Activated Algerian kaolin’s as low-coast potential adsorbents for the removal from industrial effluents of Derma Blue R67 acid dye: kinetic and thermodynamic studies

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Keywords: Activated Kaolins, Tannery dye, Kinetic, Thermodynamic of Adsorption

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Abstract

The tanning industry, particularly the discharges from the dyeing process, induces environment pollution, causing hence human health problems. The treatment of the effluents by using low cost clays would have an important economic and environmental interest, as it would promote the local clays from the Algerian East. In the present work**,** we tested two Algerian kaolin clays, DjebelDebagh "DD3" and Tamazert “KT2**”**. These two clayswere firsttreated by acid in orderto enhance their retention capacities,and then characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), surface area measurements (BET method), surface charge (PZNPC), and electrophoretic mobility (Zetaphoremeter). The adsorption experiments were done using the Derma Blue R67 acid dye, commonly used in the tanning industry. The results showthat the adsorption is efficient and feasible at ambient temperature, and well described by the Langmuir model indicating a monolayer covering of the clay by the acid dyemolecules.The adsorption kinetics follows a two-type process onto KT2 kaolinite, whereas onto DD3, it only follows the pseudo-second-order model. Thus, it is concluded that the Algerian local kaolin clays are goodadsorbent candidates for wastewatertreatments.

Keywords:ActivatedKaolins,Tannery dye, Kinetic,Thermodynamic of Adsorption

Introduction

Textile and tannery effluents are among the most polluting industrial wastes, and the problem of treatment and disposal of such wastes requires much attention. A certain amount of dye is lost in the manufacturing processes and remains in their effluents. Moreover, it may be released in aqueous mediumsuch as in river streamswhich become coloured. Moreover, tanning dyes like textile dyesaretoxic to living organisms due to their low biodegradability and persistence in the environment, and their presence in wastewater represents risk to human health (Jain et al. 2003). Therefore, effluents have to be treated carefully before discharge. However, the removal of dyes remains usually the key point. For example, in Algeria, domestic and industrial raw wastewaters are discharged in the environment and cause pollution, which is an increasing threat forwater resources and public health. On the estimated base of amounts of industrial effluents discharged by100 industrial units, industrial textile and tannery companies, 22%produce a volume of 100 to 130 million m^3, with a pollution load of more than 55,000 tons of biologic oxygen demand (BOD5). The treatment capacity of existing industrial effluents represent about 20million m^3/year, some 10% of the volume of wastewater generated(Rapport sur l’état et l’avenir de l’environnement 2005).There are several methods for dye removal such as biological treatment (Kapdan and Kargi 2002; Allegre et al. 2006),coagulation/flocculation(Cooper 1993), ozone treatment(Allegre et al. 2006; Cooper 1993),chemical oxidation and photocatalytic processes (Clark et al. 1994), membrane processes(Allegre et al. 2006;Cooper 1993), and adsorption (Cooper 1993;Gupta et al. 1997). Among these methods, 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 concentrations(Gupta et al. 2006). However, the choice of the adsorbent is based on economical and practical reasons.Clay is one of the well-known low cost natural materials, available worldwide in rocks. Among clays, the kaolin may be a good alternative low-cost adsorbent because it is the most abundant kaolinite-rich rock in Algeria. Indeed, Algeria possesses in the East, an estimated amount of millions of tons of clays that need to be promoted. Thus, the use of kaolin as adsorbent would be very convenient for removing organic pollutants and heavy metal ions (Dubey et al 2009).Although kaolinite has a low-cation exchange capacity (CEC) (3-15 meq/100 g), its adsorption properties may play an effective role in scavenging inorganic and organic pollutants from water (Rodney Harris et al 2001,Liu and Zhang 2007). However, the adsorption of anions is less efficient than for cations, due to the negative permanent surface charge of the phyllosilicate.Nevertheless, theadsorptionperformancecan be improvedby treating theclay to increase the specific surface. This can be done for example, by acid activation(Lin et al. 2004).

In this study, we focused on the adsorption of an anionic reactive dye (Derma BlueR67), which is commonly used in the Algerian tanning industry, onto acid activated Algerian clays from DjebelDebagh and El Milia regions. Up to now, only few studies were carried out on the adsorption of anionic dyes ontothese local Algerian kaolinclays (Benguella and Yacouta-Nour 2009a,Zen and El Berrichi 2014).A number of parameters wereconsidered in the adsorption experiments of this study, including the effect of initial dye concentration, initial solution, pH, acid activation, dose of adsorbent, and nature of clays. Moreover, kinetic and thermodynamic studies were done to describe the adsorbate removal rate, the residence time in the adsorbent–solution interface, and determine the feasibility and the spontaneity of the adsorption process.

Materials and methods

Materials

Two commercial raw clay materials, DD3 and KT2, weresupplied by the ceramic company ETER (Guelma, Algeria).The kaolin “DD3”, was sampled in an active kaolin mine, formed by hydrothermal alteration processes in the region of Guelma (DjebelDebagh, Algeria) (Boulmokh et al. 2007).This clay composed of halloysite and kaolinite with a ratiohalloysite/kaolinite = 1.23,is a potential adsorbent in mortars (Rabehi et al. 2012)and in adsorption of metals (Mellouk et al. 2009).The second clay material “KT2” is also composed of kaolinite and halloysite, and already enriched in clay minerals by the ceramic company (ETER), by removing other minerals. Itcomes from El Milia deposit “TAMAZERT”fromJijel region (Algeria).The El Milia region consists of metamorphic rocks belonging to the Precambrian. The kaolin deposit is the alteration zone of gneiss, and is often in contact with micasschist. The reactive dye used as adsorbate is abifunctional dye, soluble in water, commonly in use in the tanning industry. Itwas provided by the CromogeniaCompany (Spain)and itscommercial name isDerma Blue R67.The complete structure diagram of the dye is not available. A synthetic test dye solution was prepared by dissolving accurately weighed amounts of dye (1g/L) in distilled water and subsequently diluted to the required concentrations.The pH value of the initial dye aqueous solutions were measured at 25 °C with a Consort C831 potentiometer.

Clay preparation and characterization methods

In order to obtain the acid-activated clays DD3 and KT2, the acid treatment wascarried out with 0.1N H_2SO_4acid (Benguella and Yacouta-Nour 2009b).We added 5 g of natural clay (DD3 or KT2) to 100 mL of the 0.1 N H_2SO_4aqueous solutionandagitationwas applied during 4 h. The solution was filtered and then washed several times with distilled water. The filtrate was put in a drying oven for 12 h at approximately 60°C. After drying and crushing in a mortar, very fine particles were obtained.The cation-exchange capacity (CEC) was measured in order to evaluate the potential adsorption sites ofthe clays. It was determined using the Hexammine cobalt (III) chloride saturation method coupled with UV–VIS spectrophotometer Photo lab Spectral WTW. The chemical composition of the clays was measured by X-ray fluorescence (XRF).The pH of the solution was adjusted with a 0.1 mol/L NaOH or HCl solution using a “HANNA Instruments” model pH meter that was equipped with a combined pH electrode.The X-ray diffraction (XRD) of the random-powdered clays before and after activation was carried out by XRD on a Bruker D5000 (2-30° 2θscanning angle) and the program MacDiff (version 4.2.) was used to estimate the relative contents of each clay mineral species based on the area of their (001) basal reflections (Petschick 2000). The following diagnostic treatments were performed for parallel-oriented specimens of the clays:ethylene glycol and hydrazine solvations overnight, and heating at 490 °C for 4 h.The surface morphology of DD3 and KT2 natural and modified clays was investigated by scanning electron microscopy (JEOL JSM-6390 LU) operating at 5∼30 kV.To examine these clays, the samples were coated with a conducting layer of gold and carbon by sputter coating**.** The surface area of all samples was measured by adsorption of nitrogen at liquid nitrogen temperature according to the BET-method, using a Micromeritics ASAP**.** The Points of Zero Net Proton Charges (PZNPC) were determined from potentiometric titration at different ionic strengths(Kosmulski2009). The electrophoretic mobilities of the clay particles were measured at 20 ± 2 ◦C by using a Zetaphoremeter as described elsewhere (Jada and Erlenmeyer 2012).

Batch adsorption Studies

Adsorption studies were performed in batch to assess the adsorptive capacities of natural and synthetic sorbents, and to obtain the rate and the equilibrium data. Adsorption experiments were carried out in 500 mL conical flasks, filled with various dye concentrations ranging from 20 to 200 mg/L, containing 4 g ofclayand agitated at a constant stirring speed of 450 rpm at natural pH (4.0)for 120 min. Aliquots of 2 mL of the solution were sampled at suitable time intervals. The samples were then centrifuged for 15 min at 5000 rpm, and the left out concentrations in the supernatant solution were analysed.The equilibrium concentrations of dye were determined by measuring the absorbance at the maximum wavelength of the dye (610 nm forDerma Blue R67 at pH =5.6) with an UV–VIS spectrophotometer (PhotolabSpektral WTW).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:

$$Q_t = (C_0 - C_t)\ V/m \quad \mathbf{(1)}$$

$$P\% = 100(C_o - C_t)/C_i \mathbf{(2)}$$

Where C_0 and $C_t$are the initial and liquid-phase concentrations of the dye solution (mg/L) at any time *t*, respectively, Vthe volume of dye solution (L), and ‘m’ is the mass of kaolinite sample used (g).The effect of pH on the removal of the dye was investigated by mixing 20 mL of the dye solution with 4 g of clay in a solution with an initial dye concentration of 20 mg/ L at 20°C for 120 min with constant agitation, and over a pH range of 2–9.The effect of the initial dye concentration on dye removal was investigated by mixing 20 mL of the dye solution with 4 g of solid without adjusting the pH at 20°C for 200 min with agitation. The initial dye concentrations were varied from 10 to 100 mg/L. Different amounts of the adsorbent (0.5–8 g) were used to examine the effect of the adsorbent dosage on the adsorption of the dye. All the experiments were performed in duplicate.

Results and discussion

Characterization of adsorbents

The chemical composition indicated that the raw clays were rich in Si,and Al,and contained only small amounts of Fe, Ca, Mg, Na and K(Table 1).

Table1. Chemical composition of DD3, and KT2 raw clays expressed in mass percentage of oxides

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

The low concentrations of these elements confirmthe high content of the raw clay material in kaolin-type minerals. Thathigh degree of purity of the clay materialgeneratesthe rheological and physico-chemicals propertiesof the raw material,required in the ceramic industry.The apparent values of the point of zero charge of the various clay amphoteric surfaces, in their natural state, were determined for two ionic forces. It is to notice that it was not possible to determine a clear common intersection point (CIP) (Kosmulski2009).Of the potentiometric titration curves at the two ionic strengths. The DD3 clay exhibits high apparent PZC (point of zero charge) value (5.3-7.3) compared to the apparent PZC of the KT2 clay (4.5-6.2) and the standard KGa-2 sample (3.4)(from the Source Clays Repository of the Clay Minerals Society) (Errais et al. 2012).This indicates that the DD3 natural clay may present positive adsorption sites at particle edges, available for anionic dyes, already at pH values ranging between 5.3 and 7.3, unlike the KT2 clay which needs lower pH values to enhance the adsorption of anions.The CEC values after the activation of the clay samples, decreased respectively, from 30 to 15meq/100 g, and from 15 to 9 meq/100 g for KT2 and DD3 respectively. However, the activation lead to an increase of theirS_{BET} valuesfrom 24 to 31 m^2/gand from 49 to 65 for KT2 and DD3 respectively, suggesting hence an increase in their available adsorption sites. The higher S_{BET}value for the activated DD3 (65 m^2/g) as compared to the activated KT2 (31 m^2/g) suggests a more pronounced acid activation of the DD3 sample and development of surfaces at the expense of the pore sizes which slightly decrease.

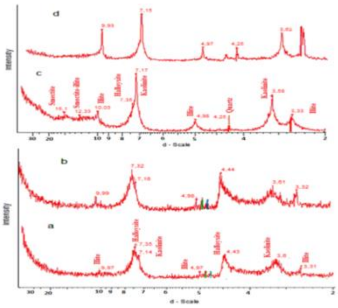

Fig. 1.XRD patterns of the natural and activated clays; (a and c): natural DD3, KT2;

(b and d): activated DD3, KT2.

The XRD results for DD3 and KT2 clays before and after activation are shown in Fig. 1. The 7.14 Å,and 7.35 Åbasal spacings or d_{001}spacingsof the DD3clay may be attributed to kaolinite and dominant halloysite respectively (Fig. 1a and c). The basal spacings or d_{001} spacing values of KT2 are similar to those of DD3, but with intensities indicating a dominance of kaolinite. Other reflections attributed to quartz, calcite as impurities are observed for both natural kaolins, as also minor amounts of illite. Moreover, there are traces of smectites and interstratified illite/smectites in KT2 clay.The slight increase of the basal spacings in the activated DD3 (7.33 Å), and KT2 (3.59 Å) clays (Fig. 1b, and d)after ethylene glycol treatment indicate that the acid treatment affected the structure of the components and that the interlayer spaces expanded. Furthermore, acid treatment with H_2SO_4 0.1N, dissolved the major impurities such as calcite, quartz and dolomite for both materials, as well as the traces of smectite and interstratified illite/smectite in KT2. Thus, illite shows a higher cristallinity in KT2.

Adsorption studies

Effect of contact time and initial dye concentration

The initial concentration of the dye is an important driving force to overcome the mass transfer resistance of the dye from the aqueous and the solid phase. Theshape of the curves for DD3, and KT2 clays is similar and approximately independent on the initial dye concentration. The amount of dye removed by theactivated DD3 and KT2 clays, increase as function of the initial concentration of the dye (from 20 to 200 mg/L)and reaches 22-25 mg/g for the maximum concentration of dye considered in this study.Both clays are efficient to adsorb Derma Blue R67with higher rates for DD3. The adsorption for the activated DD3 and KT2 clayswas rapid in the first 2 min followed by a slow increase until reaching equilibrium after about 10 min. At the beginning, the adsorption rate was very fast as the dye ions were adsorbed on the external surfaces of the clay, until they reached saturation. Then the dye ions entered into the pores of the adsorbent particles and were adsorbed by the internal surfaces of the solid particles. This process took a relatively short time and the adsorption was rapid. Theadsorption capacity increased with increasing initial dye concentration. A similar trend was reported for the adsorption of dyes such as Malachite Green onto treated sawdust(Garg et al. 2003), reactivedyes onto dried activated sludge (Aksu 2001)and anionic dye (Reactive Red 120) on Fouchana clay (Errais et al. 2011).

Effect of pH

The pH is an important parameter modulating dye adsorption efficiency(Bousher et al. 1997).The effect of pH on the adsorption capacity of DD3 and KT2 was investigated between pH 3.0 and 9.0, at 20°C. Generally, at low solution pH, the percentage of dye removal decreases for cationic dye adsorption, while it increases for anionic dyes,due to creation of positively charged adsorption sites. The reverse is observed at a high solution pH.The data obtained in the present work indicate that the adsorption of Derma Blue R67 dye on DD3 clay is unaffected by pH over the whole range explored, and an average value of 2.5 mg/g was observed for the adsorbed amount Qt. This may suggest that the dye adsorption onto DD3 may have mainly occurred on sites which are not pH dependent. For KT2 clay, the adsorption enhancement at pH 3 compared to pH 9 is very slight (0.02 mg/g for C_0 = 20mg/L) and may be related to amphoteric sites. Similar results were reported for the adsorption of anionic dyes by cross-linked cationic starch(Renault et al 2008)and cross-linked quaternary chitosan (Rosa et al 2008).The maximum uptake of Derma Blue R67 on KT2 was found to be at pH 2.This behaviour can be explained on the basis of changes in the surface charge of KT2’s amphoteric sites. At lower pH, the H^+ ion concentration in the aqueous system increased and the surface of KT2acquires positive charge by absorbing H^+ ions. The positively charged surface sites on KT2 favour the adsorption of anionic dye due to the electrostatic attraction, causing an increase in dye adsorption. As the pH of the aqueous system increases, the numbers of negatively charged sites increase by absorbing OH^-ions. As the KT2 surface gets negatively charged at high pH, a significantly high electrostatic repulsion exists between the negatively charged surface of KT2 and anionic dye molecules, leading to a decrease in dye adsorption.Similar results were reported for the adsorption of anionic dyes by cross-linked cationic starch(Renault et al 2008),cross-linked quaternary chitosan (Rosa et al 2008), by pullulan microspheres (Constantina et al 2013) and Diphosphonium-intercalated montmorillonite (Makhoukhi et al 2010).

Effect of clay amount

The effect of the adsorbent dosage (varying from 0.5 g to8 g) on the Derma Blue R67 dye removal was investigated at 20°Cwith a fixed initial dye concentration of 20 mg/ L, at pH 4. Initially,a rapid increase in the adsorption upon increasing theadsorbent dosage is due to a higher number of adsorption sites.In the presence of 1.5 g of the adsorbent, the removal of the dye from the solution was almost completely achieved (99%). However, on increasing the adsorbent load, there is no improvement of the quantity of the dye adsorbed, which means that 1.5 g and 4 g of DD3 and KT2 respectively, are the optimal amounts of clay necessary to remove dye at a concentration of 20 mg/Lcorresponding to 9.88mg/g for DD3 and 2.46 mg/g for KT2. A similar behaviour was observed for cationic starch derivatives (Khalil and Aly 2004)and anionic dyes (Azocarmine B (AzB), Acid Orange 7 (AO), Methyl Orange (MO), Ponceau 6R (P6R), and Congo Red (CR) adsorbed on pullulan microspheres (Constantina et al 2013).

Effect of temperature and thermodynamics

Temperature is one of the most important factors in adsorptionprocess. This was investigated for the adsorption of Derma Blue R67 dye on activated clays as a functionof temperature (20°C– 50°C) (Table 4). Generally,temperature has two major effects on the adsorption process.Increasing the temperature induces an increase in the diffusionrate of adsorbate molecules onto the adsorbent surface, thereby diminishing mass transfer resistance in liquid phase as a result of the reducedviscosity of bulk solution (Dogan et al 2006).The amount of Derma Blue R67 dye adsorbed onto activated KT2 and DD3 clays, increases slightly with the increase in temperature (Table 2). This may be due to increasing the mobility of the dye molecules, and an increased access to the active sites for the adsorption with increasing temperature(Senthilkumaar et al 2006).Thermodynamic parameters such as standardfree energy change (ΔG^0), enthalpy change (ΔH^0) and entropy change (ΔS^0) were calculated using the following equations:

$$\Delta G^\circ = -RT\ln Kc \qquad \textbf{(3)}$$

$$\mathrm{Kc}={}^{\mathrm{qe}}/_{\mathrm{Ce}} \qquad (4)$$

and thevan't Hoff equation

$$\ln\mathrm{Kc}=(\Delta S°/R)-(\Delta H°/RT) \qquad \mathbf{(5)}$$

where, Kc (L/mg) is the equilibrium constant;q_e and C_e arethe equilibrium concentrations of adsorbate in the liquid phase (mg/L) and on the solid phase (mg/g)respectively; T is the temperature in Kelvin, and R is the gas constant (8.314 J/mol K). The values of the enthalpy (ΔH^o) and entropy (ΔS^o) were determined respectively from the slope and intercept of the plot of lnKc versus 1/T. As can be seen from Table 2, the Gibbs free energy of adsorption (ΔG°) is slightly positive, very close to 0 for DD3, and slightly negative for KT2. In both cases, ΔG°slightly decreaseswhen T increases, suggesting that the adsorption process is possible at ambient temperature but morespontaneous at higher temperature,especially for KT2, despite a small increase in the adsorbed amount. The values of the change in enthalpy (ΔH°) were positive, which show thatthe process is endothermic in nature. The positive values of ΔS^oreflect increased randomness at the solid–solution interface during dye adsorption.

Adsorption isotherm

The adsorption isotherm indicates how the adsorbate molecules are distributed between the liquid and the solid phases when the adsorption process reaches an equilibrium state (Adamson 1990). The isotherm data were analyzed by fitting them to theLangmuir and the Freundlich isotherm models (Langmuir 1918, Freundlich 1906)**.**These models are described in Eqs. (**6**) and (**7**), respectively:

Langmuir equation

$$\frac{1}{q_e}=\frac{1}{q_m}+\frac{1}{q_m\,b\,c_e} \qquad \mathbf{(6)}$$

Where C_e is the equilibrium concentration in (mg/L), q_e the amount adsorbed at equilibrium,expressed in (mg/g), q_m the maximum amount adsorbed expressed in (mg/g), and b is the energy of adsorption (Langmuir constant, L/mg). The values of q_m and b were calculated from the slope and intercept of the linear plot Ce/qe versus Ce. The slope $1/q_m$ corresponds to the complete monolayer coverage (mg/g) and the intercept is $1/(q_m b)$.

Freundlich equation:

$$lnqe=lnK_F+\frac{1}{n}lnCe \qquad \mathbf{(7)}$$

Table2. Thermodynamic parameters for the adsorption of Derma Blue R67 onto activated KT2 and DD3 clays at different temperatures (without control of pH)

Clays	T (K)	293	303	313	323
DD3	Qt (mg/g)	2.37	2.48	2.49	2.50
	ln Kc	-0.08	-0.07	-0.06	-0.055
	ΔG° (kJ/mol)	0.19	0.17	0.16	0.15
	ΔH° (kJ/mol)	0.56			
	ΔS° (J/mol)	1.28			
KT2	Qt (mg/g)	2.25	2.26	2.26	2.27
	ln Kc	1.42	1.50	1.72	1.95
	ΔG° (kJ/mol)	-3.45	-3.78	-4.48	-5.24
	ΔH° (kJ/mol)	14.18			
	ΔS° (J/mol)	59.8			

WhereK_F and n are Freundlich constants, calculated from the slope and intercept of the Freundlich plot. It has been shown that an n value between 1 and 10 represents a good adsorption potential of the adsorbent.The values of the Langmuir and Freundlich constants are shown in Table 3 that also gives the correlation coefficient reflecting the adjustments between the experimental data and the data calculated using the Langmuir and Freundlich models respectively.

Our results indicate that the Langmuir model gives the best fit to the experimental data for both DD3 and KT2 clays, which means that the dye molecules form a monolayer on the clay surface. Furthermore, the Freundlich exponent 1/n gives an indication of the favorability of the dye adsorption on the clay. Thus, values of 1/n <1.0 represent favorable adsorption conditions as obtained in the present study, were less than unity, indicating the favorable adsorption of Derma Blue onto DD3 and KT2 (Namasivayam et al 1994).

Adsorption kinetics

The solute uptake rate is an important parameter in the understanding of the kinetic mechanism which controls the adsorption of the dye onto activated DD3 and KT2 clays. This was evaluated using the pseudo-first-order (Lagergren 1898)**,** the pseudo-second-order (Ho and Mckay 1998b), the intra-particle diffusion (Weber and Morris 1963)**,** and the Elovich models according to Eqs (8)–(11):

$$\log\frac{(q_e - q_t)}{q_e} = -\frac{K_1 t}{2{,}3} \quad \textbf{(8)}$$

$$\frac{t}{q_t} = \frac{1}{2Kq_e{}^2} + \frac{t}{q_e} \quad \textbf{(9)}$$

$$q_t = k_i t^{1/2} + C \quad \textbf{(10)}$$

where qt and qe represent the amounts of the adsorbed dye at time t and at equilibrium (mg/g), respectively; K_1(1/min), K_2(g/mg min), and K_i (mg/g min$^{1/2}$) are the rate constants respectively for the pseudo-first order, the pseudo-second order and the intra-particle diffusion models for the adsorption process; t is the time (min); and C is the intercept on the y axis (mg/ g).

Table 3. Langmuir and Freundlich isotherm constants for the adsorption of Derma Blue R67 on the KT2 and DD3 clays (adsorbent amount 4 g, 20 mL of 20–200 mg/L dye solution, without control of pH, agitation time of 120 min).

Models	Equations	clay type	Parameters
Langmuir	$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m\, b\, c_e}$	DD3	q_m= 38.46 b =0.24 R^2 = 0.99
		KT2	q_m= 5.58 b = 0.33 R^2 = 0.92
Freundlich	$lnq_e = lnK_F + \frac{1}{n} lnCe$	DD3	K_F = 0.79 1/n=0.31 R^2 = 0.74
		KT2	K_F = 1.27 1/n= 0.52 R^2 = 0.89

The pseudo-first-order kinetic model describes the adsorption of a solute from liquid solution (Lagergren 1898, Ho and McKay 1998a) and is nowadays widely used in different fields of pollutants adsorption from wastewater. The pseudo-second-order model assumes that the chemisorption is the mechanism of the adsorption of adsorbate on the adsorbent.The values of the parameters obtained from the analysis of data according to the investigated kinetic models are shown in Table 4.The coefficient of determination R^2 was calculated, to evaluate the most appropriate model adjusting the data.The Elovich equation is often used when the adsorbing surface is heterogeneous. The linear form of Elovich equation is given as (Elovich 1959):

$$q_t = 1/\beta\ (\alpha\beta) + 1/\ \beta\ \ln t \quad \textbf{(11)}$$

where α (mg/g min) is the initial adsorption rate constant and the parameter β (g/mg) is related to the extent of surface coverage and activation energy for chemisorption. The values of α and β can be calculated from the plot of qt against ln t. The values of the constants α and β are given in Table 4.

The R^2 values for both clays were found to be higher for the pseudo-first-order and pseudo-second-order models than those obtained for the Elovich model and intra-particle diffusion models. The pseudo-second-order and the pseudo-first-order models describe and fit the experimental data very well, for activated KT2. However, for activated DD3, only the pseudo-second-order model yielded the best fit of the experimental data. Therefore, the adsorption of Derma Blue R67 onto DD3 kaolin can be explained by a chemical sorption process, whereas onto KT2 clay may be two processes were involved in the adsorption of Derma Blue R67 dye.

Table 4. Kinetic parameters of the adsorption of the anionic Derma Blue R67 dye onto clays

Models		Pseudo-first order	Pseudo-second-order	Intra-particle diffusion	Elovich
Parameters	DD3	K_1= +0.161 q_m = 35.62 R^2= 0,81	K_2 = 376.135 q_m =2,37 R^2= 1 qe= 2 ,37	Ki = 0,002 C = 2,35 R^2= 0.75	α= 0,006 β =166.66 R^2= 0,85
	KT2	K_1 = +0.958 q_m = 2.181 R^2= 0.991	K_2 = 121.22 q_m = 2.28 R^2=1 q_e= 2.27	Ki = 0,01 C = 2,154 R^2= 0,238	α = 0,005 β = 200 R^2= 0,533

Electrophoretic mobilities of DD3 and KT2 clays

The electrophoretic mobilities were measured for both activated and non-activatedDD3andKT2 clays, before and after adsorption of the blue dye, in order to determine the surface charge of the clay particles and its evolution in function of pH (Fig.2(a, b) and Fig.3(a,b)).The results indicate that several factors affect the electrophoretic mobility of the clays:

1)The activation makes the clay more hydrophilic and increases itelectrophoretic mobility in the whole pH range investigated.

2)As can be seen in Fig.2(a, b) and in Fig.3(a,b), the adsorption of dye decreases systematically the electrophoretic mobility magnitude ofthe both activated and non-activated clays. The adsorption of dye likely screens and/or reduces the electric charges of the clay.

3) After adsorption of the dye, the electrophoretic mobility of the clay is higherfor the activated as compared to the non-activated sample. This difference in behaviors resultsfrom the clay available adsorption sites created upon activation, and which remain uncovered by the dye molecules.

4) The KT2 clay, whether activated or not, is more hydrophilic than the DD3 clay.

5) The increase in the adsorption of the dye appears to be related to an increase in the specific surface area (due to the activation of the clay), or to an increase in the hydrophobicity of the clay. In fact, the DD3 sample (activated or not) is more hydrophobic than the KT2. Thus, DD3 has fixed more dye molecules than KT2 in both cases (activated and non-activated).

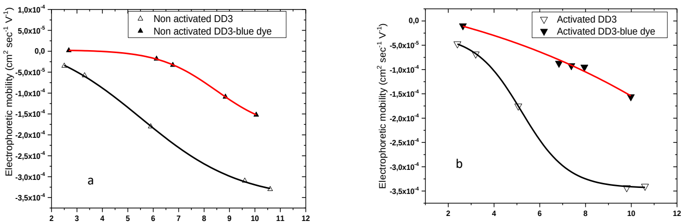

Fig.2. a). Electrophoretic mobilities versus the aqueous phase pH of the non-activated DD3 clay before and after adsorption of Derma Blue R67. b). Electrophoretic mobilities versus the aqueous phase pH of the activated DD3 clay before and after adsorption ofDerma Blue R67

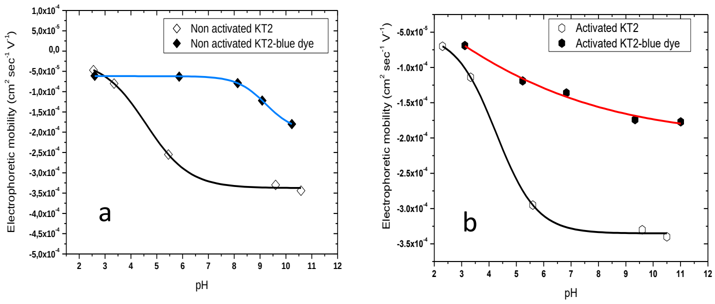

Fig. 3 a. Electrophoretic mobilities versus the aqueous phase pH of the non-activated KT2 clay before and after adsorption of Derma Blue R67. Fig. 3 b. Electrophoretic mobilities versus the aqueous phase pH of the activated KT2 clay before and after adsorption of Derma Blue R67 dye.

Structure of clays after adsorption

Observations by scanning electron microscopy (SEM) were performedto investigatethe change in morphological features of activated DD3 and KT2 before and after dye adsorption (Derma Blue R67). The surface morphology of both clays before adsorption is different from that after adsorption. Activated DD3 has larger pores between particles before adsorption than after adsorption (Fig.6a andb). The same was noticedfor activated KT2 (Fig.4 c and d). Further, the micrographs shown in Fig.4 b and 4 d indicate 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 reliefs of particles and porosity of the aggregates. On the contrary, the clay before adsorption exhibits well distinguishable particles and a porous structure (Fig. 4 a and c).

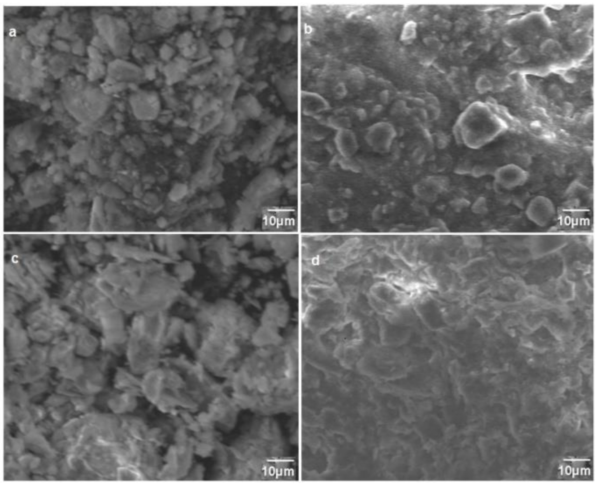

Fig.4. SEM image of DD3 (a) and KT2 (c) activated clays before adsorption of Derma Blue R67 dye, and after adsorption of Derma Blue R67 dye (b:DD3; d:KT2).

Conclusion

Two kaolinite and halloysite-rich kaolin clays, respectively, the DD3 (halloysite-dominant) from DjebelDebagh (Guelma), and the KT2 (kaolinite-dominant) from Tamazert (El Milia region), were activated, and their capacitieswere compared in the removal of effluents'Derma Blue R67 dye used in tannery. Both activated clays were efficient in the removal of the dye from aqueous solution.The synthetic effluent's discoloration by using the acid activated DD3 samplewas more pronounced and the claysurfaces were more developed, as compared to the KT2. The adsorption processes on the bothactivated clays werepossible at ambient temperature, slightly favoured by higher temperatures, and the process wasendothermic in nature. Good agreement pour DD3 was found betweenthe experimental data and the predicted values obtained by using the Langmuir model, indicating the formation of a monolayer of the dye molecules on the clay surfaces. Moreover, the calculated positive values of the entropy's variations results likely from scarce disorder in the adsorbed dye molecules film at the solid–solution interface.The kinetic study indicates that the adsorption of Derma Blue R67 on the halloysite-rich DD3 clay is rather of chemical nature, whereas twotypes of processes may be involved intheadsorptiononto the kaolinite-rich KT2 clay. The overall data show the high potential of the activated kaolin clays for the treatment of dyeing's waste water.

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