹). Chemical analysis of the solid leads to a 1.53 SiO₂/Al₂O₃ ratio and confirms the structural characterization results (**table II**), which showed that mineral is mainly composed of kaolinite with trace amount of smectite and mica ^[1].

Tannery waste water preparation

The SPE Technique (Solid Phase Extraction) is to retain analyte and to concentrate the sample of tannery. The protocol of extraction adopted is as follows: 200 mL of filtered effluent are treated on a cartridge C18 (500 mg, 6 ml) with a flow of 5 mL/min. The eluted fraction is acidified at pH 3.5 and filtered on a Lichrolut cartridge EN with a flow of 15 mL/min. After preconcentration the adsorbents are dried to avoid the hydrolysis of the trapped aqueous solutions. Each cartridge is then treated in the following way.

The Lichrolut cartridge is eluted by it by twice 5 mL of methanol to a flow of 1 mL/min. A contact of 5 min between two elutions is necessary to

desorb the aqueous solutions effectively.

The cartridge C18 is eluted with 3 different solvents to obtain fractions containing of made up of polarity and different functional groups. Elution was thus carried out successively with: 5 mL of hexane (fraction A), 5 mL of a mixture dichloromethane-hexane (4:1 v/v) (fraction B), and 5 mL of a mixture methanol-dichloromethane (9:1 v/v) (fraction C).

The four fractions A, B, C and D obtained are evaporated under flows of nitrogen, then taken again by 2 mL of suitable solvent.

Method of organic compounds in tannery wastewater

Organics in the tannery waste water fractions were analyzed by coupled gas chromatography – mass spectrometry. The analyzer used is an Autosystem-Turbomass of Perkin-Elmer. The mass spectrometer was operated in the electron impact ionization mode with an ionizing energy of 70 eV and an emission current of 200 mA. The ion source temperature was 280 °C. The column, type: WCOT CP SIL 5 CB de Chrompack, Length : 25 m, interne Diameter : 0.10 mm , phase thickness 0,10 µm was programmed has follow: initial isotherm 2 min at 40°C, ramp 1 de 30°C/min. Isotherm 12 min at 100°C, ramp 25°C/min, isotherm finale 20 min at 300°C. Helium was used as the carrier gas at 68.947 Pa (10 psi). The injection volume was 2 mL in a splitless mode. Results obtained are presented in table IV.

Solutions obtained in the sorption isotherm were analysed by ICP-AES with detection limit 0.002 mg/L.

Qualitative and semi quantitative analyze by ionic chromatography

A complementary analysis by ionic chromatography was carried out by the laboratory TERA Environment. The results obtained are presented in table III.

Table III: Quantitative analysis of tannery waste water.

	Fluorure (ppm)	Acetate (ppm)	Propionate (ppm)	Formiate (ppm)
Sample	2.9	18.5	3.0	7.9
D.L.	0.29	1.29	1.69	0.78

D.L – detection Limit

Table IV: Organic compounds in tannery waste water

Compounds	Fraction
Nonane	A
Decane	A
Tridecane	A
tetradecane	A
Others alkanes with undermined number of C	A
Acetic acid	B
propionic acid	B
Undecanoic acid	B

Tetradecanoic acid	B
Pentadecanoic acid	B
oleic acid	B
Dibutyl phthalate	B et D
1,2,4-benzene tricarboxylic acid-1,2-dimethyl ester	B
Acetic acid, 2-propenyl ester	B
1,2,4-benzene tricarboxylic acid-1,2-dimethyl ester	B
1-propène-2-ol acetate	B
pentaacetate	B
2-heptanaone	B
Benzophenone	B et C
nonanal	B
undecanal	B
benzene	B
pyridine	A et D
dimethyl amine	D
alanine	D
dimethyl pentanol	D
2,4-bis(1,1-dimethyl) phenol	D

A- Hexane; B- Dichloromethane/hexane (4:1 v/v); C - methanol-dichloromethane (9:1 v/v); D – Dichloromethane.

3.2. Method of chromium adsorption on clay in presence of organic compounds.

3.2.1. Solution preparation

A 100 mmol.L⁻¹ chromium(III), sodium acetate, sodium propionate, and sodium citrate solutions were obtained from dissolution of analytical grade reagent CrCl₃.6H₂O 96% min from Labosi, C₂H₃NaO₂.3H₂O 99% from Fluka, C₃H₅O₂ 99% from Sigma respectively in deionised water.

3.2.2. Adsorption experiment

Five millilitres of sodium nitrate solution as well as aliquots of the 10⁻¹ mol.L⁻¹ stock chromium solution and organic stock solution were added to 0.50 g of the clay in the 50mL centrifugation tube. The ionic strenght of the medium is stabilized by 10 mL nitrate solution of sodium with 0,1 M and the pH was adjusted between 2.5 and 7 by drop wise addition of 0.1mol.L⁻¹ HCl or NaOH. The clay suspensions were stirred for 24 h at room temperature. pH suspensions were measured with pH-meter Orion research and centrifuged in Beckman Avanti J-20 à 12500 tprs during 15 min. Supernatant were filtered with sterile filter Rotilabo and the residual chromium concentrations in the filtrate were measured with I.C.P. AES (Perkin Elmer Optima 3300 DV). % chromium adsorbed was calculated using formula:

$$\%Cr_{ads} = \frac{100x([Cr]_0 - [Cr]_{eq})}{[Cr]_0} \quad (1)$$

Were [Cr]₀ is the Initial chromium concentration; [Cr]_{eq} is the chromium concentration in equilibrium.

4. Results and discussions

Results from adsorption of chromium alone are shown in Figure 5. Initial sorption value is about 30% at pH 2.5. Sorption increases from pH 2.5 to pH 5.0 where adsorption is nearly complete (99%). Beyond, the curve shows constant adsorption level up to pH 7.

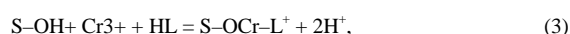
The curve resulting from modelling (**figure 5**) presents a percentage of adsorption of 42% at pH 2.7 a value slightly higher than the experimental one. As the pH increases this curve become similar to the experimental one. They are identical from pH 4.5. In this study we considered adsorption only on the strong site. Concurrently to $\text{SoCr}(\text{OH})_2$ the less stable compounds like SoCr^{+2} and SoCrOH^+ are formed.

Adsorption of chromium in the presence of organics compounds (acetate or propionate) are shown in Figure 6 and Figure 7, respectively. The comparison between the curve obtained in presence of acetate and those obtained in presence of propionate show the same behaviour because they have the same thermodynamics constants.

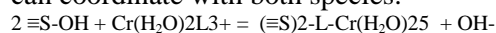
With low concentration of organics compound (1 mmol/L) we did not observe any variation between adsorption without organic compound. But, on contrary, with concentration of 5 mmol/L curve show a change in adsorption. It can be seen that chromium (III) adsorption onto kaolinite is depended to organic compounds concentration: as the organic compound concentration increases, less is adsorption of the chromium (III) onto kaolinitic clay. Adsorption rate without organic compound is higher than that of 5 mmol/L of organic compound which is also higher than 10 mmol/L of organic compounds. Further studies extended to other

organic compounds over acetate and propionate may allow having more details about the organic compound nature influence.

Chromium is complexed by anthropogenic complexants such as acetate and propionate. Complexation will alter chromium reactivity, affecting properties such as catalytic activity, toxicity, and mobility^[23]. The adsorption of a heavy metal onto the surface of a hydrous oxide is also represented as the formation of a metal complex. As hydrous oxide surfaces display amphoteric properties, they are able to coordinate with ligands as well. These three components metal, ligand, and reactive surface afford the formation of a ternary complex. This ternary complex can be exceedingly stable and may possess properties, which are very different from those of the individual component species. The formation of a ternary surface complex can be explained by two different mechanisms. First, bonding of the complex occurs through the metal to the surface:



Where L represents the ligand and S-OH represents a hydroxyl functional group on the oxide surface. The surface complex is designated as “metal-like” or “type A”^[24]. This mechanism is usually characterized by increasing adsorption with increasing pH (**Figure 3**). Second, the ligand may form a bridge between the surface and the metal, which is only possible when it is multidentate so it can coordinate with both species:



Here, none of the 2 ligands studied are multidentate, meaning that only the first hypothesis can occur. In that case, the phenomenon increases with increasing pH values, which can be observed on **figure 5**.

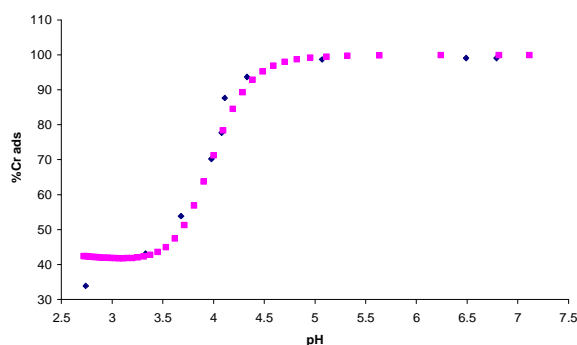


Figure 5: Chromium adsorption on kaolinite. Experimental conditions: Cr concentration 6.10^{-4} M; Solid/liquid ratio 1/100; at room temperature; reaction time 24 hours. ♦ - Experimental curve, ■ – Fitted curve

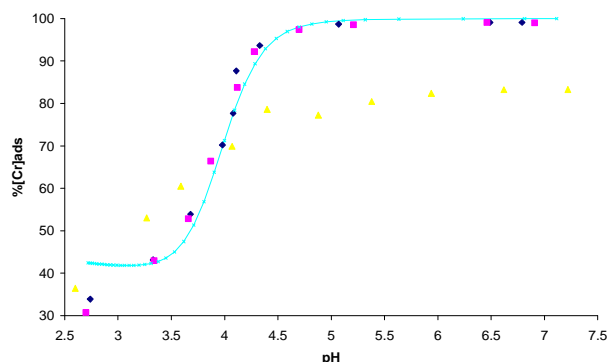


Figure 6: Adsorption of chromium in the presence of sodium acetate (filled squares 1mol/L, filled triangle 10mmol/L) vs without organic ligand (filled diamonds). Experimental conditions: Cr concentration $1.4 \cdot 10^{-3}$ mol/L; mass solid/liquid ratio 1/100. Full line: model curve.

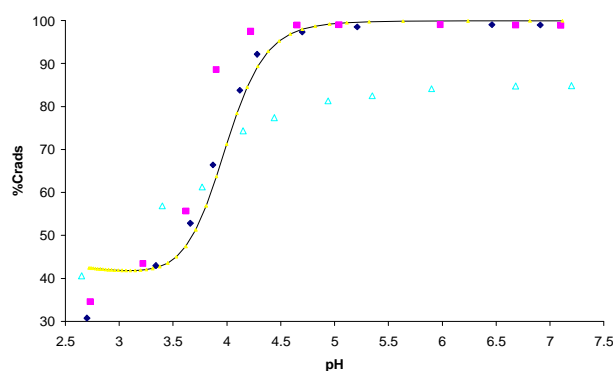


Figure 7: Adsorption of chromium in presence of sodium propionate (filled squares, filled triangle 10mmol/L) vs without organic ligand (filled diamonds). Experimental conditions: Cr concentration $1.4 \cdot 10^{-3}$ mol/L; mass solid/liquid ratio 1/100. Full line: model curve

5. Conclusions

The present study shows that the present Mali Kaolinite clay sample is specific because its properties are different from that of pure kaolinite. It is a good adsorbent for the metallic cation.

Chromium (III) adsorption on this kaolinite is larger compared to chromium sorption on large particle Kaolinite. It is strongly pH dependant.

We have a strong adsorption (approximately 99% at $\text{pH} \geq 5$). It must be noted that low organic compounds concentration does not affect chromium adsorption on clay (fig.5, 6 and 7); that was confirmed by model PHREEQC. With a 10 mMol/L organic compounds concentration, chromium adsorption rate falls down and does reach 80%. Adsorption rate doesn't reach this value when the raw wastewater from tannery is directly adsorbed onto MB clay. In this case, we only have about 15% adsorption rate, possibly due to other compounds organics or not.

The difference between curve without organic and curve with organic may be due to the complexation of chromium by ligand (organics). The chromium –

acetate or chromium - propionate complexes occurrences are highly pH dependant.

Thus, in this study, we have identified the phenomenon which prevents chromium to be adsorbed onto MB clay of Mali in tannery effluents. In perspective it would be interesting to explore methods allowing eliminating the organics before waste water treatment by kaolinitic clay minerals.

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6. References

- [1] Samaké D., Thomas F., Pléa M., Greneche J. M., Poinson C., Debionne J. L., Charlet L., 2012 : A natural nanokaolinite clay from Marakabassi (Mali) for Chromium (III) removal in tanning effluents : I. Structure and surface characterization (2012). *J. Soc. Ouest-Afr. Chim. 034 ; 1- 11*
- [2] Agency for Toxic Substances and Disease Registry (ATSDR). Toxicological profile for chromium (2000). US Department of Health and Human Services, Public Health Service, Atlanta, GA.
- [3] Eisler, R., Laurel, M.D. Chromium hazards to fish, wildlife, and invertebrates: a synoptic review. Biological Report 85 (1.6), Contaminated Hazard Reviews Report 6. US Department of the Interior, Fish and Wildlife Service (1986).
- [4] Xuyuan Gu, Les Evans, J. Surface complexation modelling of Cd (II), Cu (II), Ni(II), Pb (II) and Zn (II) adsorption onto kaolinite. *Geochim. Cosmochim. (2007). Acta 72, 267-276.*
- [5] Ferris, A. P. and Jepson, W. B. The cation exchange capacities of kaolinite and the preparation of homoionic clays (1976). *J. Colloid Interf. Sci. 51, 245-259. J. Colloid Interf. Sci. 210, 43 - 54.*
- [6] Bolland, M. D. A., Posner, A. M. and Quirk, J. P. Surface charge on kaolinites in aqueous suspension (1975). *Aust. J. Soil Res. 14, 197-216.*
- [7] Newman A. C. D., Brown G. The chemical constitution of clays. In *Chemistry of Clays and Clay Minerals* (ed. Newman, A.C.D.) (1987). Mineralogical Society Monograph no. 6, London, England, 1-128.
- [8] Sposito, G. *The Surface Chemistry of Soils* (1984). *Oxford University Press*, New York
- [9] Motta, M. M. and Miranda, C. F. Molybdate adsorption on kaolinite, montmorillonite, and illite: constant capacitance modelling (1989). *Soil Sci. Soc. Am. J. 53, 380-385.*
- [10] Alberga, L., Holm, T., Tiravanti, G. and Petruzzelli, D. Electrochemical determination of cadmium sorption on kaolinite (1994). *Environ. Technol. 15, 245-254.*
- [11] Brady, P. V., Cygan, R. T. and Nagy, K. L. Molecular controls on kaolinite surface charge. *J. Colloid Interf. (1996). Sci. 183, 356-364.*
- [12] Wieland E. and Stumm W. Dissolution kinetics of kaolinite in acidic aqueous solutions at 25°C. *Geochim. Cosmochim. (1992). Acta 56, 3339-3355.*
- [13] Huertas, F. J., Chou L., Wollast R. Mechanism of kaolinite dissolution at room temperature and pressure: Part I, surface species. *Geochim. Cosmochim. Acta 62 (1998), 417-431.*
- [14] Spark, K. M., Wells, J. D., Johnson, B. B. Characterizing trace metal adsorption on kaolinite (1995). *Eur. J. Soil Sci. 46, 633-640.*
- [15] Schindler, P.W. Hochella, M.F.Jr., White, A.F. (Eds.), *Mineral-Water Interface Geochemistry*, in: *Reviews in Mineralogy* (1990), *Mineralogical Society of America. Washington, DC*, p. 281.
- [16] Lackovic K., Angove M. J., Wells J. D. and Johnson B. B. Modelling the adsorption of Cd(II) onto Mulloorina illite and related clay minerals (2003). *J. Colloid Interf. Sci. 257, 31-40.*
- [17] Parkhurst D.L. and Appelo C.A.J. (1999) - User's guide to PHREEQC (version 2). A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. U.S. Geological Survey Water-Resources Investigations Report 99-4259, 312 p.
- [18] Barral, J. P., Dicko, M. K.. Soil degradation, case of the Niger Authority (fr). Ministère français de la coopération, Institut d'Economie Rural, Travaux et études 1(1996). www.springerlink.com.
- [19] Marlet, S., N'Diaye, M. K.. Evolution temporelle et variabilité spatiale des indicateurs de la dégradation des sols par alcalinisation et sodisation de l'Office du Niger- Tome 1, synthèse. Pôle Systèmes Irrigués, Etude et travaux (1998).
- [20] (http://www.cr.usgs.gov/projects/GWC_coupled/phreeqc/index.html)
- [21] Fendorf, S.E., Lamble, G.M., Stepleton, M.G., Kelly and M.J. Sparks D.L. Mechanisms of chromium (III) sorption on silica. 1. Cr (III) surface structure derived by extended X-ray absorption fine spectroscopy (1994). *Environ. Sci. Technol 28, 284-289.*
- [22] Sajidu, S.M.I., Persson, I., Masamba, W.R.L., Henry, E.M.T., Kayambazinthu, D. Removal of Cd²⁺, Cr³⁺, Cu²⁺, Hg²⁺, Pb²⁺ and Zn²⁺ cations and AsO₄³⁻ anions from aqueous solutions by mixed clay from Tundulu in Malawi and characterisation of the clay (2006), *Water SA 32 (4) 519-526.*
- [23] Torapava, N. hydration, solvation and hydrolysis of multicharged Metal Ions. Doctoral Thesis 2011 Swedish University of Agricultural Sciences Uppsala.
- [24] Benjamin, M.M., Leckie, J.O., Conceptual model for metal-ligand-surface interactions during adsorption *Environmental Science and Technology* (1981) 15, 1050-1057