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Physico-chemical characterization and valorization of swelling and non-swelling Moroccan clays in basic dye removal from aqueous solutions

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Abstract

The aim of the present work was to study the application of natural clays to remove a cationic dye (methylene blue (MB) chosen as a pollutant model) from wastewater. Rhassoul-clay and Red clay investigated in this study were extracted from two different sites in Morocco. These clays have different swelling properties. A comparison of their affinity towards cationic dye help to understand the limiting factors controlling the adsorption process. Rhassoul clay and Red clay were characterized using powder X-ray diffraction, Scanning Electron Microscopy, X-ray Fluorescence spectroscopy and surface area measurement (BET). The adsorption capacities of the solids were measured using batch sorption studies as a function of contact time, pH, temperature and initial concentration. Pseudo-second-order model and intraparticle diffusion model were applicables to describe the MB adsorption on both adsorbents. Langmuir and Freundlich isotherms were employed to determine adsorption mechanism. According to the results, the Langmuir model was more suitable to describe MB adsorption on both adsorbents. The maximum monolayer adsorption evaluated with this model is 166.7 mg g⁻¹ and 18.7 mg g⁻¹ for Rhassoul-clay and Red clay, respectively. The temperature exhibited a positive effect on MB adsorption. According to Gibbs energy and enthalpy, the adsorption process was spontaneous and endothermic for both clays, but was more favorable for Rhassoul clay. Hence, Rhassoul clay exhibits much higher adsorption capacity than Red clay. The both clays studied could be potentially used for the removal of cationic dye from wastewater.

Keywords: Effect of temperature; Intra-particle diffusion; Kinetics of adsorption; Moroccan clays; Methylene blue;

63 **1. Introduction**

64 Industries such as textile, paper, plastic, and leather are the main sources of dyes discharge in
65 aquatic systems (Doğan et al., 2007). Due to their important molecular weight and their
66 complex structure, dyes resist to biodegradation. Hence, they accumulate in water stream and
67 present a potential risk for aquatic organisms and humans. Dyes toxicity depends on their
68 chemical form. For example, azo dyes are the most toxic since reduction products are
69 aromatic amines which are carcinogenic compounds (Chen, 2006). Indigo dyes also exhibit
70 significant toxicity. Human exposure to this family of dyes causes skin irritation, gastric
71 disorder, eczema and breathing difficulties (Srivastava et al., 2004). Basic dyes like
72 methylene blue (MB) present also an important menace to human health (Rafatullah et al.
73 2010). In Morocco, textile industry involves 160 000 employees and represents the first
74 industrial employer in the country (Gebrati et al., 2010). Among the textile companies, 29 %
75 are specialized in dying activities. The Moroccan scientific community reported numerous
76 studies on the treatment of effluents from dying industry by using several technologies such
77 as coagulation-flocculation, nanofiltration, and photocatalysis. Abouzaid et al. (2005) studied
78 the combination of coagulation-flocculation-nanofiltration and found that this process
79 exhibited a good ability to remove organic pollutants. Total discoloration of textile effluents
80 was observed with rejection of 98 % of soluble organic matter and 99 % of salts.
81 Photocatalysis was applied by Gebrati et al. (2010). The results showed a removal rate of 53
82 % for chemical oxygen demand COD and 89 % for discoloration of industry effluents.
83 Adsorption process is the most efficient technology for dyes removal. Adsorbents can be of
84 biomass origin such as grass waste, walnut shells, rice husk, algal waste or industrial origin
85 such as red mud and fly ash (Miyaha et al 2018; Hameed, 2009; Chowdhury, 2009; Gupta et
86 al., 2004; Kumar et al., 2005; Vilar et al., 2007). All of them exhibited a high capacity to
87 remove basic dyes but adsorbents from biomass need preliminary treatments to enhance their
88 adsorption efficiency, and adsorbents from industrial origin can generate a secondary source
89 of pollution. Considering this, clays are considered as good candidates to remove cationic
90 dyes since they occur naturally and abundantly, no supplementary treatment is needed, and
91 they do not provide any secondary pollution. Clays present interesting physico-chemical
92 properties such as low permeability, high porosity, high cation exchange capacity and large
93 specific surface area, allowing efficient dyes adsorption (Bentahar et al., 2016; Christidis et
94 al., 1997). Dyes adsorption on clays is generally attributed to an ion exchange mechanism and

linked to the surface specific area of the adsorbent (Li et al., 2011, Bagane and Guiza, 2000). The permanent negative charge related to isomorphic substitution in the interfoliar space of swelling clays improved the adsorption capacity of cationic elements (Azejjel et al., 2009) or dyes (Hong et al. 2009). Regarding non-swelling clays, an increased adsorption of MB was reported when clay was treated with NaOH (Ghosh and Bhattacharyya, 2002). Whatever the kind of clay, the electrostatic interaction between adsorbate and adsorbent is an important parameter conditioning adsorption efficiency (Al-Ghouti et al. 2003). A nowadays challenge is to promote the use of naturally occurring solids, without any preliminary treatment for environmental applications. This is both for an economical point of view, since naturally occurring materials are less expensive than manufactured ones, and for an ecological point of view, since these materials will prevent secondary pollution effects. Recent papers investigated adsorption of dyes on natural minerals (illite or kaolinite) (Mouni et al., 2018; Omer et al., 2018; Özmetina et al., 2018). One difficulty with data provided in these papers is that studies were carried out on only one kind of solid, illite on one hand (Mouni et al., 2018) and kaolinite on the other hand (Özmetina et al., 2018), some other authors investigated the effect of temperature on natural clay mainly composed of a mixture of illite and kaolinite (Omer et al., 2018).

The objective of this work was to provide a complete adsorption study (kinetic effects, equilibrium effects, temperature effects) for two naturally occurring Moroccan clays (Rhassoul-clay and Red clay). Rhassoul-clay and Red clay have different physicochemical properties, and could be promising candidates to remove MB from water. Rhassoul-clay is mainly composed of stevensite, a swelling clay that belongs to the smectite family characterized by a large surface specific area and high cationic exchange capacity. Its texture presents both micro and mesopores. Furthermore, an important negatively charged reaction site was found on its surface related to the isomorphic substitution (Bouna et al. 2010). Therefore, a strong capacity to attract cationic dyes could be expected, as previously shown for methyl violet (Elass et al. 2011). For this kind of clay, the electrostatic attraction was the dominant mechanism controlling the adsorption processes. Other swelling clays like bentonite and montmorillonite also exhibited a good affinity toward cationic dyes (Hong et al. 2009; Li et al. 2011). Red clay consists mainly of kaolinite, a non-swelling clay with a low CEC. Previous study reported that kaolinite with low CEC can be valorized as adsorbent for MB in relatively low concentration (Ghosh and Bhattacharyya, 2002). Red clay is very abundant in North of Morocco and essentially used in ceramic industry. Its valorisation in water treatment

should give an added value to this low-cost mineral resource and give more information about the influence of clay composition for dyes adsorption.

Studying adsorptive behavior of a swelling clay (Rhassoul-clay) and a non-swelling clay (Red clay) towards MB in identical experimental conditions and under various physico-chemical parameters (pH, contact time, temperature, MB initial concentration) could allow us to state about the importance of edge sites and exchange sites reactivity, and to evaluate which parameter is important regarding each kind of surface sites. Finally, considering the whole results one could be able to select which one of natural, low-cost and easy to provide clays could be used in Morocco for dyes removal from wastewater.

2. Materials and methods

2.1 Materials

The adsorbents are clayey materials, extracted from two different sites of Morocco. Red clay was collected on the Mediterranean coast of Morocco in Oued Laou, at 44 km from Tétouan while Rhassoul-clay was collected from Jbel Rhassoul located at the East side of the Middle Atlas Mountains. The samples were used in their natural state without chemical modification. They were crushed and sieved to obtain particle below 0.1 mm. The mineralogical content of solids were determined by diffractometer model Phillips Xpert-pro using $\text{CuK}\alpha$ radiation at 45 kV and a scanning speed of $0.039^\circ \text{ s}^{-1}$. Chemical characterization of the samples was carried out using an X-ray fluorescence spectrometer (WDXRF, S4 Pioneer from BRUKER). BET surface area was measured by a Multi-point Beckman Coulter surface analyzer SA 3100 with N_2 gas as adsorbate. The morphology of the clays was investigated using Scanning Electron Microscopy (SEM) (Quanta FEG 250). The cation-exchange capacity (CEC) was determined according to hexamino-cobalt method (Orsini and Remy, 1976). Zeta potentials of solid particles were measured in clay/water system at ($m/v = 1 \text{ g L}^{-1}$) in pH of suspension and in function of different pH values using a Zetasizer Nano Z (Malvern Instruments).

2.2 Reagents

The MB was used in this study as adsorbate and was purchased from Fisher scientific. Its chemical formula is $\text{C}_{16}\text{H}_{18}\text{ClN}_3\text{S}$. pH was adjusted using micro-volumes of nitric acid (Fluka, 69 % first grade) and sodium hydroxide (Fluka, purity 98%) solutions at 0.01 M. Hexaamminecobalt was used to determine the cation exchange capacity. It was prepared at 5

$\times 10^{-3}$ M from hexaamminecobalt chloride (Fluka, purity $\geq 99\%$). All reagents used in this study were prepared using a high purity deionized water .

2.3 Adsorption studies

The adsorption experiments were realized using batch method at room temperature. Polypropylene tubes of 50 ml were used as reactors. The solid/liquid ratio used for all adsorption studies was 2.5 g L^{-1} and 1.25 g L^{-1} for Red clay and Rhassoul-clay, respectively. These ratios were determined according to recommendations made in Roy et al (1991) EPA procedure. When necessary, the pH of the suspensions was adjusted all along the duration of experiment by adding few drops of dilute HNO_3 or NaOH in order to get a constant pH around 8 for Rhassoul-clay and 5 for Red-clay, corresponding respectively to the natural equilibrium pH of each clay. At the end of experiments, the equilibrium pH was measured and found to be constant for each clay. A tube rotator was used to shake the suspensions at 50 rpm. The centrifugation was made at the end of experiment using a Sigma 3–30 K centrifuge. The supernatants obtained were filtered using $0.45 \text{ }\mu\text{m}$ cellulose acetate filters. The concentrations of methylene blue were measured by a UV-vis spectrophotometer (Metertech) at $\lambda_{\text{max}} = 660 \text{ nm}$. The adsorbed quantity of methylene blue was calculated as follows:

$$q_e = \frac{(C_i - C_f)V}{m} \quad (1)$$

Where C_i (mg L^{-1}) is the initial MB concentration, C_f (mg L^{-1}) is the concentration of MB in final solution, q_e (mg g^{-1}) is the amount of MB adsorbed at equilibrium, m (g) is the mass of adsorbent and V (L) is the volume of solution.

2.3.1 Kinetic experiments

The initial concentration of MB was fixed at 40 mg L^{-1} and 130 mg L^{-1} for Red-clay and Rhassoul-clay, respectively. These conditions were imposed by the differences in the adsorption capacity. The experiments were carried out without adjusting the initial pH of the solutions. Experiments with increasing contact times, ranging from 10 min to 4 hours, were carried out.

2.3.2 Effect of pH

The initial MB concentration used is 40 mg L⁻¹ and 130 mg L⁻¹ for Red-clay and Rhassoul-clay, respectively. The pH values varying from 3 to 12. The contact time was fixed at 60 min and corresponded to the time necessary to reach adsorption equilibrium for both adsorbents.

2.3.3 Effect of temperature

The effect of temperature was investigated at four temperatures 20, 25, 30, and 35 °C. The initial MB concentration used is 40 mg L⁻¹ and 130 mg L⁻¹ for Red-clay and Rhassoul-clay, respectively. The experiments were carried out on a shaking thermostated plate at 50 rpm. The experiments were carried out without adjusting the initial pH of the solutions.

2.3.4 Adsorption isotherms

The adsorption isotherms were realized as a function of MB concentration. The experiments were carried at the natural equilibrium pH of each clay. The initial MB concentration varied from 20 mg L⁻¹ to 100 mg L⁻¹ for Red-clay and 100 mg L⁻¹ to 200 mg L⁻¹ for Rhassoul-clay.

3. Kinetics and isotherm model

3.1 Kinetic models

Adsorption kinetic is primordial to evaluate the equilibrium time necessary for the retention of pollutants from aqueous solution and to select the appropriate adsorption conditions.

In this study, the pseudo-first-order, pseudo-second-order and intraparticle diffusion models were used to investigate the mechanism of adsorption and rate controlling steps. The aim of these models is to formulate the general expression to describe the adsorption kinetics on solid surfaces for the solid-liquid adsorption system. These models were employed in many studies to describe the adsorption of dyes on solid sorbents (Albadarin and Mangwandi, 2015; Borah et al., 2015; Doğan *et al.*, 2007; Eren, 2010; Sun *et al.*, 2015; Yan *et al.*, 2015). Ho and McKay (1999) indicated that application of a sample kinetic model such as first or second-order models to describe the adsorption on solid surface is often incorrect because of the heterogeneity of the solid and the diversity of sorption phenomena. On one hand, they have also reported that the pseudo first order kinetic model was widely applied and they showed that the rate limiting step was mainly diffusion when the process follows the pseudo-first order kinetic model. On the other hand, the pseudo-second order model is based on the assumption that the rate-limiting step may be chemical adsorption involving valence forces through electron sharing or exchanging between sorbent and sorbate.

3.1.1. Pseudo-first-order model

The pseudo-first-order kinetic model was proposed by Lagergren (1898) and is expressed by YalÇin et al., (2005) as follows:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (2)$$

Where K_1 is the rate constant (min^{-1}), q_e and q_t represent the MB adsorbed per unit weight (mg g^{-1}) at equilibrium and at any time t , respectively.

When the pseudo first order kinetic is applicable, the plot of $\log (q_e - q_t)$ against t should give a linear relationship, and consequently K_1 and q_e are obtained from the slope and intercept respectively.

3.1.2. Pseudo-second-order model

The pseudo-second-order kinetic is expressed as follows (Tseng et al., (2003)):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (3)$$

Where k_2 is the rate constant of pseudo-second order ($\text{g mg}^{-1} \text{min}^{-1}$). If the pseudo second-order kinetic is applicable, plot of (t/q_t) against t should give a linear relationship. From this representation, the constants K_2 and q_e can be determined.

3.1.3. Intraparticle diffusion model

The intraparticle diffusion model assumes that intraparticle diffusion is the only rate-controlling step. The mathematical expression for this model is (Kismir and Aroguz, 2011) :

$$q_t = k_3 t^{0.5} + c \quad (4)$$

Where k_3 is the intraparticle diffusion rate constant ($\text{mg g}^{-1} \text{min}^{-0.5}$) and c is a constant. The values of k_3 and c can be evaluated from slope and intercept of the plot of q_t versus $t^{0.5}$. The value of c gives an indication of the thickness of the boundary layer. High intercept value means important effect of boundary layer (Banerjee and Chattopadhyaya, 2017). In some cases the plot q_t versus square root time can show multi-linearity which indicates that several steps occur in the process.

3.2 Isotherms models

Several empirical models were employed to characterize interaction adsorbent/adsorbate. Langmuir and Freundlich models are often useful for describing adsorption process and were consequently applied in this study.

The Langmuir model supposes that the adsorbent surface is ideally uniform and there are no interactions between adsorbate molecules on adjacent sites. While Freundlich model consider that the adsorbent surface is heterogeneous.

The expression of Langmuir isotherm model can be expressed as:

$$\frac{C_e}{q} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \quad (5)$$

Where q_m is the maximum monolayer adsorption, K_L is the equilibrium constant of Langmuir related to the energy of adsorption and C_e is the concentration of solute at equilibrium.

The expression of Freundlich isotherm model can be represented as:

$$q = K_f C_e^{\frac{1}{n}} \quad (6)$$

Where K_f is Freundlich constant gives indication of the adsorption affinity of adsorbents and $1/n$ is an another constant that represents the intensity of adsorption.

4. Results and discussion

4.1 Characteristics of Red-clay and Rhassoul-clay

The mineralogical composition of Red-clay and Rhassoul-clay was characterized in a previous work (Bentahar et al. 2016). As shown in Figure 1, kaolinite, illite, and quartz are the major phases in Red-clay while in Rhassoul-clay a presence of stevensite, quartz, calcite and dolomite was observed. The SEM micrograph of the fine fraction particles of Rhassoul and red clay reveal roughness, irregular layer structure and large aggregates consisting of micrometre-sized platelets. The particles seem to be stuck together. The microstructure is characterized by a randomly oriented platelets and porous surface morphology (Fig. 2). The data given in table 1 shows the proportion of different elements existing in the Red-clay and Rhassoul-clay. These results were obtained by X-ray fluorescence analysis. Red-clay is mainly composed of Al_2O_3 , SiO_2 , Fe_2O_3 , and CaO , while Rhassoul-clay is mainly composed of SiO_2 , and MgO . The specific surface area (SSA) and cation exchange capacity (CEC) are given in Table 2. The swelling propriety of Rhassoul-clay was clearly demonstrated by the

high values of its CEC ($83,3 \text{ meq.}100 \text{ g}^{-1}$) and its SSA ($119 \text{ m}^2\text{g}^{-1}$). In aqueous solution the SSA of swelling clay can reach $800 \text{ m}^2 \text{ g}^{-1}$ (Yukselen and Kaya, 2008). For red clay the measured SSA and CEC are $22.4 \text{ m}^2 \text{ g}^{-1}$ and $35 \text{ meq.}100\text{g}^{-1}$, respectively. Zeta potential was measured at equilibrium pH for the two solids, as illustrated in the Table 2. A net negative charge was detected on the surface of both adsorbents. This parameter can promote the adsorption of MB by an electrostatic attraction between negatively charged surface and positively charged dye molecule.

4.2 Adsorption kinetics

Figure 3 shows the effect of contact time on the adsorption of MB onto Red-clay and Rhassoul-clay. No initial adjustment of the pH-value was performed. Naturally, Rhassoul-clay tends to equilibrate at pH 8 and Red-clay tends to equilibrate at pH 5. The adsorption of the two samples was initially rapid, and then became nearly constant after 60 min. These results are correlated with previous studies which have shown that adsorption equilibrium was reached rapidly, sometimes before 30 min of contact (Almeida et al., 2009; Hajjaji et al., 2006). This fast reaction is interesting when considering natural clays as potential dyes adsorbant. Compared to Red-clay, Rhassoul-clay exhibited a higher uptake of MB. To study the adsorption kinetic of MB onto both clays, three models were used: the pseudo first-order kinetic, the pseudo-second-order kinetic (Fig. 4), and the intraparticle diffusion (Fig. 5). The kinetics parameters and the correlation coefficients of kinetics models were presented in Table 3. For pseudo-first-order kinetic the correlations coefficients obtained were 0.97 and 0.71 for Red-clay and Rhassoul-clay, respectively. While the correlations coefficients of pseudo second-order kinetics were 0.99 for Red-clay and 1 for Rhassoul-clay. Furthermore the q_m values calculated by pseudo-second-order (Table 3) are very consistent with experimental q_m values which confirm that the pseudo-second-order is more suitable to model the adsorption kinetics of Red-clay and Rhassoul-clay than the pseudo-first-order model. These results are coherent with previous studies on methylene blue adsorption kinetics on sepiolite and pyrophyllite (Künce and Şener, 2010; Zhang et al., 2015). Application of the pseudo second-order to our two solids implies that the rate –limiting step may be a chemical adsorption involving valency forces through sharing or exchanging of electrons between adsorbent and adsorbate (Ho and McKay, 1999). Intraparticle diffusion kinetic model is illustrated in figure 5. Presence of two straight lines was observed for Rhassoul-clay and Red clay, indicating that adsorption process of MB took place in two stages. Similar finding was observed by Gil et al. (2011) on pillared clays. The authors observed a decrease of the

diffusion rate when the contact time was increased, and they concluded that the free path of the molecules in the pore was reduced, blocking some molecules during the diffusion process. The first linear section was attributed to the surface adsorption into the micropores and the second linear section corresponded to adsorption on the external surface. The rate constant corresponding to the first linear section was higher for Rhassoul-clay than for Red clay, and the rate constant for the second linear section was lower for Rhassoul-clay (almost zero) than for Red clay (Table 3). Considering Gil et al. (2011) interpretations, we can conclude that adsorption on Rhassoul-clay occurred mainly onto the microporous part of the clay, and occurred both on microporous and on the external surface of Red clay. Compared to pillared clays investigated by Gil et al. (2011) Rhassoul-clay exhibited an interesting diffusion rate, without any surface modification.

4.3 Effect of pH

The effect of pH on MB adsorption onto Red-clay and Rhassoul-clay was investigated under varying pH value from 3 to 12. As presented in the Fig. 6, adsorption capacity of MB by the two adsorbents increased slightly with increasing pH. For Red-clay, a drop of adsorption is observed between pH 3 and 7, while for Rhassoul-clay a slight increase occurs between pH 3 to 5, then a plateau is reached between pH 5 to 7, and a second increase occurs from pH 7 to 12. It is well known that alkaline pH improves significantly dye adsorption (Almeida et al., 2009). This behavior is due to deprotonation of the reactive edge surface sites, provoking an increase in the number of negative charge on the adsorbent surface and consequently improves the adsorption capacity of the cationic dye. In the case of swelling clays, this deprotonation of edge surface sites is combined to the permanent negative charge of the Rhassoul-clay.

To evaluate the impact of pH on surface solid, a measure of surface charge of adsorbents was realized as a function of pH, and without MB. The fig. 7 shows that surface charge of Red clay is highly dependent on the pH, and becomes more negative at high pH. This variation of charge is attributed to the deprotonation of silanols (SiOH) and aluminols (AlOH) groups on edge sites which are highly pH-dependent surface sites. Similar behavior was observed for other aluminosilicates clays (Gücek et al., 2005; Zhao et al., 2003). For Rhassoul clay, pH evolution does not influence significantly the zeta potential. This is due to the permanent negative charge arising from the interfoliar space. From these results we can conclude that

adsorption of MB occurs at the surface of edge sites of Red-clay, whereas it occurs both at the surface of edge sites and in the interfoliar space of Rhassoul-clay.

4.4 Effect of temperature

The determination of thermodynamic parameters is important to understand the effect of temperature on adsorption. $\Delta_R H^\circ$ and $\Delta_R S^\circ$ of MB adsorption on Rhassoul-clay and Red-clay were determined consecutively to experimental data collected at different temperatures.

Knowing that Gibbs Energy depends on enthalpy, entropy and temperature:

$$\Delta_R G^\circ = \Delta_R H^\circ - T \Delta_R S^\circ \quad (7)$$

$$\text{And} \quad K_d = \frac{Q_e}{C_e} \quad (8)$$

where K_d is the distribution coefficient. The adsorption enthalpy $\Delta_R H^\circ$ and the adsorption entropy $\Delta_R S^\circ$ can be calculated with the Van't Hoff equation:

$$\ln(K_d) = \frac{\Delta_R S^\circ}{R} - \frac{\Delta_R H^\circ}{RT} \quad (9)$$

Where R is the universal gas constant ($8.314 \text{ J mol}^{-1}\text{K}^{-1}$). The plot of $\ln(K_d)$ against $1/T$ represented in Fig. 8, is a straight line, hence $\Delta_R H^\circ$ and $\Delta_R S^\circ$ (supposed to be independent of T) can be calculated from slope and intercept respectively.

The effect of temperature of MB adsorption on Red clay and Rhassoul clay was examined at 20, 25, 30 and 35 °C without adjusting pH. Naturally, the pH equilibrated around 8 for Rhassoul-clay and around 5 for Red-clay. Temperature change from 20 to 35°C did not influence the equilibrium pH measured after each experiments. The results (Table 4) show that the temperature increase leads to an increased adsorption capacity of MB for both clays. From 20°C to 35°C, the adsorption capacity (Q) increased of 11% for Red-clay and 15% for Rhassoul-clay. Considering this evolution, the thermal effect is benefic for both solids, and slightly more favorable for Rhassoul clay. This is explained by the swelling properties of this clay. Indeed, a temperature increase can enlarge the expandable layer, consequently allowing an easier diffusion of MB molecules (Weng and Pan, 2007). Negative values of $\Delta_R G^\circ$ were observed for the two clays indicating the spontaneous nature of the adsorption. The values of $\Delta_R G^\circ$ were found to decrease with increase of temperature indicating that the adsorption processes of MB onto the Rhassoul-clay and Red-clay were more favorable at high

temperature. Enthalpies values for Red-clay and Rhassoul-clay were positive and of the same order of magnitude, indicating (i) that adsorption process is endothermic (Almeida et al., 2009; Doğan et al., 2007), and (ii) adsorption is equivalent in terms of energy for both clays. The values of ΔS° calculated by the intercept of the plot $\ln k_d$ versus $(1/T)$ were given as 132.35 J mol⁻¹ for Red-clay and 168.01 J mol⁻¹ for Rhassoul-clay. The positive value of $\Delta_R S^\circ$ reflects the affinity of these two adsorbents for the MB. Entropy values were of the same order of magnitude for both solids.

From these data, we can conclude that adsorption of MB on Red-clay and Rhassoul-clay is a spontaneous reaction, that is favored when temperature is increased. Enthalpy and entropy values were of the same order of magnitude for both solids, indicating that adsorption is thermodynamically equivalent at the surface of both systems. The main difference between the two solids resides in their adsorption capacity (Q).

4.5 Adsorption isotherm

Adsorption of MB on Rhassoul-clay and Red-clay was examined as a function of initial concentration of MB at naturally equilibrated pH (around 8 for Rhassoul-clay and 5 for Red-clay). Initial MB concentration has a negligible effect on equilibrium pH. The results obtained were modeled using two empirical models: Langmuir and Freundlich models. The adsorptions isotherms are presented in Fig. 9. Rhassoul-clay and Red-clay exhibited a good correlation with Langmuir model, suggesting that adsorption is limited with monolayer coverage and the surface is energetically homogeneous. The constants and the correlation coefficients calculated by Langmuir and Freundlich are given in the table 5. From these results Rhassoul-clay is the most effective adsorbent for methylene blue. This clay possesses the highest maximal adsorption capacity (166 mg g⁻¹) compared to the adsorption capacity of MB on Red-clay (18.83 mg g⁻¹). The ability of Red clay to remove MB is coherent with its CEC relatively low. Indeed, adsorption occurs only on the edge surface sites of the clay. The comparison of adsorption capacity of Rhassoul-clay and Red clay with others adsorbents reported in literature is presented in table 6. Adsorption capacity of Rhassoul clay was high when compared to the majority of adsorbents. While Red clay exhibited a comparable adsorption capacity with some natural adsorbents. Al-Futaisi et al. (2007). The adsorption properties of Rhassoul-clay is clearly linked to its swelling properties: its important cation exchange capacity resulting from the high negative charge at the clay surface due to the isomorphous substitution (Chen et al., 1999; Hong et al., 2009). Adsorption mainly occurs by

ion exchange on the interfoliar space of the Rhassoul clay. These findings are in agreement with some previous studies (Al-Futaisi et al., 2007; Li et al., 2011). However, some researchers highlighted a discrepancy between methylene blue adsorption and cation exchange capacity (Hajjaji and El Arfaoui, 2009; Ruiz-Hitzky and Serratosa, 1998). The nature of exchangeable cation affects drastically the distribution of methylene blue on the clays surface. Cations with an important hydration capacity such as Na^+ , Li^+ , Mg^{2+} , Ca^{2+} improve adsorption of cationic dye by ion exchange (Cenens and Schoonheydt, 1988; Yukselen and Kaya, 2008). On the other hand, MB intermolecular interactions can influence adsorption process (Klika et al., 2007). Indeed, MB has a tendency to form aggregates in the solution at high equilibrium concentrations. At low concentration (7×10^{-6} M) the monomer species are predominant (Hajjaji et al., 2006). At higher concentrations, MB aggregates as dimers and trimers in the contact of clay particle surfaces (Li et al., 2011). Formation of dimers and trimers of MB at the surface of Rhassoul-clay could explain that adsorption do not reach a plateau in figure 9b (as a function of initial concentration), contrary to figure 9a. Regarding the experimental conditions used for adsorption isotherms on Rhassoul-clay, MB was introduced in concentrations ranging from 3.10^{-4} M to 6.10^{-4} M, which are significantly higher than the concentration recommended by Hajjaji et al. (2006). Since the nature of clay and nature of exchangeable cation influence relatively the ratio of dimers and trimers species, this should be deeply investigated. The dimension of MB molecule and its orientation are the key parameters to understand the adsorption mechanism. It is assumed that MB molecule presents a rectangular shape with dimensions $17 \text{ \AA} \times 7.6 \text{ \AA} \times 3.25 \text{ \AA}$ (Hang and Brindly, 1970). The orientation of this molecule was found to be arranged in tilted or perpendicular fashion (Kaneko et al., 2003; Bujdak et al., 2003). This orientation is appropriate to the basal plan of clay surface, particularly swelling clays.

5. Conclusion

The main factor controlling the adsorption processes of methylene blue on Rhassoul clay and Red clay is adsorption capacity of the clay, pH, and initial concentration of methylene blue. The kinetic adsorption of MB on the two adsorbents is important and equivalent. Adsorption was found to be spontaneous and thermodynamically equivalent for Rhassoul clay and Red clay. Nevertheless, this point should be deeply investigated since two different kinds of surface sites are concerned (exchange sites for Rhassoul clay and edge surface sites for Red clay), justifying that we were expecting thermodynamic discrepancies. Adsorption was found to be more favorable in the pH range from 7 to 12 for both clays. Regarding the

results obtained in this study, Rhassoul clay is the most efficient adsorbent. Red clay considered also as good adsorbents for MB, This clay exhibited an adsorption capacity better than some natural adsorbents recognized by their high adsorption potential like zeolite(see table 6). Thus the both of clays can be used as a low cost adsorbent for the removal of cationic dye from wastewater. Nevertheless, adsorption reversibility should be deeply investigated to confirm the efficient of these clays are, and to confirm which of surface sites (ion exchange or edge surface) are sufficiently strong to prevent release of cationic dye according to physico-chemical conditions.

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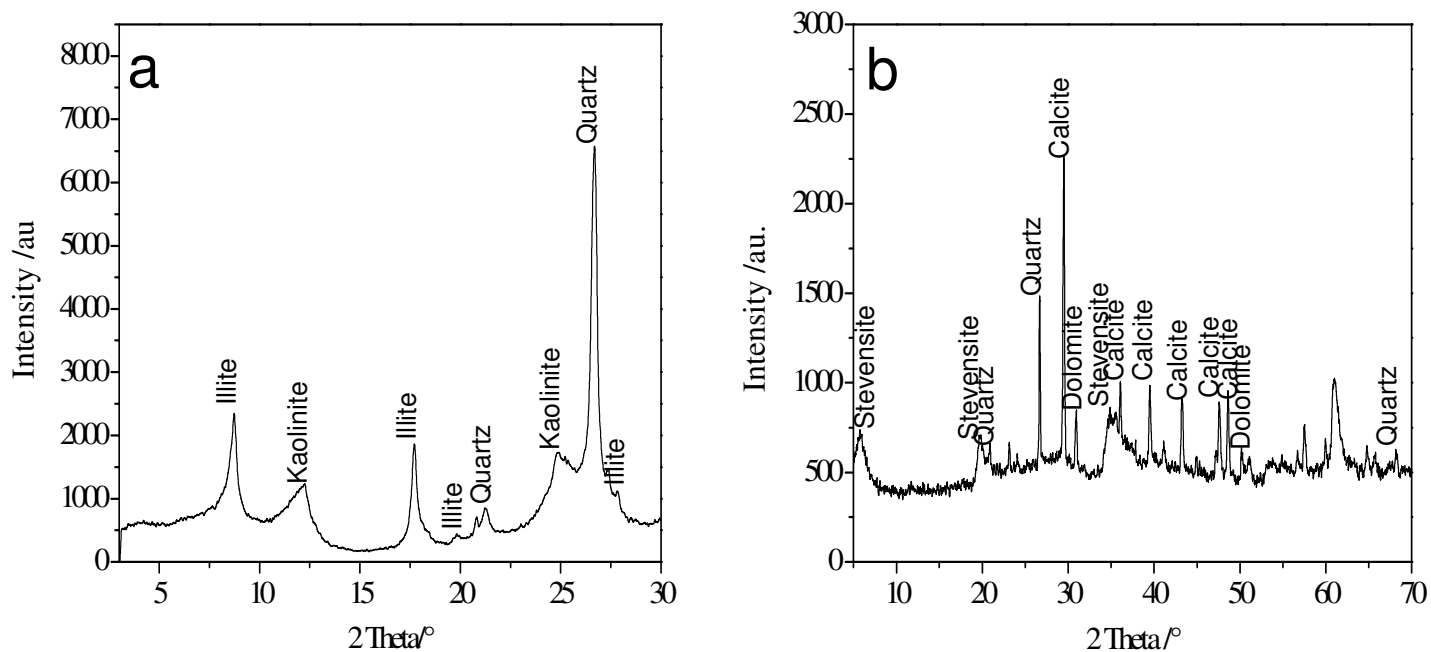


Fig. 1 X-ray patterns of Red-clay (a) and Rhassoul-clay (b)

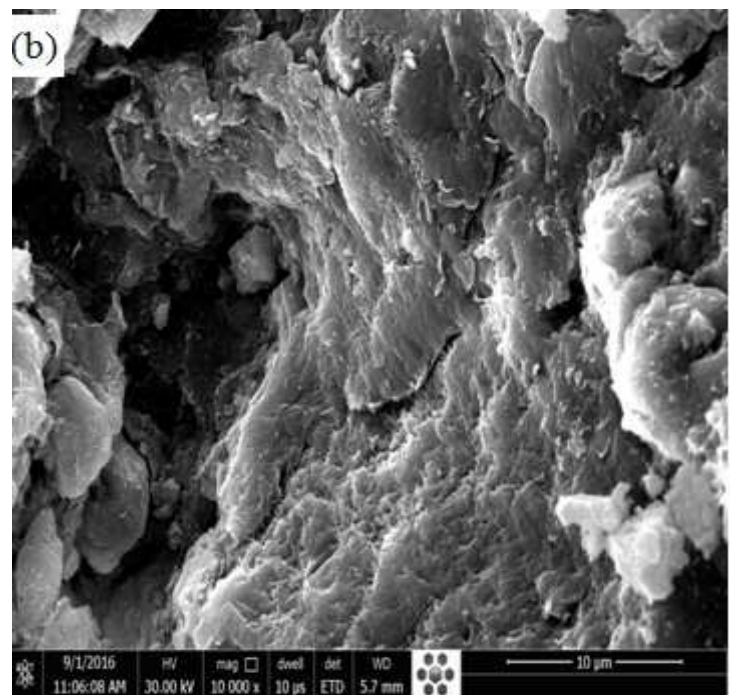
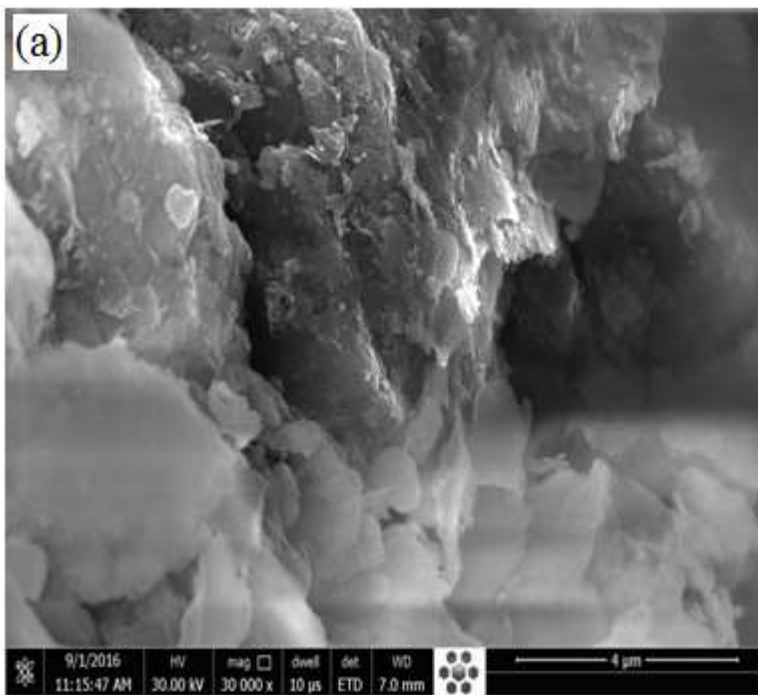
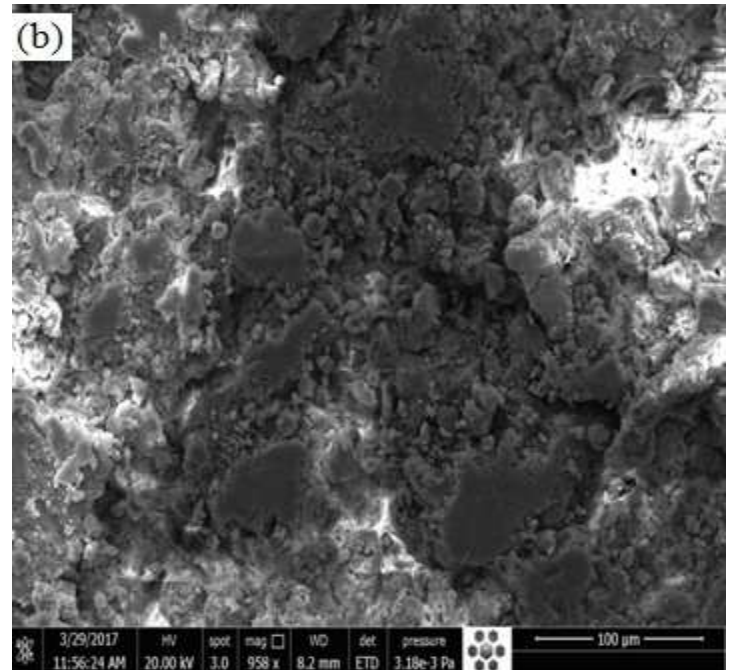
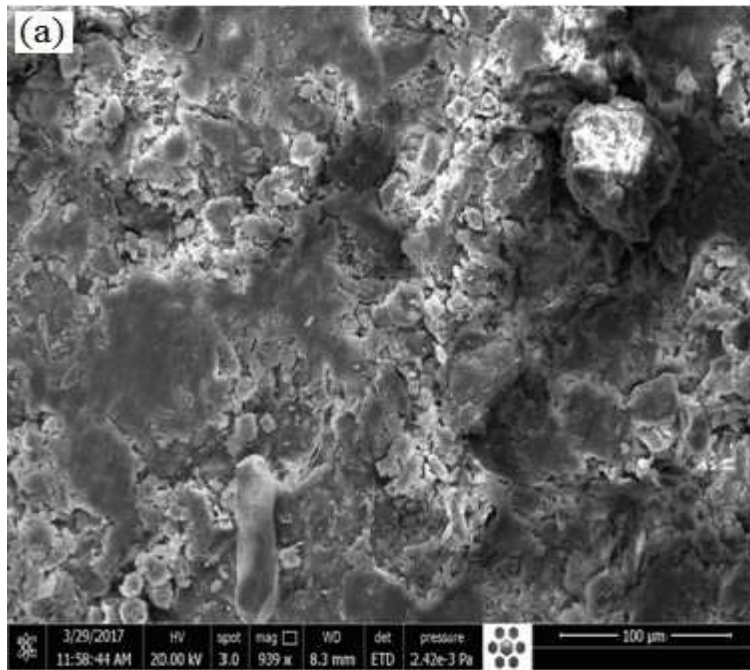


Fig. 2 SEM micrographs of Red clay (a) and Rhassoul clay (b)

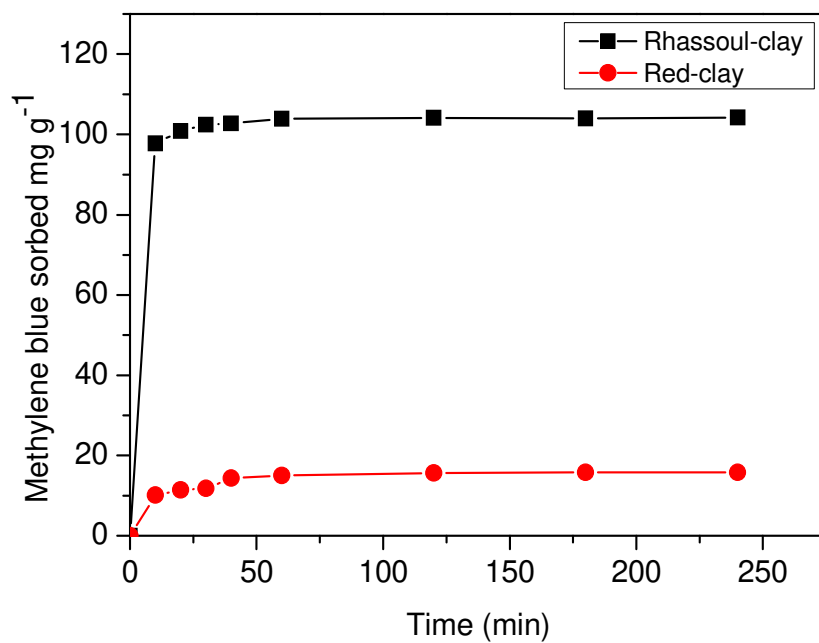


Fig. 3 Methylene Blue sorption on Red-clay and Rhassoul-clay as function of time. Red clay ($m/v = 2.5 \text{ g L}^{-1}$, $[\text{MB}] = 40 \text{ mg L}^{-1}$, $\text{pH}_{\text{eq}} = 5$), Rhassoul-clay ($m/v = 1.25 \text{ g L}^{-1}$, $[\text{MB}] = 130 \text{ mg L}^{-1}$, $\text{pH}_{\text{eq}} = 8$).

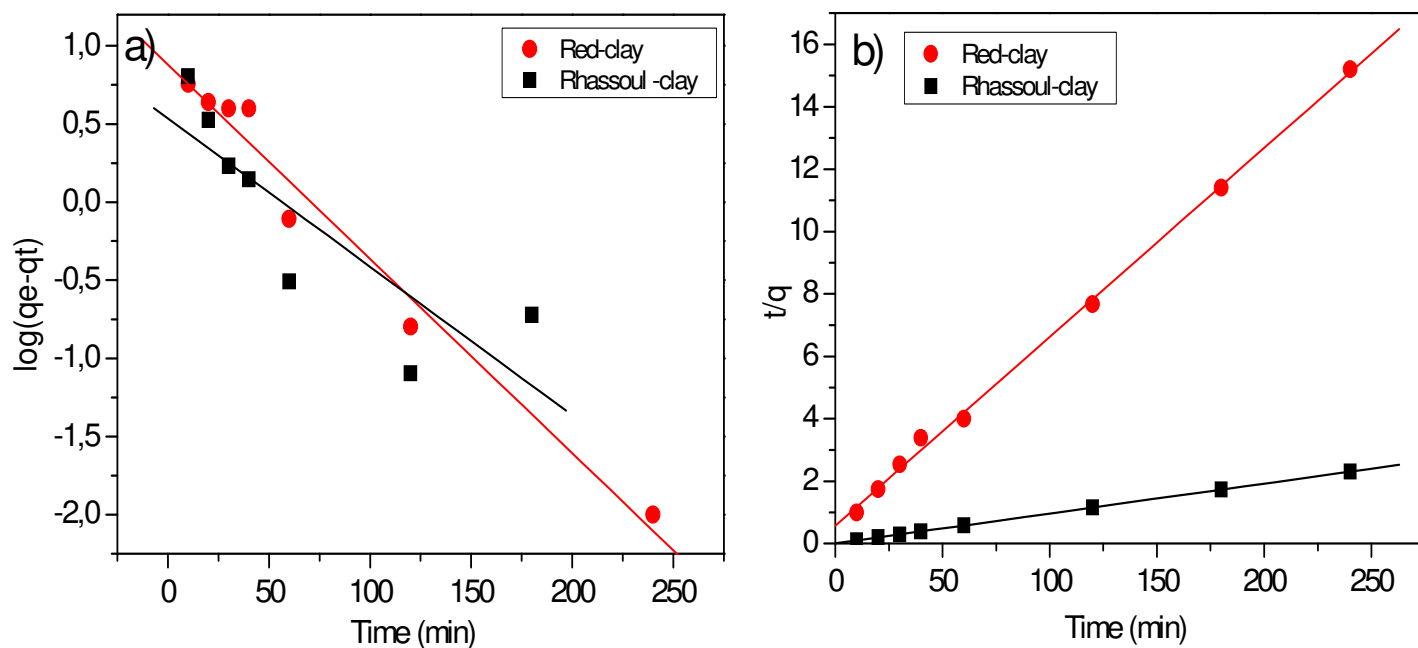


Fig. 4 (a) Pseudo-first-order kinetics and (b) Pseudo-second-order kinetics for MB adsorption onto Red clay and Rhassoul-clay.: Red clay ($m/v = 2.5 \text{ g L}^{-1}$, $[MB] = 40 \text{ mg L}^{-1}$, $pH_{eq} = 5$), Rhassoul-clay ($m/v = 1.25 \text{ g L}^{-1}$, $[MB] = 130 \text{ mg L}^{-1}$, $pH_{eq} = 8$).

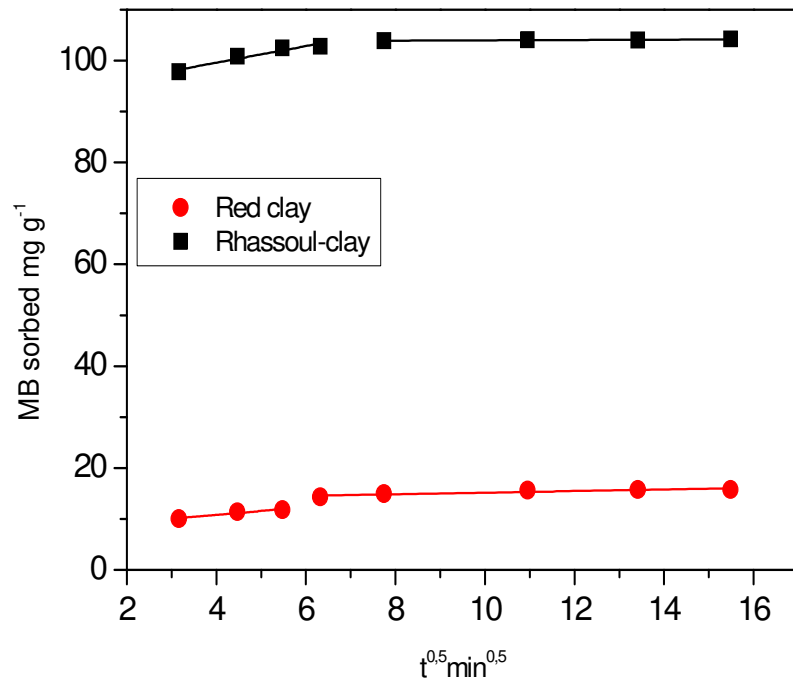


Fig. 5 Intraparticle diffusion plots for MB adsorption onto Red clay and Rhassoul-clay. Red clay ($m/v = 2.5 \text{ g L}^{-1}$, $[MB] = 40 \text{ mg L}^{-1}$, $pH_{eq} = 5$), Rhassoul-clay ($m/v = 1.25 \text{ g L}^{-1}$, $[MB] = 130 \text{ mg L}^{-1}$, $pH_{eq} = 8$).

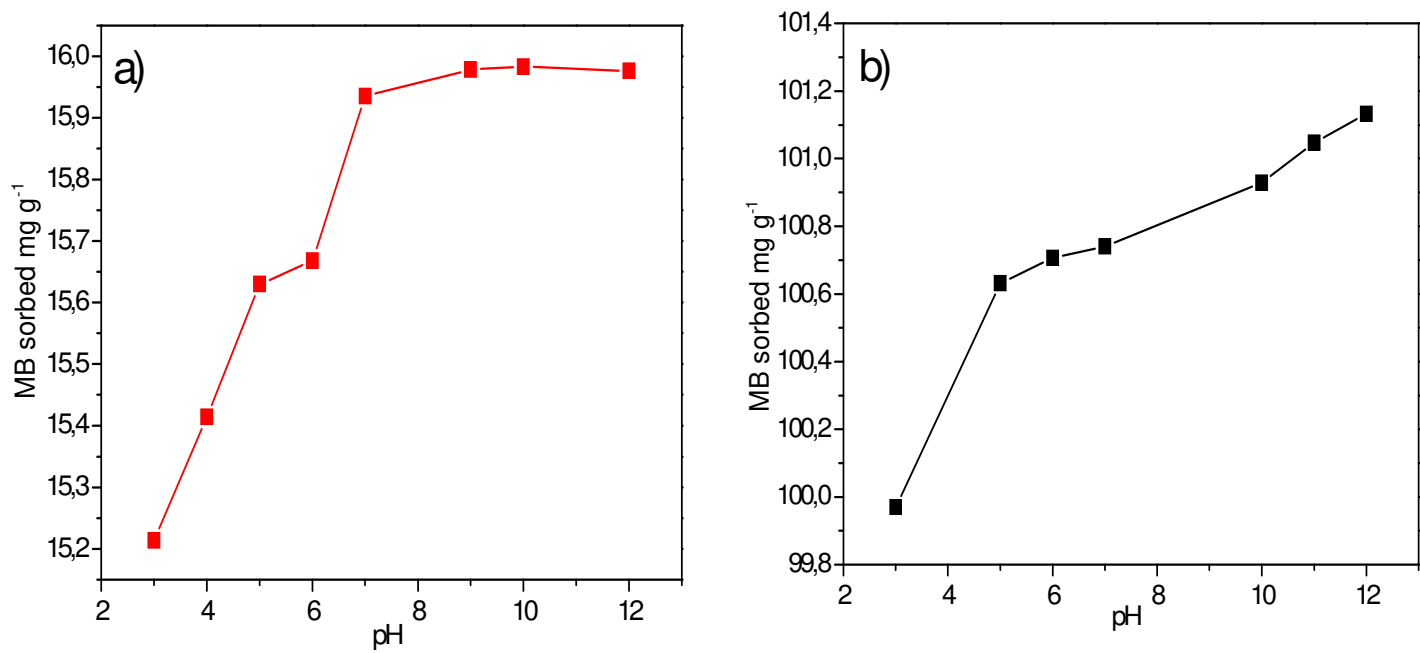


Fig. 6 Effect of pH on the adsorption of MB onto Red-clay (a) and Rhassoul-clay (b). 60 min of stirring. Red clay ($m/v = 2.5 \text{ g L}^{-1}$, $[MB] = 40 \text{ mg L}^{-1}$), Rhassoul-clay ($m/v = 1.25 \text{ g L}^{-1}$, $[MB] = 130 \text{ mg L}^{-1}$).

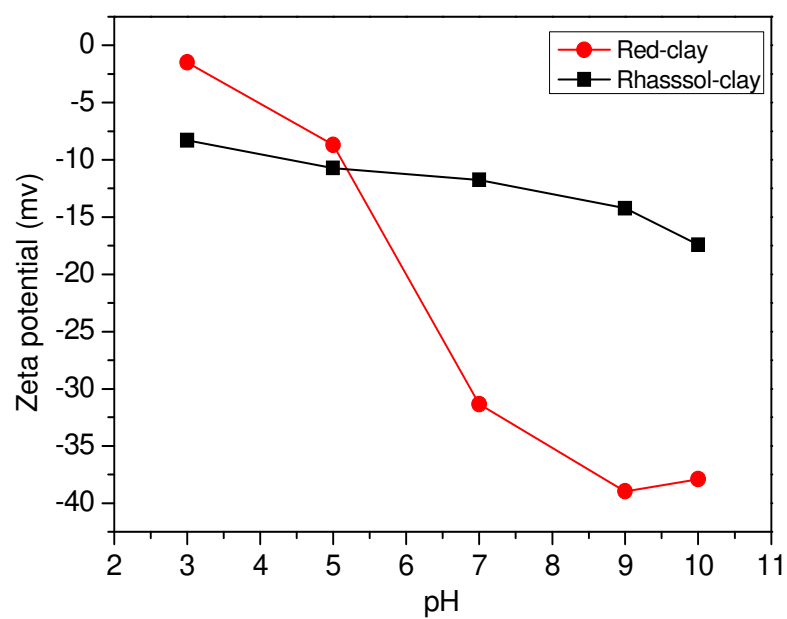


Fig. 7 The variation of zeta potential of Red-clay and Rhassoul-clay in function of pH. (m/v = 1 g L⁻¹, time 60 min, stirring speed 50 rpm).

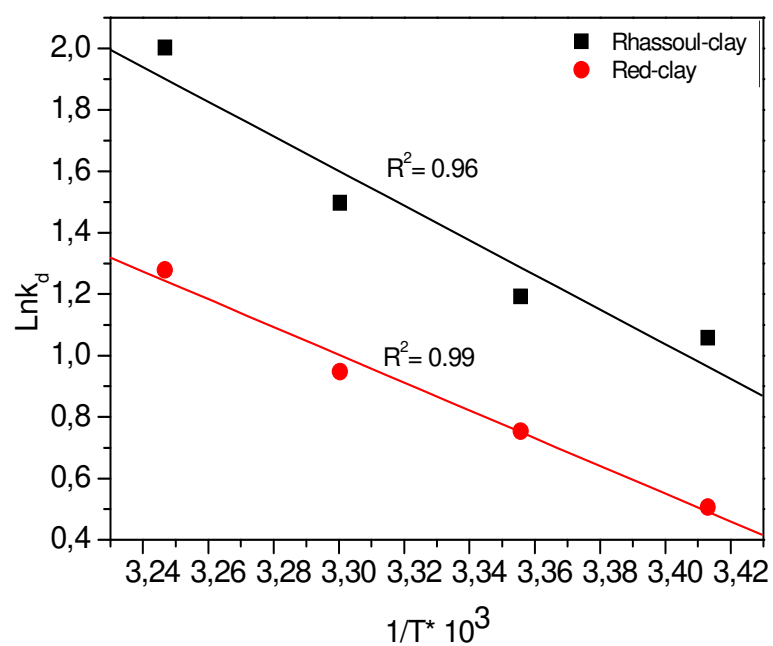


Fig. 8 Plot of $\ln K_d$ versus T^{-1} : estimation of thermodynamic parameters for the adsorption of MB onto Red-clay and Rhassoul-clay. Red clay ($m/v = 2.5 \text{ g L}^{-1}$, $[\text{MB}] = 40 \text{ mg L}^{-1}$, $\text{pHeq} \approx 5$), Rhassoul-clay ($m/v = 1.25 \text{ g L}^{-1}$, $[\text{MB}] = 130 \text{ mg L}^{-1}$, $\text{pHeq} \approx 8$).

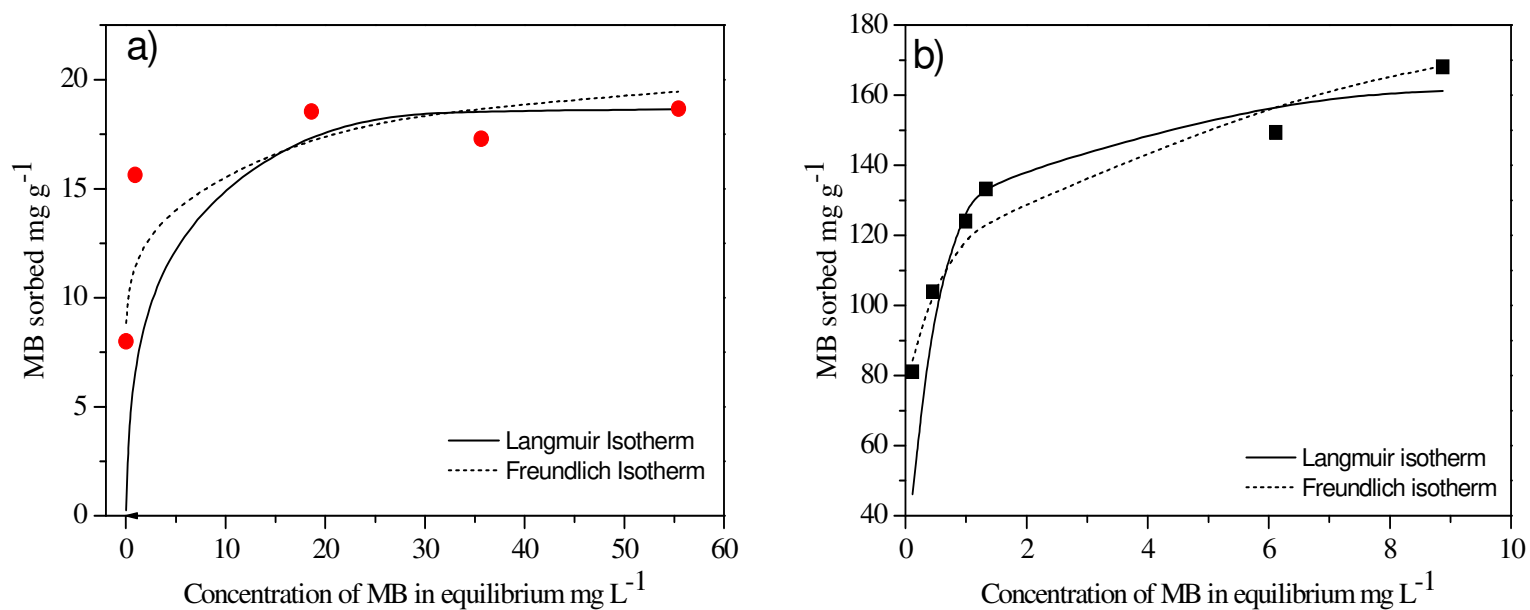


Fig. 9 Adsorption isotherms of MB onto Red-clay (a) and Rhassoul-clay (b). 60 min of stirring. Red clay ($m/v = 2.5 \text{ g L}^{-1}$), Rhassoul-clay ($m/v = 1.25 \text{ g L}^{-1}$).

*All figures was created using OriginLab software

Table 1 Mineral composition of adsorbents

Samples	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	Na ₂ O	K ₂ O	LOI
Red-clay	47.8	16.2	7.5	2.4	7.6	0.9	2.1	15.0
Rhassoul-clay	49.0	4.4	1.9	20.1	5.4	0.5	1.2	7.0

Table 2 Physicochemical properties of adsorbents

	Red-clay	Rhassoul-clay
CEC (meq. 100g ⁻¹)	35	83.3
BET (m ² g ⁻¹)	22.4	119
Zeta potential (mV)	-25.3	-25.1

Table 3 Kinetics parameters for adsorption of MB on clays.

Adsorbents	Q _{exp} (mg g ⁻¹)	Pseudo first order			Pseudo second order			Intraparticle diffusion			
		Q _{max}	K ₁	R ²	q max	K ₂	R ²	K	R ²	K'	R ²
		(mg g ⁻¹)	(min ⁻¹)		(mg g ⁻¹)	(g.mg ⁻¹ min ⁻¹)		(mg g ⁻¹ min ^{-0.5})		(mg g ⁻¹ min ^{-0.5})	
Red-clay	15.8	7.6	0.03	0.97	16.5	6.4×10 ⁻³	0.99	0.76	0.97	0.15	0.91
Rhassoul-clay	104.2	3.4	0.02	0.71	104.1	16.5×10 ⁻³	1	1.62	0.96	0.03	0.79

Table 4 Thermodynamic parameters for adsorption of methylene blue on clays

	Red-clay				Rhassoul-clay			
Temperature (°C)	Q (mg g ⁻¹)	ΔG° (kJ mol ⁻¹)	ΔH° (kJ mol ⁻¹)	ΔS° (J mol ⁻¹)	Q (mg g ⁻¹)	ΔG° (kJ mol ⁻¹)	ΔH° (kJ mol ⁻¹)	ΔS° (J mol ⁻¹)
20	13.5	-1.2	37.6	132.4	83.3	-2.4	46.9	168.0
25	14.1	-1.9	—	—	85.6	-3.2	—	—
30	14.5	-2.3	—	—	90.2	-4.1	—	—
35	15.0	-3.2	—	—	96.0	-4.9	—	—

Table 5 Freundlich and Langmuir isotherm constants determined for Red-clay and Rhassoul-clay

Adsorbents	Freundlich isotherm			Langmuir isotherm		
	1/n	K_f	R^2	K_l	Qmax (mg g ⁻¹)	R^2
Red-clay	0.09	13.5	0.92	2.3	18.83	0.99
Rhassoul-clay	0.15	119.0	0.96	3.3	166.7	0.99

Table 6 Comparison of methylene blue adsorption on various adsorbents

Adsorbents	MB adsorption capacity (mg g ⁻¹)	References
surfactant modified montmorillonite	254	Fan et al 2017
walnut shells	187.9	Miyaha et al 2018
Rhassoul-clay	166	This study
activated carbon from chitosan flakes	143.53	Marrakchi et al 2017
carbon/montmorillonite nanocomposites	138.1	Tong et al 2018
Palm kernel fiber	95.4	El-Sayed et al 2011
Natural clay	62.5	Omer et al 2018
Kaolin	52.76	Mouni et al 2018
Palygorskite	51	Al-Futaisi et al 2007
activated lignin-chitosan pellets	36.25	Albadarin et al 2017
Red-clay	18.83	This study
Zeolite	16.37	Han et al 2009
Raw kaolin	13.99	Ghosh and Bhattacharyya, 2002
Raw Coal fly ash	5.06	Li et al 2018