

Physico-Chemical Characterization of Two Dabou Clays with a View to Use Them in the Treatment of Dyeing Wastewater

Wilfried Aristide Atsé¹, Marc Marie-Maurice Mélédege Essi¹, Bi Irié Hervé Gouré Doubi², Mahamadou Kamagaté³, Aké Pierre Aké¹, Alfred Niamien Kouamé¹

¹Laboratory of Constitution and Reaction of Matter, Félix Houphouët Boigny University, Abidjan, Côte d'Ivoire

²Biological Sciences Training and Research Unit, Péléforo Gon Coulibaly University, Korhogo, Côte d'Ivoire

³Central Analysis Laboratory, University of Man, Man, Côte d'Ivoire

Email: wilfriedaatse@gmail.com

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Abstract

This work falls within the general framework of the valorization of the clays of Ivory Coast in order to propose innovative solutions in the resolution of certain problems related to development such as the depollution of water. Its main objective is therefore to study the physico-chemical properties of two Dabou clays with a view to using them in chemical processes for the treatment of dyeing wastewater. The results of the chemical analysis and the ray diffraction showed that the DAB 1 and DAB 2 samples are clays of the kaolinitic type consisting mainly of kaolinite with 51.17% for DAB 1 against 65.81% for DAB 2 and quartz with respectively 41.76% and 25.8% for DAB 1 and DAB 2. They also contain relatively large amounts of goethite with 9.96% for DAB 1 and 12.8% for DAB 2. The specific surfaces measured in both samples are greater than 25 m²/g. All the results of the physico-chemical characterization, in particular the presence in significant quantity of clay minerals, the presence of iron compounds and the large specific surface area of both samples, allow the conclusion that they can be used in adsorption studies and in the heterogeneous Fenton process for water treatment.

Keywords

Clays, Physico-Chemicals, Water Treatment

1. Introduction

Water is indispensable in all human daily activities. Water is also an effective means of transporting and spreading pollution, as it is involved in several activi-

ties such as the industrial ones (paper, food processing, textiles). As drinking water resources are affected and the amount of wastewater is increasingly important, this phenomenon is the cause of most environmental concerns [1]. The European Directive 2013/39 of 12 August 2013 begins with this preamble: “Chemical pollution of surface water poses a threat to the aquatic environment, with effects such as acute and chronic toxicity in aquatic organisms, accumulation of pollutants in the ecosystem and loss of habitats and biodiversity, and also poses a threat to human health. As a matter of priority, causes of pollution should be identified and emissions of pollutants should be dealt with at source, in the most economically and environmentally effective manner.” It then agrees that to reduce treatment costs and improve water quality, “the development of innovative water treatment technologies could be stimulated”.

Advanced oxidation processes (AOP) are a wide category of treatment processes based on the production of powerful oxidants, mainly hydroxyl radicals. The Fenton process is one of the known POAs. The use of the Fenton process in a homogeneous phase has several disadvantages, in particular its relatively high cost of treatment linked to the need for specific reaction conditions (pH, temperature) and to the production of ferrous sludge. To overcome these drawbacks, the use of solid catalysts is an attractive solution [2]. Heterogeneous Fenton catalysts can be classified into two categories: synthetic and natural catalysts. Synthetic catalysts are generally prepared by inserting iron into a solid material called a support. The choice of support type for heterogeneous Fenton catalysts is of paramount importance as the ability of the iron ion to react with hydrogen peroxide is affected by the size and structure of the support [3]. Different matrices are used as supports. Clays [4] [5] [6], zeolite [7] [8] [9], silica gel [10] and activated carbon are the most widely used supports in the literature. There is great interest in the use of activated carbons as a heterogeneous Fenton catalyst support. Research on low cost, high surface area and environmentally friendly activated carbon has increased to establish the benefits of its use in wastewater treatment technologies. Although the cost of producing activated carbon can be reduced, iron impregnation methods are expensive and costly. Natural catalysts, contrary to synthetic ones, do not require the iron insertion step before being used in the heterogeneous Fenton process. Laterite is an example of natural catalysts. It can be used directly as a catalyst in the Fenton process because it naturally contains iron. Unlike activated carbon, the existing literature on the use of laterite as a heterogeneous Fenton catalyst is limited [11]. The most widely used adsorbent for water effluents treatment is activated carbon. This adsorbent is an imported product whose cost increases that of effluent treatment. The use of clays as adsorbents is of interest in the treatment of industrial wastewater. Clays have a wide variety of uses due to their physico-chemical properties [12] [13] [14]. In addition, studies carried out from 1963 to 1969 by La Société pour le Développement Minier (SODEMI) showed that Côte d’Ivoire is full of numerous clay deposits [15]. In order to promote the use of these local clays in water treatment, two clay samples from Dabou, a city located in the

South of Côte d'Ivoire, namely in the region of the great bridges, were used in this study. These clays are scientifically little known. In effect, works on the use of youhouill clay (Dabou) as a heterogeneous Fenton catalyst is almost non-existent in the literature. The objective of this study is therefore to carry out a physico-chemical and mineralogical characterization of this clay in order to conclude on the possibility of using it in the depollution and treatment of industrial wastewater.

2. Materials and Experimental Techniques

2.1. Clay Samples

The clay materials used in this study come from the region of Dabou located in the south of Côte d'Ivoire. The two samples referenced DAB 1 and DAB 2 were taken from the same well at a depth of 4 m and 4.1 m respectively. The sampling site is located at coordinates 05°21'29"N and 04°3'18"W. The samples were first dried and then ground and sieved at 100 µm before carrying out the various physico-chemical characterization tests.

2.2. Experimental Techniques

The elementary chemical analysis of the clay samples was carried out by plasma emission spectrometry ICP-AES (Inductively Coupled Plasma-Atomic Emission Spectrometry) using an ANTON Paar type spectrometer.

The analysis of the samples by X-ray diffraction (XRD) was carried out using a multifunction diffractometer GBC-EMMA. It made it possible to determine the mineral phases present in the two clay samples. The identification of the mineral phases was made by comparing the diffractograms obtained with the database of the ICDD (International Center for Diffraction Data) using the EVA software (Brukers AXS).

The results of the X-ray diffraction and chemical analysis were used to evaluate the semi-quantitative mineralogical composition using the works by [16] [17] which is the following **Equation (1)**:

$$T(a) = \sum_{i=1}^n M_i P_i(a) \quad (1)$$

With: $T(a)$: content (%) of element a in the material;

M_i : content (%) of mineral i in the material;

$P_i(a)$: proportion of element a in mineral i .

The thermal behavior of the clay samples was studied by Differential Thermal Analysis (DTA) coupled with Thermogravimetric Analysis (TGA). The thermograms were recorded from room temperature to 1200°C. with a temperature rise of 5°C/min using a NETZSCHSTA type device.

The Fourier transform spectrometer Perkin Elmer Spectrum 1000 was used to record the infrared spectra of the two samples.

The morphology of the samples was observed using a Scanning Electron Microscope (SEM) of the HIROX SH 4000 M type with a Bruker detector, XFlash 6/30.

The specific surface was determined by the BET method. The measurements were carried out after degassing the samples at 200°C. for 16 h, with the Micromeritics TriStar II apparatus.

The density of the powders was measured using a micromeritics AccuPyc II 1340 helium pycnometer.

3. Results and Discussion

Table 1 presents the results of the chemical analysis of the two clay samples.

The results of the chemical analysis show that the two samples contain significant amounts of silica SiO_2 with 67.54% and 58.21% respectively for DAB 1 and DAB 2. They also contain alumina Al_2O_3 with 21.87% for DAB 1 and 28.11% for DAB 2. The high silica and alumina contents show that these two samples are aluminosilicates [18]. DAB 1 is richer in silica than DAB 2. However, it contains less alumina Al_2O_3 , iron oxide Fe_2O_3 , potassium oxide K_2O and titanium oxide TiO_2 than DAB 2. The lack of calcium oxide CaO and magnesium oxide MgO suggests that the samples contain very little or no compounds rich in calcium (calcite, dolomite, smectites, etc.) and magnesium (chlorite). Besides these two major oxides, they contain a relatively large amount of iron oxide, which suggests the presence of ferric phases. In the literature [19] [20]. Iron is found in soils in the form of oxide and oxy-hydroxides, the most important of which are Hematite ($\alpha\text{-Fe}_2\text{O}_3$), Maghemite ($\gamma\text{-Fe}_2\text{O}_3$), Goethite ($\alpha\text{-FeOOH}$), Lepidocrocite ($\gamma\text{-FeOOH}$) and Ferrihydrite ($\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ with $0.5 < x < 2.5$). DAB 2, which contains approximately 11.55% of Fe_2O_3 , can be qualified as lateritic clay. Indeed, according to [21], a lateritic clay content in Fe_2O_3 is between 10% and 50%. In addition, the high iron content in these samples (8.95% in DAB 1% and 11.55% in DAB 2) could, through the Fenton reaction, induce the production of hydroxyl radicals [22]. Furthermore, the oxides K_2O , Na_2O and TiO_2 are present in small quantities. The values of the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios are 2.07 and 3.09 respectively for DAB 1 and DAB 2. These ratios are high compared to those generally encountered for kaolinites which are 1.18 [23]. These high ratios suggest the presence of free silica and clay minerals of the 2:1 type [13]. The low TiO_2 and K_2O contents could suggest the presence of small quantities of compounds rich in titanium (anatase and rutile) and potassium (illite, muscovite, etc.) in the samples. **Figure 1** presents the X-ray diffractograms of the samples studied.

The diffractograms reveal that the two samples have the same mineralogical composition because the characteristic lines of the mineral phases highlighted are perfectly superimposed. These are kaolinite (12.48°; 35.24°; 55.5°), Illite

Table 1. Chemical composition (wt%).

Samples	SiO_2	Al_2O_3	Fe_2O_3	CaO	K_2O	MgO	Na_2O	TiO_2	$\text{SiO}_2/\text{Al}_2\text{O}_3$
DAB 1	67.54	21.87	8.95	-	0.51	-	0.08	1.05	3.09
DAB 2	58.21	28.11	11.55	-	0.65	-	0.09	1.38	2.07

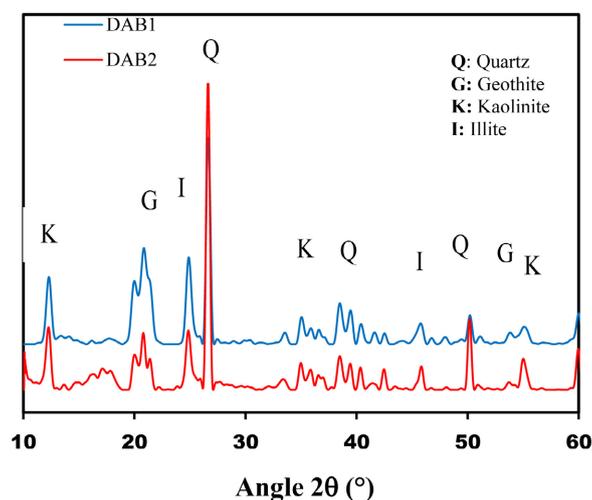


Figure 1. X-ray diffractograms of clay samples.

(25.16° and 46.14°), quartz (26.98°; 39.36°; 50.18°) and goethite (21.06° and 54.4°).

The results of the chemical analysis combined with those of the X-ray diffraction made it possible to determine the semi-quantitative mineralogical composition of the two samples. The results obtained are presented in **Table 2**.

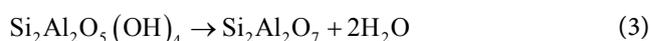
The results of the mineralogical composition reveal that the two samples consist mainly of kaolinite (51.17% and 65.81%). DAB 2 is richer in kaolinite (65.81%), illite (5.51%) and goethite (12.80%) than DAB 1. However, it contains a higher quartz content. The presence of goethite in relatively large quantities could make both samples particularly adsorptive. Indeed, the work by [19] [24] using clay materials from Côte d'Ivoire to remove phosphates showed that the content in goethite improved the adsorption capacity of the clay samples used.

The ATD/ATG thermograms of the two clay samples are shown in **Figure 2**. On these thermograms, several thermal transformations were observed during heating.

- The first endothermic peak observed around 70°C associated with a loss of mass of about 1% on the thermograms of the two samples is related to the departure of hygroscopic water. This phenomenon does not lead to a modification of the crystal structure of the material [19].
- The second endothermic peak of low amplitude between 300°C and 330°C, with a mass loss of about 1.5%, is generally the consequence of the dehydroxylation of goethite into hematite according to **Equation (2)** [25].



- A third endothermic peak of high intensity around 510°C, accompanied by a loss of mass of around 8% is observed on the two thermograms. This loss would be due to the dehydroxylation of kaolinite and illite according to **Equation (3)**.



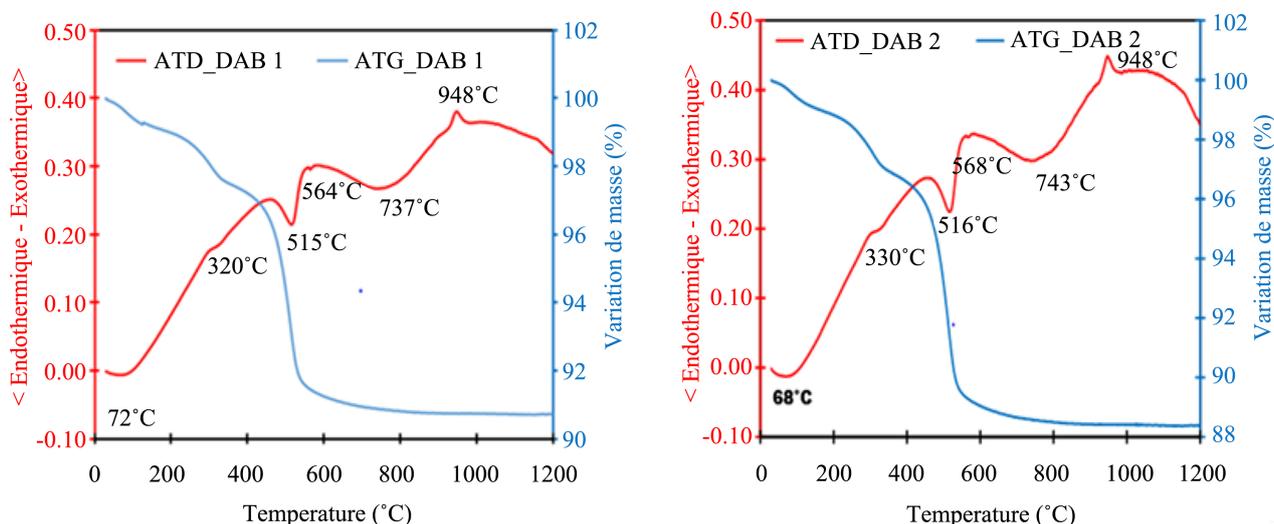
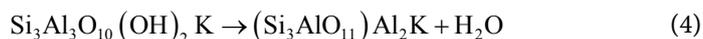


Figure 2. Differential thermal and thermogravimetric analyses of samples.

Table 2. Semi-quantitative mineralogical compositions of DAB 1 and DAB 2.

Samples	Quartz	Kaolinite	Illite	Goethite	Total
DAB 1	41.76	51.17	4.32	9.96	107.21
DAB 2	25.08	65.81	5.51	12.80	109.20

- We have the allotropic transformation of quartz round 565°C ($\alpha \rightarrow \beta$).
- Between 650°C and 850°C , the thermograms show a spread endothermic phenomenon which would correspond to the dehydroxylation of illite. This reaction takes place according to **Equation (4)** [26].



- Finally, the exothermic peak without mass loss at 948°C is linked to the structural reorganization of metakaolinite into spinel which is a more stable compound and into amorphous silica. This reaction takes place according to the following **Equation (5)**:



Figure 3 shows the combined infrared spectra of the two clay samples recorded in the $4000 - 400\text{ cm}^{-1}$ frequency range. The spectra show broadly the same vibrational bands and are identical to those generally observed in clay materials.

On the spectrum of the two samples, the bands observed at 3700 , 3650 and 3620 cm^{-1} correspond to the vibration bands of the OH groups of kaolinite [27] [28]. The bands at 3650 and 3700 cm^{-1} correspond to the stretching vibrations of the OH hydroxyls located in the interlayer space. These are the outer hydroxyls [29]. The band at 3650 cm^{-1} would be due to the coupling of two external hydroxyls in phase opposition and the band at 3700 cm^{-1} would be attributed to an external hydroxyl group forming an angle of 76° with the crystallographic axis

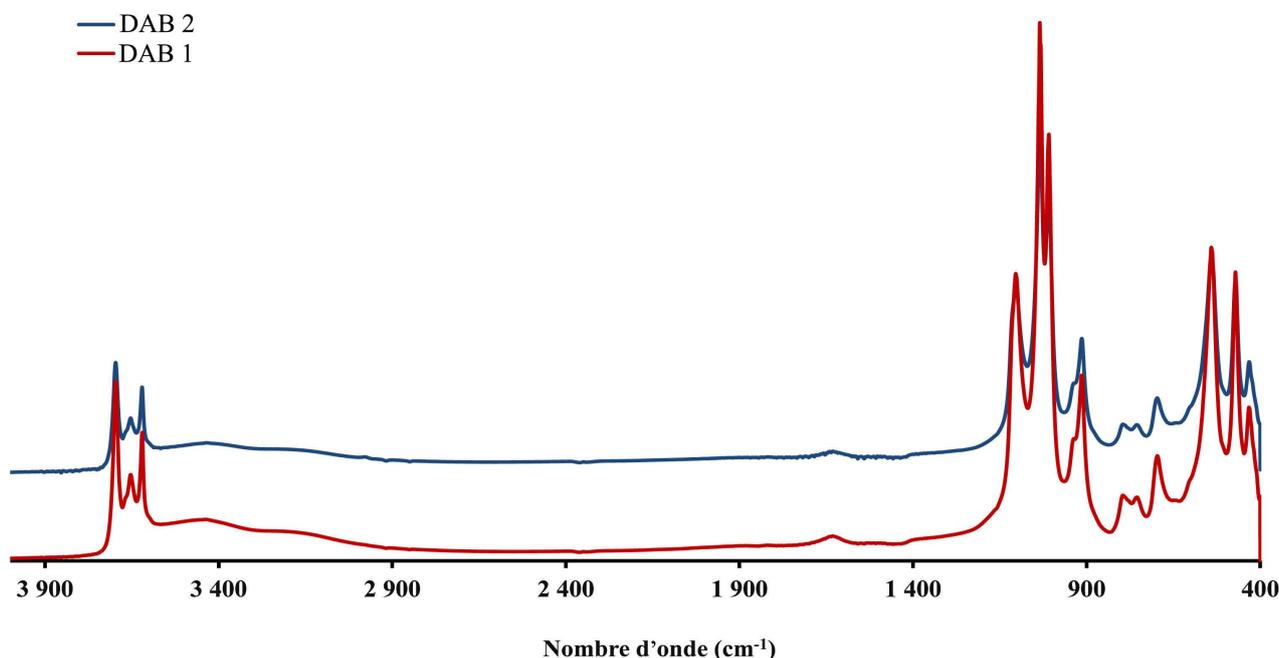


Figure 3. Infrared spectra of DAB 1 and DAB 2 samples.

according to the work by [30]. The intensity of the band at 3700 cm^{-1} , which is large compared to that of the band at 3620 cm^{-1} , indicates that both samples contain kaolinite. Indeed, according to [28] for a kaolinite, the intensity of the band at 3700 cm^{-1} (external OH) > the intensity of the band at 3620 cm^{-1} (internal OH). The band at 3620 cm^{-1} corresponds to the vibrations of the internal hydroxyls located between the Si_2O_5 tetrahedral interlayer and the octahedral layer [13] [31]. The same band is also characteristic of the OH⁻ bond of the illitic phase at 3620 cm^{-1} . The medium intensity band at 914 cm^{-1} and the weak band at 1610 cm^{-1} are attributed respectively to the deformation vibration of the OH-Al groups of the dioctahedral 1:1 and 2:1 clay [28] and of the H-OH bonds of adsorbed water [32] [33] [34] [35]. Also, the average intensity band at 914 cm^{-1} corresponds to the band related to the Al-OH deformation vibrations of kaolinite and also to the Fe-OH bond of goethite [13] [36] [37] [38]. The intense bands at 1010 , 1030 and 1100 cm^{-1} correspond to the elongation vibrations of Si-O and Si-O-Si in the tetrahedral layer of adsorbed phyllosilicates [28] [34] [35]. The intense band at 1100 cm^{-1} corresponds to the vibrations of the Si-O bond of the kaolinite [31] [37] [38]. At 1030 cm^{-1} we observe the band due to Si-O-Si vibrations of illite and kaolinite [13] [39]. The band at 1610 cm^{-1} on the spectra is related to absorbed hygroscopic water [40]. The bands of average intensity at 696 , 755 and 796 cm^{-1} observed on the IR spectrum correspond to the stretching vibrations of the Si-O-Al bonds and to the OH hydroxyls perpendicular to the surface (also called translational OH) [27] [29] [32] adsorbed. The bands at 755 and 530 cm^{-1} are attributable to the Si-O-Al bonds of the kaolinite [30] [41]. The bands of average intensity at $432 - 471$ and 540 cm^{-1} correspond respectively to the vibrations of deformation of Si-O [42] [43] and deformation

of Si-O-Al bonds (Al in tetrahedral and/or octahedral site) [30] [40]. Furthermore, the bands at 471 cm^{-1} and 540 cm^{-1} are either due to vibrations from deformations of the Si-O bonds, or due to vibrations of the Fe-O bonds [44]. The results of the infrared analysis show that both samples are rich in kaolinite, quartz, goethite and illite, which corroborates the results of the X-ray diffraction.

Figure 4 shows the microstructure of the two clay raw materials.

The morphology of the two samples presents sheets in the form of platelets with a complex structure. Platelets with irregular contours are stacked on top of each other (crystals joined face to face) so as to form clusters whose thickness can reach $100\text{ }\mu\text{m}$.

Table 3 presents the surface area and density measurements of the two samples.

The specific surface of DAB 2 ($25.72\text{ m}^2/\text{g}$) is in the $10 - 30\text{ m}^2/\text{g}$ range of kaolinites) [45] [46]; which confirms that this sample is rich in kaolinite by referring to the results of the mineralogical composition. The specific surface of DAB 1 ($39.16\text{ m}^2/\text{g}$) is slightly higher than that of DAB 2. This higher value can be explained on the one hand by the large quantity of clay minerals (kaolinite and illite) because the smaller the particles of a soil, the greater its specific surface area [47]. On the other hand, it would be linked to the high rate of iron compounds in this sample (12.8% goethite). Indeed, it has been shown in the literature a linear evolution of the specific surface of clays of the kaolinitic type as a function of the rate of iron compounds [48].

DAB 1 has a lower density than DAB 2.

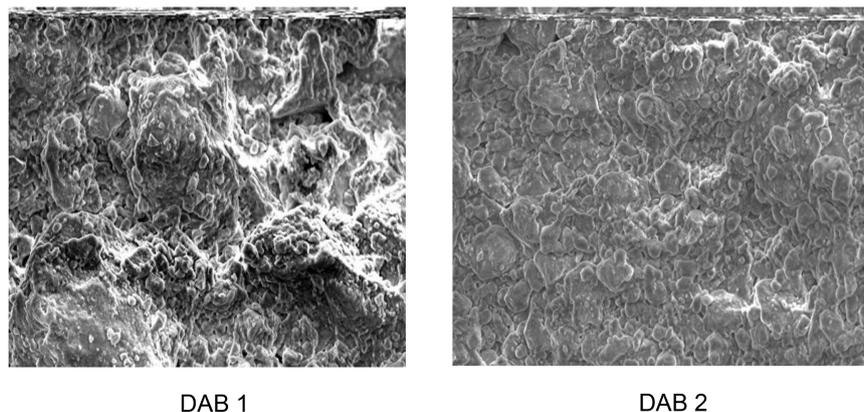


Figure 4. SEM analysis of DAB 1 and DAB 2.

Table 3. Specific surfaces and densities of DAB 1 and DAB 2 samples.

Sample	DAB 1	DAB 2
Specific surface (m^2/g)	39.16	25.72
Apparent density (g/cm^3)	2.47	2.72

4. Discussion

Among the catalysts used for the Fenton reaction, the tendency is to use clay materials. ICP-AES data indicate the presence of the oxides SiO_2 , Al_2O_3 , Fe_2O_3 within the two samples, respectively in the proportions 67.54 wt%, 21.87 wt% and 8.95 wt% for DAB 1 and 58.21 wt%, 28.11 wt% and 11.55 wt% for DAB 2. The iron content determined by ICP-AES is around 9 wt% to 12 wt%. This average is higher than that given by the literature [22]. XRD results show the presence of Kaolinite, quartz, illite and goethite. The FTIR analysis has confirmed XRD results. It also appears the presence of iron probably intercalated within the clays. The SEM indicates a sheet morphology in agreement with the previous results. Finally, the high values of the specific surfaces measured show that our samples are clays of the lateritic type because the values of the specific surface are between 10 and 30 m^2/g [45]. This result shows that these samples can be used as catalysts in adsorption reactions as well as in heterogeneous Fenton-type reactions. Such iron-rich natural minerals with large specific surface areas are potential precursors of the Fenton reaction for the depollution of textile dyes. Indeed, the great production of OH radicals due to the iron content predicts a high yield of the reaction.

5. Conclusion

The main objective of this study was to determine the physico-chemical properties of two local clays in order to use them in the treatment of dyeing wastewater. At the end of this work, it appears that the DAB 1 and DAB 2 clays taken from the same well at different depths have the same chemical and mineralogical composition. Indeed, the results showed that they are clays of the kaolinitic type consisting mainly of kaolinite (51.17% and 65.85% respectively for DAB 1 and DAB 2) and quartz (41.76% for DAB 1 and 25.08% for DAB 2). The large amount of clay minerals (Kaolinite and Illite) shows that these clays can be used in adsorption studies that will be implemented in the treatment of dyeing wastewater. Furthermore, these samples contain a relatively large amount of iron compounds (goethite) which justifies a large specific surface area (>25%) in both of them. The presence of goethite and the large specific surface of the samples lead to the conclusion that these clays can be exploited in the heterogeneous Fenton process for the depollution of dyeing wastewater.

Conflicts of Interest

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

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