Keywords— Kaolin, Bentonite, acid activation, anionic dyes, adsorption kinetics

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 bordeau 3B, derma blue R67 and the 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 (XRF), X-ray diffraction, Fourier Transform IR, Scanning Electron Microscopy (SEM) to obtain information about their structure and surface texture. The adsorption kinetics was investigated using the parameters such as contact time, amount of clay, solution initial dye concentration and acid activation. The adsorption capacity of all three dyes on local kaolinite clays exceeds 90% observed after 40 to 80 min. Compared to adsorption experiments on bentonite, the results show that the kaolin has the best adsorption capacity for anionic dyes under the experimental conditions of this work.

I. INTRODUCTION

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, electrochemical, dilution, filtration, flotation, 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 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 of heavy metal ions [4], [5]. Kaolinite has a low-cation exchange capacity (CEC) (3-15mequiv./100 g) and the adsorption properties may play an effective role in scavenging inorganic and organic pollutants from water [6], [7]. 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 kaolinite over a range of physicochemical conditions that are important to identify various natural environmental systems, on Algerian kaolinite from Djebel Debagh “DD3” and EL Milia “KT2” in which Algeria possesses estimated at millions of tons, in the East, and that need to be valorised. 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.

II. EXPERIMENTAL

A. 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 by ETER (ceramic company,Guelma, Algeria). The type of kaolin is much rarer other clay minerals [8]. The second kaolin used “KT2” is an Algerian kaolin treated and enriched by ceramic company (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 0.1N H$_2$SO$_4$ acid [9]. The cation-exchange capacity (CEC) was measured in order to evaluate the potential use of these clays for adsorption. It was determined using the cobalt hexaammine chloride saturation method using a UV–VIS spectrophotometer. The decrease CEC values after deactivation from 13.87 meq/100 g to 10.5 of DD3 and 27.62 meq/100g to 21.17 of KT2, previously air-dried overnight at 120 °C mainly due to dealumination.

Chemical compositions in mass % of natural KT2 and DD3 obtained by X-ray fluorescence (XRF) are listed in Table I.

### Table I. X-ray fluorescence analysis: oxide composition (%) of natural “KT2” and “DD3” kaolins

<table>
<thead>
<tr>
<th>Kaolins</th>
<th>Components (mass %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SiO$_2$</td>
</tr>
<tr>
<td>DD3</td>
<td>41.97</td>
</tr>
<tr>
<td>KT2</td>
<td>49.30</td>
</tr>
</tbody>
</table>

LOI: Loss on ignition at 1000°C

### B. Characterisation

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 Proanalytical diffractometer using Ni filtered Cu-K$_\alpha$ radiation ($\lambda$=1.5406Å, 30 kV, 30 mA and automatic monochromator). The diffractograms were recorded in the range 20 = 6–65°. The scanning speed was 1°/min. The FTIR spectra of natural and treated KT2 and DD3 with H$_2$SO$_4$ acid were obtained in the region 400–500 cm$^{-1}$ by using FT-IR spectrometer, type Perkin Elmer Spectrum one model, at room temperature dispersed in KBr discs. The morphologies of natural and activated bentonite were examined using a scanning electron microscopy (Model JEOL JSM 6390 LU).

### C. Dyes Solutions

The reactive dyes used as adsorbates are bifunctional dyes, they were provided by the Stahl Iberica of Spain and they were industrially used in tanning industry, with commercial names: coriacide bordeau 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 the samples 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 bordeau 3B (pH was 6.1), derma for 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 addition of clay but only after few minutes once dye adsorption started.

### D. 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. 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 Tamzert “KT2” kaolins.

The adsorption process was conducted by adding a known amount of activated clays Tamzert “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 5000 rpm and the left out concentration in the supernatant solution were analysed through UV visible at 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 %) were calculated using the following equations:

$$Q_t = \frac{(C_0 - C_t)V}{m}$$  \hspace{1cm} (1)

$$P\% = \frac{100(C_0 - C_t)}{C_t}$$  \hspace{1cm} (2)

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

### III. RESULTS AND DISCUSSION

#### A. Characterisation of DD3 and KT2 kaolins

The raw kaolins were rich in SiO$_2$ (>40%), in Al$_2$O$_3$ (>30%) and contained only small amounts of Ca$^{2+}$, Mg$^{2+}$, Na$^+$ ions.
However, titanium oxide (TiO₂) is present in traces amounts for KT2 in all their crystalline forms such as the anatase and the rutile and the low manganese oxide content is present in DD3. The low concentrations of these minerals generate the rheological and physico-chemicals properties which are direct influence on quality of raw material.

Physical characterization of layer structure for DD3 and KT2 before and after activation was conducted by X-ray diffraction. The XRD results for kaolins before and after activation shown in Fig. 1. The interlayer spacing or d₀₀₁ 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 [10]. The KT2 and DD3 clays yielded, 5 to peaks in the range of 6–40° (2θ). The basal spacing (d₀₀₁) of DD3 and KT2 natural kaolins are 7.26, 3.50 Å, respectively attributed to kaolinite (Figure 1a and c). Other reflections attributed to quartz, calcite as impurities are observed for both natural kaolins. The increase of basal spacing in DD3 (7.33 Å) and KT2 (3.59 Å) activated (Fig. 1b and d) indicate the acid treatment affect slightly the structure of the components and expanded the interlayer spaces. Furthermore, acid treatment with H₂SO₄ 0.1N, dissolves major impurities such as calcite, quartz and dolomite for both materials.

The infrared spectroscopy constitutes for the 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 spectrums 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 3620.64 and 3750 cm⁻¹, which might be ascribed to the stretching frequencies of the OH functional groups of co-ordination water and of the hydration OH stretching. The absorption peaks between 1620 and 1630.53 cm⁻¹ can be taken as both due to OH stretching vibration and δ(H₂O) deformation. The rest of the bands between 450 and 1095 cm⁻¹ in natural clays are due to stretching vibration of Si–O, Si–O–Si, OH attached to (Al³⁺, Fe³⁺, and Mg²⁺) 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 [11].

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. DD3 activated has larger pores between particles than DD3 non activated (Fig. 3a and b). Also, natural KT2 appears to be highly compact than activated KT2 (Fig. 3c and d). It is seen that in all non activated kaolins the inter-particle pores are smaller compared to the activated kaolins.

B. Adsorption studies

B.1 Effect of contact time

The influence of contact time on removal of blue derma R67, coriacide bordeaux 3B and coriacide brown 3J by 4g of
activated Tamazert "KT2", Djebel Debagh “DD3” kaolins or bentonite at pH 4 and 20°C with an initial dye concentration 20mg/l are shown 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 [12].

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%).

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 bordeau 3B.

The effect of clay nature on dye adsorption observed in this study was explained by electrostatic interaction between kaolinite or bentonite and dye molecules. As the pH of the system (dye +kaolinite) is acid (pH=4), knowing that the pH has a relatively high value for kaolinite (2 – 4.6) [13], the number of negatively charged sites decreases and the number of positively charged sites increases in activated DD3 and KT2. The lower adsorption of anionic dyes on activated bentonite is because of the low presence of H+ ions competing with dye anions for the adsorption sites.

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 4g 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. The adsorption capacity increased with increasing initial dye concentration and the process was faster at low concentrations (20mg/L) than high concentration (200mg/L) because the adsorption sites took up the available dye more quickly (Fig. 6). 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 [14]. 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 [12].

B.4 Effect of acid-activation

The adsorption rate of derma blue R67 on the acid activated and no activated DD3 kaolin was investigated at 20°C and pH = 4 as a function of time (Fig. 7). The removal percent of derma blue on the kaolinite surface increased with kaolinite treated. The fact that the adsorption of tanning dye increase with DD3 activated, may be due to transforming of SOH groups to SOH₂⁺ groups on kaolinite surface according to the following reaction [15]:

\[ S - OH + H^+ = SOH_2^+ \]  

IV. 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 bordeau 3B was highly dependent on initial dye concentration and acid-activation. 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 was attained after 10 to 80 min for anionic dyes by comparison with activated bentonite, the adsorption capacity is low for all the three anionic dyes and the time to reach equilibrium was 80 to 140 min. These results could be explained by the electrostatic attraction between the positively charged surface and the negatively charged dye molecule in the acidic medium (natural pH=4). Compared to standard bentonite clay, activated DD3 and KT2 have a good and high potential for adsorption removal of anionic dye from aqueous solution.

REFERENCES
