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A natural nanokaolinite clay from Marakabassi (Mali) for Chromium (III) removal in tanning effluents : I. Structure and surface characterization

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Abstract : Clay from Marakabassi close to Niono (Mali) with interesting morphology and adsorption capacity is characterized in anticipation of its possible use for chromium (III) adsorption. Chemical analysis, XRD and infrared spectroscopy show that the major mineral is poorly crystallized kaolinite (71%), the other minerals being smectite/illite (14%), quartz and nanometric goethite. TEM images reveal nanometric size of the clay crystallites (90 nm in average), the thickness of which is estimated around 20 nm from XRD and low pressure gas adsorption. The material displays large specific surface area (64 m2/g) and 1 cation exchange capacity (0.34 Meq/kg). Mössbauer spectrometry excludes Fe^{II}/Al^{III} substitution, the only possible origin of permanent charge in kaolinite. The electrophoretic behaviour of the sample is relatively independent of pH (z = -27mV above pH 4) and ionic strength (IEP at pH 2 only observed for 0.1 mol/l ionic strength), i.e. close to that of montmorillonite, which points to the presence of montmorillonite layers at the basal surfaces of kaolinite particles.

Keywords: kaolinite clay, crystal-chemistry, surface properties, electric charge.

Une argile nanokaolinitique naturelle de Marakabassi (Mali) pour l'enlèvement du chrome (III) dans les effluents de tannerie : I. Structure et caractérisation de surface

Résumé : Une argile de Marakabassi près Niono (Mali) avec une morphologie et capacité d'adsorption intéressante est caractérisée en prévision de son utilisation possible pour l'adsorption du chrome (III). L'analyse chimique, la diffraction aux rayons X et la spectroscopie infrarouge montrent que le minéral principal est une kaolinite mal cristallisée (71%), les autres minéraux étant la smectite / illite (14%), de quartz et de goethite nanométrique. Les images TEM révèlent la taille nanométrique des cristallites d'argile (90 nm en moyenne), dont l'épaisseur est estimée à 20 nm à partir de la diffraction aux rayons X et de l'adsorption de gaz à basse pression. Le matériau a montré une grande surface spécifique (64 m²/g) et une capacité d'échange cationique (0.34 m_{Eq}/kg). La spectrométrie Mössbauer exclut la substitution FeII/AIIII, la seule origine possible de la charge permanente de la kaolinite. Le comportement électrophorétique de l'échantillon est relativement indépendant du pH ($\zeta = -27$ mV avec le pH au dessus de 4) et la force ionique (PEI à pH 2 observée uniquement pour la force ionique 0.1 mol /l), soit proche de celle de la montmorillonite, qui pointe vers la présence de la couches de montmorillonite sur les surfaces de basales de particules de kaolinite.

Mots clés : Kaolinite, Argile, chimie cristalline, Propriétés de surface, charge électrique.

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1. Introduction

Decontamination of waste waters from industry and craft-industry in order to decrease their environmental impact, has become an important issue at the international level. This is particularly the case for effluents from metallurgical and chemical industries, ceramics, electro-galvanization. More specifically, in Mali, textile industries and tanneries are potential sources of water pollution by chromium ions. Chromium ions cause serious cases of acute toxicity and diseases such as lung cancer and kidney failure. Various methods such as ion exchange, electro-dialysis, reverse osmosis and hydrometallurgical technologies have been used in parallel with precipitation and adsorption for chromium removal from environmental aqueous solution ^[1]. Anyway, clays readily adsorb heavy metal ions, and their use as adsorbent appears to be a very appropriate method to treat these effluents. Clays, and particularly kaolinite, are abundant clay minerals in Mali^[2] and their use as an adsorbent would be very convenient for the treatment of industrial effluents. Furthermore it is observed that kaolinite in effluents show a higher selectivity for transition and heavy metal ions due to the presence of pH-dependent adsorption sites ^[3]. Thus, metal ion retention by estuarine sediments could be better modeled with kaolinite than with smectite.

It is considered that the adsorption of heavy metal ions and complexes on clay minerals occurs as a result of ion exchange, surface complexation, hydrophobic and electrostatic interaction ^[4]. Consequently, removal of metal cations by clay minerals is controlled by parameters such as clays charge characteristics. Charge characteristics include the magnitude of the active sites and the exchange cation capacity which has two components: one hand, the permanent negative charge generated by isomorphous substitutions within the octahedral and tetrahedral sheets of the silicate layers, and on the other hand the pH dependent charge arising from dissociation of edge hydroxyl groups. The pH-dependent charge may also be contributed by dissociation of other acid groups present such as humic acids particularly in non purified clay minerals^[5]. In addition to the clay charge properties, metal uptake is also influenced by the metal ion's self characteristics such as its radius, charge size and hard / soft acid - base properties, which determine its solubility and reactivity ^[6].

In the present work a natural kaolinitic soil from Marakabassi with interesting morphologic and adsorption capacity is presented. In the present paper, its mineralogical composition, textural and surface reactivity properties are studied in order to evaluate its ability to adsorb metal ions from aqueous solutions. A companion paper is dedicated to the adsorption mechanisms of Cr III, and to the potential use of such clay for the treatment of tannery wastewaters.

2. Field site

The clay used in this study was collected in Marakabassi (MB), a small town close to Niono (Mali). Sampling area is South of "lower Kala" (12 degrees North), near Niono, a city located 115 km North of Segou, 350 km North-East of Bamako (Fig. 1). The area is presently irrigated for agricultural purpose. The underground structure includes three geological units of different thickness ^[7]: the infra Cambrian substratum, the Continental Terminal and the alluvial coverage. The infra Cambrian substratum, (580-400 million years old), consists of sandstone and schist and is crossed by fractured systems, diaclases and fissures allowing important circulation of water. The roof of this horizon is located 30 m depth. In the Continental Terminal, (25 to 28 millions years old), layers of clays, sandy clays and sands are intercalated with levels containing gravels, quartz and clayey or sintered lateritic horizons. Its thickness varies from 10 to 60 meters. The alluvial deposits were formed when the Western African craton subsidence occurred and comprise old or recent alluvia brought by the river Niger, fossil or current. The deposit is 5 and 10 meters thick. Three pedological and morphological units can be distinguished in the Niger dead delta ^[8] high sandy lifting, depressions between the sandy heights and decantation basins. The high sandy lifting comprises different types of Seno soils. They consist in sands and silts and are located on both sides of the old outflows; they were often used as a background for the irrigation channels installation. The depressions between the sandy heights are soils of Danga type. They consist in decantation basins and small lifting made up of muddy and clay-muddy materials covering clayey deposits. 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 clay fraction amount increases from Seno to Danga, Dian and Moursi soils. Clays are of illite, kaolinite and smectite types.



Figure 1: Map of South-East Mali, and localization of Niono

3. Materials and methods

3.1. Preparation of the clay

After collecting, the clay was manually ground. For the present study, separation of the $< 2 \ \mu m$ grain size fraction was performed by sedimentation according to the Stokes law, after destruction of the organic matter by oxygen peroxide, and pyrophosphate dispersion.

3.2 Chemical, Structural and Surface characterization

Chemical analysis of the clay material was performed with a Quantometer Jobin Yvon 70-P with ICP (Inductively Coupled Plasma) after sample fusion in lithium metaborate and dissolution in deionized water.

X-Ray diffraction patterns were recorded using a D8 Bruker diffractometer with a Co K α radiation (λ = 1.7890 Å). The rough sample was analyzed by powder diffraction. The < 2 µm fraction was analyzed as an oriented preparation, then after soaking with ethylene-glycol in order to detect the presence of swelling clays, and after 550°C heating in order to confirm the presence of illite.

For TEM studies, an aliquot of $< 2 \mu m$ clay fraction was suspended in ethanol under ultrasonication and a drop of resulting suspension was evaporated on a carbon coated copper grid. Observations were performed using a Philips CM20 transmission electron microscope operating at 200 kV equipped with an EDX energy dispersive X-ray spectrometer.

Infrared spectra were recorded in transmission geometry on KBr pellets made of 19 % clay in KBr using a Bruker Fourier Transform Interferometer IFS 55.

Mössbauer spectra were recorded on the raw sample at room temperature using the miniaturised Mössbauer spectrometer MIMOS, ^[9], and at 300 K and 77 K on the < 2 μ m fraction of the clay material by means of a conventional transmission spectrometer using a ⁵⁷Co (Rh) source and an α -Fe foil as calibration sample. The Mössbauer spectra were fitted by using the MOSFIT program developed by ^[10].

TGA and TDA diagrams were recorded on a SETARAM MTA microbalance with a 5°C/mn heating rate from ambient temperature to 900°C under Ar sweep.

Cation exchange capacity was measured by the cobaltihexamine method.

Low pressure adsorption isotherms of argon and nitrogen at 77 K were recorded on a lab-built automatic quasi-equilibrium volumetric setup ^[11, 12] using the protocol given by ^[13].

Electrokinetic measurements were obtained by electrophoresis using a Zetaphoremeter IV from the CAD Instrumentation Company. The electrophoretic mobility was converted into the Zeta potentiel after the Smoluchowski equation. The measurements were achieved in 10^{-1} , 10^{-2} and 10^{-3} M NaNO₃ solutions prepared in ultra pure water.

4. Results and discussion

4.1 Chemical composition and morphology

Chemical and TEM-EDX analysis of the dry adsorbent yielded the composition in weight percentages given in **Table I**. A first indication on the nature of the silicate minerals in the sample is given by the Si and Al contents. The SiO₂/Al₂O₃ oxide ratio, 1.53, is intermediate between that of kaolinite (1.18) and smectite (2.36). Similarly, the atomic ratio Si/Al is 1.22. Therefore, it can be expected that the MB sample contains, besides kaolinite, SiO₂ and 2:1 clays such as smectite or illite. The presence of small amounts of these clays is suggested by MgO, Na₂O and K₂O. Fe₂O₃ can be attributed to iron oxide particles or substitutions in the crystal network of clays. CaO is attributed to carbonate. The Marakabassi clay is essentially composed of very small clay particles, most of them below 0.5 μ m, with angular shape and low contrast (**Fig. 2**). A very small number of iron oxide particles are observed. Fe and Mg are uniformly distributed over the clay particles, and are interpreted as substituents in the crystal array of the clays and intergrowth of nanocrystalline grains of goethite. The heterogeneous dispersion of Si with small spots of high Si density reveals the presence of SiO₂ nanoparticles.

Table I: Results of chemical analysis of Marakabassi clay by Inductive Coupled Plasma (ICP) and TEM-EDX.

ІСР	SiO ₂	Al ₂ O ₃	TiO ₂	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	MnO	Loss on ignition
Wt %	45.75	29. 90	1.00	6.03	0.81	0.75	0.10	0.67	0.02	13.04
EDX	Si	Al	0	Fe	Ca	Mg	Na	K	Mn	
Wt%	25.30	19.82	47.35	5.94	0.63	0.43	0.1	0.43	0	
At %	18.96	15.47	62.30	2.24	0.33	0.38	0.09	0.23		



Figure 2 : TEM images and EDX analyses of the Marakabassi clay (< 2 μ m fraction).

4.2. Mineralogy

The X-Ray powder diffractogram of the initial material in Fig. 3 is dominated by the equidistances of kaolinite at 7.19, 4.46, 2.56, 3.57 Å. The presence of 2:1 clays is indicated by the modulation around 18 Å for smectite and at 10.18 and 2.35 Å for illite/mica.The degree of crystalline order of kaolinite can be quantified by calculating the Hinckley Index ^[14], which is the sum of the heights of reflexions (010), and (111) measured from the inter-peak background, divided by the height of the (010) peak measured from the general background. Hinckley The index of the Marakabassy clay is 0.42, which indicates a low degree of order, according to the general scale which ranges from 0.2 to 1.5 (Fig. 3). The X-ray pattern of an oriented preparation of the <2 μ m fraction (Fig 3) confirms the dominance of

kaolinite over quartz, smectite and illite. The halfheight width of the 001 peak of kaolinite at 7.19 Å introduced in the Scherrer equation yields a thickness of 26 nm, which suggests a highly anisotropic shape of the kaolinite particles. Expansion of smectite by ethylene glycol shifts the 15.32 Å line towards 17.12 Å. The small intensity of this line indicates that smectite is present in very low amount. Thermal treatment at 550°C releases a small amount of illite, identified by the remaining 10.30 Å line, and of quartz. The recorded X-ray patterns do not allow to quantify the clay minerals present in sample MB. However, the amounts can be approached using the results above. If the hypothesis is made that Mg (Table 1) is present as octahedral substitution in 2:1 clays, at an average rate of 0.5 atoms per half cell, the amount of 2:1 clays (here smectite and illite/mica) can be estimated at 14 g per 100 g of sample.



Figure 3: X-Ray diffractograms of the Marakabassi clay (Co-K \square radiation). a) Powder diagram of the raw material – b) Oriented preparation of the <2 μ m fraction – c) Calculation of the Hinckley index. K: kaolinite – I: illite – S: smectite – Q: quartz

The IR spectrum presented in Fig. 4 confirms the predominance of the kaolinite phase, as shown by the strength of the 4 OH stretching modes at 3697 cm⁻¹, 3670 cm⁻¹, 3652 cm⁻¹ (external OH) and 3620 cm⁻¹ (internal OH) belonging to the octahedral OH-Al groups as indicated in **Fig. 4** $^{[15,16]}$. The intensity and resolution of the 3670 cm⁻¹, 3652 cm⁻¹ modes generated by the coupling of two of the three external OH oscillators allow to quantify the cristallinity of the clay as proposed by ^[17] and ^[18]. They defined a criterion named p2, as the intensity ratio of the 3670 cm⁻¹ and 3652 cm⁻¹ modes: $p_2 =$ $(I/Io_{3670 \text{ cm}-1}) / (I/Io_{3652 \text{ cm}-1})$. The value of p2 is lower than 1 for a well crystallized kaolinite, it increases when the amount of crystalline defects increases. Here, the 3670 cm⁻¹ mode is poorly resolved, and p2 is higher than 1 indicating a poorly crystallized kaolinite, as already shown by XRD (Fig. 3).

The stretching modes of external OH groups (figure 4) which represent the proton motion in front of the Al-O bond generate an absorption mode at 915 cm⁻¹ exhibiting on the high frequency side a shoulder at 938 cm⁻¹. The resolution of this 938 cm⁻¹ stretching mode is also an index of the kaolinite crystallinity. A shoulder at 3598 cm⁻¹ identified as OH-Fe³⁺-Al stretching mode, is associated to the 878 cm⁻¹ bending mode (Fig. 4): it reveals the presence of Fe^{3+} ions in substitution to Al in the octahedral sheet of clay particles. The wide stretching mode at 3447 cm⁻¹ associated with the 1638 cm⁻¹ bending mode of molecular water indicates that a large amount of water is bound to the clay. In addition the stretching mode at 1424 cm⁻¹ is assigned to the presence of carbonate and the triplet at 796 cm⁻¹, 780 and 753cm⁻¹ to the stretching modes of SiO₂.



Figure 4: Infrared spectra of < 2 μm fraction. a) Complete spectrum, b) Domain of OH stretching (linear baseline between 3750 and 3550 cm⁻¹), c) Domain of OH bending

The status of Fe appears on the 300 K Mössbauer spectrum of the raw material (Fig. 5), which essentially consists of a quadrupolar doublet with a isomer shift of 0,35 mm.s⁻¹ characteristic of octahedral Fe^{III} in clays ^[19] and a quadrupolar splitting at 0,53 mm.s⁻¹. This information is also present on the Mössbauer spectra of the fine fraction. From the 300 K spectrum recorded at 12 mm.s⁻¹, one observes clearly at the centre a quadrupolar doublet while the outer part remains rather flat; suggesting the absence of Fe based magnetic phases. When collecting the 300 K Mössbauer spectrum at 4 mm/s, one observes a small peak at about 2 mm.s⁻¹ in addition to the prevailing quadrupolar doublet. The refinement of this spectrum requires at least 2 quadrupolar components. As listed in Table 2, the isomer shift value of the main component (98 %) is typical of High Spin state Fe³⁺ located in octahedral coordinence while that of the minor component has to be rather attributed to the presence of Fe^{2+} . Such a description has been successfully achieved with the large velocity spectrum, giving rise to the same qualitative and quantitative conclusions. Furthermore the slight asymmetry of the intense central doublet could be assigned to the contribution of a low percentage of Fe³⁺ in tetrahedral coordinence which does not exceed 5%.

At 77 K (Fig. 5), a magnetic sextet with broadened

and asymmetrical lines occurs in addition to the central quadrupolar doublet. The fitting model involves two quadrupolar doublets and at least 2 magnetic components to well describe the sextet (see hyperfine data listed in **Table II**).

The refined values of hyperfine parameters confirm previous conclusions, i.e. a majority of Fe^{3+} and a minority of Fe²⁺. Taking into account the values of the quadrupolar shift, the magnetic component is assigned to ultrafine particles of goethite. Indeed it is well established that the Néel temperature of goethite is about 400 K and the confinement effect into nanometer size particles originates the presence superparamagnetic fluctuations: both of the quadrupolar structure at 300 K and the magnetic one at 77 K suggest particles of goethite less than 15 nm. The broadening and asymmetry of the lines might be due to grain size distribution (5-15 nm), the role of the matrix and/or the presence of other elements (Al ...). It is difficult to give deeper and reasonable description. The nanometric grain size of goethite is attributed to its growth in a restricted volume, for example as an intergrowth with kaolinite nanometer size particles. That is confirmed by the TEM-EDX images of Figure 2 on which Fe distribution overlaps on that of Si.



Figure 5: Mössbauer spectra of the Marakabassi clay. a) Raw sample (MIMOS), b) < 2 μ m sample at 300°C and 12 mm.s⁻¹, c) < 2 μ m sample at 300 K and 4 mm.s⁻¹, d) < 2 μ m sample at 77 K and 4 mm.s⁻¹

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Т°К	Velocity (mm.s ⁻¹)	Isomeric shift (IS) (mm.s ⁻¹)	Line width (mm.s ⁻¹)	Quadrupolar splitting (QS) (mm.s ⁻¹)	Fe ³⁺ %	Fe ²⁺ %
300	4	0.26	0.46	0.52	98	
		0.98	0.47	2.58		2
300	12	0.33	0.49	0.50	97	
		0.97	0.50	2.42		3
77	12	0.45	0.55	0.48	74	
		1.11	0.50	2.64		2
		0.48	0.61	- 0.31	15	
		0.50	0.61	- 0.15	9	

Table II : Characteristics of Mossbauer spectra of the fine clay fraction (Figure 5).

From these measurements, it appears that Fe^{3+} occurs mainly in octahedral coordinence (98 %) while Fe^{2+} content remains extremely low. Fe^{3+} is consequently related to kaolinite and goethite. Chemical analysis shows that its occurrence in the clay sample in less than 6% in weight: thus goethite represents less than 2% of the whole sample that is obviously not detectable in XRD patterns and IR spectra.

Fe-OH-Al bonds were also observed on the IR spectra (**Fig. 4**), which supports that Fe^{III} substitutes Al in the octahedral sheet of the present clays. Fe^{III} in iron oxides is significant, as observed by the presence of the characteristic sextuplet. Fe^{II} was not observed, since its characteristic feature (IS 1 and QS 1.3) is absent from the Mössbauer spectrum (**Fig. 5**). Therefore, the Fe substitution in the octahedral sheet of the clays does not affect their CEC.

The weight loss recorded during annealing of the clay up to 900°C (Fig 6) occurred mainly in two steps. The first weight loss (6 %) is due to elimination of molecular water between 25 °C and 90 °C with the maximum loss at 55 °C. It can be attributed essentially to interlayer and surface water in smectite and kaolinite. The second major weight loss (8 %) occurs at 473 °C. It is attributed to the dehydroxylation of the kaolinite crystal, although the temperature is significantly lower than that of well crystallized kaolinite, expected at 515 °C. There are several origins of such unusually low dehvdroxvlation temperature. First, the small size of the kaolinite particles promotes their reactivity ^[20]. Then, iron substituting octahedral sites promotes dehydroxylation of kaolinite by increasing the structural disorder ^[21, 22]. Finally, the conditions of thermal analysis also influence the dehydroxylation:

the low heating rate (5°C. min⁻¹) under Ar sweep may result in lower dehydroxylation temperature than those given as references, which are generally recorded in air at a heating rate of 10°C.min⁻¹. Stoichiometrically, kaolinite generates 14% of weight loss upon thermal dehydroxylation around 500°C^[23]. Therefore, the actual amount of 8% weight loss recorded for the MB clay corresponds to 57% of kaolinite. However, studies on the influence of particle size on thermal dehydroxylation of kaolinite ^[20] clearly show that size reduction of pure kaolinite (the well-known KGa1 and KGa2 samples) by grinding and ultrasound results in structural and superficial effects according to the treatment time. The surface areas increased up to 60 m².g⁻¹, the XRD reflexions were broadened, and substantial changes in the thermogravimetric curves occurred. Weight loss up to 3.97% appeared upon dehydration below 140 °C, the two dehydroxylation stages (230-440°C and 440-1000°C) produced respectively up to 4.35% and 9.44%, which corresponded to a sum of 13.79% characteristic for pure kaolinite dehydroxylation. In the present study, all the features of ground kaolinite are observed, including a weight loss of 2% around 250°C.





The kaolinite content of the MB clay, calculated from the sum of the weight losses in the two dehydroxylation stages, i.e. 10%, is then 71.4%. From the above results, an estimation of the mineralogical composition of the MB clay can be proposed: 71% Kaolinite, 14% smectite/illite, 2% Goethite, 13% (the complement to 100%) SiO₂.

4.3 Surface properties

The N₂ and Ar low pressure adsorption isotherms (Fig. 7) describe the adsorption of the gas in the range of six orders of magnitude below the average monolayer, which occurs around $P/P_0 = 0.1$, i.e. $LnP/P_o = -2.3$. The isotherms presented here are derivative isotherms. In order to quantify the heterogeneous distribution of surface energy, the experimental curve is decomposed in a sum of theoretical local derivatives. Each of the local derivative represents adsorption on a single surface patch, each of which being characterized by the median adsorption energy (the maximum), the lateral interaction between adsorbed molecules (the half-height width), and a geometric area which represents a proportion of the total area occupied by the gas molecules. The parameters of the theoretical local derivatives (Table III) are adjusted so that their sum fits the experimental data. The experimental curves show two major modulations, corresponding to two major energy domains. The most energetic domain (respectively at $LnP/P_0 = -$ 11 and -13 for Ar and N₂) is attributed to the edges of the clay particles, which bear reactive silanol and aluminol groups. The less energetic domain (respectively at $LnP/P_0 = -4$ and -6 kT for Ar and N_2) is attributed to the basal faces of the clay particles, on which saturated siloxane and/or aluminol groups are present ^[11,12,13]. The specific surface area of the edges can be calculated from the sum of the theoretical local derivatives used to model the most energetic domain, which accounts for 20.5 % of the total surface area. Such proportion corresponds to a very anisotropic hexagonal prism of diameter/height ratio 20. This result is strongly supported by the particle sizes below 500 nm and the low contrast observed by SEM (Figure 2), and by the 26 nm thickness calculated from the X-ray diffractogram. In line with the morphology of the studied clay, its total surface area of $69.5 \text{ m}^2/\text{g}$ (Table 3) is unusually high for clays, the N₂ BET specific surface area of which ranges generally around 20-30 m².g⁻¹. This high surface area can be an explanation for the weight loss of 6% observed below 130°C in the thermogravimetric analysis. Assuming that the hydrated surface carries two water layers, which is generally the case for mineral surfaces at room humidity (50-60%), and the crosssectional area of adsorbed water being close to 0.1 nm^{2} ^[2], the adsorbed water content is 4.2 %. The complement to 6%, i.e. 1.8%, can then be attributed to interlayer water in smectite.

The cation exchange capacity (CEC) measured by the cobaltihexamine method is 0.34 e-.kg⁻¹. This

high CEC value cannot be attributed only to 2:1 clays, which represent 14% in mass, and contribute for 0.14 e-.kg⁻¹ of CEC according to an average CEC of 1 e-.kg⁻¹. The rest of the CEC, i.e. 0.2 e-.kg⁻¹ ¹ is attributed to kaolinite. In the case of kaolinite, the CEC is generally located on the dissociated edge charges, and represents 0.1 e-.kg⁻¹. Permanent charge is generally considered as insignificant for kaolinite compared to montmorillonite, but yet represent 0.01 - 0.08 e-.kg⁻¹ ^[25]. In fact Al^{III}/Fe^{II} substitutions in the crystal lattice have been evidenced only exceptionally ^[26]. In the present case, infrared and Mössbauer spectra (Figures 4 and 5) indicate that isomorphic substitution of Al^{III} by Fe^{III} occurs, but the absence of Fe^{II} precludes a permanent charge from this origin. A significant part of the CEC of the Marakabassi clay is then not explained at this point.



Figure 7: Low pressure N_2 and Ar derivative adsorption isotherms on the $<2\,\mu m$ fraction. The isotherms are decomposed into theoretial local derivative isotherms. Grey lines: experimental data. Fine black lines: local theoretical derivatives.

The pH variation of Zeta (ζ) potential of the < 2 µm fraction acordind to the pH in 10⁻¹, 10⁻² and 10⁻³ M NaNO₃ electrolyte is shown in Figure 8. In the pH domain from 4 to 10, the ζ potential is quasi-stable around –25 mV, independently of the pH and ionic strength. A shift towards -20 mV is recorded at pH below 4 in 10⁻² and 10-3 M Na NO₃. In 10⁻¹ M

NaNO₃ the ζ potential is reversed at pH 2.2, which defines an Iso-Electric Point.

Table III: Parameters used to fit the experimental derivative gas adsorption isotherms (Figure 7). LnP/Po: position of the maximum of the theoretical local derivative. □/kT: broadening of the local curves. The specific surface area (SSA) was calculated on the nitrogen adsorption isotherm.

-	LnP/Po kT	□/kT	SSA m²/g	SSA %
	-10.7	0	7.6	13.3
	-7.9	0	3.2	5.7
Argon	-6.8	0	9.3	16.3
	-4.0	0.4	36.7	64.7
		Total	56.8	100.0
	-14.5	0	65	93
	1	v	0.5	2.5
	-12.7	1	7.8	11.2
	-12.7 -10.4	1 0.4	7.8 3.9	11.2 5.6
Nitrogen	-12.7 -10.4 -7.9	1 0.4 -0.8	7.8 3.9 18.8	11.2 5.6 27.1
Nitrogen	-12.7 -10.4 -7.9 -5.6	1 0.4 -0.8 0.69	7.8 3.9 18.8 19.1	11.2 5.6 27.1 27.5
Nitrogen	-12.7 -10.4 -7.9 -5.6 -2.6	1 0.4 -0.8 0.69 0	7.8 3.9 18.8 19.1 13.4	11.2 5.6 27.1 27.5 19.3

The surface charge of kaolinite originates from the proton dissociation of amphoteric silanol and aluminol groups at the hydroxyl – terminated edges planes of the particles. Therefore one would expect a strong dependence of the corresponding ζ potential to the pH and secondary to the ionic strength, as generally observed for metal oxides, and as predicted Poisson-Boltzmann theory of electric double layer. The electrokinetic behaviour of the Marakabassy clay fraction (Figure 8) is clearly in contradiction with the above expectations. Recent works report similar observations [27, 25, 28, 29]. These observations parallel those made on montmorillonite, which show strong potential independence of the electrokinetic potential to pH and ionic strength due to the dominance of the ^[30,31,32,25,33].The charge permanent crystalline montmorillonite-like electrokinetic behaviour of kaolinites is generally attributed to interstratified kaolinite/smectite impurities, and to montmorillonite layers at the surface of kaolinite particles, especially in the case of poorly ordered kaolinite ^[34,35,25]. In the present study, the Mössbauer analyses clearly show absence of Fe^{II} in the Marakabassi clay (Fig. 5), the surface properties of which must then be attributed to surface montmorillonite 1 layers. Unambiguous observations of such structures can only be achieved by HRTEM after delicate and complicated preparation ^[35]. In contrast, the presence of montmorillonite layers on top of kaolinite particles significantly impacts their electrokinetic behaviour, which is easily measurable by electrophoresis (Fig. 8).



Figure 8: Zeta potential of the < 2 $\mu m.$ Evolution with pH in $10^{-1},\,10^{-2},$ $10^{-3}\,M\,NaNO_3.$

5 Conclusion

The present study shows that in the MB clay sample the main mineral is a badly crystallised nanometric kaolinite with Fe^{III}/Al^{III} octahedral substitution. Additional minerals are smectite (14%), quartz and goethite. The nanometric size and strong anisotropy (20% of lateral faces) of the particles result in high surface area ($64 \text{ m}^2.\text{g}^{-1}$). The presence of montmorillonite layers on both sides of the kaolinite stacks results in high CEC (0.34) $e-.kg^{-1}$) and montmorillonite-like electrokinetic behaviour ($\zeta = -27$ mV above 4). These properties define a very favourable substrate for the adsorption of metallic cations by complexation and cation exchange.

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