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Equilibrium, kinetics and thermodynamics studies of textile dyes adsorption on modified Tunisian clay

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Abstract: The adsorption capacity of two anionic textile dyes (RR120 and BB150) on DMSO intercalated Tunisian raw clay was investigated with respect to contact time, initial dye concentration, pH and Temperature. The equilibrium data were fitted into Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherms. The kinetic parameters were calculated using pseudo-first order, pseudo second-order, intra-particle diffusion and Elovich kinetic models. The thermodynamic parameters (ΔH°, ΔS° and ΔG°) of the adsorption process were also evaluated.

Keywords: Tunisian clay, DMSO, adsorption isotherm, kinetics model, anionic dyes.

Introduction

The pollution of water and soil, accidentally or willingly, by some chemicals products from industry (dyes, heavy metals, phenols, ...) or agriculture (pesticides, fertilizer, ...) is the main source of environmental degradation. Textile industries produce large amounts of wastewater containing high concentrations and unfixed number of dyes, salts and other organic compounds. This is one of the major industrial sources of water pollution in developing countries. In Tunisia, 2094 textile industries reject approximately 7502 m^3 of wastewater per day [1]. It is so crucial to proceed to a pretreatment of wastewater before leaving the industry.

Several methods have been applied to decolorize the wastewater rejected from textile industries. We cite as examples: adsorption [2-5], ion exchange [6,7], flocculation-coagulation [8]…etc.

The use of natural materials and especially clay minerals [9] as adsorbent to remove textile dyes from wastewater by adsorption process seems to be the good way due to the abundance of the clay and the low cost of the process.

In this context, in our previous work [10] we have studied the capacity of a Tunisian raw clay, collected from Nabeul region, to remove two anionic dyes RR120 and BB150 used in a textile industry located at the same region.

The present work concerns the study of the capacity of adsorption of both mentioned dyes on Nabeul raw clay modified by a cationic surfactant: the Dimethyl sulfoxide (DMSO). Various parameters of the adsorption process were highlighted such as pH solution, contact time, initial dye concentration and adsorption temperature. The kinetics data of the adsorption process were fitted by pseudo-first-order, pseudo-second-order, intra-particle diffusion and Elovich kinetic models. The equilibrium data were analyzed using Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherm models. The thermodynamic parameters of the adsorption process were also evaluated.

Materials and Methods

Raw material and reagent

Nabeul raw clay (NRC) was collected from a clay deposit in the region of Nabeul located in the North-East of Tunisia. Mineralogical characterization showed that the raw clay fraction is a mixture of kaolinite and illite with the presence of quartz and carbonate as impurities[10]. The cationic exchange capacity of the raw clay was found to be equal to 74.85 meq per 100g of fired clay[10]. The specific surface area of the raw clay was found equal to 23.26 $m^2.g^{-1}$ and the average pore diameter is of 130.105Å[10].

The compound dimethyl sulfoxide (DMSO) was used without purification. Reagent grade solvents (methanol and ethanol) were used.

The anionic dyes (RR120 and BB150) chosen in this work were provided from a cotton dyeing industry located in Nabeul. The characteristics and chemical structure of both dyes are given in reference[10].

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Functionalization of the raw clay

The functionalized hybrid material was synthesized according to the method in reference[11]. A mixture of 70g of clay, 630 ml of DMSO and 70 ml of distilled water was stirred for 96h at 70°C. The treated clay particles, named NRC-DMSO, were isolated by centrifugation at 4000 rpm for 15 min, washed with distilled water, methanol and ethanol then dried in a vacuum oven at 70°C for 24h.

Characterization of the modified clay sample

X-Ray Diffraction patterns were performed on a bruker X-ray diffraction unit model with radiation Cu-Kα (1.541874 Å) at room temperature in 40kV and 20mA at a scan speed of 1.2°.min^{-1}.

The infrared absorption spectra of a KBr pressed pellet of the powdered clay before and after DMSO intercalation were recorded in the range 4000-400 cm^{-1} using a brucker alpha type spectrophotometer. KBr pellets were prepared by mixing 10 wt% clay with 90 wt% KBr and pressing.

Batch adsorption Study

The adsorption of both mentioned dyes on NRC-DMSO was carried out in aqueous solution in a batch system by suspending a series of 0.3g of the modified clay in 100ml aqueous solution of desired dye concentration. Adsorption experiments were conducted at a constant agitation speed of 450 rpm by varying the pH of solution from 3 to 9, the adsorbent concentration from 0.3 to 6g.L^{-1}, the contact time from 10 to 130 min, the initial dyes concentrations from 20 to 200mg.L^{-1} and the temperature from 20 to 50°C. The solid and liquid phases were separated by centrifugation. The final dye concentration in the liquid phase was determined by a Perkin Elmer LAMBDA 24 spectrophotometer. The amount of dye q_e(mg.g^{-1}) adsorbed per gramme of NRC-DMSO at equilibrium, was calculated using the following equation:

$$q_e = (C_0 - C_e)\frac{V}{m} \tag{1}$$

Where C_0 and C_e (mg.L^{-1}) are, respectively, the initial and equilibrium dye concentration, V(mL) the volume of aqueous solution and m (g) the mass of sorbent.

Modelling

The equilibrium data were fitted using Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherm models.

Langmuir model

Langmuir isotherm model[12,13] assumes monolayer adsorption onto a surface containing a finite number of adsorption sites, uniform adsorption energies and no transmigration of adsorbate in the plane of the surface. Based upon these assumptions, Langmuir model is represented by the following equation:

$$q_e = \frac{Q_0 K_L C_e}{1+K_L C_e} \tag{2}$$

Langmuir adsorption parameters were determined by transforming equation (2) into its linear form:

$$\frac{1}{q_e} = \frac{1}{Q_0} + \frac{1}{Q_0 K_L} \times \frac{1}{C_e} \tag{3}$$

Where C_e is the dye concentration at equilibrium (mg.L^{-1}), q_e is the dye adsorbed amount at equilibrium (mg.g^{-1}), Qo is the maximum monolayer coverage capacity (mg.g^{-1}) and K_L is the Langmuir equilibrium constant (L.mg^{-1}).

Freundlich model

Here formation of multilayer adsorption is possible and the surface is assumed to be heterogeneous[14-15]. Based upon these assumptions, Freundlich model is represented by the following equation (4):

$$q_e = K_F C_e^{\frac{1}{n}} \tag{4}$$

Where K_f is the Freundlich constant (mg$^{1-1/n}$.L$^{1/n}$.g^{-1}) and n is the adsorption intensity.

Freundlich adsorption parameters were determined using logarithmic form of equation (4):

$$lnq_e = lnK_F + \frac{1}{n} lnC_e \tag{5}$$

Temkin model

Derivation of temkin isotherm[16-18] supposes that the decrease of adsorption heat is linear rather than logarithmic and that the adsorption is characterized by a uniform distribution of the bond energies up to a certain maximum binding energy. The model is given by the following equation:

$$q_e = \frac{RT}{b_T} LnK_T + \frac{RT}{b_T} LnC_e \tag{6}$$

Where b_T is Temkin isotherm constant (J.mol^{-1}.g.mg^{-1}), R is the universal gas constant (8.314 J.mol^{-1}.K^{-1}) and T is the absolute temperature (K). Temkin adsorption parameter, b_T, was determined from the slope and intercept of q_e vs LnCe plot.

Dubinin-Radushkevich model

Dubinin-Radushkevich isotherm[19-22] is generally applied to express the adsorption mechanism with a Gaussian energy distribution onto an heterogeneous surface. The model has often successfully fitted high solute activities and intermediate range of concentrations data well. The model is given by the following equation:

$$q_e = q_D \exp(-B_D[RTLn(1+1/C_e)]^2 \tag{7}$$

Where, B_D is a constant related to the adsorption energy and q_D is the theoretical isotherm saturation capacity (mg.g^{-1}). The linear form of equation (7) is:

$$Lnq_e = Lnq_D - B_D[RTLn(1+1/C_e)]^2 \tag{8}$$

Dubinin-Radushkevich adsorption parameters (q_D and B_D) were determined from the slope and intercept of Lnq_e

vs [RT Ln(1+1/Ce)]^2 plot.

The apparent adsorption energy (E_D) can be computed using equation (9):

$$E_D = \sqrt{1/2B_D} \qquad (9)$$

Adsorption kinetic

The kinetic modeling of the adsorption process gives information on the mechanism and the mode of the solutes transfer from the liquid phase to the surface solid phase.

The procedure of the kinetic adsorption study was identical to the adsorption equilibrium study where the aqueous samples were withdrawn at different time intervals and the concentrations of dyes were similarly measured. The dye adsorbed amount, q_t (mg.g^{-1}), at time t was calculated by:

$$q_t = (C_0 - C_t)\frac{V}{m} \qquad (10)$$

where C_t (mg.L^{-1}) is the dye concentrations in the liquid phase at time t.

The kinetics data were fitted using pseudo-first order, pseudo-second order, intra-particle diffusion and Elovich models.

Pseudo-first order model

It has been assumed that in this model constant adsorption rate k_1 (min^{-1}) at time t is proportional to the difference between the adsorbed amount at equilibrium, q_e, and the adsorbed amount at this moment, q_t, and that the adsorption is reversible[23]. Constant adsorption rate is deducted from the model established by Lagergren and coll.[24].

The kinetic law equation is:

$$ln(q_e - q_t) = ln(q_e) - k_1 t \qquad (11)$$

Pseudo-second order model

The equation of the pseudo-second order is often used with success to describe the kinetics of the binding reaction of the pollutants on the adsorbent[25]. This model allows the characterization of the kinetics of adsorption taking into account both the case of a fast fixation of solutes on the most reactive sites and that of a slow fixation on sites with low energy.

The kinetic law equation is:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (12)$$

Where k_2 (g.mg^{-1}.min^{-1}) is the constant adsorption rate of pseudo second-order equation.

Intra particle diffusion model

Intra-particle diffusion model was proposed by Weber and coll.[26]. The molecule is assumed to migrate by diffusion into the liquid phase and enter the pores of the solid phase.

The possibility of intra-particle diffusion was explored by using the following equation[27]:

$$q = k_{id}\, t^{0.5} + I \qquad (13)$$

Where k_{id} is the intra-particle diffusion constant rate (mg.g^{-1}.min$^{-1/2}$) and I (mg.g^{-1}) is a constant which gives information about the thickness of boundary layer.

Elovich model

Elovich equation is also used successfully to describe second order kinetic assuming that the solid surfaces are energetically heterogeneous, but the equation does not propose any definite mechanism for adsorbate-adsorbent. It has extensively been accepted that the chemisorption process can be described by this semi-empirical equation[28].

$$\frac{dq_t}{dt} = \alpha e^{-\beta q_t} \qquad (14)$$

The linear form of this equation[29] is given by :

$$q_t = (1/\beta)\, Ln(\alpha\beta) + (1/\beta)\, Ln\, t \qquad (15)$$

Where α is the initial adsorption rate (mg.g^{-1}min^{-1}), and β a parameter related to the extent of surface coverage and activation energy for chemisorption (g.mg^{-1}). The Elovich coefficients could be computed from the plots q_t vs lnt.

Results and Discussion

Characterization of adsorbent

X-ray diffraction patterns of the original and the modified clay samples are shown in Fig.1. After treatment with DMSO, diffraction peaks relative to the kaolinite phase (7.15Å and 3.58Å) disappear completely, those of illite phase decrease in intensity and new peaks were detected at 11.23Å and 3.99Å. This result indicates that DMSO is intercalated into the interlayer space of kaolinite, and the clay-DMSO composite is formed.

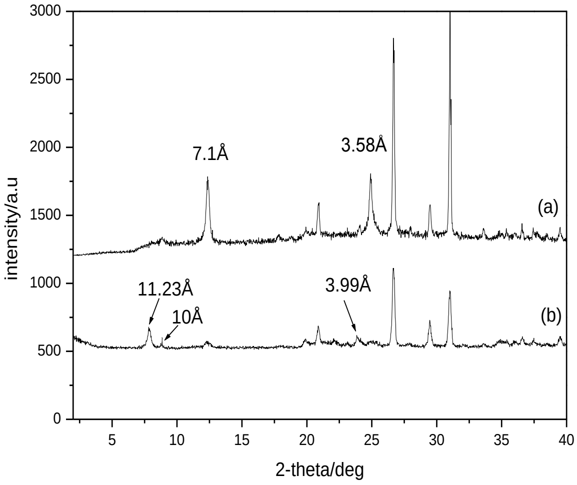


Figure 1. XRD patterns of NRC (a) and NRC-DMSO (b).

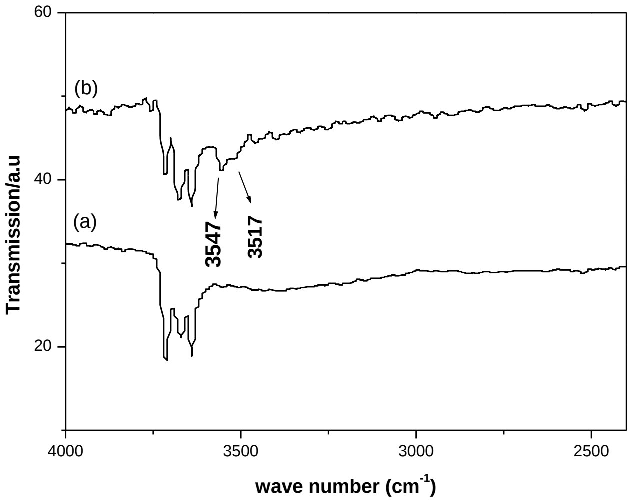


Figure 2. FT-IR spectra of NRC (a) and NRC-DMSO (b).

In Figure 2 are shown the infrared spectra of both NRC and NRC-DMSO. The assignments of the untreated raw clay bands were made in reference[10]. After treatment of the clay with DMSO, two new absorption bands centered at 3547 and 3517 cm^{-1} are observed. These bands are assigned to the inner hydroxyls forming hydrogen bonding with the sulfonyl oxygens of DMSO[30].

Effect of pH on the adsorption dyes

The pH of the solution can affect the adsorption process since it can changes the surface charge of the adsorbent, the ionization degree of functional groups of the adsorbate, as well as the mechanism of adsorption.

To highlight the effect of pH, the isothermal adsorptions of both dyes, RR120 and BB150, were carried out at different pH values from 3 to 9 (Fig.3). It should be noted that the two dyes are not altered in that pH range as shown in reference[31].

As shown in Figure 3, the adsorption capacity depends on pH. The maximum adsorption of RR120 and BB150 on NRC-DMSO is obtained at pH = 3. The decrease of the adsorption capacity when pH increases can be explained by the increase of the hydroxyl groups OH- which compete with the anionic group of both dyes in solution.

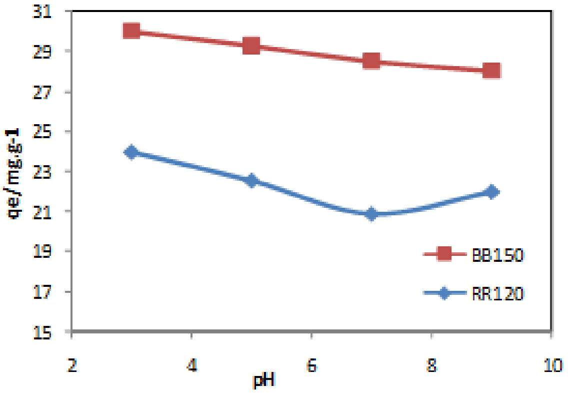


Figure 3. Effect of pH on the adsorption of RR120 and BB150 onto NRC-DMSO.

Batch experiments were carried out at different initial concentrations of both dyes from 20 to 200 mg.L^{-1} and at natural pH conditions. The corresponding curves, shown in Fig.4, are of L-type according to the Sposito[32] classification. This indicates the existence of a relatively high affinity for the solid phase (NRC-DMSO) to both studied dyes. The decrease of the adsorption rate is related to the decrease in the number of adsorption sites. The maximum adsorption capacity of NRC-DMSO is 26.9 mg.g^{-1} for RR120 and 30.12 mg.g^{-1} for BB150.

Effect of contact time

Here, adsorption experiments were conducted at different contact times varying from 10 to 130 min and at natural pH. The initial concentration of dyes was fixed at 80mg.L^{-1}. Corresponding isothermal curves are shown in Fig.5. The adsorption capacity of dyes increases rapidly and linearly with time contact up to 30 min. Between 40 min and 50 min adsorption rate decreases. From 50 min of contact time, the adsorption capacity reaches the maximum (21.6 mg.g^{-1} for RR120 dye and 30.12 mg.g^{-1} for BB150 dye) and becomes independent of contact time. The rapid adsorption during the first 30 min for NRC-DMSO is due to the abundant availability of active sites on the modified clay surface, but with the gradual occupancy of these sites, the adsorption becomes less efficient.

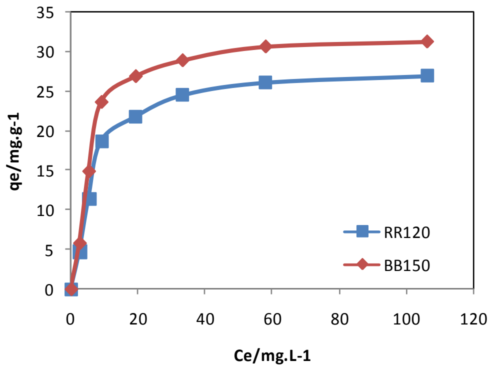


Figure 4. Effect of initial dye concentration on the adsorption of RR120 and BB150 onto NRC-DMSO

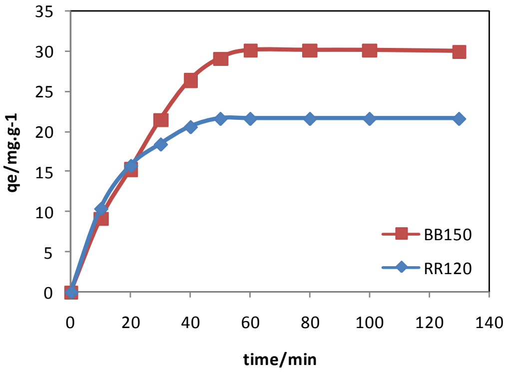


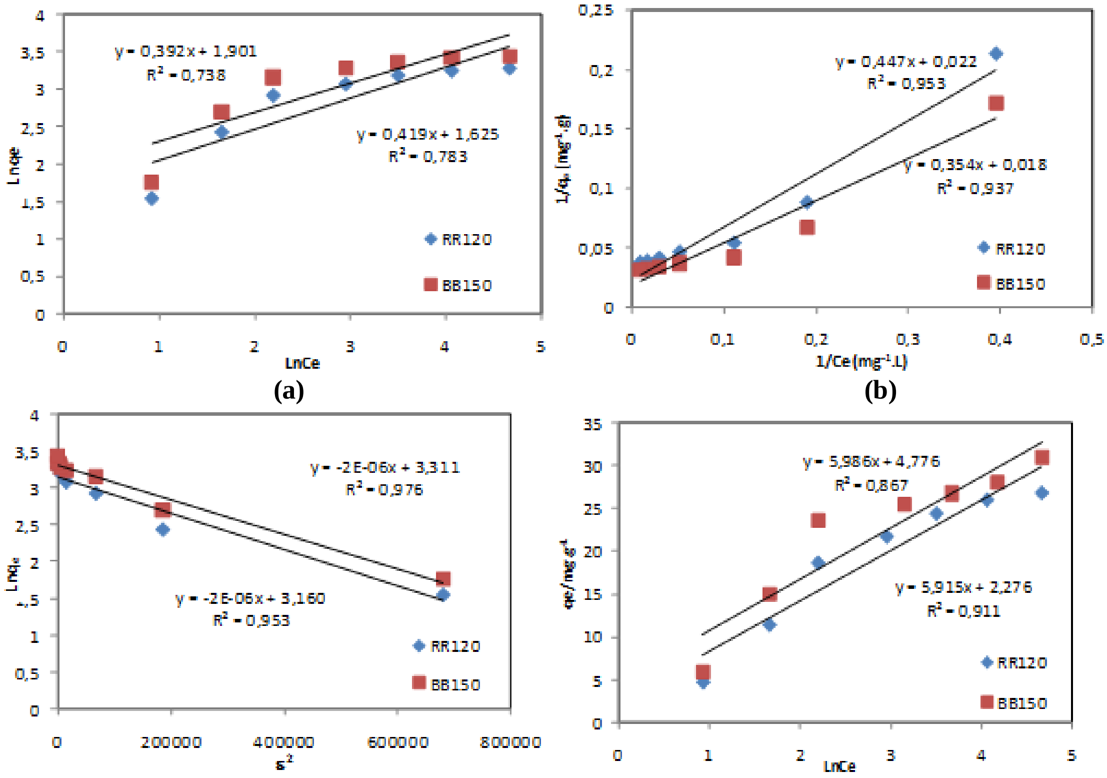
Figure 5. Effect of contact time on the adsorption of RR120 and BB150 onto NRC-DMSO

Adsorption isotherms

Fig.6 shows Langmuir, Freundlich, Temkin and Dubinin - Radushkevich isotherms for both dyes. The characteristic parameters of the different models as well as the correlation coefficients R^2 are listed in Table 1. The values of the regression coefficients indicate that the adsorption of RR120 onto NRC-DMSO can be described in a favorable manner by the Dubinin - Radushkevich and/or Langumir isotherm model where as adsorption of BB150 is described by Dubinin - Radushkevich isotherm model.

Table 1. Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherm constants for the adsorption of RR120 and BB150 onto NRC-DMSO.

dyes	Langmuir parameters			Freundlich parameters			
	K_L	Q_0	R^2	1/n	K_F	R^2	
RR120	0.049	45.454	0.953	0.392	6.692	0.783	
BB150	0.057	50	0.937	0.342	7.455	0.738	
	Temkin parameters			Dubinin - Radushkevich parameters			
	K_T	b_T	R^2	q_D	B_D	E_D	R^2
RR120	2.220	370.196	0.911	27.412	2.10^{-5}	0.5	0.953
BB150	2.43	426.652	0.867	28.210	2.10^{-5}	0.5	0.976



(a) (b)

(c) (d)

Figure 6. Langmuir (a), Freundlich (b), Temkin (c) and Dubinin-Radushkevich (d) adsorption isotherms.

Effect of temperature and thermodynamic study

The adsorption process may be exothermic or endothermic depending on both the adsorbent material and the adsorbed molecules[33]. This can be cheked knowing thermodynamic parameters including the change in free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°).

In order to calculate these thermodynamic parameters corresponding to the adsorption reaction of both dyes, RR120 and BB150, on the modified raw clay NRC-DMSO, several adsorption experiments were carried out at different solution temperature from 20 to 50°C.

In Fig.7 are shown the variation of dyes quantities adsorbed on the modified clay as function of solution temperature. The adsorbed quantity of both dyes decreases significantly with the increase in temperature from 20 to 50°C.

Thermodynamic parameters including the change in free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were calculated from lnKc vs. 1/T curves represented in Fig.8. These parameters were calculated[34] by considering the following equations:

$$K_c = \frac{C_e}{C_0 - C_e} \quad (16)$$

$$\Delta G° = -RTLn(K_c) \quad (17)$$

$$ln(K_c) = -\frac{\Delta H°}{R} \times \frac{1}{T} + \frac{\Delta S°}{R} \quad (18)$$

Where K_C is the equilibrium constant, and T is the solution temperature in Kelvin.

The calculated thermodynamic parameters are illustrated in Table 2. From these results, it can be concluded that, the adsorption process is endothermic in nature for both dyes BB150 and RR120. The low values of adsorption enthalpies of RR120 (2.962 kJ.mol^{-1}) and BB150 (3.682kJ.mol^{-1}) indicate that adsorption is a physical type. Positive values of entropy show that the adsorption of both dyes on the NRC-DMSO was accompanied by an increase of disorder. This result shows that the dye molecules adsorbed on the raw clay surface are organized much random as compared with the situation in the aqueous phase.

Similarly, the negative values of ΔG° show that the process of adsorption of both dyes on the modified raw clay is spontaneous.

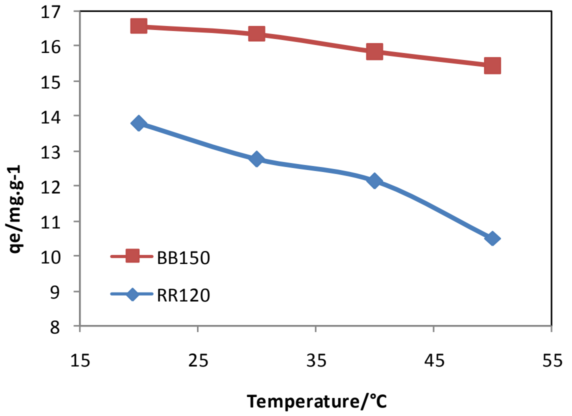


Figure 7. Effect of temperature on the adsorption of RR120 and BB150 onto NRC-

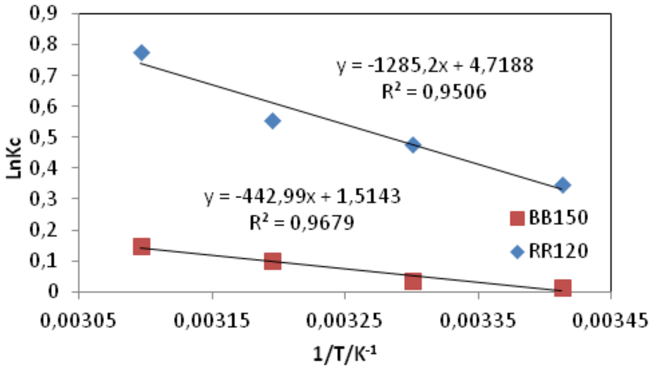


Figure 8. Thermodynamic parameters of RR120 and BB150 adsorption onto NRC-DMSO.

Table 2. Thermodynamic parameters calculated for the adsorption of RR120 and BB150 onto NRC-DMSO.

T(°C)	BB150			RR120		
	ΔH°/kJ.mol^{-1}	ΔS°/J.mol^{-1}.K^{-1}	ΔG°/J.mol^{-1}	ΔH°/kJ.mol^{-1}	ΔS°/J.mol^{-1}.K^{-1}	ΔG°/J.mol^{-1}
20	3.682	12.587	-5.721	2.962	10.126	-809.435
30			-131.591			-1201.685
40			-257.461			-1593.935
50			-383.331			-1986.186

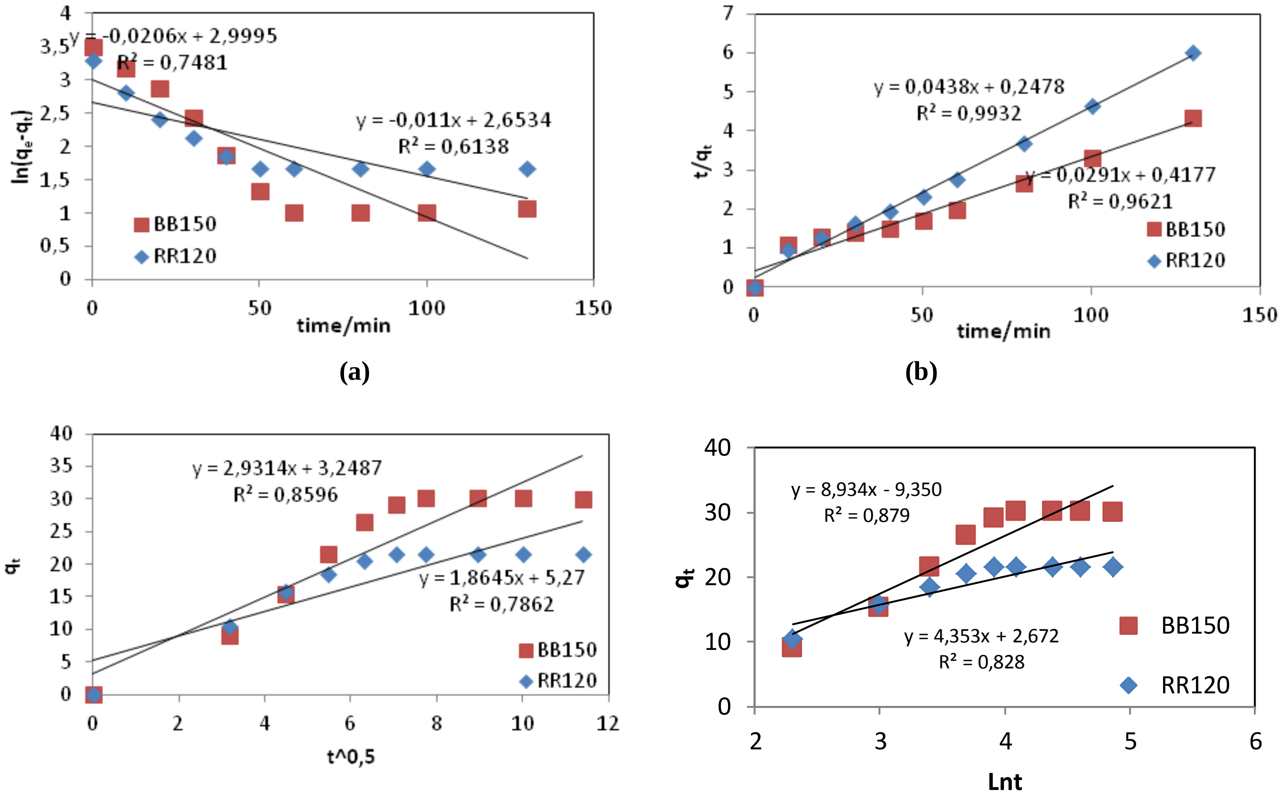
Adsorption kinetics

The experimental kinetic data of adsorption reaction of both dyes on NRC-DMSO, calculated from Eq. (10), were correlated by four kinetic models: the pseudo-first order, the pseudo-second order, the intra-particle diffusion and the Elovish model (Fig.9). In Table 3, are reported the calculated kinetic parameters of the listed kinetic models along with R^2 values. We can note that the pseudo-second order kinetic model fits better the experimental results of adsorption of both anionic dyes with a constant rate k_2 = 0.0003g.mg^{-1}.min^{-1} for RR120 dye and k_2= 0.001g.mg^{-1}.min^{-1} for BB150 dye.

Table 3: Kinetics parameters for BB150 and RR120 dyes adsorption onto NRC-DMSO.

Dyes	**$q_{e\cdot exp}$/mg.g^{-1}**	**Pseudo First-order kinetic model**			**Pseudo second-order kinetic model**		
		k_1/l.g^{-1}.min^{-1}	q_{ecalc}/mg.g^{-1}	R^2	k_2/g.mg^{-1}.min^{-1}	q_{ecalc}/mg.g^{-1}	R^2
BB150	30.12	0.046	20.065	0.748	0.001	34.482	0.962
RR120	26.9	0.025	14.19	0.613	0.0003	23.255	0.993

Dyes	**$q_{e\cdot exp}$/mg.g^{-1}**	**Intra-particule diffusion model**			**Elovich model**		
		k_{id}/mg.g^{-1}.min$^{0.5}$	I /mg.g^{-1}	R^2	α/mg.g^{-1}.min^{-1}	β/g. mg^{-1}	R^2
BB150	30.12	2.284	6.006	0.780	25.88	0.11	0.879
RR120	26.9	1.388	7.765	0.611	8.03	0.23	0.828



(a) (b)

(c) (d)

Figure 9. Pseudo- First order (a), pseudo-second order (b), Intra particle diffusion (c) and Elovish (d) kinetic models plots for the adsorption of BB150 and RR120 onto NRC-DMSO.

Conclusion

The present work was undertaken to investigate the capacity of an interstratified illite/kaolinite clay sample intercalated with dimethyl sulfoxide (DMSO) to remove both anionic dyes RR120 and BB150 from aqueous solution by adsorption. It was shown that:

a- The amount of dye adsorbed onto NRC-DMSO (26.9 g. mg^{-1} For RR120 and 30.12 g.mg^{-1} For BB150) is twice higher than for NRC (11.76 g.mg^{-1} For RR120 and 14.76 g.mg^{-1} For BB150[10]).

b- The adsorption isotherm of NRC-DMSO could be well fitted by Langmuir and /or Dubinin-Radushkevich equation in the case of RR120 dye and Dubinin-Radushkevich equation in the case of BB150 dye.

c- The rise in temperature decreases the adsorbed amount of both dyes on modified clay sample. The adsorption process is found spontaneous, endothermic and characterized by a disorder of the medium.

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