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Adsorption of tannery anionic dyes by modified kaolin from aqueous solution

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ABSTRACT

There are significant amounts of unused dyes remaining in wastewater from dyeing industry. The release of these effluents causes abnormal coloration of surface waters and there is a risk of toxicity. This research involved the efficient adsorption of anionic dyes (Coriacide Bordeaux 3B, Derma Blue R67, and Coriacide Brown 3J) used in tanning industry by local natural and treated clays; DD3 and KT2, a low-cost material abundant in highly weathered soils from Algerian East. The activated kaolins were characterized by chemical analyses, X-ray diffraction, and fourier transform IR scanning electron microscopy to obtain information about their structure and surface texture. The adsorption kinetics was investigated using the parameters such as contact time, clay nature, solution initial dye concentration, and acid activation. The adsorption capacity of all three dyes on local kaolinite clays exceeds 90% observed after 40–80 min. Compared with the adsorption experiments on Bentonite, the results show that kaolin has the best adsorption capacity for anionic dyes under the experimental conditions of this work.

Keywords: Kaolin; Bentonite; Acid activation; Anionic dyes; Adsorption kinetics

1. Introduction

Effluents from metallurgical and chemical industries, ceramics, electrogalvanization, textile industries, and tanneries are potential sources of water pollution, and the problems of treatment and disposal of such wastes require much attention. The presence of dyes in aqueous effluent such as in river stream can be noticed easily, because dyes are colored and highly visible. The discharge of dyes directly into aqueous effluent can endanger living organism and its aquatic ecology, because most dyes are toxic. They have negative environmental effects, causing oxygen impoverishment and light transmission attenuation in aquatic ecosystems affecting both fauna and flora [1]. Various physical, chemical, and biological decolorization methods such as coagulation, reverse osmosis, membrane separation process, electrochemical, dilution, filtration, flotation, softening, and reverse osmosis technologies have been proposed [2]. Several conventional methods for the treatment of effluents containing dyes are available [3], and the most efficient one is the adsorption process, because it is simple in terms of operation and can remove the contaminant even at very low

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concentration. However, the choice of the adsorbent is based on economical and practical reasons and clay minerals are natural materials with low cost. Kaolinite is the most abundant phyllosilicate mineral in highly weathered soils and its use as adsorbent would be very convenient for removing organic pollutants and heavy metal ions [4–6]. Kaolinite has a low cation-exchange capacity (CEC) of the order of 3–15 meq/100 g, and therefore it is not expected to be an ion exchanger of high order. Nevertheless, the small CEC and the adsorption properties may play an effective role in scavenging inorganic and organic pollutants from water [7,8]. Therefore, the aim of this study was to determine the adsorption kinetics of anionic dyes widely used in the tannery, such as: Derma Blue R67, Coriacide Brown 3J, and Coriacide Bordeau 3B on kaolins from Djebel Debagh "DD3" and EL Milia "KT2," which Algeria possesses reserves estimated at millions of tons, in the East, and that need to be valorized. A number of experimental parameters in this study are considered, including the effect of initial dye concentration, acid activation, and nature of clay. To explore the feasibility of this clay, Bentonite was chosen to test the adsorption capacity to release the anionic dyes after treatment.

2. Experimental

2.1. Materials

Two commercial clays, DD3 and KT2, were chosen to represent abundant raw materials without special degree of purity. The kaolin (DD3), gray in color, was obtained from the Guelma region (Djebel Debagh) in Algeria and supplied and enriched by ceramic company (ETER) (ceramic company, Guelma, Algeria). The type of kaolin is much rarer than other clay minerals [9]. The second kaolin used "KT2" is an Algerian kaolin treated and ETER. The kaolin "KT2" came from the original EL Milia deposit "TAMAZERT" in the region of Jijel (Algeria). In order to obtain the acid-activated clays (DD3) and KT2, the acid treatment was carried out with 0.1 N H_2SO_4 acid [10]. The CEC was measured in order to evaluate the potential use of these clays for adsorption. It was determined using the cobalt hexammine chloride saturation method using a UV–vis spectrophotometer. The CEC values were 13.87 meq/100 g of DD3 and 27.62 meq/100 g of KT2, previously air-dried overnight at 120°C and decreases after deactivation to 10.5 meq/100 for DD3 and 21.17 meq for KT2 mainly due to dealumination.

Chemical compositions in mass % of natural KT2 and DD3 obtained by X-ray fluorescence (XRF) are listed in Table 1. The physical properties of KT2 and DD3 before and after activation are summarized in Table 2.

2.2. Characterization

Mineralogical compositions of representative clays samples were determined by XRD using air-dried. XRD patterns of DD3 and KT2 clays (before and after activation) were collected on a X-Pert Propanalytical diffractometer using Ni filtered Cu-Kα radiation ($\lambda = 1.5{,}406$ Å, 30 kV, 30 mA, and automatic monochromator). The diffractograms were recorded in the range $2\theta = 6$–65°. The scanning speed was 1°/min. The

Table 1
XRF analysis: oxide composition (%) of natural "KT2" and "DD3" kaolins

	Components (mass %)												
Kaolins	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	NO_2	TiO_2	BaO	SO_3	MnO	LOI
DD3	41.97	38.00	0.12	0.07	0.20	–	–	–	–	–	0.75	1.34	16.80
KT2	49.30	33.50	1.59	0.40	0.08	0.09	2.75	–	0.24	–	–	–	10.50

Note: LOI: Loss on ignition at 1,000°C.

Table 2
Physicochemical properties of natural and activated adsorbents

Clays		BET surface area S_{BET} (m^2/g clay)	Average pore size D_p (nm)	Cationic exchange capacity CEC (meq/100 g) clay
Before activation	DD3	49.33	16.0 8	13.87
	KT2	24.31	13.22	27.62
After activation	DD3	65.59	12.64	10.50
	KT2	30.74	11.67	21.17

FTIR spectra of natural and treated KT2 and DD3 with H_2SO_4 acid were obtained in the region 4,000–500 cm^{-1} using FTIR spectrometer, type Perkin Elmer Spectrum one model, at room temperature dispersed in KBr discs. The morphologies of natural and activated kaolins were examined using a scanning electron microscopy (SEM) (Model JEOL JSM 6390 LU).

2.3. Dyes solutions

The reactive dyes used as adsorbates are bifunctional dyes. They were provided by the *Stahl Iberica of Spain* and simulated by aqueous solutions of organic anionic dyes industrially used in tanning industry, with commercial names: Coriacide Bordeaux 3B, Derma Blue R67, and Coriacide Brown 3J. Synthetic test dye solution was prepared by dissolving an accurately weighed amount of dye (1 g/L) in distilled water and subsequently diluted to required concentrations. Analytical samples were taken from the reaction suspensions at various time intervals during the reaction, then centrifuged to remove the suspended particulates, and the equilibrium concentrations of dye were determined by measuring the absorbance at 510, 610, and 430 nm of the Coriacide Bordeaux 3B (pH was 6.1), Derma Blue R67 (5.6), and Coriacide Brown 3J (6.3), respectively, with an UV–vis spectrophotometer (Photolab Spektral WTW). The complete structure diagrams of three dyes are not available. Intrinsic pH values of 6.1, 5.6, and 6 were measured at 25˚C with a Consort C831 potentiometer. These pH values did not vary immediately after the addition of clay, but only after few minutes once dye adsorption started.

2.4. Adsorption studies

Adsorption of tanning dyes by the different kaolin fractions was carried out in batch. Batch adsorption is a simple technique commonly utilized to assess the adsorptive capacities of natural and synthetic sorbents. Aside from the fact that it is easy to manipulate, it also helps in obtaining important information about the efficiency of a given sorbent to remove the studied solute in static conditions.

In the present study, the Algerian Bentonite, supplied by ENOF (mining products company), was chosen to test the adsorption capacity to release the anionic dyes after treatment in addition to Djebel Debagh “DD3” and treated Tamazert “KT2” kaolins.

The adsorption process was conducted by adding a known amount of activated clays Tamazert “KT2,” or Djebel Debagh “DD3,” or Bentonite into 500 mL of 100 mg/L dye solution at a constant stirring speed of 450 rpm. Dye adsorption kinetics was investigated at 20˚C and natural pH 4 for 200 min. Two milliliters of samples were drawn at suitable time intervals. The samples were then centrifuged for 15 min at 5,000 rpm and the left out concentration in the supernatant solution was analyzed through UV visible at the maximum wavelength. In order to characterize the adsorption process of dye on clay, we have discussed the effect of parameters such as contact time, initial dye concentration, and acid activation on the removal rate of dye onto clay from aqueous solution.

In the kinetic experiments, the amount of dye adsorbed at a time interval t, q_t (mg/g) or the percentage removal (P%) was calculated using the following equations:

$$q_t = (C_0 - C_t)V/m \tag{1}$$

$$P\% = 100\ (C_0 - C_t)/C_i \tag{2}$$

where C_0 and C_t are the initial and liquid-phase concentrations at any time t of dye solution (mg/L), respectively; V the volume of dye solution (L), and m is the mass of kaolin sample used (g).

3. Results and discussion

3.1. Characterization of “DD3” and “KT2” kaolins

The raw kaolins were rich in SiO_2 (>40%), in Al_2O_3 (>30%) and contained only small amounts of Ca^{2+}, Mg^{2+}, and Na^+ ions (Table 1). However, titanium oxide (TiO_2) is present in trace amounts for KT2 in all their crystalline forms, such as anatase and rutile, and low manganese oxide content is present in DD3. The low concentrations of these minerals generate the rheological and physicochemical properties which have direct influence on the quality of raw material.

The specific surface area and cationic exchange capacity of the raw and activated clays are summarized in Table 2. The specific surface area is higher for activated DD3 and KT2 suggesting a pronounced acid activation, and this is most relevant to evaluate the capacity of adsorption and more active sites being available for adsorption by DD3 and KT2 and indicating that the major part of nonporous components such as quartz was removed.

On the other hand, kaolinite has a low CEC of the order (Table 2), and therefore it is not expected to be an ion exchanger of high order. Nevertheless, the small CEC and the adsorption properties may play an effective role in scavenging anionic tannery dyes.

Physical characterization of layer structure for DD3 and KT2 before and after activation was conducted by

X-ray diffraction (XRD). The XRD results for kaolins before and after activation are shown in Fig. 1. The interlayer spacing or d_{001} spacing is measured from the top of the corresponding Si tetrahedral silica sheet (T) to the top of the Si tetrahedral sheet of the following layer [11,12].

The X-ray diffractogram of natural DD3 showed a basal reflection at 7.35 Å (halloysite) with a shoulder at 7.14 Å (kaolinite) and at 7.35 Å (halloysite) with a shoulder at 7.17 Å (kaolinite) for nonactivated KT2 (Fig. 1(a) and (c)), with a relative intensity of 100%. Also observed were illite for DD3 and smectite and illite for KT2. The low intensities indicated minor quantities of quartz at 4.25 Å for KT2 (Fig. 1(c)).

The acid activation of DD3 and KT2 modified the basal spacing in DD3 (7.31 Å) and KT2 (7.15 Å) (Fig. 1(b) and (d)), which indicates that the acid treatment affected slightly the structure of the components and expanded the interlayer spaces. Furthermore, acid treatment with H_2SO_4 0.1 N dissolves major impurities such as quartz for KT2.

The infrared spectroscopy constitutes for mineralogists a tool for characterization of the crystallinity of clays by the observation of the relative intensities of the bands of vibrations of hydroxyls of structure. The FTIR spectra of natural and activated clays are shown in Fig. 2. As we can see, all clays, natural and activated, exhibit two moderately intense bands between 3,620.64 and 3,750 cm^{-1}, which might be ascribed to the stretching frequencies of the OH functional groups of coordination water and of the hydration OH stretching. The absorption peaks between 1,620 and 1,630.53 cm^{-1} can be taken as both due to OH stretching vibration and $\delta(H_2O)$ deformation. The rest of the bands between 450 and 1,095 cm^{-1} in natural clays are due to the stretching vibration of Si–O, Si–O–Si, OH attached to (Al^{3+}, Fe^{3+}, and Mg^{2+}) groups, and the silica quartz impurities. After acid treatment, a significant difference is not observed between original and activated KT2 and DD3. Under these mild conditions, the FTIR curves showed that a weak destruction of the layers and interlayer space of activated clay was carried [13].

SEM was used to probe the change in morphological features of natural and activated kaolins DD3 and KT2. Fig. 3 shows the SEM micrographs of DD3 and KT2. The surface morphology of natural kaolin is different from that of the treated kaolin. Activated DD3 has larger pores between particles than nonactivated DD3 (Fig. 3(a) and (b)). Also, natural KT2 appears to be highly compact than activated KT2 (Fig. 3(c) and (d)). It is seen that in all nonactivated kaolins the interparticle pores are smaller compared with the activated kaolins.

3.2. Adsorption studies

3.2.1. Effect of contact time

The influence of contact time on removal of Blue Derma R67, Coriacide Bordeaux 3B, and Coriacide Brown 3J by 4 g of activated Tamazert “KT2”, Djebel Debagh “DD3” kaolins, or Bentonite at pH 4 and 20°C with an initial dye concentration 20 mg/L are shown

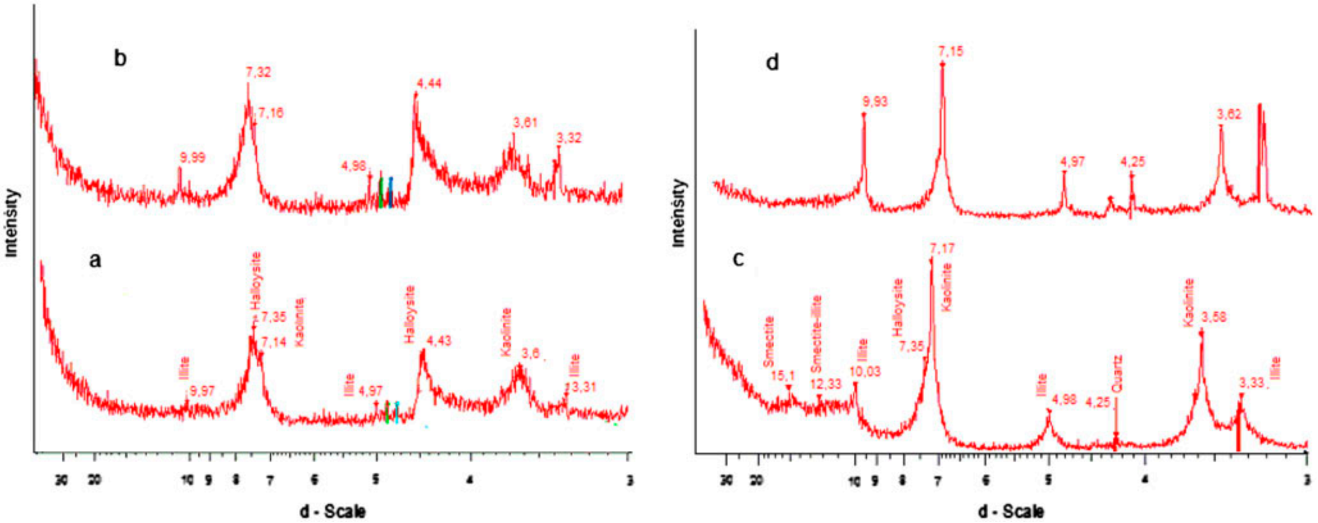

Fig. 1. XRD analysis results for the natural and activated kaolins. ((a) and (c)): Natural DD3 and KT2; ((b) and (d)): activated DD3 and KT2.

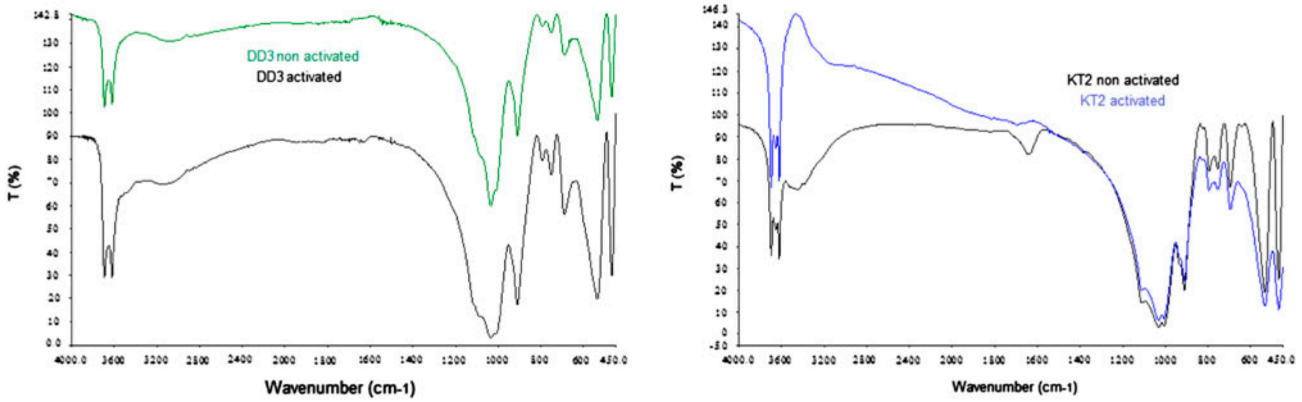

Fig. 2. Infrared spectra of natural and activated kaolins DD3 and KT2.

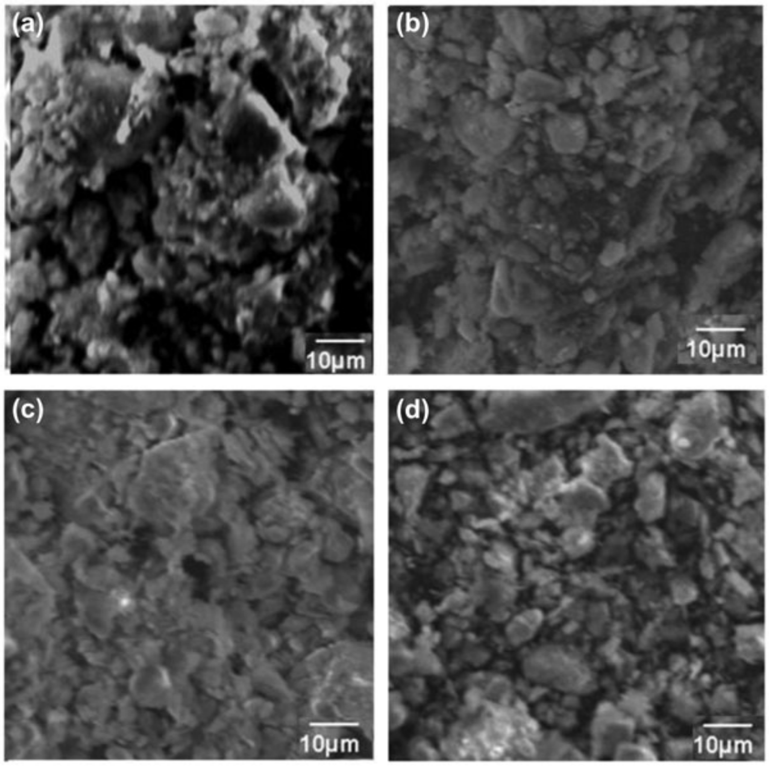

Fig. 3. SEM image of DD3 and KT2 kaolins. ((a) and (c)): Natural DD3 and KT2; ((b) and (d)): activated DD3 and KT2.

in Fig. 4. It is evident that all clays are efficient to adsorb dyes with different efficiencies and the removal of dyes was rapid and strong in the initial stages of contact time (2 min) followed by a slow increase until reaching equilibrium due to the abundant availability of active sites on the clay surface, and with the gradual occupancy of these sites, the sorption becomes less efficient. The shape of the curves for DD3, KT2, and Bentonite clays are similar. This indicates a monolayer formation of the dye on the external surface [14]. The adsorption of the activated DD3 and KT2 is faster than that of activated Bentonite for three dyes. Moreover, the maximum removal percentage of three dyes adsorbed (*P*%) is higher for the activated DD3 (98%) and for the activated KT2 (97%) than for activated Bentonite (82%).

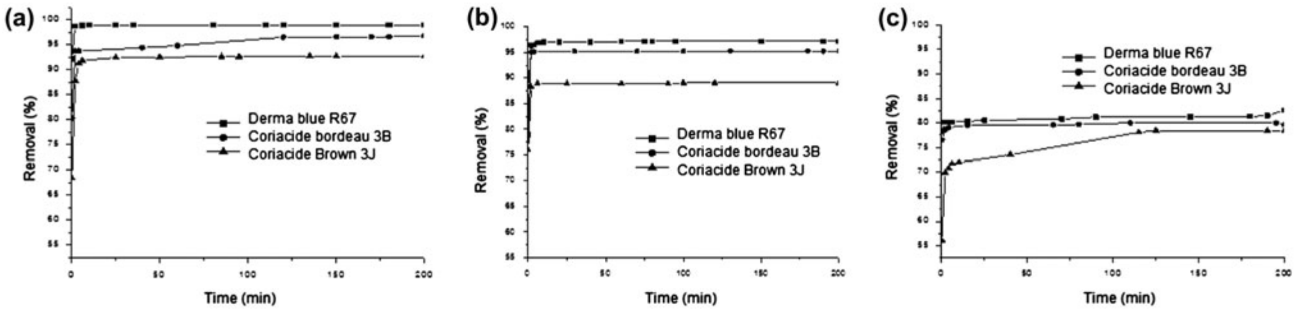

Fig. 4. Effect of contact time on the removal of three anionic dyes on activated DD3 (a), KT2 (b), and Bentonite (c).

To reach equilibrium for anionic dye as Blue Derma R67, it takes 10, 25, and 80 min for activated DD3, KT2, and Bentonite, respectively. At the equilibrium, the activated DD3, KT2, and Bentonite fixes more Blue Derma R67 than the Coriacide Brown 3J and Coriacide Bordeaux 3B. Similar results have been obtained on a textile dyes adsorbed on natural and activated Bentonite [10].

3.2.2. Effect of clay nature

Fig. 5 shows the effect of clay nature on the anionic adsorption dye at initial dye concentration of 20 mg/L at pH 4 for Derma Blue as function of contact time on 4 g of activated Bentonite, or DD3, or KT2. In order to characterize the adsorption capacity on kaolin of the anionic dye “Blue Derma R67” which was fixed more than Coriacide Bordeaux 3B and Brown 3J, we have compared with activated Bentonite. The removal of Derma Blue R67 was rapid in the initial stages of contact time (Fig. 5) and gradually decreased with lapse of time until equilibrium. The rapid adsorption observed during the first 2 min is probably due to the abundant availability of active sites on the kaolinite surface, and with the gradual occupancy of these sites, the sorption becomes less efficient. The time required to attain this state of equilibrium was termed as the equilibrium time and the amount of dye adsorbed at the equilibrium time reflected the maximum dye adsorption capacity of the adsorbent under these particular conditions [15]. The time necessary to reach this equilibrium is about 10 min for DD3 with higher removal percentage (98%). However, it appears from Fig. 5, the rapid adsorption of Derma Blue R67 on KT2 and Bentonite clays was observed during the first 4 min and this is followed by a strong increase in adsorption after 25 min for activated KT2 with higher removal percentage (97%) than that of Bentonite (80%). Thus, the main process involved in anionic Derma Blue dye adsorption on activated DD3 and KT2 kaolins may be the attraction on the broken edges of clay particles, where charges become positive at acidic pH. That is why acidic pH conditions were found to enhance the dye removal. At low pH of the system (dye + kaolin), knowing that the pH has a relatively high value for kaolinite (2–4.6) [16], there was a combined effect on both protonated clay surface and anionic dye molecules which favored the adsorption of the dye. However, the solution pH was always higher than 4, but slightly acid (5.5–6) for experiments with DD3 and KT2. That means that protonation of both clays particle edges contributed only partly to the adsorption of dye. The stronger dye-adsorbent interactions on surface adsorption sites after acid activation must also be involved in tanning dye retention on DD3 and KT2 kaolins, more particularly at low pHs. This kind of interaction must develop in different ways for Bentonite and kaolin minerals, because of their different structure and characteristics of the planar faces. This can explain the anionic dye adsorption capacity of DD3 and KT2 kaolins at acidic conditions.

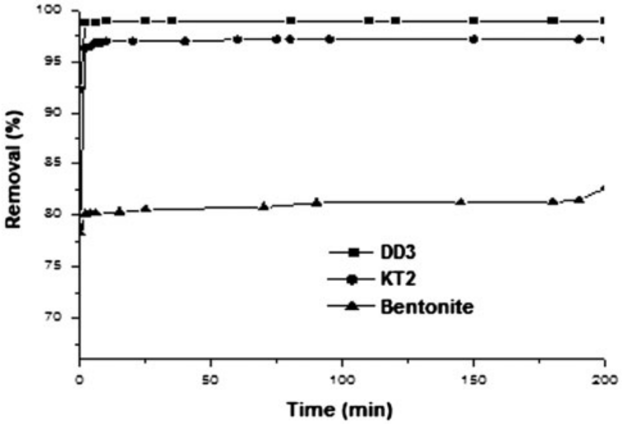

Fig. 5. Effect of clay nature on the removal of Derma Blue R67 on activated “DD3”, KT2, and Bentonite.

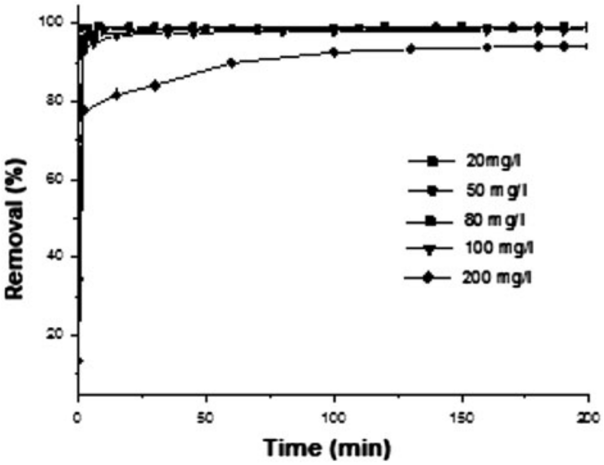

Fig. 6. The effect of initial dye concentration on the removal of Blue Derma on activated DD3.

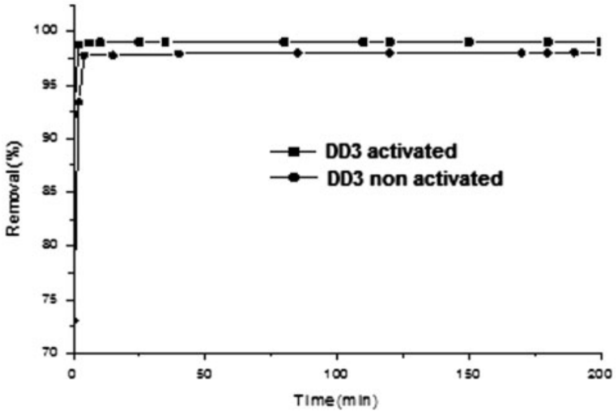

Fig. 7. The effect of acid activation on the removal of Blue Derma on DD3.

3.2.3. Effect of initial dye concentration

The amount of dyes adsorbed, removal percentage (*P*%), increases with time for all initial concentration at pH 4 for Derma Blue as function of contact time on 4 g of activated clay. When the equilibrium conditions are reached, the adsorbate molecules in the solutions are in a state of dynamic equilibrium with the molecules adsorbed by the adsorbent. It appears from Fig. 6 that the removal of dye was dependent on the concentration of the dye. The adsorption capacity increased with increasing initial dye concentration and the process was faster at low concentrations (20 mg/L) than at high concentration (200 mg/L), because the adsorption sites took up the available dye more quickly. However, at higher concentrations, dye needed to diffuse to the sorbent surface by intraparticle diffusion. Also, the steric repulsion between the solute molecules could slow down the adsorption process. The high adsorption indicates that the low initial concentration provided a powerful driving force to overcome the mass transfer resistance between the aqueous and solid phases [17]. On the other hand, the shapes of the curves are similar and approximately independent on the initial dye concentration (Fig. 6). This indicates a monolayer formation of the dye on the external surface [14].

3.2.4. Effect of acid activation

The adsorption rate of Derma Blue R67 on the activated acid and nonactivated DD3 kaolin was investigated at 20°C and pH 4 as a function of time (Fig. 7). The removal percentage of Derma Blue on the kaolinite surface increased with kaolinite treatment. The fact that the adsorption of tanning dye increase with activated DD3, may be due to transforming of SOH groups to SOH_2^+ groups on kaolinite surface according to the following reaction [18]. On the other hand, the acid activation increases the number of adsorption sites in the specific surface area (Table 2), which

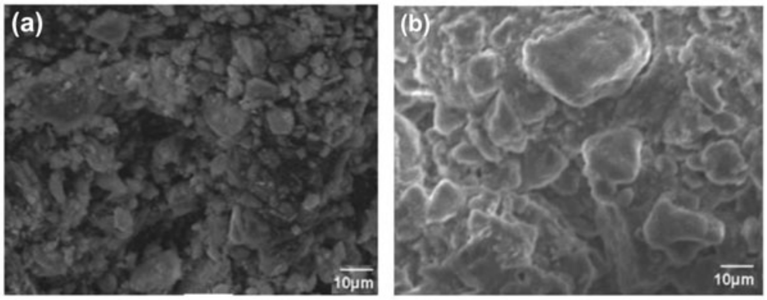

Fig. 8. SEM image of DD3 activated kaolin. (a): DD3 before adsorption of Blue Derma dye and (b): DD3 after adsorption of Blue Derma dye.

facilities the penetration of dye molecules and their accessibility to active sites in the porous structure of the DD3 and is reflected in a higher retention of anionic dye on the kaolin surface.

$$\text{S–OH} + \text{H}^+ = \text{SOH}_2^+ \tag{3}$$

3.2.5. Structure of kaolin after adsorption

The results of electron microscopy (Fig. 8) before and after adsorption dye on activated DD3 showed that the surface morphology of kaolin before adsorption is different from that after adsorption (Fig. 8(a) and (b)). Also the micrographs presented in Fig. 8(b) show clearly the dye-loaded clay coated by dye molecules over the whole surface at natural pH conditions. The dye molecules seem to have formed a void-free film masking the relief of particles and porosity of the aggregates. It seemed that the dye molecules completely filled the spaces between aggregates showing the adherence surface of the adsorbate. On the contrary, the clay before adsorption exhibits well distinguishable particles and a porous structure (Fig. 8(a)). These observations suggested adsorption on external surfaces of particles, thus masking the porosity between particles in aggregates.

4. Conclusion

Algerian kaolins, DD3 from Djebel Debagh (Guelma), and KT2 from Tamazert (El Milia region), activated by acid treatment can be employed as an effective and promising low-cost alternative adsorbents for the removal of anionic dyes from tannery wastewater. The adsorption of Derma Blue R67, Coriacide Brown 3J, and Coriacide Bordeaux 3B was highly dependent on the initial dye concentration, acid activation, and clay nature. A comparative study of adsorption evidences the high adsorption capacity of the three tanning dyes on the activated DD3 and KT2 than activated Bentonite. An increase in the initial dye concentration enhances the interaction between tanning dyes and kaolins "DD3 and KT2", resulting in greater and fast adsorption capacity with the equilibrium attained after 20–60 min for anionic dyes by comparison with activated Bentonite, whose adsorption capacity is low for all the three anionic dyes and the time to reach equilibrium was 80–140 min. The results showed that the adsorption anionic dyes on activated DD3 and KT2 could be explained by the main efficient adsorbing sites on adsorbent surface for anionic dye molecules. Furthermore, the experimental conditions (acidic medium, activated adsorbent, and low temperature) of kinetics adsorption study were found to enhance dye removal with great adsorption efficiency. Compared with standard Bentonite clay, activated DD3 and KT2 kaolins have a good and high potential for adsorption removal of anionic dyes from aqueous solution. Therefore, it may be promising low-cost alternative adsorbents for removing anionic reactive dyes from dye wastewater.

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