Desalination and Water Treatment
www.deswater.com
doi: 10.1080/19443994.2016.1168584

57 (2016) 27954–27968
December

Taylor & Francis
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Discoloration of textile effluent by natural clay improved through the presence of dyeing additives

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Received 22 October 2015; Accepted 10 March 2016

ABSTRACT

The aim of this work was to investigate the possible mechanisms of adsorption of anionic dyes from effluents onto natural clay, and particularly the influence on the adsorption of dyeing additives, released in the effluents with the dyes. Batch experiments with an anionic dye (RR120) at different conditions showed that the adsorption was enhanced at high ionic strength, low pH and in the presence of the additive such as CHT Catalase derived from enzymatic products. On the contrary, the presence of another additive, Duralkan (nitrogenated polycondensate, formaldehyde and metal free), had a negative effect. Experimental methods, such as Fourier transform infrared spectroscopy, electrophoretic mobility and streaming induced potential, allowed us to evidence that CHT Catalase when mixed with RR120 neutralizes the dye and decreases the repulsion between RR120 molecules and the clay negative surfaces, thus favouring adsorption. However, the additive Duralkan does not neutralize the dye, but interacts with the clay, thereby competing with the dye for the clay surface reactive sites, leading hence to adsorption reduction. The efficient discoloration of effluents by clay suggests that in overall, the negative effect of some additives on adsorption is overcome by the positive effect of others. Thus, crude clay may be a promising adsorbent to treat effluents containing dyes and chemical additives.

Keywords: Adsorption; Textile dyeing additives; Natural clay; Streaming induced potential; FTIR; Electrophoretic mobility

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Presented at the International Conference on Industrial Waste and Wastewater Treatment and Valorization (IWWTV 2015) May 21–23, 2015, Athens, Greece

1. Introduction

Water shortage is a short-term crucial concern in the Mediterranean regions subject to arid climate and overuse of water resources in agriculture and industries, such as the textile dyeing activities. Indeed, the textiles and clothing industries in the Mediterranean region consume millions of cubic metres of groundwater, most of which are not recyclable [1]. Moreover, textile dyeing operations use different chemical classes of dye and additional chemicals, depending on the textile produced, which results in a very mixed wastewater [2] containing residual dyes, auxiliary chemicals, surfactants, chlorinated compounds and salts [3]. The dyes are difficult to remove from textile wastewaters because they are resistant to degradation by conventional biological treatments. The degradation is even more difficult when dyes are mixed with additional chemicals [4,5]. Thus, dyes may affect the environment to which they are discharged and may be toxic to various organisms [1,6]. Thereby, improving the treatment of these effluents is a major concern for the environment and human health. It is also a great challenge that would help the Mediterranean countries in the conservation of water resources, for example through the reuse of the treated wastewater for irrigation.

There has been much research devoted to the various methods of treating effluents in the textile industry, as reported elsewhere [7]. The adsorption from water onto activated carbon appears to be the best method for eliminating dye, but although effective, this adsorbent is expensive and difficult to regenerate after use. In the last few years, various organic and inorganic materials have been tested as alternative adsorbents of organic pollutants in effluents [8–25]. Clay minerals are inorganic alternative adsorbents that provide several advantages due to their low cost, abundant availability, non toxicity and high potential of pollutant adsorption. Clays are able to adsorb cations under natural conditions, but their adsorption capacity for anions is small [26,27], unless their surface charge is modified by surfactants, or in acidic conditions that increase the complexation of anions on the amphoteric crystal edges [28–30]. However, several studies have noticed the efficiency of untreated clay for the discolouration of effluents containing anionic dyes, which should be difficult considering the anionic character of the dyes and the negative charge of the natural clay [31–37]. The natural clay used (Fouchana clay), which is a mixture of smectite, kaolinite and illite, was able to remove up to 98% colour from effluents containing anionic dyes mixed with the additional chemicals used in the dyeing process [36,37]. This finding is interesting in the context of sustainable treatment using natural clay, but raises a question: do the chemicals used in the dyeing process, and released in effluents with dyes, have an influence on the adsorption of anionic dyes onto clay, and if yes, to what extent?

In the present work, at first the experimental results are presented that illustrate the efficient treatment of real effluents by the Fouchana clay. Second, to answer to the above-mentioned question and propose possible mechanisms involved in the adsorption processes, we investigated the interaction of Fouchana clay with an anionic dye (RR120 dye), in the presence of two chemical additives, commonly used in the dyeing process of a textile industry, and at different conditions (pH, salinity). These interactions in the clay–dye-additive system were highlighted by Fourier Transform Infra Red spectroscopy (FTIR) analyses, streaming induced potential (SIP) measurements, isotherm modelling and estimation of thermodynamic parameters, knowing the surface properties of the clay and the chemical characteristics of the RR120 dye.

2. Materials

The adsorbent material used in this work is clay from the Northeast of Tunisia, commonly called Fouchana clay. It was characterized in a previous study [33] and consists of smectite, kaolinite and illite. Fouchana clay's physico-chemical characteristics are summarized in Table 1. Two real effluents discharged at the end of two Tunisian textile industry processes (referred to as A and B) were tested: effluent A comes from the dyeing and finishing of cotton fabrics, and effluent B from the denim washing. The processes and chemicals are described elsewhere [34]. The textile dyeing additives and the dye investigated in this study are chemicals commonly used in the cotton dyeing procedure from the "A" industry. The additives are released in the effluent, with the dye molecules that were not fixed on the cotton fabric. They are of different chemical natures and ionic forms and were described more in detail elsewhere [37]. A synthetic mixture of these chemicals, associated with the dye, has been used in the adsorption and desorption experiments.

In order to better understand the interactions in the clay–dye-additive systems, we focused on an anionic dye as adsorbate (C.I. Reactive Red 120). It is a bifunctional azo-based chromogen dye incorporating bis (monochloro-s-triazine) (Fig. 1). Its molar mass is $M_{\mathrm{w}} = 1{,}338\ \mathrm{g\ mol^{-1}}$, and the absorption maximum wavelength in the visible range ($\lambda_{\max}$) is 535 nm.

Table 1
Physical and chemical characteristics of Fouchana clay

Parameter	Unit	Fouchana clay <2 μm fraction
Specific surface	$m^2 g^{-1}$	80[a]
CEC (cationic exchange capacity)	C mol kg^{-1}	34.3[b]
Smectite	%	60
Kaolinite	%	30
Illite	%	10
SiO_2	% (w)	52.1
CaO	% (w)	1.01
Na_2O	% (w)	0.02
Al_2O_3	% (w)	22.7
MgO	% (w)	2.17
Fe_2O_3	% (w)	9.15
K_2O	% (w)	2.46
TiO_2	% (w)	0.916

[a] This study: BET method.

[b] Metson method.

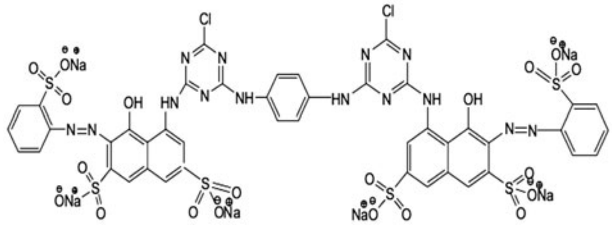


Fig. 1. Molecular structure of C.I. Reactive Red 120 (RR120).

In addition, we focused on two neutral additives in particular, CHT Catalase and Duralkan FSR (Table 2), to investigate different adsorption efficiencies in the clay–dye-additive system [35]. CHT Catalase is an enzymatic auxiliary for destroying residual peroxide after textile bleaching. Duralkan FSR is a nitrogenated polycondensate, formaldehyde and metal free. It is a fixing agent to improve the wet fastness of direct and reactive dyeing.

3. Methods

3.1. Measurement of the physico-chemical parameters of effluents

Concerning the effluents, the pH was determined according to ISO 10523 [38], using a TW 330 pH metre. The concentration of the suspended matter (SM) in the water was determined by filtering (pore size of 1 μm) and drying at 105˚C for 2 h [39]. The chemical oxygen demand (COD, mg O_2 L^{-1}) is the O_2 concentration consumed by the dissolved and suspended oxidizable organic matter in 1 L of water, which was measured according to the standard titration method [40]. The biochemical oxygen demand (BOD_5) was determined electrochemically by the measurement of oxygen consumption of the effluent after 5–7 d incubation at 20˚C [41]. The total phosphorus (Pt) was determined by the colorimetric method using ammonium molybdate [42]. The total Kjeldahl nitrogen (TKN) was determined by the Kjeldahl method after mineralization with selenium [43].

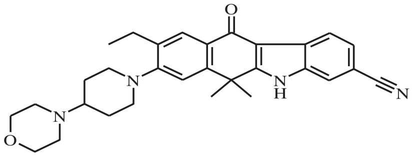
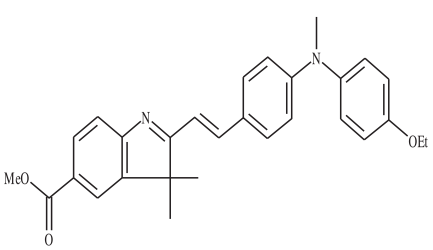
3.2. FTIR analyses

The interactions between the RR120 dye, the additives and the clay were highlighted through FTIR analyses, using a Nicolet 200w model Fourier transform infrared spectrometer. The samples were ground and sieved at 100 μm. The infrared analyses of the clay were conducted on a Perkin–Elmer spectrophotometer using a pressed KBr pellet technique; 1 mg of clay mixed with 100 mg of bromide potassium KBr was homogenized and compressed at 10 T cm^{-2}. The spectra were recorded in the region from 400 to 4,000 cm^{-1} with a spectral resolution of 2 cm^{-1}.

3.3. Microelectrophoresis

The surface charge of the clay particles in function of pH was determined by measurements of the electrophoretic mobility (U_e) of the particles and using Zetaphoremeter II model Z3000 as described elsewhere [44]. A clean electrophoresis chamber was filled with a dilute clay aqueous dispersion submitted to an

Table 2
Characteristics of the studied textile dyeing additives

Additives	Chemical name	Chemical formula	Molecular structure	Molecular weight (g mol^{-1})
CHT Catalase	9-Ethyl-6,11-dihydro-6,6-dimethyl-8-[4-(4-morpholinyl)-1-piperidinyl]-11-oxo-5H-benzo[b]carbazole-3-carbonitrile CAS number 86352-20-7	$C_{30}H_{34}N_4O_2$		482.62
Duralkan	3H-Indole-5-carboxylicacid, 2-[2-[4-[(4-ethoxyphenyl)methyl amino]phenyl]ethenyl]-3,3-dimethyl-,methyl ester CAS number 86352-20-7	$C_{29}H_{30}$ N_2 O_3		454

electrical field for a few seconds. The tension applied in the electrophoretic cell was 100 V, and the pH of the clay aqueous dispersion was adjusted between 2.5 and 12.5 by adding aliquots of either HCl or NaOH solutions. At least three experiments were achieved for each sample. It should be emphasized that no sedimentation was observed during the measurements, even at low pH values, due to the low particle sedimentation rate. The mobility U_e is calculated according to Eq. (1):

$$U_\mathrm{e}\ \left(\mathrm{cm^2\ V^{-1}\ s^{-1}}\right) = 10^{-4}\ v\ \left(\mathrm{\mu m\ s^{-1}}\right)/E\ \left(\mathrm{V\ cm^{-1}}\right) \qquad (1)$$

where v (μm $\mathrm{s^{-1}}$) is the clay particle velocity measured at ambient temperature using the Zetaphoremeter II apparatus and E (V $\mathrm{cm^{-1}}$) the electric field applied to the clay aqueous dispersion.

3.4. SIP measurements

The surface charge evolutions, of RR120 dye in the presence of the additive CHT Catalase, and of the clay in the presence of the RR120 dye mixed with CHT Catalase, were investigated by measurements of the SIP. The measuring cell of the apparatus (Müteck PCD03) is composed of a cylindrical poly (tetrafluoroethylene) (PTFE) container with a PTFE piston inside. An amount of 10 mL of aqueous dye titrated with an additive, or clay dispersion titrated with the dye mixed with additive, was filled into the gap (0.5 mm) between the container wall and the piston, and various amounts of titrants were then added. The clay particles or dye molecule are adsorbed on the container wall, and the aqueous solution is forced to move along the container wall, due to the sinusoidally up and down movements of the piston. This induces the separation of the counter ions from the particle or molecules and their motion and produces a measurable SIP [45]. The SIP's charge and value evolution as a function of the addition of titrant reflects the evolution of the surface charge of the clay particles or dye molecules during titration, and thus informs on the adsorption or not, of the titrant onto the titrated species. The experimental conditions were at natural pH, ambient temperature, with a concentration of 0.48 mg $\mathrm{L^{-1}}$ of RR120 dye solution and 96 mg $\mathrm{L^{-1}}$ of clay suspension.

4. Adsorption and desorption experiments

The experiments for the determination of the physico-chemical characteristics of effluents before and after adsorption onto Fouchana clay were performed by mixing a volume of 1 L of wastewater with 100 g of natural clay in natural pH.

The adsorption experiments were performed in batch at different conditions (pH, temperature, ionic strength). An aqueous solution of RR120 dye, or dye with a chemical additive, was added to the Fouchana clay suspension and agitated for 1 h [34,35]. The supernatant was then collected and centrifuged for 15 min at 3,600 rpm. The concentration in the supernatant solution was analysed using a spectrograph (Jobin Yvon, TRIAX 320), by monitoring the absorbance changes at $\lambda_{\max} = 535$ nm. The amount of dye adsorbed per unit mass of Fouchana clay at time t, q_t (mg $\mathrm{g^{-1}}$) was calculated following Eq. (2):

$$q_t = (C_0 - C_t)V/m \qquad (2)$$

To express the percentage of dye removal (R), the following Eq. (3) was used:

$$R\ \% = 100(C_0 - C_t)/C_0 \qquad (3)$$

where C_0 is the initial concentration of the dye solutions (mg $\mathrm{L^{-1}}$) and C_t is the concentration at any time t; q_t is the dye concentration on the adsorbent at any time t (mg $\mathrm{g^{-1}}$), V the volume of dye solution (L) and m (g) the mass of the clay sample.

The desorption experiments were conducted by immersing the clay loaded with dye and additives in 50 mL of deionized water for 2 h at room temperature. The samples were collected and centrifuged for 15 min at 3,600 rpm, and the dye concentration in the supernatant solution was analysed using the same apparatus as for adsorption experiments.

5. Results and discussion

5.1. Treatment of effluents using the Fouchana clay

The treatment of the effluents by Fouchana clay has proved very effective, since the COD decreased by 95.7 and 83.5% for effluents A and B, respectively, the $\mathrm{BOD_5}$ by 98.5 and 97.5% and the concentration of SM by 82.3 and 84.7% (Table 3). The values of $\mathrm{BOD_5}$ and COD met the conditions for release in public hydraulic, and the pH value after treatment of effluent A corresponded to acceptable values for release in aquatic environment ($6.5 < \mathrm{pH} < 8.5$; NT 106.02, 1989), which was not the case for effluent B. Moreover, the salinity increased slightly, which is likely due to a release of $\mathrm{Ca^{2+}}$ and $\mathrm{SO_4^{2-}}$ ions from dissolution of gibbsite that is present in the Fouchana natural clay.

Table 3
Percentage of change in physico-chemical characteristics of A and B textile dyeing industries' effluents after treatment by Fouchana clay

	Effluent A treated (%) Percentage change	Effluent B treated (%) Percentage change
Salinity (g L^{-1})	+13.3	+50
BOD_5 (mg O_2 L^{-1})	−98.5	−97.5
COD (mg O_2 L^{-1})	−95.7	−83.5
Pt^a (mg L^{-1})	nd	−98.6
TKN^b (mg L^{-1})	nd	−79.6
SM^c (mg L^{-1})	−82.3	−84.7

[a] Total phosphorous.
[b] Nitrogen Kjeldahl.
[c] Suspended matter.

5.2. Adsorption of RR120 dye onto Fouchana clay

The effective treatment of the effluents, and particularly of effluent A containing anionic dyes, raises the problem of the mechanism involved in the successful adsorption of anionic molecules on clay particle surfaces which are themselves negatively charged. In order to better understand this mechanism occurring in real effluents' treatment, we focused on the adsorption of RR120 anionic dye onto Fouchana clay in the presence and absence of additives and on the characterization of the clay surface charge.

5.2.1. Electrophoretic mobility

Measurements of the electrophoretic mobility in aqueous dispersions were taken to investigate the surface charge of the bare clay particles as function of pH and the modifications identified after adsorption of RR120 dye (Fig. 2). The results show that the clay particles have negative surface charges in the pH range investigated (2.5–12.5). Furthermore, as seen in Fig. 2, no isoelectrical point (IEP) is observed for Fouchana clay composed of smectite, kaolinite and illite, contrary to what is observed for the Birdwood kaolinite clay [46]. The magnitude of the electrophoretic mobility also increases from 0.5 to about 4.0 $\mu m\ s^{-1}\ V^{-1}\ cm^{-1}$ when the pH increases from 2.5 to 12.5. This change in electrophoretic mobility with the pH can result from contributions of the aluminol silanol groups and their broken bonds at the clay edge's amphoteric surfaces, and from the silanol groups of the basal surface (permanent charge). Sondi et al. [47], likewise, did not find any IEP for illite and smectite suspensions. The authors speculate that these two kinds of minerals have their surface charge dominated by their permanent negative charge. Relative to the number of permanent charges, there are a small number of amphoteric groups located on the edge of the clay sheets, which may vary in charge as a function of pH. Therefore, these variable surface charges are not numerous enough to cause charge reversal when changing the pH. Thus, considering that the RR120 dye surface charge is negative, as it results from the ionisation of the sulphonate groups, it is expected that increasing the pH would enhance the negative surface charge of the Fouchana particles and hence decrease the adsorption of the dye. On the contrary, lower pH conditions would, however, increase the number of positive charges on the amphoteric clay particle edges and lead to enhanced adsorption of the anionic molecules on these sites.

The clay–dye system after adsorption remains negatively charged throughout the pH range studied, but the amplitude of the variation in pH is much lower

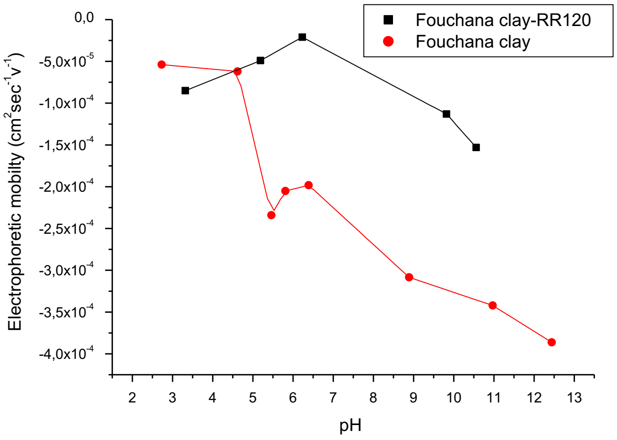


Fig. 2. Electrophoretic mobility ($cm^2\ s^{-1}\ v^{-1}$) of aqueous dispersions of Fouchana clay particles as function of the pH of the aqueous phase, before and after adsorption of RR120 dye.

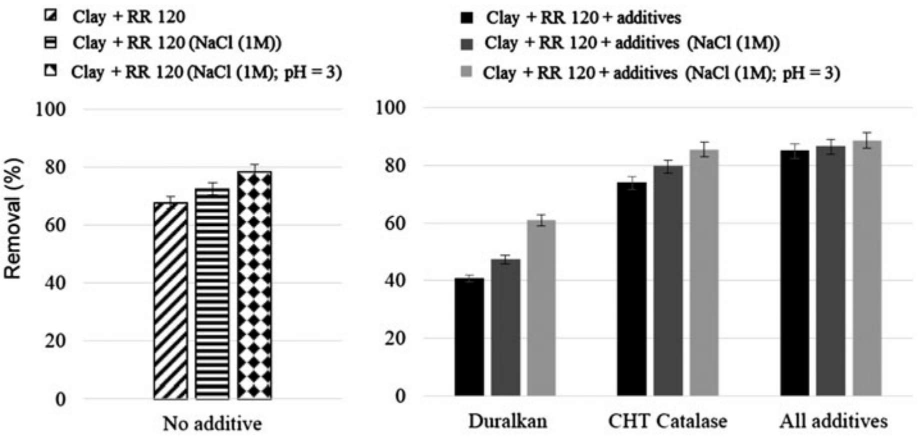


Fig. 3. Removal rate of RR120 dye by Fouchana clay at ambient temperature, at dye concentration of 25 mg/L, (a) in the absence and (b) in the presence of dyeing additives at high ionic strength, *I*, (NaCl, *I* = 1 M) and at pH ≈ 3.

than before adsorption of dye. This seems to indicate a significant negative contribution of the permanent negative charge of the clay, in the measurement of the electrophoretic mobility, as describe Zbik and Frost [46] for kaolinite. This also means indirectly the absence of contribution of the amphoteric surfaces because they have been neutralized through the adsorption of dye.

5.2.2. Effect of additives, ionic strength and pH

Fig. 3 illustrates the results of adsorption experiments when selected additives were mixed separately with the RR120 dye, with the mixture of all additives, and with high ionic strength conditions (NaCl 1 M) and low pH (≈3).

The amount of dye adsorbed by the clay varies with the nature of the added chemical. The mixture of all additives allows a significantly better adsorption of the dye than the only clay (85 and 67%, respectively) and also results in the highest amount of adsorbed dye among all the tested conditions. Taken individually, it appears that the additive CHT Catalase slightly enhances the adsorption of RR120 molecules, compared to the experiment using only clay, whereas Duralkan has a limiting effect, for which the amount of dye adsorbed on clay was only 40%.

The amount of dye adsorbed increased with high ionic strength, either with or without additives (Fig. 3) (77% removal without additive, up to 88% with all additives). This effect of ionic strength may be explained by the Gouy-Chapman theory of the electrical double layer (EDL) at solid–water interface. The EDL thickness decreases when the ionic strength of the aqueous phase increases, which favours the interaction between the adsorbate molecules and the adsorbent particles, and results in an increase in the amount of adsorbed dye. As for high ionic strength, a decrease in pH had always a positive effect on the removal of dye. The maximum amount of dye adsorbed was recorded with all additives (92% removal) (Fig. 3). The enhancement in the removal of dye at lower pH values was expected following the electrophoretic mobility measurements' results (Section 5.2.1); it is explained by a decrease in the amount of OH^- ions which compete with RR120 dye anions in solution, which advantages the adsorption of the dye onto clay.

In general, a high ionic strength (NaCl 1 M), combined with low pH (≈3), enhances the adsorption of RR120 onto clay, whatever the additive. This phenomenon was clearly observed in the case of the addition of Duralkan which showed the lowest efficiency in the adsorption of RR120, but with a significant improvement when ionic force was increased and pH was lowered.

5.2.3. Adsorption isotherms and thermodynamic parameters

The adsorption equilibrium isotherms enable describing how the adsorbate molecules distribute between the liquid and the solid phases at equilibrium [48,49]. The adsorption equilibrium is a dynamic process achieved when the rate at which molecules adsorb onto a surface is equal to the rate at which they desorb [50]. As already observed previously, the amount of RR120 adsorbed on Fouchana is higher in the presence than in the absence of CHT Catalase, and increases in both cases rapidly for low concentrations

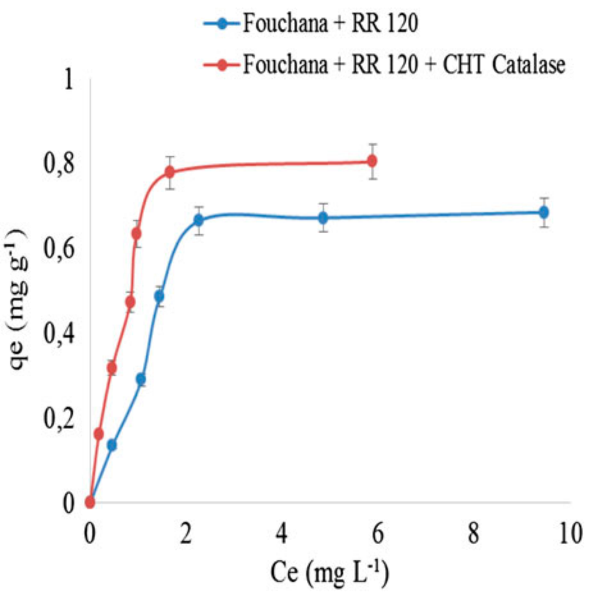


Fig. 4. Isotherm for the adsorption of RR120 dye onto Fouchana clay as a function of dye equilibrium concentration (C_e, mg L^{-1}), in the presence and absence of CHT Catalase.

of dye in solution, until reaching a plateau corresponding to the saturation of the adsorption sites (Fig. 4). The maximum amount of dye removed by 3 g of clay is achieved for a dye concentration of $C_i = 20$ mg L^{-1} and 25 20 mg L^{-1}, in the presence and in the absence of CHT Catalase, respectively. Both adsorption isotherms are of L-type according to the classification of Sposito [51], which is characterized by a slope increasing with the concentration of the substance in solution. This is the result of a relatively high affinity of the adsorbed substance for the solid phase, coupled with a decrease in the number of adsorption sites.

Different isotherm models (Langmuir, Freundlich, Dubinin–Radushkevich) were used to describe the interaction of RR120 dye with the clay adsorbent and in the system clay-RR120-CHT Catalase. Moreover, the correlation coefficient (R^2) and the sum square error (SSQR) were calculated to analyse the fitting degree of the isotherm, with the experimental data.

The Langmuir isotherm assumes that sorption occurs at specific homogeneous sites within the adsorbent [52]. The Freundlich isotherm describes the equilibrium on heterogeneous surfaces and hence does not assume monolayer capacity [53]. The Dubinin–Radushkevich (D–R) isotherm model [54] allows distinguishing between physical and chemical adsorption [55,56]. The parameters calculated for the different models are listed and compared in Table 4, with the experimental adsorption capacity and the predicted adsorption capacity. The values of the regression coefficients and standard errors indicate that the Langmuir model is the best to describe the adsorption of RR120, onto the Fouchana clay, with and without the additive CHT Catalase. These results indicate that a monolayer rather than a multilayer of RR120 molecules is adsorbed on homogeneous sites of the Fouchana clay. The value of the mean adsorption energy at ambient temperature (0.158 kJ mol^{-1}) using the Dubinin–Radushkevich model is slightly lower than the reported energies for ion exchange mechanisms (0.6–25 kJ mol^{-1}) [57,58] indicating that the adsorption process may be, however, rather of a physical than of a chemical nature. In the presence of additives, although the adsorption rate is higher, the RR120 molecules still form an adsorbed monolayer on Fouchana clay. The mean adsorption energy (0.0063 kJ mol^{-1}) calculated by the Dubinin–Radushkevich model is much lower than in the experiment without additives (0.158 kJ mol^{-1}), indicating that much weaker forces

Table 4
Isotherm equations, constants, correlation coefficients (R^2) and sum square errors (SSQR) for the adsorption of RR120 onto Fouchana clay, with and without the addition of CHT Catalase

Model	Equation	RR120	RR120 + CHT Catalase
Langmuir	$1/q_e = 1/(q_m K)$ $(1/C_e) + 1/q_m$	q_m (mg g^{-1}) = 5.5, K_L (mg L^{-1}) = 0.049, $R^2 = 0.998$, SSQR = 0.12	q_m (mg g^{-1}) = 10.9, K (mg L^{-1}) = 0.026, $R^2 = 0.998$, SSQR = 0.048
Freundlich	$q_e = K_F C_e^{1/n}$	$n = 1.039$, K_F (mg g^{-1}) = 0.6, $R^2 = 0.956$, SSQR = 0.09	$n = 1.044$, K_F (mg g^{-1}) = 0.59, $R^2 = 0.994$, SSQR = 0.26
Dubinin–Radushkevich	$q_e = q_m \exp(-\beta\varepsilon^2)$ $\varepsilon = RT \ln(1 + 1/C_e)$	q_m (mg g^{-1}) = 2.3, β = 2E−05, $R^2 = 0.913$, SSQR = 0.06, $E = 0.158$ kJ mol^{-1}	q_m (mg g^{-1}) = 2.2, β = 2E−05, $R^2 = 0.858$, SSQR = 0.09, $E = 0.00632$ kJ mol^{-1}

are needed for the sorption of RR120 molecule on the clay substrate in the presence of the additives.

The influence of temperature on the process of sorption of RR120 onto clay was approached by estimating changes in the free energy of the sorption reaction (ΔG°) given by Eq. (4):

$$\Delta G^\circ = -RT \ln K^\circ \tag{4}$$

where ΔG° is the standard free energy change (J mol^{-1}); R is the ideal gas constant, 8.314 J mol^{-1} K^{-1}; T is the absolute temperature (K) and K° is the equilibrium constant given by the distribution coefficient of adsorbate (q_e/C_e) and the Van't Hoff relation (Eq. (5)):

$$\ln K^\circ = (\Delta S^\circ/R) - (\Delta H^\circ/RT) \tag{5}$$

where ΔH° and ΔS° are the enthalpy and entropy of the sorption reaction, respectively.

The ΔG° values are negative in the temperature range studied (Table 5), which shows the feasibility and spontaneity of the adsorption process of RR120 molecules at ambient temperature, up to 323.15 K. It is, however, to note that the Gibbs free energy increases at higher temperatures, indicating a decrease in the affinity of RR120 towards Fouchana clay.

5.2.4. Infrared spectra after clay–dye-additive interaction

FTIR analyses were performed to highlight the interactions in the clay–dye-additive system. The spectra are presented elsewhere [35], and Table 6 summarizes the identified functional groups and bonds that appear or change in the clay–dye-additive system compared to the bare clay, the clay after adsorption of dye, the anionic dye alone and the additives Duralkan or CHT Catalase alone.

Without additives, infrared spectra show the interaction between Fouchana clay and the adsorbed RR120 dye by a slight intensity increase in the Al–Al–OH group's characteristic band from the clay sheet [59] (Table 6) which is most likely due to the interaction between hydrogen bonds and the N–H group of RR120 molecule. Moreover, the appearance of the absorption band approximately 1,450 cm^{-1}, specific of RR120 molecule's S=O groups, confirms the sequestration of the dye by the clay matrix.

Table 5
Standard free energy (ΔG°) for adsorption of RR120 dye onto Fouchana clay at different temperatures

T (K)	ΔG° (J mol^{-1})
293.15	−1,075
303.15	−307
313.15	−122
323.15	−68

The spectra after adsorption are significantly different when Duralkan or CHT Catalase are mixed with the dye, although both additives are neutral and have approximately the same mass. The major difference is that interactions with the clay are evidenced with Duralkan, whereas no interaction could be observed with CHT Catalase.

In case of adsorption of RR120 mixed with Duralkan, it appears that the C=N group of the Duralkan molecule interacts with the OH group of the clay. Furthermore, the (Al–Al–OH) group of the clay sheet interacts with the (NH) and (C_{ar}–N) groups of the Duralkan molecule. This suggests that two types of reactive sites in the clay sheet interact with the additive. In particular, the Al–Al–OH groups which are situated at the amphoteric surfaces of the clay, and which are the main adsorption sites for the dye as identified previously, may be less available for the dye adsorption. That means that there may be a competition between Duralkan and dye molecules at these reactive sites, in favour of the additive, which may explain the low adsorption rate in presence of Duralkan.

The IR spectra of RR120 adsorbed on clay are identical with or without the presence of CHT Catalase additive during adsorption (Table 6). The specific absorption bands observed without CHT Catalase, which confirm the sequestration of RR120 by the clay matrix, are still observed in the presence of the additive. This tends to indicate that CHT Catalase, contrary to the dye, does not interact with the clay; thus, it does not compete with the dye for reactive sites of the clay as observed with Duralkan. Thereby, the adsorption of the dye is favoured by the maximum availability of the reactive sites of the clay.

5.2.5. Surface charge evolution during adsorption

The measurements of the streaming potential allow studying the evolution of charges of a solution or a suspension of particles, during addition of a titrant. Two experiments of titration were performed in order to better understand the interactions and changes in surface charge in the systems: dye-additive and clay–dye-additive. Thus, in the first experiment, we added CHT Catalase to a solution of RR120 dye, and in the

Table 6
Absorption frequencies of functional groups identified by Infrared (IR) spectroscopy and occurring chemical bonds in the system Fouchana clay-RR120, and Fouchana clay-RR120-additive (Duralkan or CHT Catalase)

	Frequencies (cm^{-1})	Bonds	Comments
Clay + RR120	1,450	υ (S=O) from RR120	The appearance of the absorption band around 1,450 cm^{-1} specific of the S=O group confirms the sequestration of RR120 by the clay matrix
	3,400	υ (Al–Al–OH) from clay	There is a widening of the vibration band of the clay Al–Al–OH group towards 3,400 cm^{-1}; this is probably due to the interaction of hydrogen bonds with the N–H group of RR120
Clay + RR120 + Duralkan	1,670	υ(OH) from clay	There is an extension of the characteristic band of the clay OH group; this vibration band moves from 1,625 towards 1,670 cm^{-1} through interaction with the (C=N) group of the Duralkan molecule
	3,400	υ (Al–Al–OH) from clay	There is a widening of the vibration band of the clay Al–Al–OH group towards 3,400 cm^{-1} by interaction with the (N–H) group of Duralkan molecule.
	2,950–2,900	υ (C–N) from Duralkan	Two absorption bands appear at 2,950 and 2,900 cm^{-1} which are specific of the C–N group; this indicates the sequestration of the Duralkan molecule by the clay matrix
	1,100–1,470	υ (C_{ar}–N) from Duralkan	The absorption bands appearing in the wave range from 1,470 to 1,100 cm^{-1} confirm the interaction of the (C_{ar}–N) group of Duralkan with the clay lattice
Clay + RR120 + CHT Catalase			There are no changes compared to the spectrum of the Clay + RR120

second, the mixture RR120 dye-CHT Catalase was added to a suspension of clay particles.

Fig. 5(a) displays the curve of the induced normalized streaming potential (SIP) of RR120 dye, as function of the volume of CHT Catalase that was added. The SIP of the dye progressively decreased from −1 to −0.1 mV, indicating that the additive CHT Catalase neutralized most of the negative charges of the RR120 dye molecules. The SIP of the clay particles, after addition of the mixed RR120 dye-CHT Catalase

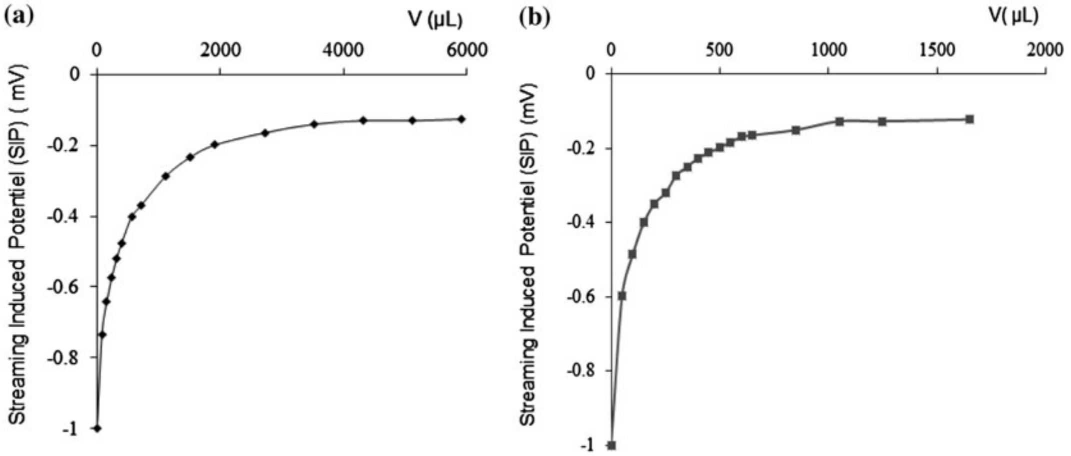


Fig. 5. Normalized SIP: (a) of RR120 dye as function of the volume of CHT Catalase added and (b) of the clay particles as function of the added volume of the RR120-CHT Catalase complex.

(Fig. 5(b)), also decreased from −1 to −0.02 mV, which is also very weakly negative (−0.02 mV). This indicates that the clay particles' surface charge approximates neutrality after the addition of the near-neutral complex, and that adsorption took place. These results may explain the improvement of RR120 adsorption on Fouchana clay, as CHT Catalase neutralizes the negative charges of the RR120 dye and decreases the repulsion between the anionic dye molecules and the clay surfaces with negative permanent charge.

5.3. Desorption studies

The desorption experiments indicate that the lowest desorption rate is observed when all additives together are mixed with the RR120 dye solution. Additionally, when CHT Catalase is added, a limited proportion of dye is released from the clay. Duralkan showed the worst efficiency in RR120 adsorption improvement along with a high desorption rate. It is to notice that desorption rate without additives is also high (Table 7). The mixture of all additives has a positive effect on RR120 molecule retention, which may be explained either by a stronger influence of additives such as CHT Catalase which neutralizes the dye than additives such as Duralkan which hold the reactive sites of the clay, or an interaction between the additives that strengthened the bonding of the dye with clay.

5.4. Adsorption process

From the different approaches presented in this study, several points can be highlighted.

The electrophoretic measurements suggested a major contribution of the amphoteric surfaces of the clay in the adsorption of the anionic dye onto Fouchana clay.

This hypothesis is consistent with the Langmuir model that best describes the experimental results. In fact, this model indicates that the adsorbent clay has a uniform distribution of reactive sites which, according to the zetametry study, would be preferentially localized on the broken bonds at clay edges.

The SIP measurements showed that the additive CHT Catalase interacts with the dye in solution, by neutralizing the negative charged groups. The IR spectroscopy also showed that there was probably no interaction between CHT Catalase and the clay, thus leaving reactive sites on the clay sheet, free for the adsorption of dye. Thus, the enhancement of dye adsorption onto clay in case of addition of CHT Catalase to the dye solution may result from two phenomenons: (1) interaction between the dye molecule and the additive prior to adsorption, rendering the dye molecule less negative and (2) no interaction of the additive with the clay and thus, no competition with the dye for reactive sites on the clay surface. This high availability of reactive sites may explain the low desorption, as the dye molecule may have several hooks sites and thus be more strongly retained.

In the case of the additive Duralkan, the IR spectroscopy showed that the additive interacted with the clay rather than with the dye. Thus, Duralkan may not have been able to reduce the negative charge of the dye molecule as did CHT Catalase, probably due to a lack of active sites that have hindered its electrostatic interaction with the RR120 dye. Moreover, the strong interaction of the additive Duralkan with the clay may have blocked adsorption sites which were no more available for the dye. Therefore, it did not favour the adsorption of dye onto clay. Furthermore, the desorption study showed that the retention of the dye by the clay was weaker than when CHT Catalase is added, either because the bonds were weaker, or because the large dye molecule could not cling to multiple reactive sites because they were lacking.

The mixture of all the additives improved the adsorption of dye, more than did the CHT Catalase, which indicates a synergic effect of the additives that favour adsorption. Moreover, the additive Duralkan, although limiting the adsorption, did not cancel the positive effect of the efficient additive CHT Catalase.

Table 7
Desorption rate of RR120 dye, compared to the adsorption rate on Fouchana clay as a function of the nature of the additive

	Desorption rate (%)
Fouchana clay + RR120	29
Fouchana clay + RR120 + Duralkan	22
Fouchana clay + RR120 + CHT Catalase	9
Fouchana clay + RR120 + all additives	6

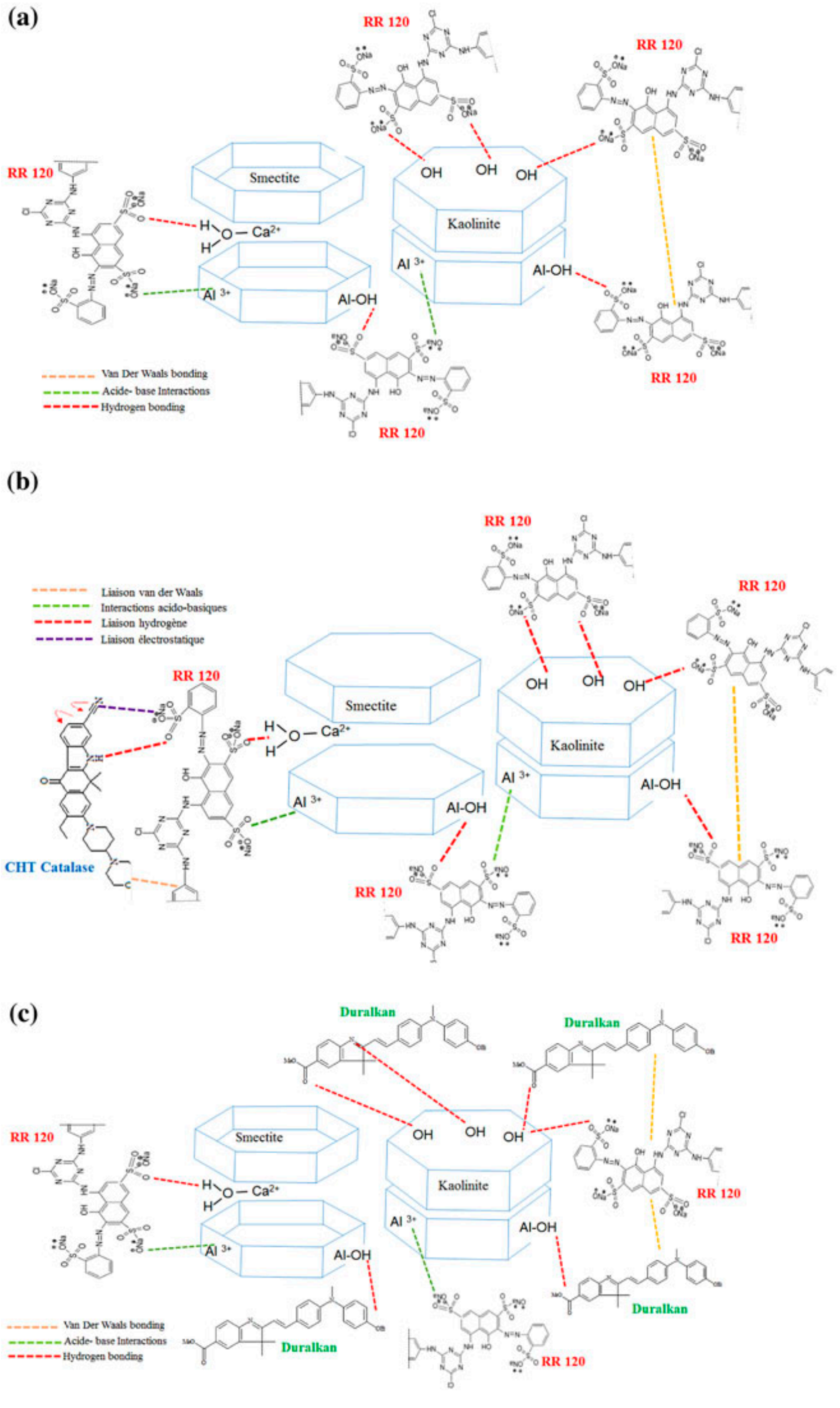


Fig. 6. Adsorption processes on smectite and kaolinite clay sheets (a) of the RR120 dye molecules, (b) of RR120 in the presence of the additive CHT Catalase and (c) of RR120 in the presence of the additive Duralkan.

The different results and hypotheses presented above have allowed making assumptions of mechanisms of interaction resumed by a schematic illustration (Fig. 6(a)–(c)).

5.4.1. Interaction between Fouchana clay and the RR120 dye molecule

Fouchana clay consists essentially of smectite and kaolinite clay minerals. Thus, the adsorption of the dye molecule could be explained by the interactions of different types depending on the clay type (Fig. 6(a)).

In the case of smectite:

(1) Hydrogen bonds between the SO_3^- groups of the dye and the hydroxyl groups of the octahedral layer of the clay and with the hydrated cations Ca^{2+} in the interlayer space (Fig. 10(a)).
(2) Van der Waals interactions between the dye molecules attached by cations Ca^{2+} and those adsorbed at the surface of the clay.

In the case of kaolinite:

(3) Interactions by hydrogen bonding between the SO_3^- groups of the dye and acid groups of the surface at the level of OH outer planes of kaolinite (Fig. 6(a)).

In the case of both smectite and kaolinite:

(4) Acid–base interactions can be established at the edges of the sheets between Al^{3+} (Lewis acid) and SO_3^- groups of the dye (Lewis base).

5.4.2. Interactions between Fouchana clay and the complex RR120-CHT Catalase

The dye-CHT Catalase expected interactions may be electrostatic interactions, hydrogen bonds or Van der Waals interactions (Fig. 10(c)). The move by intramolecular electron pair conjugation of nitrogen in the additive CHT Catalase may create positive charges that favour the electrostatic attraction of the SO_3^- groups of RR120 dye molecules. The SO_3^- groups of RR120 dye may also be linked by hydrogen bond with the NH group of the additive CHT Catalase. These dye-additive interactions tend to neutralize the negative charge of the dye molecules, and therefore induce the weakening of dye–dye, but also of dye–clay repulsions. Moreover, as shown in Fig. 6(b), several types of interactions may occur simultaneously between the RR120 dye molecule and CHT Catalase, due to the big dye molecule size, thereby strengthening the dye-additive combination, and ensuring the neutralization of negative charges. In that situation, the nearly neutralized RR-120–CHT Catalase complex may more easily overcome the repulsion with the negative charged surface of the clay, and adsorption may be facilitated. IR spectroscopy suggested that no interaction may occur between CHT Catalase and the clay, only RR120 dye seems to interact with the clay, thus the adsorption of the dye molecule associated with the additive could be explained by the same interactions as described previously for the system clay–dye (Fig. 6(a)).

5.4.3. Interactions between Fouchana clay, RR120 and Duralkan

Contrary to CHT Catalase, it is assumed that Duralkan did not interact with the dye but directly with the clay surface at different sites (Fig. 6(c)):

(1) Hydroxyl groups at the broken edges of the sheet of kaolinite and smectite.
(2) Acid groups of the surface at the level of OH outer planes of kaolinite.

The reactive sites remaining for the adsorption of the dye may be hydrogen bonds with a $H_2O\text{-}Ca^{2+}$ group of the clay (in the interlayer space of the smectite), or Al^{3+} (Fig. 10), and the sites left by the Duralkan molecules at the level of OH outer planes of kaolinite, and hydroxyl groups at the broken edges of the sheet of kaolinite and smectite.

6. Conclusion

In this research, we investigated the influence of chemical additives present in the dyeing wastewaters, on the effluents treatment by adsorption, and we investigated particularly the adsorption of an anionic dye, onto natural clay. The results showed that the adsorption capacity of the clay was enhanced in the presence of an additive derived from enzymatic products (CHT Catalase). On the contrary, the presence of the additive Duralkan reduces the adsorption of the dye on clay. Further, the adsorption rate was improved at high ionic strength and at low aqueous phase pH values. In the presence of CHT Catalase, the anionic dye molecules tend to be neutralized and may thus easily overcome the repulsion interaction occurring between them and the negatively charged clay surface, hence enhancing their adsorption on the mineral. Duralkan additive, on the contrary, does not neutralize the dye molecules, but it interacts with the clay, thus making the adsorption harder for the dye, as resulting from the lack of reactive sites on the clay surface. Nevertheless, after all, it seems that the positive effect on the dye adsorption brought by the CHT Catalase was not overcome by the negative effect observed in the presence of the other additives in the real effluent.

The overall data showed that naturally existing clay may be promising adsorbents for the effluents treatment in the textile dyeing industry that release dyes and various chemical additives. Moreover, the additives, and the aqueous phase high ionic strength conditions, contribute to the efficiency of colour removal, which is in line with a more sustainable treatment without pre-treatment of the adsorbent clay.

Acknowledgements

This work was performed within the framework of the PHC UTIQUE French-Tunisian project (12G21002) with support from the French Ministries of Foreign Affairs (MAE) and Education and Research (MESR), and the Tunisian Ministry of Higher Education and Scientific Research.

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