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Characterization of Clay Materials from Ivory Coast for Their Use as Adsorbents for Wastewater Treatment

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Abstract

In order to contribute to the valorisation of the clay materials of Ivory Coast in the depollution of wastewater, the physicochemical and mineralogical characterization of three clay samples taken in Agboville (AGB), Bingerville (BIN) and Katiola (KAT) was carried out. The objective of this work was to compare the properties of the clays in order to identify the one that is likely to have interesting adsorptive capacities to clean up contaminated water. These clays were studied by chemical analysis, X-ray diffraction, scanning electron microscopy and thermal analysis. In addition, their specific surface areas and cation exchange capacities were determined. The AGB clay is composed of 75.51% kaolinite, 14.20% illite and 9.26% quartz. The BIN clay contains 52.21% kaolinite, 6.23% illite, 17.50% quartz and 15.71% goethite. As for the KAT clay, it contains 48.08% kaolinite, 3.55% illite, 20.14% smectite, 6.11% quartz and 16.86% goethite. Their thermal behavior and microstructure are in agreement with their mineralogy. The measured specific surface areas and cation exchange capacities are consistent with literature values. The KAT clay has the highest specific surface and cation exchange capacity. In the light of the results obtained, the KAT clay appears to be more effective in depolluting water than the BIN and AGB clays.

Keywords

Insert Clay, Characterization, Depollution of Water, Kaolinite, Smectite

1. Introduction

The issue of drinking water is a major challenge for developing countries, including Ivory Coast. Indeed, in these countries where industrialization and urbanization are rapid, the effluents from anthropic activities, rich in pollutants, are generally not well treated and are released into nature, causing enormous pollution of surface and groundwater. Among the anthropic sources of pollution, we can point out: the mining activity, the metallurgical and iron and steel industry, the fertilizers and pesticides applied in the cultivation of the grounds, the incinerators and ashes of incineration of the waste, the medical waste, the waste dumps of cities, the emissions of the factories and the explosion engine, the effluents of the sewers and the sludges of sewage... [1]. Numerous researches have shown that waters of Côte d'Ivoire are contaminated by chemical species due to anthropic activities [2] [3]. It is necessary to find inexpensive and easy to implement methods to treat these effluents before they are released into nature. Commonly adopted techniques for removing pollutants from water include chemical precipitation, lime coagulation, ion exchange, reverse osmosis and solvent extraction. These methods are less effective when the concentration of pollutants in the effluent is low. Therefore, adsorption can be an alternative technology for the removal of pollutants, which are present in very low concentrations in aquatic environments [4]. In this context, several studies have invested in the search of effective materials (adsorbent) to clean up contaminated water. Ouédraogo *et al.* showed that the properties of a laterite from Burkina Faso gave it an adsorbent power in the removal of arsenic [5]. Sawdust has been proven to remove unwanted material from water [6]. Mimanne *et al.* proved that the interesting characteristics (large specific surface and cationic exchange capacity) of an activated carbon and a montmorillonite from Algeria allowed a good removal of Pb and Cd [7]. Several other materials such as: powdered corn cobs [8], activated carbons [9], wood powders [10], clays [11]... with interesting properties have also been proven in the decontamination of contaminated water.

Among so many materials, clays, of which the Ivory Coast has many deposits [12], presents interesting adsorption properties in relation to their mineralogy and physicochemical properties [7] [13].

The objective of this study is to characterize from the point of view of mineralogy and physicochemical properties, three samples of clays from Ivory Coast in order to better appreciate their ability to clean up contaminated water.

2. Materials and Methods

2.1. Clay Materials

The clay samples used in this study are referenced: AGB, BIN and KAT. The AGB sample was collected at Grand-Morié (5°59' north latitude and 4°08' west longitude) in the Agnéby Tiassa region of southern Ivory Coast. The BIN sample was extracted in Bregbo (5°18' north latitude and 3°50' west longitude), a town in the municipality of Bingerville, in the Abidjan district of southern Ivory

Coast. The KAT sample was taken from the City of Katiola (8°08' north latitude and 5°06' west longitude) in the Hambol region of northern Ivory Coast. The sampling was carried out based on the fact that the clays in the south of Côte d'Ivoire are very often rich in kaolinite and those in the north contain a significant amount of smectite [14] [15]. The images of the studied clays are shown in **Figure 1** below.

All analyses were performed on these raw clays sieved to 63 μm and their fine fractions saturated with sodium or magnesium.

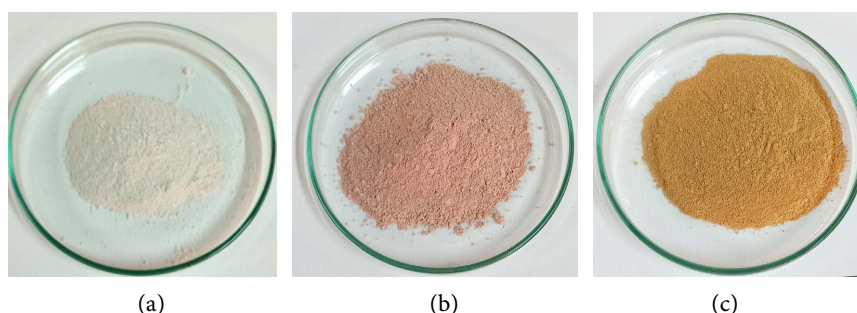


Figure 1. Images of the AGB (a), BIN (b) and KAT (c) clay samples.

2.2. Extraction of the Fine Fraction

The pure clay fraction was obtained by the granulometric separation technique based on sedimentation [16]. It made it possible to obtain fine fractions of clay saturated with sodium or magnesium: BIN-Na, BIN-Mg, AGB-Na, AGB-Mg, KAT-Na and KAT-Mg.

2.3. Chemical Analysis

The chemical analysis was carried out on the raw clays by atomic emission spectrometry coupled to an inductive plasma (ICP-AES type Spectro Arcos) for major elements. The study of trace elements was carried out using a mass spectrometer coupled by induction to a plasma (ICP-MS type Agilent 7800). Before analysis, the samples were mineralized in an acidic mixture ($\text{HNO}_3 + \text{HCl} + \text{HF}$).

2.4. X-Ray Diffraction (DRX)

The DRX study was performed on an ARL equinox 100 diffractometer operating at 45 Kv and 0.9 mA. The measurements were performed on the 63 μm sieved raw clays totally disoriented and on the oriented legs of the fine clay fractions. The monochromatic radiation used for the measurements is the copper K_α ($\lambda_{\text{Cu}} = 1.5406 \text{ \AA}$). To differentiate “swelling” 2:1 clay minerals, such as smectites, from non-swelling minerals, oriented legs saturated with ethylene glycol were analyzed by diffractometer. Samples heated to 500°C were also analyzed. This treatment aims to destroy the kaolinite phases in order to distinguish them from the illite phases.

2.5. Scanning Electron Microscopy (SEM)

The surface images of BIN, AGB and KAT clays were zoomed up to 40,000 times and observed with an Auger spectrometer type JEOL JEAMP 9500F (JEOL Ltd, Tokyo, Japan). The work was performed under a voltage of 20 kV, a low current of 1 nA and a pressure lower than 2×10^{-7} Pa. The surfaces of the samples were previously sputtered with a gold layer.

2.6. Thermal Analysis

Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA) were carried out simultaneously using an apparatus of type SDT 650 - TA Instruments, at a rate of temperature rise of $10^\circ\text{C}/\text{min}$ from room temperature to 1200°C , under helium scavenging. 10 mg of raw clay powder, saturated with sodium or magnesium were used for each analysis.

2.7. Measurement of Specific Surface

The measurement of the specific surface area was carried out by volumetric nitrogen adsorption at 77 K using a Tristar II surface and porosity analyser from Micromeritics. The samples of raw clays, saturated with sodium or magnesium, were previously degassed at 120°C overnight in a VacPrep type sample preparation system under primary vacuum.

2.8. Measurement of the Cation Exchange Capacity (CEC)

This measurement was performed by displacement of exchangeable cations by the hexammine ion cobalt (III) $[\text{Co}(\text{NH}_3)_6]^{3+}$ at 99%, follow-up of the dosage by spectrophotometry. This method was described by Morel [17]; Mantin and Glaeser [18] then by Remy and Orsini [19]. In a 50 mL centrifuge tube, 20 mL of cobaltihexammine chloride solution of concentration 16.6×10^{-3} M is mixed with 1 g of clay. The normality of the cobaltihexammine ion in the solution is 0.05 N. The resulting mixture is rotated for 2 hours to reach equilibrium and then centrifuged at 19000 rpm for one hour. After centrifugation, the supernatant is collected and filtered at $0.45 \mu\text{m}$. The cobaltihexammine ion present in the supernatant is determined by colorimetry using a spectrophotometer (absorption band at 472 nm). A calibration line established from five standard solutions (normality = 0.01; 0.02; 0.03; 0.04 and 0.05 N) of cobaltihexammine is used as reference.

The CEC is calculated using the following relationship (remainder method) (Equation (1)):

$$\text{CEC} = \frac{(C_i - C_f) * V}{m} * 100 \quad (1)$$

With: C_i and C_f the initial and residual concentrations expressed in normality; V : volume of solution in mL; m : mass of sample in grams.

To verify the CEC and to determine the cations responsible for the compensation of the surface charges of the clays, the concentrations of the displaced ca-

tions (Mg^{2+} , Fe^{3+} , Al^{3+} , K^+ , Ca^{2+} , Na^+ and Mn^{2+}) in solution are determined by ICP-AES. The sum of these contents constitutes the chemical cation exchange capacity (chemical CEC) determined by the following relation (Equation (2)):

$$\text{CEC}_{\text{chemistry}} = \sum_i [M_i] * v_i * \frac{V}{m} * 10^3 * 100 \quad [20]. \quad (2)$$

$[M_i]$: concentration of the species considered in mol/L, v_i : valence of the ion; V : volume of solution in L and m : mass of sample in g. The CEC is expressed in meq/100g. This study was carried out on raw clays.

3. Results and Discussion

3.1. Chemical Composition of Clays

Chemical analysis reveals that for all the chemical species studied, the same oxides are generally found but in variable proportions (**Table 1**). The contents of SiO_2 (from 41.52% to 50.87% (mass)) and Al_2O_3 (from 20.57% to 34.62%) are the most important, which clearly indicates the silico-aluminous nature of the clays studied. These predominant elements are followed by the iron oxide (Fe_2O_3) content. The Bingerville and Katiola clays are the richest in Fe_2O_3 , with contents of 15.71% and 16.86% respectively. This high iron content in these samples is consistent with the pink and orange colors observed for BIN and KAT respectively. The AGB clay contains a low iron content (1.21%) which is a consequence of the white color of the sample. Then come the other oxides (TiO_2 , K_2O , CaO , MgO , Na_2O , MnO and P_2O_5). The presence of more or less important K_2O , indicates a probable existence of illite in these clays. The existence of smectite in the Katiola clay is suggested by the relatively important presence of calcium oxide in the KAT sample. The high values of mass loss following calcination (10.51% and 17.60%) could be explained by the natural character of the clays [21].

The presence of trace elements (**Table 2**) can be related to the adsorption capacity of clays. The contents of metals (Hg, Pb and Cd) and arsenic in these clays

Table 1. Composition of major oxides (% by mass) of BIN, AGB and KAT clays.

Samples	SiO_2	Al_2O_3	Fe_2O_3	K_2O	Na_2O	MgO	MnO	TiO_2	CaO	P_2O_5	LOI
BIN	44.83	22.64	15.71	0.72	0.68	0.52	0.00	0.82	0.00	0.10	14.08
AGB	50.87	34.62	1.21	1.64	0.41	0.07	0.01	0.18	0.03	0.02	10.51
KAT	41.52	20.57	16.86	0.41	0.02	0.52	0.02	0.92	1.41	0.01	17.60

Table 2. Minor element composition of BIN, AGB and KAT clays (expressed in ppm).

	As	Ba	Be	Bi	Cd	Co	Cr	Cu	Hg	Mo	Ni	Pb	Sb	Sn	Zn
BIN	18	260	1.6	0.36	0.12	2.5	130	6	-	0.9	17	27	0.62	2.5	23
AGB	0.55	228	6.5	2.54	0.05	2.03	25	14.1	-	0.30	6.35	39	-	2.43	48.2
KAT	1.6	203	2.12	1.27	0.12	32	830	86.6	-	1.20	400	10.6	0.14	1.71	130

are clearly lower than the regulatory thresholds (AFNOR NF U 41,044 and WHO standard) [22] [23]. Moreover, mercury was not detected in all samples. This result confirms the possibility of using these clays as adsorbents for water depollution.

3.2. Mineralogical Composition

3.2.1. Total Rock

The diffractograms obtained are shown in **Figure 2** and **Figure 3**. The results for the AGB and BIN samples are very similar. The peaks identified: $d_{hkl} = 7.20 \text{ \AA}$ (12.28°); 3.58 \AA (24.85°); 3.09 \AA (28.87°) and 2.34 \AA (38.44°) and $d_{hkl} = 10 \text{ \AA}$ (8.84°); 5 \AA (17.72°), 4.46 \AA (19.89°), 2.56 \AA (35.02°), 2.48 \AA (36.19°) and 1.99 \AA (45.55°), show respectively the essential presence of kaolinite and illite phases, to which is added that of quartz ($d_{hkl} = 4.26 \text{ \AA}$ (20.84°); 3.35 \AA (26.59°); 3.24 \AA (27.51°); 2.29 \AA (39.31°); 2.13 \AA (42.40°); 1.82 \AA (50.08°) and 1.66 \AA (55.30°)). In addition to these minerals, sample BIN contains goethite (d_{hkl} located at 2.25 \AA (40.04°)). The KAT clay also contains the minerals mentioned above, plus a smectite peak (d_{hkl} located at 12.19 \AA (7.25°)).

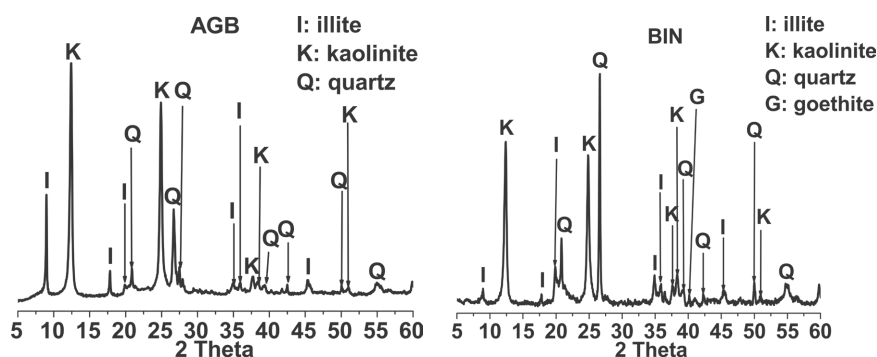


Figure 2. Diffractograms of Agboville (AGB) and Bingerville (BIN) clays.

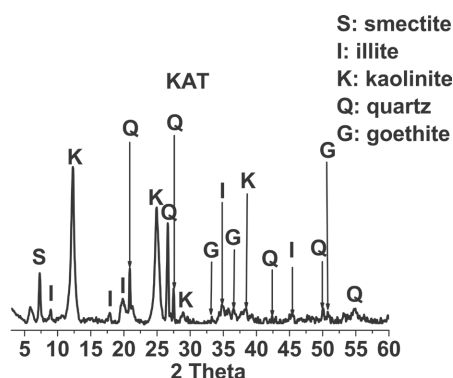


Figure 3. Diffractogram of the Katiola clay (KAT).

3.2.2. Clay Fraction

Oriented deposition analysis of fine clay fractions, saturated with ethylene glycol and calcined at 500°C (**Figure 4** and **Figure 5**) confirmed the previously indexed peaks.

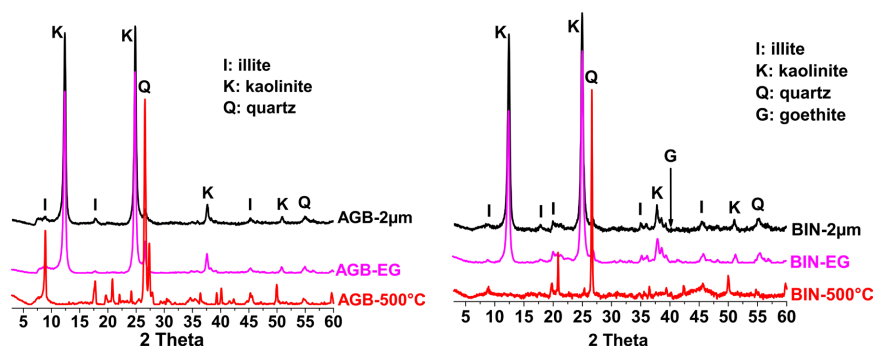


Figure 4. X-ray diffractograms of oriented preparations of AGB and BIN clays (2 µm: fine clay fraction at 2 µm; EG: ethylene glycol and clays heated to 500°C).

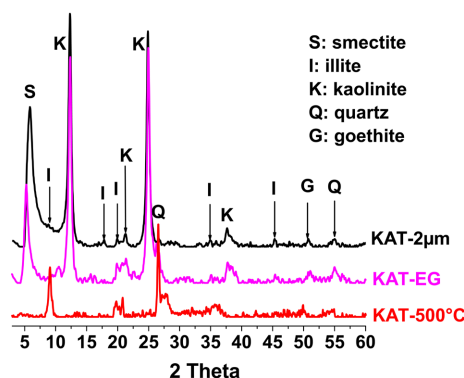


Figure 5. X-ray diffractograms of oriented KAT clay preparations (2 µm: fine clay fraction at 2 µm; EG: ethylene glycol and KAT heated to 500°C).

The smectite peak, which appears at an inter-reticular distance of 12.19 Å in the disoriented powder, expands to 15 Å (5.89°) in the oriented deposition analysis of the magnesium-saturated clay fraction. This expansion is related to the hydration of Mg²⁺ ions in the interfoliar space. After treatment with ethylene glycol, this peak increases to 17.12 Å (5.16°) and to 9.78 Å (9.03°) upon calcination. This observation is in agreement with the work of Mache *et al.* on the study of Sagba smectites in Cameroon [24]. In their study, the smectite peak detected at 13.40 Å in the untreated sample, increases to 16.66 Å after ethylene glycol treatment and to 9.56 Å after calcination.

3.3. Mineralogical Proportion of Clays

The calculation of the mineralogical percentages (Table 3) of the clays was carried out from their chemical composition, the data of qualitative mineralogical analysis and by using the following relation developed by Njopwouo (Equation (3)) [25]:

$$T_a = \sum_{i=1}^n M_i * P_i(a). \quad (3)$$

where T_a = content (mass %) of oxide a in the clay

M_i = content of mineral i (%) in the clay

$P_i(a)$ = proportion of oxide a in mineral i

Table 3. Mineralogical percentages of clays.

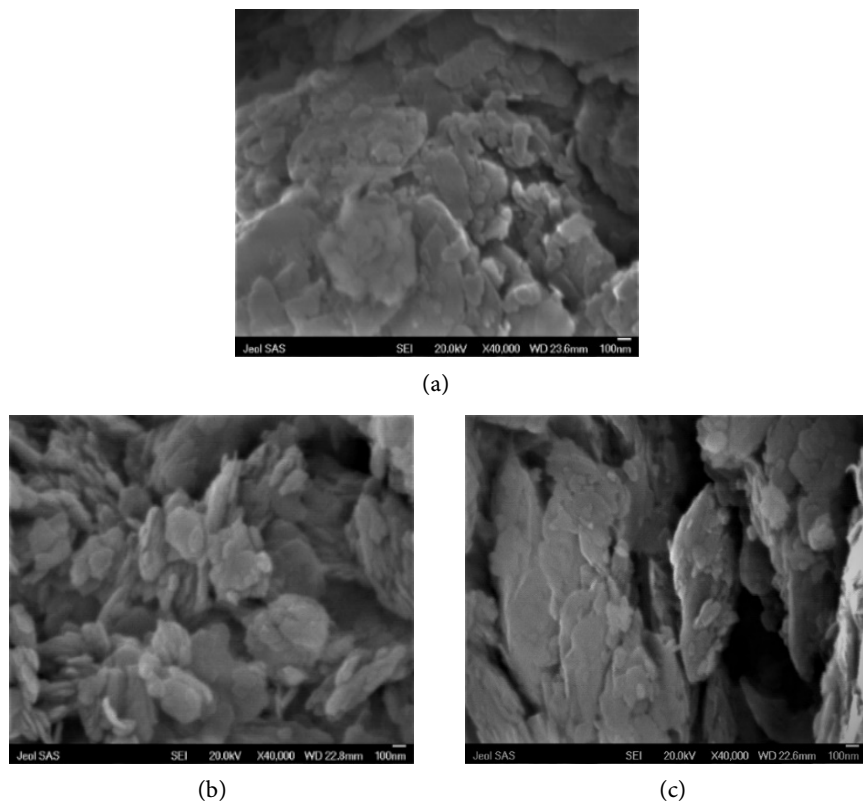
Samples	% Kaolinite	% Illite	% Smectite	% Quartz	% Goethite	Total
BIN	52.21	6.23	-	17.50	15.71	91.65
AGB	75.51	14.20	-	9.26	-	98.97
KAT	48.08	3.55	20.14	6.11	16.86	94.74

Kaolinite is the main clay mineral present in these 3 samples with a proportion varying from 48.08% to 75.51%. All clays also contain illite (3.55% to 14.20%). Smectite was detected only in the KAT sample at 20.14%. The higher kaolinite content (75.51%) and the non-existence of goethite in the AGB clay are consistent with the white color of this sample.

Many works [26] [27] [28] [29] have shown that smectite type clays have large specific surfaces and consequently have much greater adsorption capacities than kaolinitic clays. The presence of iron oxyhydroxide in particular goethite also improves the adsorption capacity of clays [30] [31] [32]. In their works, Sei *et al.* [33] noted that goethite-rich kaolinites had a greater phosphate adsorption capacity and that this reactivity decreased significantly after deferrification.

3.4. Scanning Electron Microscopy (SEM)

Images of the AGB, BIN, and KAT clays ($\times 40,000$ magnification) are shown in **Figure 6** below.

**Figure 6.** Scanning electron microscopy of AGB (a), BIN (b) and KAT (c) clays.

The images reveal large aggregates consisting of platelets of pseudo-hexagonal geometry stacked on top of each other. These randomly oriented platelets are found in all samples. According to Caillère *et al.*, clay minerals of the kaolinite type are presented in the form of hexagonal platelets with more or less marked alterations according to the degree of crystallinity [34]. These images suggest that the kaolinite present in these clays is disordered. Work has shown that iron-rich kaolinites are most often disordered [35] [36] [37] [38]. Moreover, these results confirm those of the XRD and show that kaolinite is present in significant quantities in all the clays studied. Indeed, several researches have shown that the clayey materials of Ivory Coast contain essentially kaolinite, with in rare cases traces of swelling minerals (smectite) [14] [15] [33].

3.5. Differential Calorimetric and Thermogravimetric Analysis

3.5.1. AGB and BIN Clays

Figure 7 shows the thermograms of raw clays, treated with sodium or magnesium from Agboville and Bingerville.

The AGB and BIN clays show two mass losses associated with endothermic events:

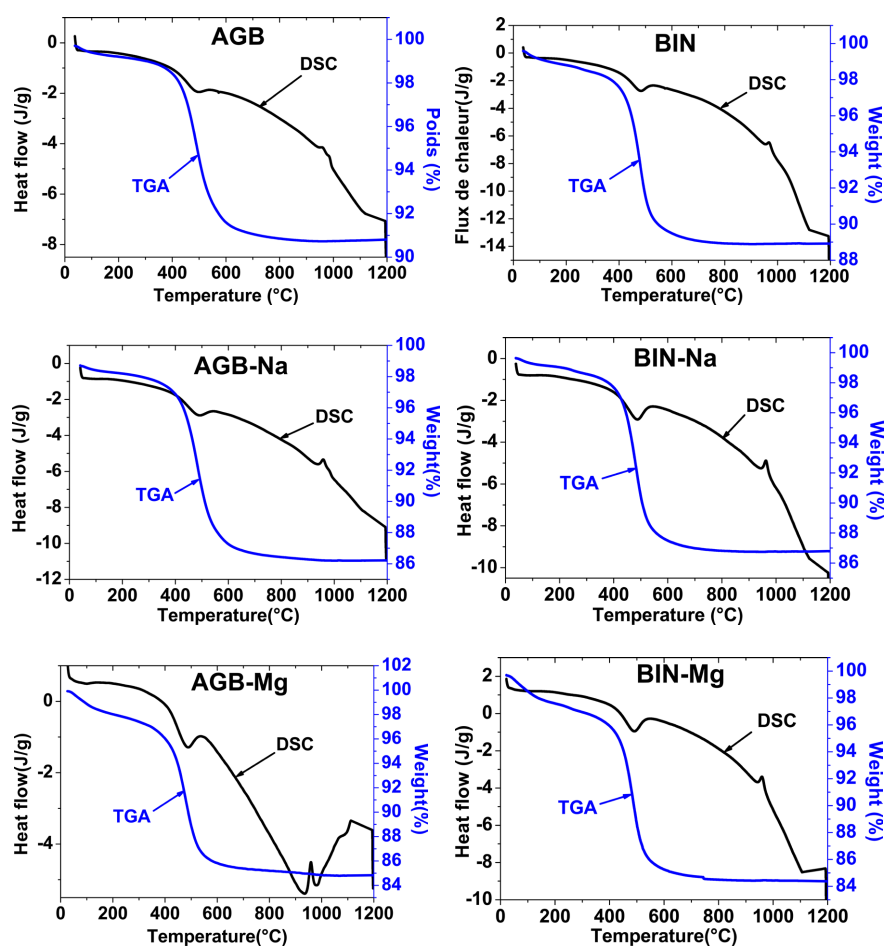


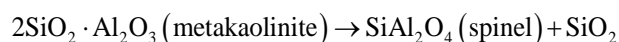
Figure 7. Thermograms of clay from Agboville and Bingerville.

- A small loss of mass between 25 °C and 200 °C, due to the departure of hygroscopic water [14].
- An important loss of mass from 400 °C to 800 °C associated with an endothermic peak around 480 °C. This thermal accident corresponds to the dehydroxylation of kaolinite (transformation of kaolinite into metakaolinite), according to the following reaction: $\text{Si}_2\text{Al}_2\text{O}_5(\text{OH})_4 \rightarrow \text{Si}_2\text{Al}_2\text{O}_7 + 2\text{H}_2\text{O}$ [39].

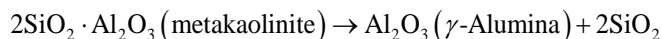
The appearance of this endothermic peak at a temperature below 530 °C, suggests that AGB and BIN are extremely disordered kaolinitic clays, according to the Smykatz-Kloss classification [40].

- Around 960 °C, an exothermic peak not associated with a mass variation is attributable to a structural reorganization of metakaolinite linked to 3 reactions:

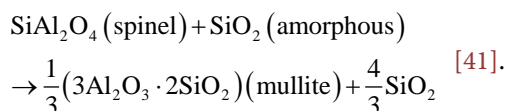
Formation of a spinel structure phase and extraction of amorphous silica:



Evolution of aluminium to VI coordination:



Mullite formation and amorphous silica extraction:



This exothermic phenomenon is subject to various interpretations in the literature. Indeed, some authors exclude the formation of mullite at this temperature. However, Pialy states in his work that: "In the case of very disordered kaolinites, there would be direct formation of mullite. Moreover, very slow heating rates would favour the segregation of metakaolinite and the appearance of the spinel structure phase." [42]. The analysis of the diffractogram of the Agboville clay heated to 960 °C shows the simultaneous presence of mullite and spinel phase (Figure 8). This result is corroborated by the thesis of Gridi-Bennadji who states that generally, the spinel phase and mullite form simultaneously below 1100 °C [43].

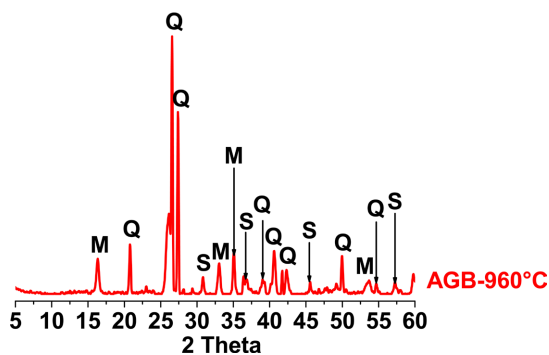


Figure 8. Diffractogram of Agboville clay heated to 960 °C (M: Mullite; S: Spinel).

- At 1112.57°C, AGB-Mg shows an exothermic peak attributable to the nucleation of a second generation of mullite. This additional mullite formation peak is in agreement with the work of Maitra *et al.* [44] and Viswabaskaran and Gnanam [45] who affirmed in their work that the magnesium oxide (MgO) used as additive intervenes in a positive way in the formation of the mullite.

3.5.2. KAT Clay

The thermograms of the Katiola clay show 3 mass losses associated with thermal reactions on the DSC curves (Figure 9). These 3 observed mass losses suggest that the mineralogical composition of this clay is a little different from those of AGB and BIN.

We observe:

- Two consecutive mass losses between 25°C and 300°C (appearing as a split) due to the departure of hygroscopic water and interfoliar water. These two losses of mass confirm the presence of clay mineral of type 2:1.
- From 400°C to 800°C, a significant mass loss associated with an endothermic peak is observed and is attributed to the dehydroxylation of the phyllosilicates contained in the clay samples [24].
- An exothermic event around 900°C due to the recrystallization of minerals such as quartz and/or mullite [46]. This peak is of low intensity in the case of treated samples and does not appear in the case of raw clay.

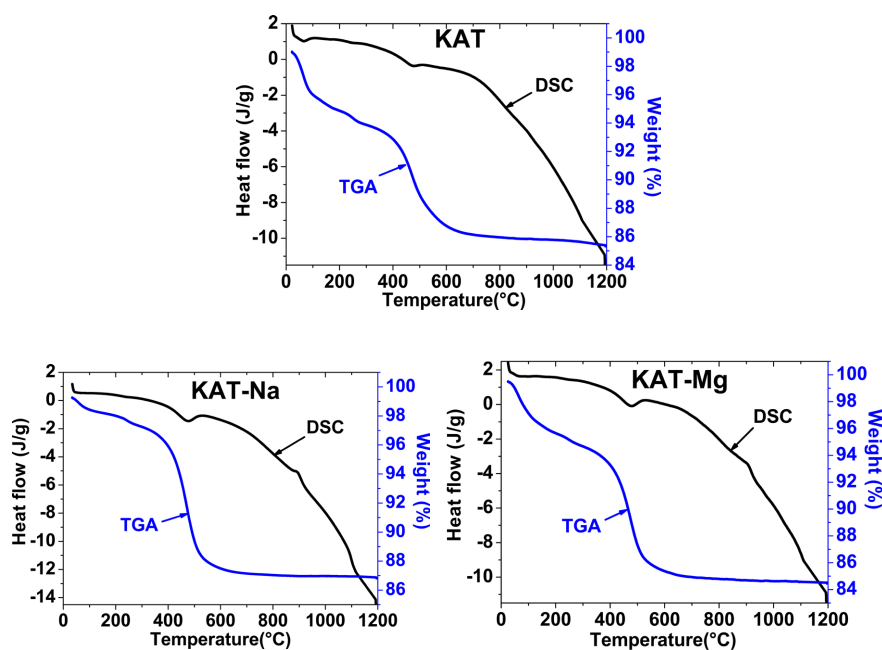


Figure 9. Thermograms of Katiola clay.

3.6. Specific Surface of Clays

The BET method was used to compute the specific surface areas from the nitrogen adsorption isotherms at 77 K [47]. Even if the samples are mesoporous, the

criterion of Rouquerol *et al.* [48] was used to accurately select the range of relative pressures for the calculation of the specific surfaces. The N₂ adsorption isotherms are presented in **Figure 10**. They show almost the same pattern and are typical of mesoporous adsorbents such as clays. The determination of the specific surface area requires the use of the BET relationship (Equation (4)) in the appropriate range of relative pressures ($0.05 \lesssim P/P_0 \lesssim 0.35$ for the samples of this study):

$$\frac{P}{n_{ads}(P_0 - P)} = \frac{C - 1}{Cn_m} \frac{P}{P_0} + \frac{1}{Cn_m} \quad [47]. \quad (4)$$

where P is the equilibrium pressure, P_0 is the saturating vapor pressure at the temperature considered, n_{ads} is the number of molecules adsorbed at the equilibrium pressure and C is the characteristic constant of the gas-solid system. The plot of the line $\frac{P}{n_{ads}(P_0 - P)} = f\left(\frac{P}{P_0}\right)$ allows to determine both C and n_m . The specific surface is then determined by the relation (Equation (5)):

$$S_{BET} = \sigma \cdot N_A \cdot n_m. \quad (5)$$

With N_A the Avogadro number ($6.023 \times 10^{23} \text{ mol}^{-1}$) and σ is the surface area occupied by a gas molecule. In the case of nitrogen adsorption at 77 K, $\sigma = 16.2 \text{ \AA}^2$.

The values of surface areas are presented in **Table 4**.

These values vary from 18.0 to 48.5 m²/g; 31.4 to 53.7 m²/g and 31.0 to 50.1 m²/g respectively for the crude, sodium-saturated and magnesium-saturated clays. In general, the fine fractions obtained by sedimentation have larger specific surface areas than the corresponding raw samples. The specific surface areas of AGB and BIN clays are in agreement with those of kaolinitic clays in many studies [33]-[49]. Although both samples contain the same clay minerals, BIN, which is richer in iron, has a larger surface area than AGB in agreement with the work of Sei *et al.* [33]. Indeed, iron oxyhydroxides (goethite) contribute strongly to the specific surface [50]. The higher surfaces of the KAT samples are related to the presence of smectite and goethite detected in this sample. The values obtained with the KAT sample are in good agreement with those of Mache *et al.* [24] compared to the study of a smectite from Sagba in Cameroon (33 - 90 m²/g). However, these values are lower than those of a pure smectite (80 m²/g) [51] and this is related to the fact that the Katiola clay is a mixture of smectite and other clay minerals such as kaolinite and illite detected in DRX. It should be noted that the presence of other mineral phases due to rock alteration can also affect the specific surface area of the samples. Gupta and Bhattacharyya [52]

Table 4. Specific surface values of raw clays, saturated with sodium or magnesium.

S_{BET} (m ² /g)	AGB	AGB-Na	AGB-Mg	BIN	BIN-Na	BIN-Mg	KAT	KAT-Na	KAT-Mg
	18.0	31.4	42.5	31.7	38.5	31.0	48.5	53.7	50.1

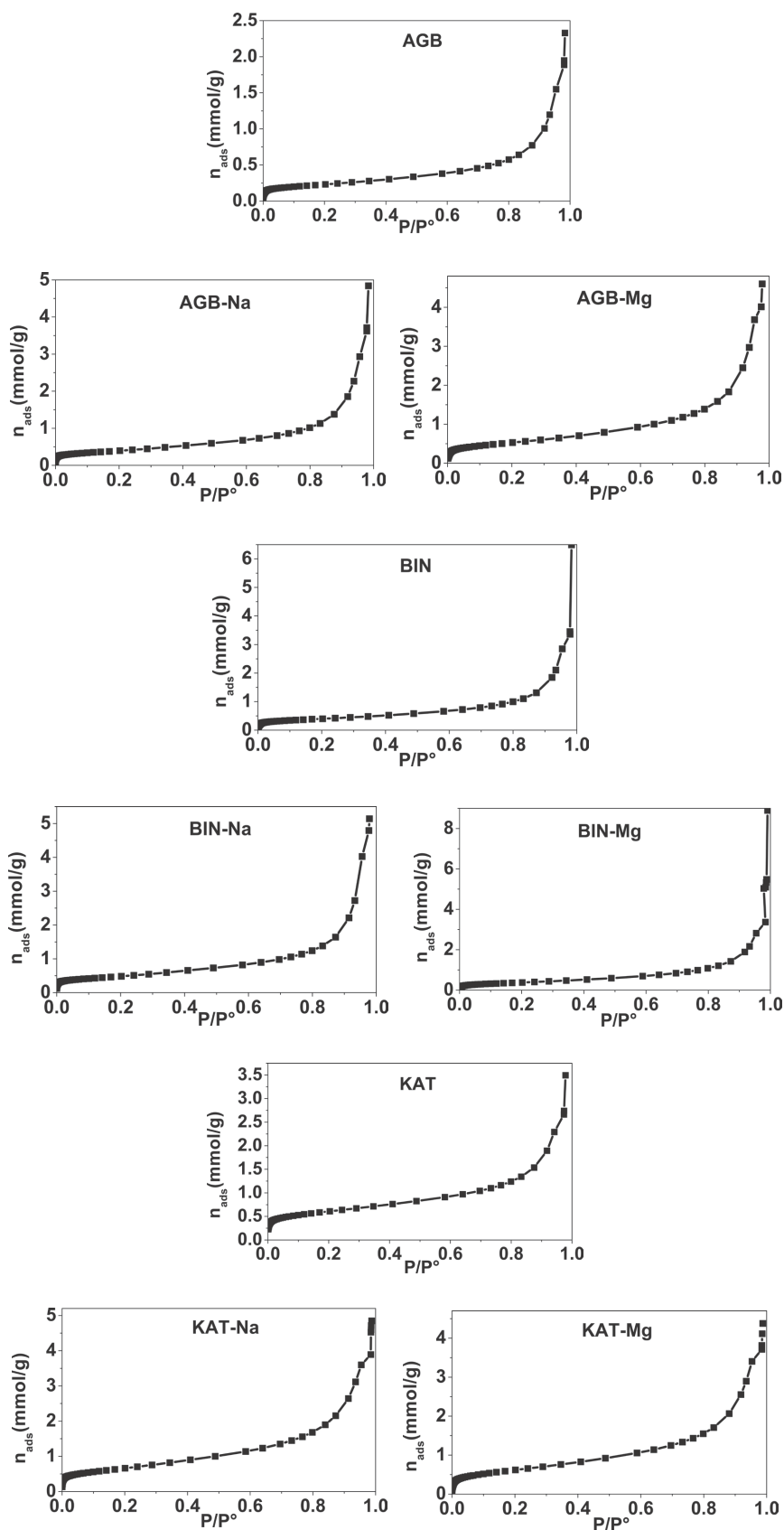


Figure 10. Nitrogen adsorption isotherms at 77 K on AGB, BIN and KAT samples.

studied the removal of Pb, Cd and Ni from a kaolinitic and montmorillonitic clay. For specific surface values varying from 3.1 to 18.7 m²/g for kaolinitic clays and from 3.8 to 19.8 m²/g for montmorillonitic clays, they obtained maximum adsorption capacities varying from 6.8 to 11.5 mg/g for kaolinites and from 21.1 to 31.1 mg/g for montmorillonites. As the specific surface values measured in the present study are much higher, we can assume that the clays studied will have interesting adsorption capacities.

3.7. Cationic Exchange Capacity (CEC) of Clays

Table 5 below shows the CEC values obtained by determination of remaining cobaltihexamine ions (CEC) and by displacement of the cations responsible for surface charge compensation (CEC_{chemistry}).

The CEC values of BIN and AGB clays are 6.18 and 6.67 meq/100g respectively. That of Katiola clay (KAT) is 35.47 meq/100g. The CEC determined by the cobaltihexamine method and that determined by the sum of major cations determined by ICP-AES (chemical CEC) are slightly different for BIN and AGB. Most of the cationic compensation is provided by aluminium for BIN (CEC_{Al} = 4.36 meq/100g). Whereas for the AGB clay, the cationic compensation is essentially assured by Ca, Mg and Na (CEC_{Ca} = 1.17 meq/100g; CEC_{Mg} = 1.93 meq/100g and CEC_{Na} = 1.43 meq/100g). Concerning the Katiola clay, the CEC chemistry and cobaltihexamine are practically identical. Ca and Mg are essentially the cations responsible for the charge compensation of the KAT clay (CEC_{Ca} = 8.18 meq/100g; CEC_{Mg} = 25.88 meq/100g).

The CEC of BIN and AGB are well within the range of cation exchange capacity values of a kaolinite (3 to 15 meq/100g). This confirms that AGB and BIN are mostly kaolinite. The discrepancy between the cobaltihexamine and chemical CEC values for BIN and AGB clays could be explained by the presence of other ions not measured but contributing to the cationic compensation [53]. The CEC value of the KAT clay is significantly lower than that of pure smectite (CEC = 80 to 120 meq/100g). This result confirms that the Katiola sample does not consist solely of smectite. Indeed the Katiola clay is a mixture of 3 clay minerals: kaolinite, illite and smectite. This observation is corroborated by Gourouza *et al.* [54] who qualified a Niger clay as mixed (semi-kaolinitic and semi-smectitic). This measurement indicates that of these three clays, KAT has the highest exchange capacity.

Table 5. Cation exchange capacity (CEC) expressed in meq/100g.

Samples	Al	Ca	Mg	Mn	Na	K	CEC _{chemistry}	CEC
BIN	4.36	0.10	0.11	0.02	0.45	0.06	5.10 ± 0.08	6.18 ± 0.01
AGB	0.01	1.17	1.93	0.04	1.43	0.25	4.83 ± 0.07	6.67 ± 0.02
KAT	0.01	8.18	25.88	0.67	0.29	0.04	35.07 ± 0.24	35.47 ± 0.03

4. Conclusions

The objective of this work was to study the physicochemical properties of 3 clays collected in Agboville (AGB), Bingerville (BIN) and Katiola (KAT) with the intention of using them later as adsorbents in water treatment. To achieve this goal, the first step was to determine their chemical and mineralogical compositions. Then, the reactions and thermal transformations were studied. Finally, the specific surface area and the cation exchange capacity were measured. The chemical composition, determined by ICP-AES and ICP-MS techniques, showed that the main oxides are SiO_2 , Al_2O_3 and Fe_2O_3 . Iron is present in significant quantities in the BIN and KAT samples. The K_2O content (0.41% to 1.64%) indicates the presence of illite in these clays. The relatively high CaO content (1.41%) in the KAT clay suggests the presence of smectite in the clay. In addition, the content of harmful elements (Hg, Pb, Cd and As) in the samples is below their toxicity threshold according to the AFNOR NF U 41,044 and WHO standards. Mineralogical characterisation by X-ray diffraction (XRD) confirmed the assumptions made during the chemical analysis. The study shows that these clays consist of kaolinite and illite. In addition to these clay minerals, the KAT sample consists of smectite. These clay minerals are associated with quartz and goethite (15.71% and 16.86% respectively in BIN and KAT). Thermal analysis and scanning electron microscopy confirmed that the clays are predominantly kaolinite. The specific surface area and cation exchange capacity values clearly indicate that AGB and BIN are kaolinitic clays. Whereas the sample KAT is a mixed clay, KAT shows the best values for specific surface area and cation exchange capacity.

All the properties determined suggest that the clays studied have interesting adsorption capacities, in particular the Katiola clay. These clays could be used in the depollution of contaminated waters, the experimental study being the subject of our future work. Moreover, the properties of these clays could be intensified by the intercalation between their sheets, of big iron polycations (bridged clay) in order to improve their adsorption capacity.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

References

- [1] Aranguren, M.M.S. (2008) Contamination en métaux lourds des eaux de surface et des sédiments du Valde Milluni (Andes Boliviennes) par des déchets miniers. Approches géochimique, minéralogique et hydrochimique. Thèse de Doctorat, Université Paul Sabatier-Toulouse, Toulouse, 381 p.
- [2] Kinimo, K.C., Yao, K.M., Marcotte, S., Kouassi, N.L.B. and Trokourey, A. (2018) Distribution Trends and Ecological Risks of Arsenic and Trace Metals in Wetland Sediments around Gold Mining Activities in Central-Southern and Southeastern Côte d'Ivoire. *Journal of Geochemical Exploration*, **190**, 265-280.

- <https://doi.org/10.1016/j.gexplo.2018.03.013>
- [3] Yapi, Y.H.A., Dongui, B.K., Trokourey, A., Barima, Y.S.S., Essis, Y. and Atheba, P. (2014) Evaluation de la Pollution Métallique des Eaux Souterraines et de Surface dans un Environnement Minier Aurifère à Hiré (Côte d'Ivoire). *International Journal of Biological and Chemical Sciences*, **8**, 1281-1289.
<https://doi.org/10.4314/ijbcs.v8i3.41>
- [4] Moonis, A.K., Rifaqat, A.K.R. and Mohammad, A. (2008) Heavy Metal Pollution and Its Control through Non Conventional Adsorbents (1998-2007): A Review. *Journal of International Environmental Application and Science*, **3**, 101-141.
- [5] Ouedraogo, R.D., Bakouan, C., Sorgho, B., Guel, B. and Bonou, L.D. (2019) Caractérisation d'une Latérite Naturelle du Burkina Faso en Vue de l'Élimination de L'arsenic (III) et L'arsenic (V) dans les Eaux Souterraines. *International Journal of Biological and Chemical Sciences*, **13**, 2959-2977.
<https://doi.org/10.4314/ijbcs.v13i6.41>
- [6] Shukla, A., Zhang, Y., Dubey, P., Margrave, J.L. and Shukla, S.S. (2002) The Role of Sawdust in the Removal of Unwanted Materials from Water. *Journal of Hazardous Materials*, **95**, 137-152. [https://doi.org/10.1016/S0304-3894\(02\)00089-4](https://doi.org/10.1016/S0304-3894(02)00089-4)
- [7] Mimanne, G., Benhabib, K., Benghalem, A. and Taleb, S. (2014) Etude de l'Adsorption des Métaux Lourds (Pb et Cd) en Solution Aqueuse sur Charbon Actif et Montmorillonite Sodée de L'ouest Algérien. *Journal of Materials and Environmental Science*, **5**, 1298-1307.
- [8] Adie, D.B., Olarinoye, N.O., Oke, I.A., Ismail, A., Lukman, S. and Otun, J.A. (2010) Removal of Lead Ions from Aqueous Solutions Using Powdered Corn Cobs. *The Canadian Journal of Chemical Engineering*, **88**, 241-255.
<https://doi.org/10.1002/cjce.20264>
- [9] Mohan, D. and Singh, K.P. (2002) Single- and Multi-Component Adsorption of Cadmium and Zinc Using Activated Carbon Derived from Bagasse an Agricultural Waste. *Water Research*, **36**, 2304-2318.
[https://doi.org/10.1016/S0043-1354\(01\)00447-X](https://doi.org/10.1016/S0043-1354(01)00447-X)
- [10] Chakravarty, P., Sarma, N.S. and Sarma, H.P. (2010) Biosorption of Cadmium (II) from Aqueous Solution Using Heartwood Powder of Areca Catechu. *Chemical Engineering Journal*, **162**, 949-955. <https://doi.org/10.1016/j.cej.2010.06.048>
- [11] Dos Anjos, V.E., Rohwedder, J.R., Cadore, S., Abate, G. and Grassi, M.T. (2014) Montmorillonite and Vermiculite as Solid Phases for the Preconcentration of Trace Elements in Natural Waters: Adsorption and Desorption Studies of As, Ba, Cu, Cd, Co, Cr, Mn, Ni, Pb, Sr, V, and Zn. *Applied Clay Science*, **99**, 289-296.
<https://doi.org/10.1016/j.clay.2014.07.013>
- [12] Andji, J.Y.Y., Sei, J., Touré, A.A., Kra, G. and Njopwouo, D. (2001) Caractérisation Minéralogique de Quelques Echantillons d'Argiles du Site de Gounioubé (Côte d'Ivoire). *Journal de la Société Ouest-Africaine de Chimie*, **11**, 143-166.
- [13] Ouakouak, A. and Youcef, L. (2016) Adsorption of Cu²⁺ Ions on Powder Activated Carbon and a Sodique Bentonite. *Larhyss Journal*, **27**, 39-61.
- [14] Konan, K.L., Sei, J., Soro, N.S., Oyetola, S., Gaillard, J.M., Bonnet, J.P. and Kra, G. (2006) Caractérisation de Matériaux Argileux du Site d'Azaguié-Blida (Anyama, Côte d'Ivoire) et Détermination des Propriétés Mécaniques de Produits Céramiques. *Journal de la Société Ouest-Africaine de Chimie*, **21**, 35-43.
- [15] Gueu, S. (2019) Élimination des Acides Humiques Présents dans l'Eau par Adsorption et/ou Photocatalyse. Thèse de Doctorat, Institut Nationale Polytechnique Houphouët-Boigny (INPHB), Yamoussoukro, 121 p.

- [16] Robert, M. and Tessier, D. (1974) Méthodes de Préparation des Argiles des Sols pour des Etudes Minéralogiques. *Annales Agronomiques*, **25**, 859-882.
- [17] Morel, R. (1958) Observations sur la Capacité d'Echange et les Phénomènes d'Echange dans les Argiles. *Bulletin du Groupe Français des Argiles*, **10**, 3-8.
<https://doi.org/10.3406/argil.1958.942>
- [18] Mantin, I. and Glaeser, R. (1960) Fixation des Ions Cobalthexammines par les Montmorillonites Acides. *Bulletin du Groupe Français des Argiles*, **12**, 83-88.
<https://doi.org/10.3406/argil.1960.974>
- [19] Remy, J.C. and Orsini, L. (1976) Utilisation du Chlorure de Cobalthexamine pour la Détermination Simultanée de la Capacité d'Echange et des Bases Echangeables des Sols. *Bulletin de l'AFES Science du Sol*, **4**, 269-275.
- [20] Aran, D., Maul, A. and Masfaraud, J.F. (2008) A Spectrophotometric Measurement of Soil Cation Exchange Capacity Based on Cobalthexamine Chloride Absorbance. *Comptes Rendus Chimie*, **340**, 865-871. <https://doi.org/10.1016/j.crte.2008.07.015>
- [21] Traoré, K., Blanchart, P., Jernot, J.P. and Gomina, M. (2007) Caractérisation Physicochimique et Mécanique de Matériaux Céramiques Obtenus à Partir d'Une Argile Kaolinitique du Burkina Faso. *Comptes Rendus Chimie*, **10**, 511-517.
<https://doi.org/10.1016/j.crci.2006.12.009>
- [22] Baize, D., Deslais, W. and Saby, N. (2007) Teneurs en Huit Eléments en Traces (Cd, Cr, Cu, Hg, Ni, Pb, Se, Zn) dans les Sols Agricoles en France. Résultats d'une collecte de données à l'échelon national. Rapport final simplifié, 49 p.
- [23] Matech, F., Zaakour, F., Moustahfer, K. and Chems, Z. (2014) Concentrations en Eléments Traces Métalliques dans les Sols Irrigués par les Eaux Usées Versées dans l'Oued Merzeg (Casablanca-Maroc). *European Scientific Journal*, **10**, 121-138.
- [24] Mache, J.R., Signing, P., Njoya, A., Kunyukubundo, F., Mbey, J.A., Njopwouo, D. and Fagel, N. (2013) Smectite Clay from the Sabga Deposit (Cameroon): Mineralogical and Physicochemical Properties. *Clay Minerals*, **48**, 499-512.
<https://doi.org/10.1180/claymin.2013.048.3.07>
- [25] Njopwouo, D. (1984) Minéralogie et Physico-Chimie des Argiles de Bomkoul et Balengou (Cameroun). Utilisation dans la Polymérisation du Styrène et dans le Renforcement du Caoutchouc Naturel. Thèse de Doctorat, Université de Yaoundé, Yaoundé, 300 p.
- [26] Gu, S., Kang, X., Wang, L., Lichtfouse, E. and Wang, C. (2019) Clay Mineral Adsorbents for Heavy Metal Removal from Wastewater: A Review. *Environmental Chemistry Letters*, **17**, 629-654. <https://doi.org/10.1007/s10311-018-0813-9>
- [27] Es-sahbany, H., Hsissou, R., El Hachimi, M.L., Allaoui, M., Nkhili, S. and Elyoubi, M.S. (2021) Investigation of the Adsorption of Heavy Metals (Cu, Co, Ni And Pb) in Treatment Synthetic Wastewater Using Natural Clay as a Potential Adsorbent (Sale-Morocco). *Materials Today: Proceedings*, **45**, 7290-7298.
<https://doi.org/10.1016/j.matpr.2020.12.1100>
- [28] Mnasri-Ghnimi, S. and Frini-Srasra, N. (2019) Removal of Heavy Metals from Aqueous Solutions by Adsorption Using Single and Mixed Pillared Clays. *Applied Clay Science*, **179**, Article ID: 105151. <https://doi.org/10.1016/j.clay.2019.105151>
- [29] Ma, J., Khan, M.A., Xia, M., Fu, C., Zhu, S., Chu, Y., Wu, L. and Wang, F. (2019) Effective Adsorption of Heavy Metal Ions by Sodium Lignosulfonate Reformed Montmorillonite. *International Journal of Biological Macromolecules*, **138**, 188-197.
<https://doi.org/10.1016/j.ijbiomac.2019.07.075>
- [30] Borggaard, O.K. (1982) The Influence of Iron Oxides on the Surface Area of Soil.

- Journal of Soil Science*, **33**, 443-449.
<https://doi.org/10.1111/j.1365-2389.1982.tb01779.x>
- [31] Borggaard, O.K. (1983) Effect of Surface Area and Mineralogy of Iron Oxides on Their Surface Charge and Anion-Adsorption Properties. *Clays and Clay Minerals*, **31**, 230-232. <https://doi.org/10.1346/CCMN.1983.0310309>
- [32] Borggaard, O.K. (1983) The Influence of Iron Oxides on Phosphate Adsorption by Soil. *Journal of Soil Science*, **34**, 333-341.
<https://doi.org/10.1111/j.1365-2389.1983.tb01039.x>
- [33] Sei, J., Jumas, J.C., Quiquampoix, H. and Staunton, S. (2002) Role of Iron Oxides in the Phosphate Adsorption Properties of Kaolinites from the Ivory Coast. *Clays and Clay Minerals*, **50**, 219-224. <https://doi.org/10.1346/000986002760832810>
- [34] Caillère, S., Hénin, S. and Rautureau, M. (1982). *Minéralogie des Argiles*. 2^e Édition, Masson, Paris.
- [35] Mestdagh, M.M., Vielvoye, L. and Herbillon, A.J. (1980) Iron in Kaolinite: II. The Relationship between Kaolinite Crystallinity and Iron Content. *Clay Minerals*, **15**, 1-13. <https://doi.org/10.1180/claymin.1980.015.1.01>
- [36] Herbillon, A.J., Mestdagh, M.M., Vielvoye, L. and Derouane, E.G. (1976) Iron in Kaolinite with Special Reference to Kaolinite from Tropical Soils. *Clay Minerals*, **11**, 201-220. <https://doi.org/10.1180/claymin.1976.011.3.03>
- [37] Tchoubar, B., Plançon, A., Clinard, C. and Sow, C. (1982) Caractéristiques Structurales des Kaolinites Désordonnées. *Bulletin de Minéralogie*, **105**, 477-491.
<https://doi.org/10.3406/bulmi.1982.7569>
- [38] Mestdagh, M.M., Herbillon, A.J., Rodrigue, L. and Rouxhet, G.P. (1982) Evaluation du Rôle du Fer Structural sur la Cristallinité des Kaolinites. *Bulletin de Minéralogie*, **105**, 457-466. <https://doi.org/10.3406/bulmi.1982.7567>
- [39] Konan, L.K., Soro, J., Andji, J.Y.Y., Oyetola, S. and Kra, G. (2010) Etude Comparative de la Déshydroxylation/Amorphisation dans Deux Kaolins de Cristallinité Différente. *Journal de la Société Oust-Africaine de Chimie*, **30**, 29-39.
- [40] Smykatz-Kloss, W. (1974) *Differential Thermal Analysis: Application and Result in Mineralogy*. Springer Verlag, Berlin/New York, 185 p.
<https://doi.org/10.1007/978-3-642-65951-5>
- [41] Chen, C.Y., Lan, G.S. and Tuan, W.H. (2000) Microstructural Evolution of Mullite During the Sintering of Kaolin Powder Compacts. *Ceramics International*, **26**, 715-720. [https://doi.org/10.1016/S0272-8842\(00\)00009-2](https://doi.org/10.1016/S0272-8842(00)00009-2)
- [42] Pialy, P. (2009) Étude de Quelques Matériaux Argileux du Site de Lembo (Cameroun): Minéralogie, Comportement au Frittage et Analyse des Propriétés d'Elasticité. Thèse de Doctorat, Université de Limoges, Limoges, 130 p.
- [43] Gridi-Bennadji, F. (2007) Matériaux de Mullite à Microstructure Organisée Composés D'assemblages Muscovite-Kaolinite. Thèse de Doctorat, Université de Limoges, Limoges, 182 p.
- [44] Maitra, S., Roy, S.K. and Dwivedi, A. (2005) Role of Some Additives on the Formation of Mullite. *Industrial Ceramics*, **25**, 31-36.
- [45] Viswabaskaran, V. and Gnanam, F.D. (2003) Effect of MgO on Mullitization Behavior of Clays. *Journal of Materials Science Letters*, **22**, 663-668.
<https://doi.org/10.1023/A:1023658726104>
- [46] Da Paz, S.P.A., Angelica, R.S. and Neves, R.D.F. (2012) Mg-Bentonite in the Parnaíba Paleozoic Basin, Northern Brazil. *Clays and Clay Minerals*, **60**, 265-277.
<https://doi.org/10.1346/CCMN.2012.0600304>

- [47] Brunauer, S., Emmett, P.H. and Teller, E. (1938) Adsorption of Gases in Multimolecular Layers. *Journal of the American Chemical Society*, **60**, 309-319. <https://doi.org/10.1021/ja01269a023>
- [48] Rouquerol, J., Llewellyn, P. and Rouquerol, F. (2007) Is the BET Equation Applicable to Microporous Adsorbents? *Studies in Surface Science and Catalysis*, **160**, 49-56. [https://doi.org/10.1016/S0167-2991\(07\)80008-5](https://doi.org/10.1016/S0167-2991(07)80008-5)
- [49] Diatta, M.T. (2016) Matières Premières Argileuses du Sénégal : Caractéristiques et Applications aux Produits Céramiques de Grande Diffusion. Thèse de Doctorat, Université Assane Seck de Ziguinchor/Université de Limoges, Ziguinchor/Limoges, 158 p.
- [50] Eusterhues, K., Rumpel, C. and Kogel-Knabner, I. (2005) Organo-Mineral Associations in Sandy Acid Forest Soils: Importance of Specific Surface Area, Iron Oxides and Micropores. *European Journal of Soil Science*, **56**, 753-763. <https://doi.org/10.1111/j.1365-2389.2005.00710.x>
- [51] Hernot, F. (2016) L'argile, son Utilisation à l'Officine. Thèse de Doctorat, Université d'Angers, Angers, 127 p.
- [52] Gupta, S.S. and Bhattacharyya, K.G. (2008) Immobilization of Pb(II), Cd(II) and Ni(II) Ions on Kaolinite and Montmorillonite Surfaces from Aqueous Medium. *Journal of Environmental Management*, **87**, 46-58. <https://doi.org/10.1016/j.jenvman.2007.01.048>
- [53] Andji, Y.Y.J. (2006) Caractérisation, Typologie et Propriétés d'Usage des Argiles du Site de Gounioubé (Côte d'Ivoire). Thèse de Doctorat, Université Félix Houphouët-Boigny (UFHB), Abidjan, 234 p.
- [54] Gourouza, M., Gourouza, A., Natatou, I. and Boos, A. (2013) Caractérisation d'Une Argile Mixte du Niger. *Revue CAMES Sciences des Structures et de la Matière*, **1**, 29-39.