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Adsorption study of cationic and anionic dyes onto Moroccan natural pozzolan. Application for removal of textile dyes from aqueous solutions

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ABSTRACT

In this study, batch adsorption experiments were carried out using Moroccan natural pozzolan for the removal of methylene blue (MB) as cationic dye and Congo red (CR) as anionic dye from aqueous solutions. Experimentally, the usual parameters influenced on adsorption process were investigated. The obtained data shows that the adsorption of both dyes follows Langmuir isotherm model and the maximum adsorption capacity for MB and CR is equal respectively to 4.14 and 106.38 mg/g. kinetically, the pseudo-second-order and pseudo-first-order models provide the best correlation to the adsorption data for MB and CR respectively. Furthermore, the thermodynamic parameters of adsorption including free energy variation, enthalpy and entropy were calculated for each dye. Consequently, the adsorption process of both dyes onto natural pozzolan is spontaneous between 25 and 60°C. Furthermore, MB adsorption is exothermic with a decrease in the randomness at MB-pozzolan surface. However, CR adsorption is endothermic and shows strong affinity of CR-pozzolan system. In addition, natural pozzolan was applied for treatment of simulated textile effluents under industrial conditions in terms of salinity, pH and temperature, and demonstrated that natural pozzolan could be recommended for treatment of textile wastewater charged with soluble dyes. Finally, desorption study using HCl as eluent was clearly prove that the pozzolan is regenerative and reusable adsorbent.

Keywords: Pozzolan; Adsorption; Methylene blue; Congo red; Textile dye

1. Introduction

As any other developing countries, Morocco has experienced a real industrial revolution. Indeed, most industries such as textile and paper dyeing, plastic, food and cosmetics factories use colored matter in their production [1]. These industries generate a huge amount of colored wastewater which poured into the sea and rivers directly or without sufficient treatment. The ingestion of these colored matters can cause several problems such as eye irritation [2], skin damage, respiratory problems [3], it can also decrease fertility [4] and cause organs as the lungs and mucous membranes [5]. Methylene blue (MB) and congo red (CR) could be considered as commonly models of anionic and cationic dyes that are widely used in industries. These two dyes are considered as toxic, carcinogenic, mutagenic and teratogenic compounds due to their complex chemical composition with aromatic structure [6,7]. Moreover, they are characterized by low biodegradability (strong recalcitrance to degradation) [8]. The presence of dyes in wastewater threatens not only human health but also ecological balance [9,10]. The existence of MB and CR in water prevent the penetration of light, and

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consequently affects negatively photosynthesis process of aquatic plants [11]. In addition, blocking of sunlight can also contribute to reduction of oxygen dissolution that can cause serious problems like inhibition and destruction of both flora and fauna [12,13]. Nowadays, it is very required to treat colored effluents prior to their discharge in the environmental medium in order to prevent its pollution by soluble toxic dyes [14]. Several techniques have been used to remove MB and CR from residual effluents such as electrochemical process, encapsulation, photocatalytic degradation and membrane processes [15–18]. However, the high investment cost, and high consumption of chemical products and energy render these techniques relatively expensive [19]. Among processes of wastewater treatment, adsorption could remain the most suitable technique for removal of MB and CR from industrial wastewater because these dyes are highly soluble in water. The adsorption advantages lie in its easy and simple installation, as well as its efficient and low-cost process compared to other techniques [20]. The recent researches have been focused on the use of low-cost adsorbents that are locally available such as perlite [9], clay [21] and phosphate [11]. In this sense, using natural pozzolan in the adsorption process for wastewater treatment could be positively influenced on treatment cost. Pozzolan is commonly used in the manufacture of cements [22] and it is recently used for elaboration of flat and tubular ceramic membranes for microfiltration of textile effluent and for pretreatment of seawater for desalination [23,24]. The pozzolan is chemically and thermally stable and also it is environment-friendly raw material. Morocco has huge amount of pozzolan that is not yet exploitable. Economically, natural pozzolan is cheaper material. Therefore, it could be significantly reduced the cost of wastewater treatment. Additionally, valorization of natural pozzolan in adsorption is not only because of its low-cost and its abundance but also due to the need to valorize local geomaterials.

The main objective of this study is to investigate the adsorption and desorption of MB as a cationic dye and CR as an anionic dye onto natural pozzolan in aqueous solution through batch adsorption experiment. Furthermore, particles size, adsorbent dose, pH of the medium, initial concentration of dye, contact time and temperature of solution were studied in order to determine the kinetics, the isotherms and the thermodynamic parameters of dyes adsorption. Finally, the natural pozzolan was used for the treatment of simulated industrial textile wastewater.

2. Materials and methods

2.1. Natural pozzolan

Natural pozzolans ample was collected from Central Middle Atlas, Morroco and it was dried, crashed and sieved using a sieve of 63 µm. The pozzolan used in this work was already characterized by Achiou et al. [25]. Briefly, the pozzolan is chemically composed by SiO_2, Al_2O_3, Fe_2O_3, CaO and MgO as major oxides with other oxides such as SO_3, K_2O, Na_2O, and P_2O_5 in low amounts (Table 1). Mineralogically, the pozzolan has an amorphous structure with the presence of small minerals such as augite aluminian, forsterite and magnetite. To complete the characterization, the natural pozzolan was analyzed by Blaine surface area measurement, scanning electron microscopy(SEM), Fourier transform infrared (FTIR) and point of zero charge (ZPC) measurement.

Table 1
Chemical composition of natural pozzolan [25]

Oxides (%)	Pozzolan
SiO_2	39.04
Al_2O_3	13.42
Fe_2O_3	12.70
CaO	11.52
MgO	8.20
SO_3	0.20
K_2O	1.30
Na_2O	2.19
P_2O_5	1.09
LI*	5.99

*Loss on ignition at 1000°C.

2.2. Chemicals

MB ($C_{16}H_{18}C_1N_3S$, 82 wt.%) and CR ($C_{32}H_{22}N_6Na_2O_6S_2$, 35 wt.%) are purchased from Sigma Aldrich. The stock solutions of 100 mg/L were prepared by dissolving of dyes in distilled water. The experimental solutions with the desired concentration were prepared from stock solutions by dilution using distilled water. Sodium chloride (NaCl, 99 wt.%) was acquired from Sigma Aldrich.

2.3. Adsorption experiments

The adsorption experiments of dyes onto natural pozzolan were carried out by batch adsorption method. The pozzolan powder (≤63 µm) was added to dye solution (under magnetic stirring of 150 rpm). After the adsorption, the solution was centrifuged at 4000 rpm for 20 min. In order to study the effect of pozzolan dose, pH of the medium, initial concentration of dye, contact time and temperature of solution parameters on adsorption process, experiments were performed according to Table 2. The initial pH of solution was varied from 2 to 12 using diluted HCl or NaOH solutions (the molarity of HCl and NaOH solutions used for pH adjustment is 0.1 and 1 M).

The amount of adsorbed dye (q) is calculated using Eq. (1).

$$q = \frac{\left(C_i - C_e\right)\mathrm{V}}{m} \tag{1}$$

where C_i and C_e are the initial and equilibrium dye concentration (mg/L), respectively. V is the volume of solution (L) and m is the mass of pozzolan (g).

The average absolute value of relative error (AARE) was used to compare the predicted results with experimental data using the following equation:

$$AARE = \frac{1}{\mathrm{NDP}}\sum_{i=1}^{NDP}\frac{\left|PredictedValue - ExperimentalValue\right|}{ExperimentalValue}\times 100 \tag{2}$$

where NDP is the number of data points.

Table 2
Program of adsorption experiments

Studied parameter	Particle size (μm)	Pozzolan dose (g/L)	pH	Initial concentration (mg/L)	Contact time (min)	Temperature (°C)
Particle size	63–900	20	7	10	120	25
Pozzolan dose	63	5–40	7	10	120	25
pH	63	MB: 15 CR: 20	2–12	10	120	25
Initial concentration	63	MB: 15 CR: 20	MB: 7 CR: 2	10–600	120	25
Contact time	63	MB: 15 CR: 20	MB: 7 CR: 2	600	0–240	25
Temperature	63	MB: 15 CR: 20	MB: 7 CR: 2	600	120	25–60

2.4. Simulated dye effluent adsorption

The natural pozzolan was used for the treatment of simulated industrial effluent charged with MB, CR and salts (NaCl) at optimized conditions at room temperature [11]. Absorption experiments were carried out according to the same procedure as described in previous section. 0.50 g of pozzolan were added to 25 mL of dye solution with concentration of 50 mg/L which is approximately the average concentration in local textile wastewater [26]. The effect of NaCl concentration was investigated in the range of 0–50 mg/L. The removal efficiency (%) is evaluated using Eq. (3).

$$Removal = \frac{C_i - C_e}{C_i} \times 100 \quad (3)$$

where C_i and C_e are respectively the initial and equilibrium dye concentration (mg/L).

2.5. Desorption study

The batch desorption study was carried out using recovered pozzolan after adsorption of MB and CR dyes under conditions of that used for simulated dye effluent adsorption. The pozzolan sample was firstly washed with distilled water to eliminate unadsorbed dye and then dried at 70°C during 24 h. After, 0.15 g of pozzolan sample was added to 5 mL of HCl as desorbing agent [11]. HCl concentration was varied from 0.1 to 1 mg/L in order to evaluate the effect of desorbing agent. The percentage of dye desorbed was determined from the amount of adsorbed dye onto pozzolan and the amount of dye in the solution after desorption.

2.6. Characterization techniques

In this work, the specific surface of pozzolan powder (≤63 μm) was measured using Blaine method according to ASTM C204-11 standard. The morphology of natural pozzolan powder before and after adsorption was observed by SEM analysis operating at 10 kV (FEI Company, Quanta 200). FTIR analysis of natural pozzolan before and after adsorption of dyes was carried out using spectrometer (FTIR, Bruker EQUINOX 55) in transmittance mode with a frequency between 600 and 4000 cm^{-1}. The point of zero charge (ZPC) of pozzolan was determined by using the solid addition method [6]. The concentration of MB and CR was determined by using an UV-Vis spectrometer (UNICAM, Model UV2) respectively at wavelength of 664 and 496 nm. It should be noted that absorbance wavelength are corresponded to a max absorbance.

3. Results and discussion

3.1. Characterizations

Generally, Specific area is important parameter that is directly influenced on adsorption capacity of absorbent. On the other word, the increase of specific area relatively improves adsorption capacity [27]. The specific area of pozzolan powder (≤63 μm) was measured using Blaine method. The experimental result shows that value of specific area is found to be 0.55 m^2/g. Fig. 1 shows the SEM picture at a 2400× magnification of raw pozzolan powder (≤63 μm) used in adsorption experiments after and before adsorption. As shown in the figure, pozzolan is black due to presence of iron oxide (magnetite) and magnesium in its chemical composition. The particles before adsorption (Fig. 1a) have heterogeneous distribution as well as they are typically porous with scoriaceous and alveolar texture [23]. Consequently, this microstructure could evidently contribute to the adsorption of dyes. It is well known that the adsorption is more important with an adsorbent with higher porosity that leads to a higher specific area [27]. After adsorption, Figs. 1b and 1c show that the pores on pozzolan surface are covered, this suggests that the adsorption of MB and CR was performed. The FTIR analysis spectra for pozzolan before and after adsorption of MB and CR are presented in Fig. 2. The natural pozzolan spectrum shows the presence of predominant bands at 888 cm^{-1} (Si-O-Si symmetric stretching vibrations [28]), 979 cm^{-1} (Si-O-Si and Si-O-Al asymmetric stretching vibrations [29]), 1507 cm^{-1} (bending vibration of –OH group [30]), and bands at 2353 and 3736 cm^{-1} (stretching vibrations of –OH group [30,31]). Through the FTIR spectrum of pozzolan after MB absorption, it can be noticed that the peaks at 888 and 979 cm^{-1} are completely extinct that it would appear that Si-O-Si and Si-O-Al groups participate in MB adsorption. In the case of the pozzolan

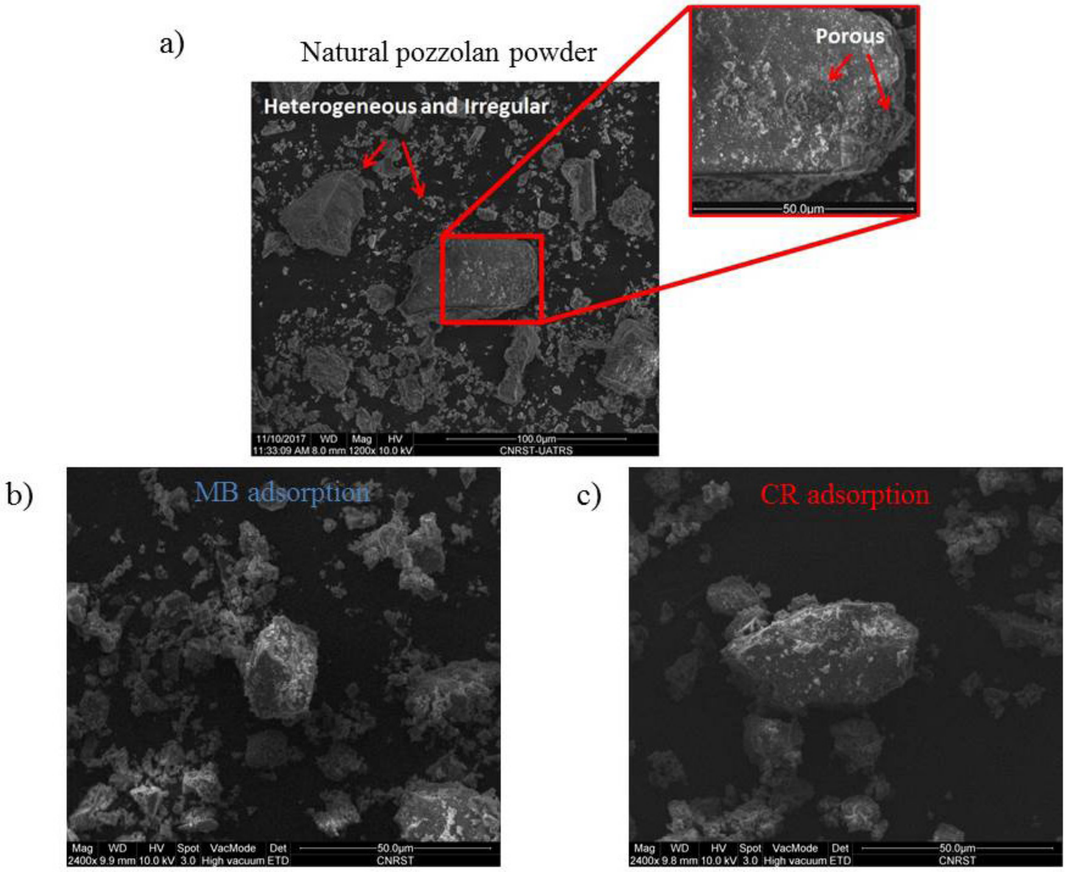

Fig. 1. SEM image of natural pozzolan before and after adsorption of MB and CR.

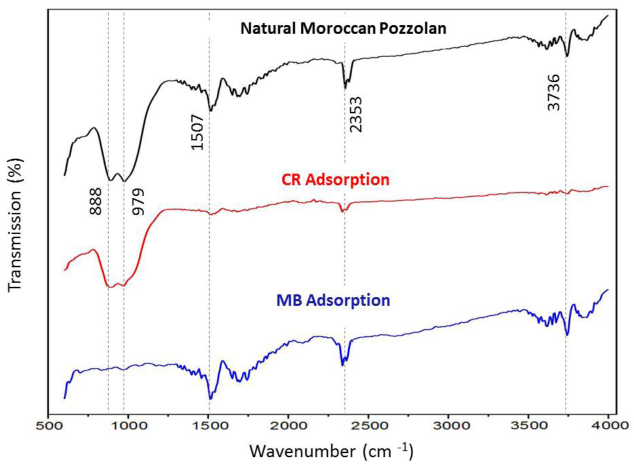

Fig. 2. FTIR of pozzolan before and after adsorption of MB and CR.

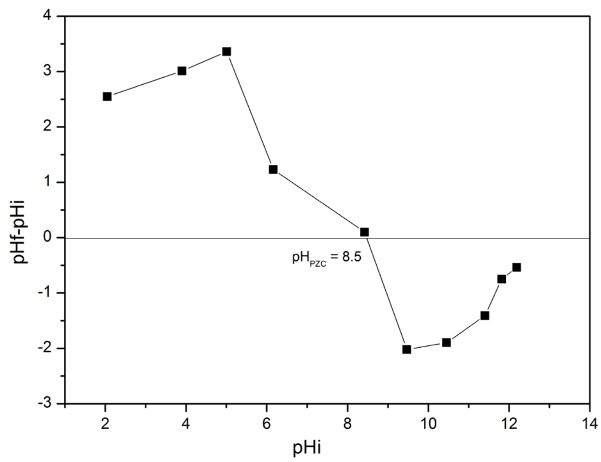

Fig. 3. pH_{ZPC} of natural pozzolan.

after CR adsorption, FTIR spectrum shows significant decrease in the intensity of the bands located at 1507, 2353 and 3736 cm^{-1} that correspond to –OH group. It can be concluded that the CR adsorption affected the –OH group. It seem to suggest that adsorption of anionic dye onto pozzolan is a physical adsorption. Van der Waals bonds could be responsible for the adsorption of CR onto pozzolan, typically, the hydrogen bond between the oxygen of the –OH group of pozzolan and the hydrogen of the NH_2^- groups of the CR [32]. pH_{PZC} corresponding to pH that surface charge of pozzolan is neutral in the aqueous medium. The value of this parameter could be easily determined from Fig. 3 which represents $pH_f - pH_i$ as a function of pH_i (pH_i and

pH_f are respectively initial and final pH). From the figure, it can be found that pH_{PZC} is equal to 8.5.

3.2. Adsorption study

According to chemical composition, natural pozzolan is composed of 52.24 wt.% of alumina and silica. The different hydroxyl groups related to silicon and aluminum located on pozzolan surface are illustrated in Fig. 4. As reported by Ghassabzadeh et al. [33], silicon and aluminum atoms at the surface tend to maintain their tetrahedral coordination with oxygen. At room temperature, these atoms complete their coordination by binding to monovalent hydroxyl groups to form silanol, silanediol and silanetriol for silicon atom, and aluminol groups for aluminum atom. In general, these groups are supposed to be one of the main responsible for adsorption phenomenon.

3.2.1. Effect of the pozzolan dose

The influence of pozzolan dose on adsorption capacity of dyes was studied in the range of 5 and 40 g/L (Fig. 5). From the figure, it can be seen that adsorption capacity decreases from 1.36 to 0.23 mg/g for MB (Fig. 5a) and from 0.44 to 0.17 mg/g for CR (Fig. 5b). However, the removal percentage of dyes is sharply increases by increasing the adsorbent dose in the range 0–20 g/L for MB and 0–15 g/L for CR. Then, the removal percentage stays constant (85.6% for MB and 68.3% for CR) even adsorbent dose is increased that means its effect is negligible. Accordingly, 20 and 15 g/L pozzolan doses are selected respectively for MB and CR as optimum values for following adsorption experiments.

3.2.2. pH effect

The pH of solution changes the surface charge of the adsorbent and the structure of the dye molecule [34]. As well known, variation of pH affects the adsorption process through the dissociation of functional groups on the adsorbent surface [35]. For pH > pH_{pzc}, the surface becomes negatively charged which favored the adsorption of cationic species. On the other hand, adsorption of anionic species is favored at pH < pH_{pzc} [36]. Consequently, the adsorption of MB is favored when the pH is above 8.5, while the adsorption of CR is favored at pH below 8.5. Fig. 6 displays the pH effect on adsorption capacity of MB onto pozzolan. As revealed by the figure, the adsorption capacity of MB on pozzolan increases when the pH increases from 2 to 7. Thereafter, it reaches a plateau of 0.66 mg/g when the pH varies from 7 to 12. The lower adsorption of MB at acidic medium is probably due to the presence of excess H^+ ions competing with the adsorption sites of cationic dye. The competition against H^+ ions decreased with the pH increase. Therefore, the equilibrium adsorption capacity increases correspondingly. The equilibrium adsorption capacity almost does not lot change at pH > 7. The pH of initial solution of MB mixed with pozzolan without any control is about 7 corresponds

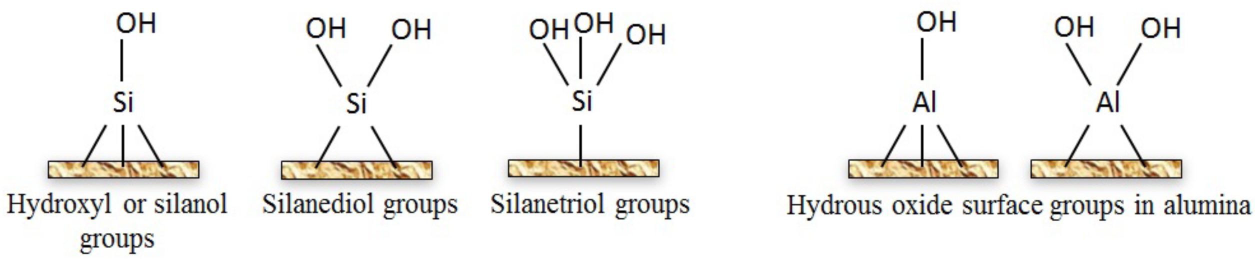

Fig. 4. Illustration of different types of silanol and aluminol groups on pozzolan surface.

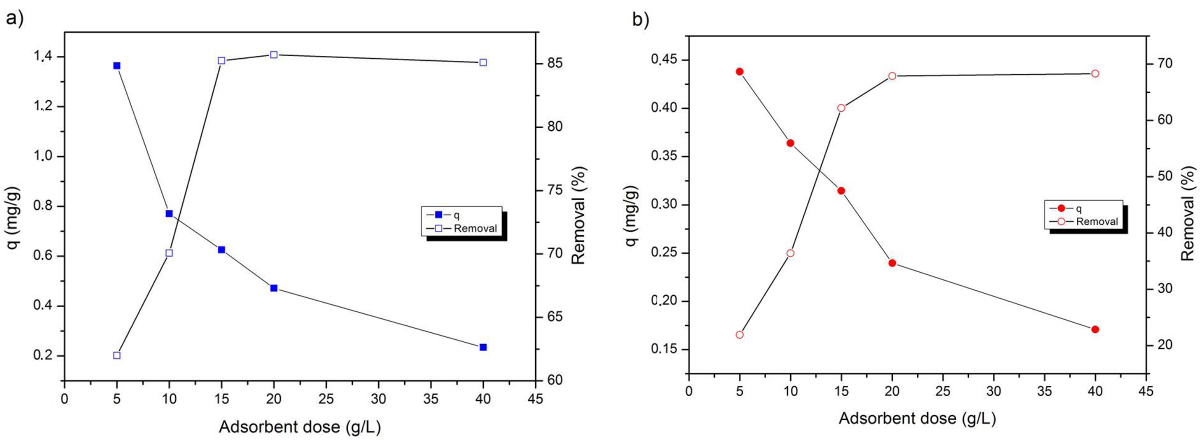

Fig. 5. Effect of the pozzolan dose on adsorption of MB (a) and CR (b).

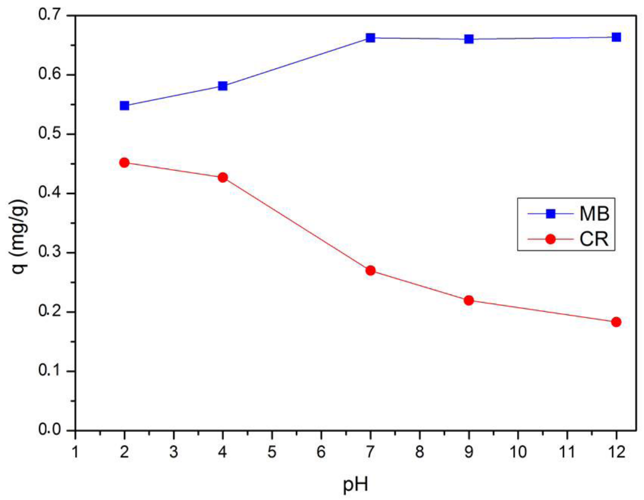

Fig. 6. Effect of the solution pH on the adsorption of MB and CR onto natural pozzolan.

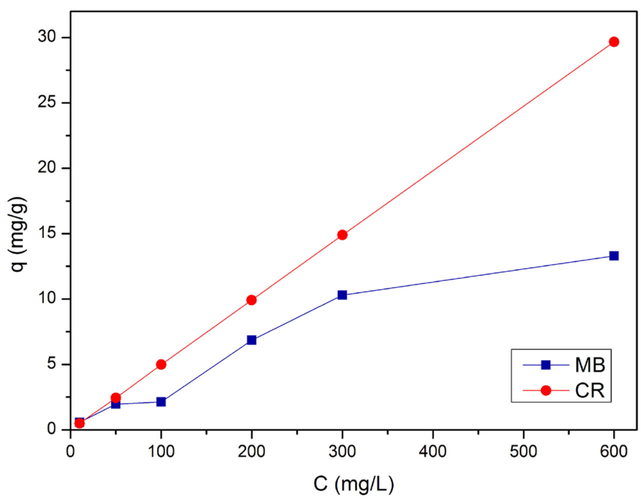

Fig. 7. Effect of initial concentration of MB and CR onto natural pozzolan.

to highest adsorption percentage. Therefore, adsorption experiments were carried out at natural pH (without any pH adjustment) for next experiment. In the case of CR adsorption, the adsorption capacity decreases from 0.45 to 0.18 mg/g while the pH increases from 2 to 12. By increasing pH of the solution, sites positively charged decrease. As result, CR adsorption is very favorable at low pH. Hence, all the succeeding investigations were performed at pH 2. Moreover, the lower adsorption of negative dye at higher pH may be due to the competition with OH^- ions that is dominant in alkaline medium. The same behavior was also reported by Munagapati et al. [37].

3.2.3. Adsorption isotherm models

Experiments of adsorption isotherm were carried out at optimum conditions and changing initial dyes concentration from 10 to 600 mg/L. Fig. 7 shows the variation of adsorption capacity of MB and CR onto pozzolan as function of initial dye concentration. From this figure, it can be seen that adsorption capacity of MB is perfectly proportional with increasing of initial concentration. In the case of CR, the more initial concentration increases the more the uptake of pozzolan also increases until reaching the saturation capacity at a higher concentration. Summing up the result, it can be concluded that the increase of initial dye concentration leads to the enhancement of the driving force at the solid–liquid interface (ion exchange, electrostatic attraction and chemical association) until the adsorption sites are completely saturated [38]. As a result, initial concentration of dyes was fixed at 600 mg/L for further absorption experiments.

In order to describe adsorption mechanism, Langmuir and Freundlich models were used to fit experimental data. Langmuir isotherm model is used to calculate the adsorption parameters and the maximum adsorption capacity corresponding to the complete monolayer coverage on the adsorbent surface [27]. The linearized form of Langmuir equation is calculated by Eq. (4):

$$\frac{1}{q_e} = \frac{1}{K_L q_m C_e} + \frac{1}{q_m} \tag{4}$$

where q_e and q_m are the amount of adsorbed dye at equilibrium and the monolayer capacity of the pozzolan (mg/g), respectively, K_L is the Langmuir constant related to the free energy of adsorption (L/mg) and C_e is the equilibrium dye concentration in solution (mg/L).

A dimensionless constant called separation factor (R_L) is calculated by Eq. (5):

$$R_L = \frac{1}{1 + K_L C_i} \tag{5}$$

where C_i is the initial dye concentration and K_L is the Langmuir constant (L/mg). R_L parameter suggests the type of isotherm to be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavorable ($R_L > 1$).

Freundlich isotherm model assumes that the adsorption capacity is related to the concentration of dye at equilibrium and the adsorption process takes place on heterogeneous surfaces [39]. The expression of Freundlich isotherm model is defined by Eq. (6):

$$\ln(q_e) = \frac{1}{n}\ln(C_e) + \ln(K_f) \tag{6}$$

where $1/n$ and K_f are isotherm constants of Freundlich isotherm related to the adsorption intensity and adsorption capacity respectively.

The experimental data of dyes adsorption onto natural pozzolan were fitted by the Langmuir and Freundlich models, and shown in Figs. 8 and 9. It should be mentioned that parameters of both models are reported in Table 3. The correlation coefficient (r^2) and AARE % values indicate that both models are able to adequately describe the relationship between q_e and C_e. However, by comparison of two models, it could be observed that Langmuir isotherm model fits equilibrium data better than Freundlich model which suggests the formation of monolayer coverage of dyes on the

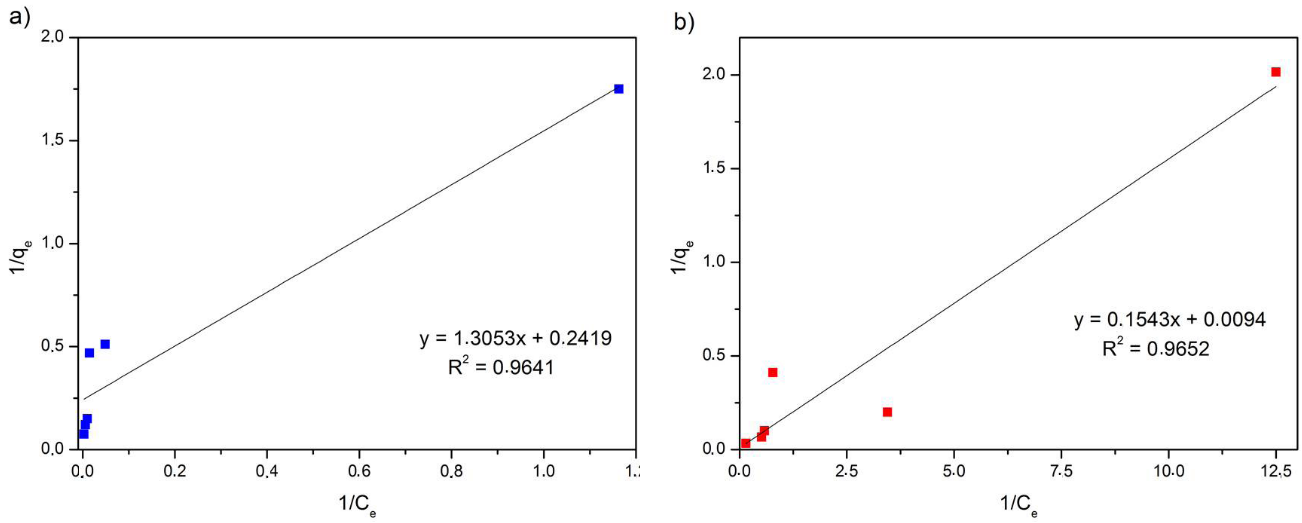

Fig. 8. Linear fitting of adsorption isotherm plot: Langmuir model for the MB (a) and CR (b) adsorption.

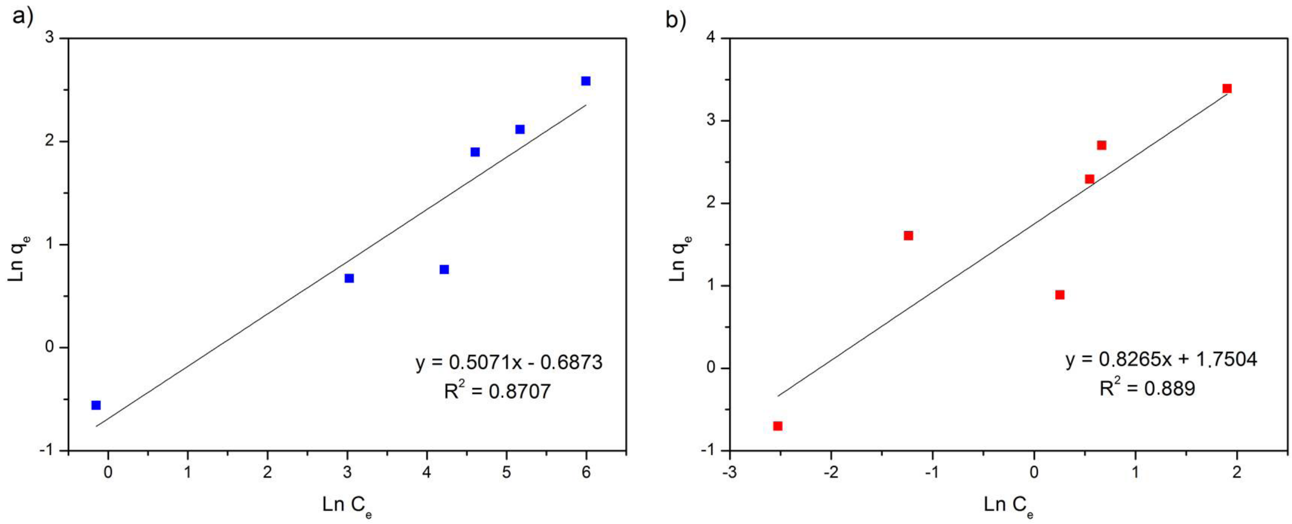

Fig. 9. Linear fitting of adsorption isotherm plot: Freundlich model for the MB (a) and CR (b) adsorption.

Table 3
Isotherm model parameters for MB and CR adsorption onto pozzolan

	Langmuir isotherm model				Freundlich isotherm model		
	K_L (L/mg)	Q_m (mg/g)	AARE (%)	R_L	K_f (L/g)	n	AARE (%)
MB	0.185	4.14	11.162	0.009	0.503	1.97	15.090
CR	0.061	106.38	4.674	0.030	5.757	1.21	9.521

surface of natural pozzolan. In addition, the R_L values are between 0 and 1 indicating that the adsorption of MB and CR onto pozzolan is favorable. The adsorption capacity of MB and CR onto natural pozzolan and other adsorbents in the literature is reported in Table 4. From this table, it can be inferred that the adsorption capacity of MB onto natural pozzolan is interesting in comparison with other adsorbents such as pyrophyllite and flay ash. On the other hand, at the same time it is still lower compared with clay materials that are generally known by their high adsorption capacity. Nevertheless, it is very evident that adsorption capacity of CR onto natural pozzolan is extremely good and competitive compared to adsorbents reported in Table 4 based not only on adsorption capacity but also on the economic view (natural pozzolan is a low-cost geomaterials). Summing up these results, it can be concluded that natural pozzolan

Table 4
Comparison of the adsorption capacity of MB and CR dyes with other adsorbents

Adsorbent	Adsorption capacity (mg/g)		Reference
	MB	CR	
Clay	58.2	–	[14]
Pyrophyllite	3.8	–	[40]
Flay ash	1.3	–	[41]
Montmorillonite clay modified with iron oxide	71.12	–	[42]
Moroccan natural phosphate	–	19.81	[11]
Leonardite	–	165.25	[36]
Cationic modified orange peel powder	–	107.144	[37]
Ag modified calcium hydroxyapatite	–	267.81	[7]
Moroccan natural pozzolan	4.14	106.38	This study

as alternative adsorbent could be successfully used for the treatment of industrial wastewater especially that charged with anionic dyes.

3.2.4. Effect of contact time and adsorption kinetics

The effect of contact time on the MB and CR adsorption onto pozzolan is illustrated in Fig. 10. As revealed by the figure, adsorption capacity of dyes onto pozzolan was rapidly increased during the first 30 and 90 min respectively for MB and CR. Then, it was gradually increased until reaching the equilibrium point that could reach 13.27 and 29.66 mg/g respectively for MB and CR. The rapid adsorption is related to the availability of active sites on the natural pozzolan surface [43]. Hence, the adsorption of MB and CR onto pozzolan reaches maximum respectively after 60 and 120 min which are selected as optimum contact time.

The study of adsorption kinetics describes the rate of uptake dyes onto pozzolan. On the other hand, adsorption kinetics helps in designing and modeling the adsorption process, and description of diffusion mechanism. Among the most common models, Lagergren first-order, pseudo-second-order and intraparticle diffusion models are used in this study to describe the kinetics of MB and CR adsorption onto pozzolan. The three models are respectively represented by Eqs. (7), (8) and (9).

$$\ln\left(q_e - q_t\right) = \ln q_e - k_1.t \tag{7}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{8}$$

$$q_t = k_i t^{1/2} + C \tag{9}$$

where q_e and q_t are the amount of adsorbed dye at equilibrium (mg/g) and the contact time t (min), respectively.

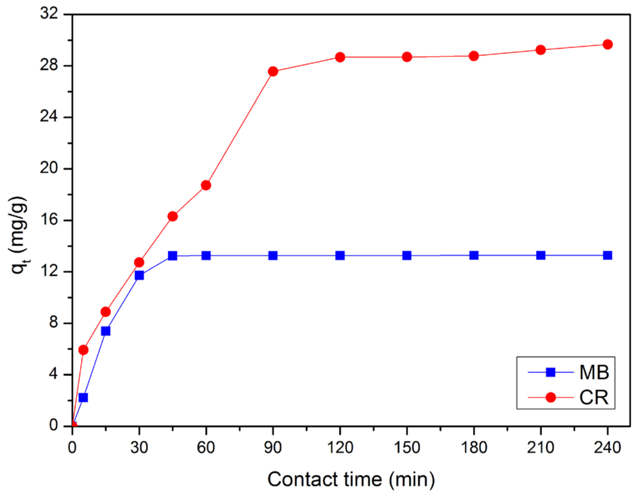

Fig. 10. Effect of contact time on the adsorption of MB and CR.

k_1 (min^{-1}) and k_2 (g/mg/min) are the rate constant of the Lagergren first-order and pseudo-second-order adsorption, respectively. k_i (mg/g/min$^{1/2}$) is the intraparticle diffusion rate constant and C (mg/g) is the intercept constant that represents the boundary layer effect of molecular diffusion.

To illustrate the result, simulation of pseudo-first-order and pseudo-second-order models were performed and displayed respectively in Figs. 11 and 12. Additionally, calculated parameters for each model, correlation coefficient as well as AARE are reported in Table 5. According to these results and that of FTIR analysis, it can be inferred that MB and CR adsorption onto pozzolan follows respectively the pseudo-second-order and the pseudo-first-order kinetics because of the good agreement between experimental and calculated data with correlation coefficient, which is greater than 0.9 for both dyes. Therefore, the finding suggests that the adsorption behavior is chemical adsorption and physical adsorption respectively for MB and CR. Meanwhile, intraparticle diffusion data is illustrated in Fig. 13 and its constants are reported in Table 5. This model describes the different steps of adsorbate transport from liquid phase to the solid phase [6]. Firstly, the adsorbate diffuses from the liquid phase to near of the adsorbent. Secondly, adsorbate diffuses to the boundary layer on the adsorbent surface. Thirdly, adsorbate transports on active adsorbent sites (intraparticle scattering). Finally, adsorbate molecules adsorb on adsorbent sites. As can be seen for both dyes, q_t vs. $t^{1/2}$ plots are not one linear curve and their intercept constant are not null. The two curves consist of two linear segments. This indicates that the adsorption of MB and CR onto pozzolan is carried out in more than one step. As reveled by Fig. 13, for the both dyes, first segment shows that adsorption of dyes is depended on intraparticle diffusion and thickness of boundary layer [44]. The second segment of MB curve is like a plateau that indicates the adsorption is only controlled by thickness of boundary layer. In the case of CR, the second segment has very lower value of k_2 (it is approximately 10 times lower than k_1) which it means that the effect of thickness of boundary layer is more dominant rather than intraparticle diffusion.

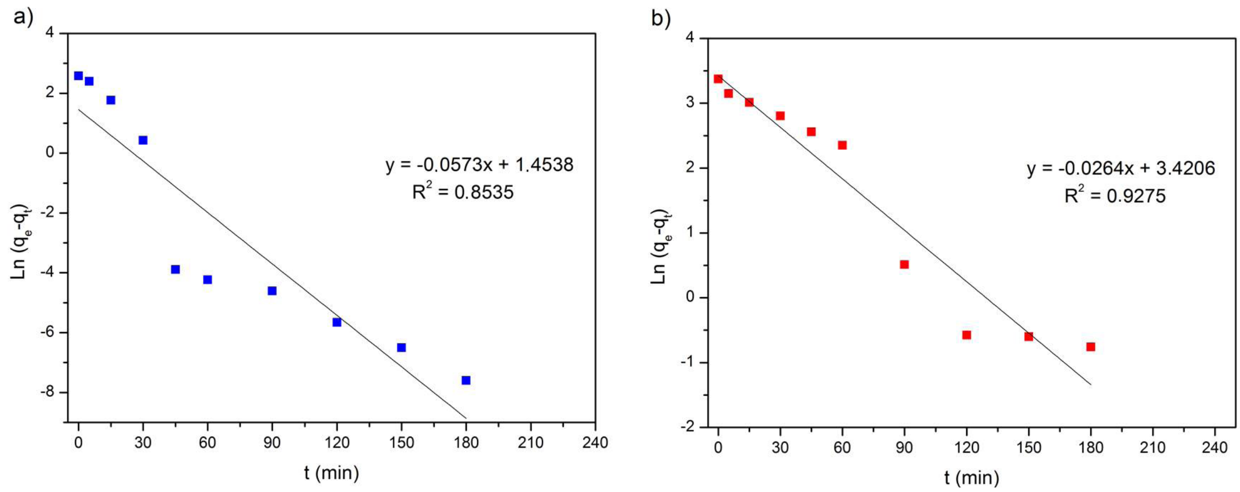

Fig. 11. Fit of pseudo-first-order kinetic model for the MB (a) and CR (b) adsorption onto natural pozzolan.

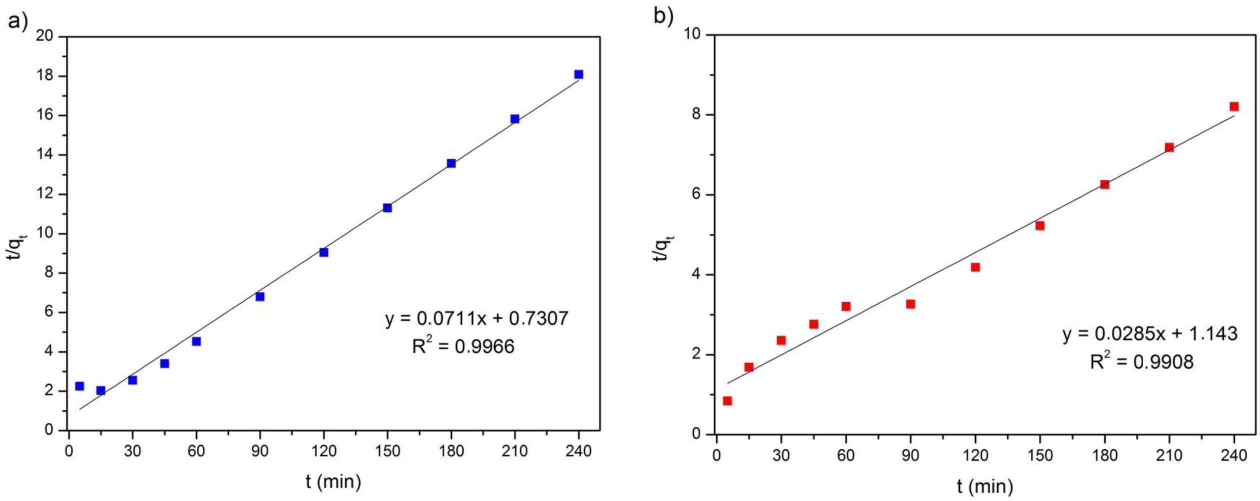

Fig. 12. Fit of pseudo-second-order kinetic model for the MB (a) and CR (b) adsorption onto natural pozzolan.

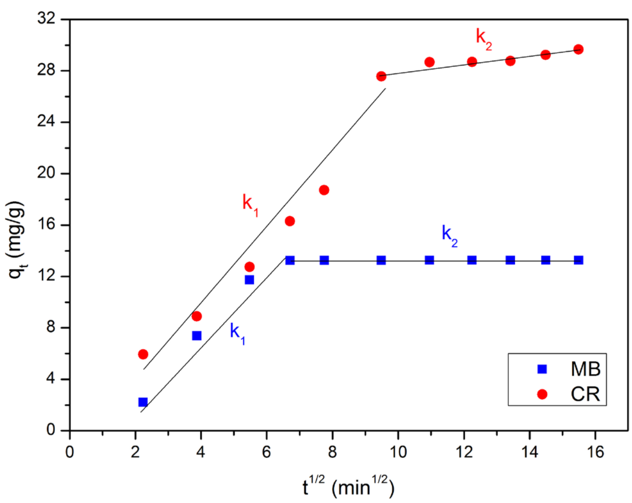

Fig. 13. Intraparticle diffusion of MB and CR adsorption onto pozzolan.

3.2.5. Adsorption thermodynamics

It is well known that thermodynamic study is fundamental in order to comprehend the nature of adsorption in terms of spontaneity and mechanism [45], and also allows determining thermodynamic parameters such as the change in standard free energy or Gibbs free energy ΔG° (J/mol), enthalpy ΔH° (J/mol) and entropy ΔS° (J/mol/K). ΔH°, ΔS° and ΔG° are calculated by following equations:

$$\ln K_d = -\frac{\Delta H}{RT} + \frac{XS}{R} \tag{10}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{11}$$

where R and T are respectively universal gas constant (8.314 J/mol K) and temperature (K). K_d is the distribution coefficient which is expressed by Eq. (12):

$$K_d = \frac{q_e}{C_e} \tag{12}$$

where q_e is absorption capacity corresponding to dye concentration C_e.

According to Eq. (10), ΔH° and ΔS° parameters can be individually calculated from the slope and intercept of the plot of ln K_d vs. 1/T.

The adsorption experiments at different temperatures (25–60°C) were performed to evaluate the influence of temperature. A typical ln K_d vs.1/T and ΔG° vs. T plots are shown in Figs. 14 and 15 respectively. The values of thermodynamic parameters are listed in Table 6. The obtained ΔG° (ΔG° < 0) values indicate that both dyes adsorption are spontaneous and favorable in the studied range of temperature (25–60°C). But, it should be noted that increasing in temperature positively affects adsorption process. The same behavior was observed by several authors using other adsorbents [45,46]. The interpretation of negative value of ΔH° is that the adsorption of MB onto pozzolan is exothermic. While the positive value of ΔH° of CR adsorption is endothermic which could be promoted by the increasing of temperature [47]. Furthermore, the negative ΔS° value of MB adsorption indicates a decrease in the randomness at MB-pozzolan surface [33]. Whereas, the ΔS° corresponding to CR adsorption is positive. This suggests that total disorder of system is increased indicating a strong CR-pozzolan affinity [47].

Table 5
Lagergren rate equation constants, pseudo-second-order rate equation and intra-particle diffusion constants

Kinetic models / parameters	MB	CR
Pseudo-first-order		
k_1 (min^{-1})	0.057	0.026
q_e (mg/g)	4.279	30.588
r^2	0.8535	0.9275
AARE (%)	6.508	3.034
Pseudo-second-order		
k_2 (g/mg·min)	0.0070	0.0007
q_e (mg/g)	14.065	35.088
r^2	0.9966	0.9908
AARE (%)	5.001	2.670
Intra-particle diffusion		
k_1 (mg/(g min$^{1/2}$))	2.516	2.8756
C_1	2.8615	2.0028
R_1^2	0.9756	0.96
k_2 (mg/(g min$^{1/2}$))	0.0023	0.295
C_2	13.233	25.024
R_2^2	0.8914	0.8799

3.3. Adsorption of simulated dye effluent

This study does not only focus on pozzolan as alternative adsorbent for adsorption of cationic and anionic dyes in order to cover majority of dyes type employed in textile industries but also investigates the possibility of treatment of textile wastewater. As known about indus-

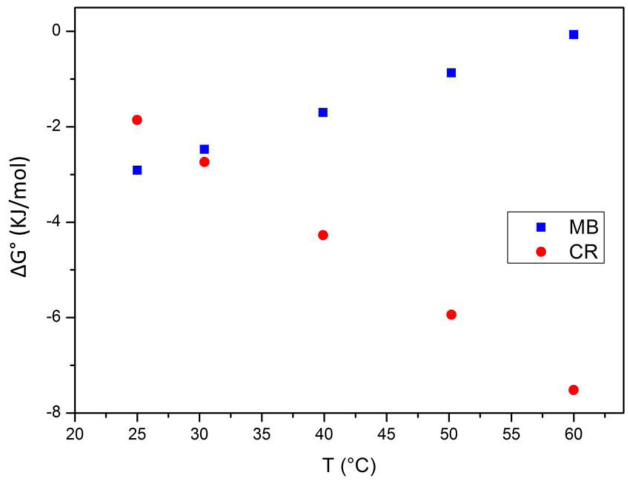

Fig. 15. Standard free energy vs. temperature.

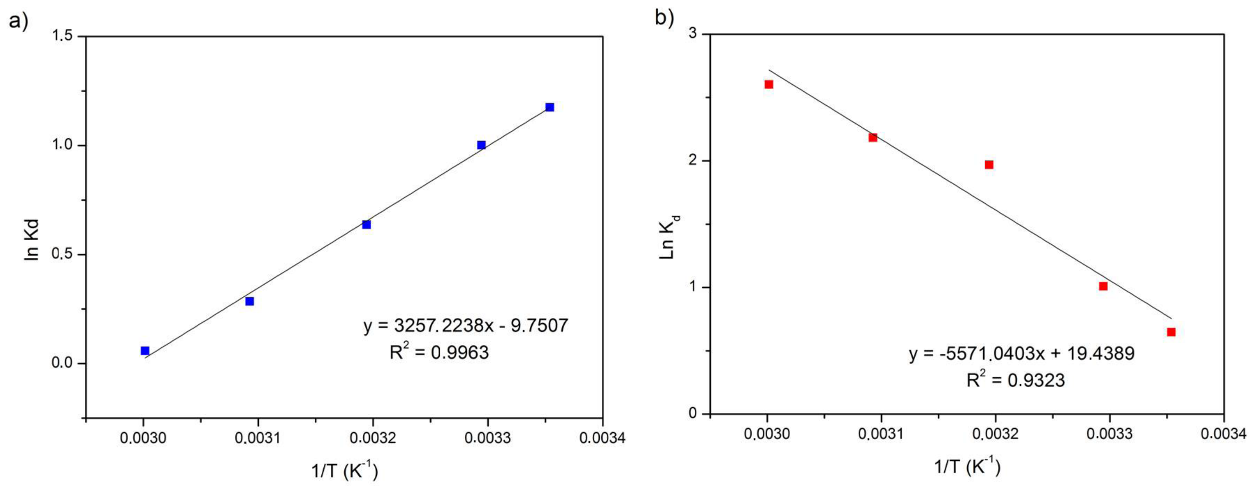

Fig. 14. Ln K_d vs. 1/T for estimation of ΔH° and ΔS° for the MB (a) and CR (b) adsorption onto pozzolan.

Table 6
Values of thermodynamic parameters for MB and CR adsorption onto pozzolan

Thermodynamic parameters	Temperature (°C)				
	25	30.4	39.9	50.2	60
MB					
ΔG° (kJ mol^{-1})	–2.91	–2.47	–1.70	–0.87	–0.07
ΔS° (kJ mol^{-1} K^{-1})	–0.08				
ΔH° (kJ mol^{-1})	–27.08				
CR					
ΔG° (kJ mol^{-1})	–1.86	–2.74	–4.27	–5.94	–7.52
S° (kJ mol^{-1} K^{-1})	0.16				
H° (kJ mol^{-1})	46.32				

trial textile wastewater, they use important amount of salt during the dyeing process [11]. To fully understand the influence of salinity on adsorption process, simulated effluents were prepared adding NaCl with concentration varied from 0 to 50 mg/L to MB and CR solutions, and then adsorption experiment were carried under optimized conditions at room temperature. Fig. 16 presents dyes removal as function of salt concentration. As it can be seen in figure, salinity of effluent influences differently on adsorption removal of dyes. MB removal is rapidly improved from 64.23 to 84.20% when NaCl concentration increases from 0 to 50 mg/L because competition between MB and other cations (Na^+ in this case) presented in effluent on negatively adsorption sites on pozzolan surface [39]. Then, MB removal remains constant even though NaCl concentration continuously increases which means that high salinity has no significant effect on the adsorption process. The opposite behavior is observed for CR. Firstly, the CR removal sharply deceases from 98.88 to 98.15% while NaCl concentration increases from 0 to 50 mg/L probably in the reason of CR molecules are neutralized with cations presented in medium and also the interaction of CR with Cl^- molecules [11]. After, by increasing salt concentration, CR adsorption is practically steady.

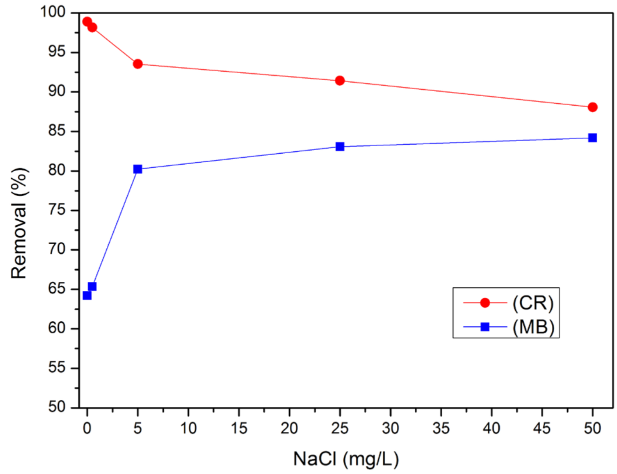

Fig. 16. Effect of NaCl concentration on adsorption efficiency of MB and CR onto natural pozzolan.

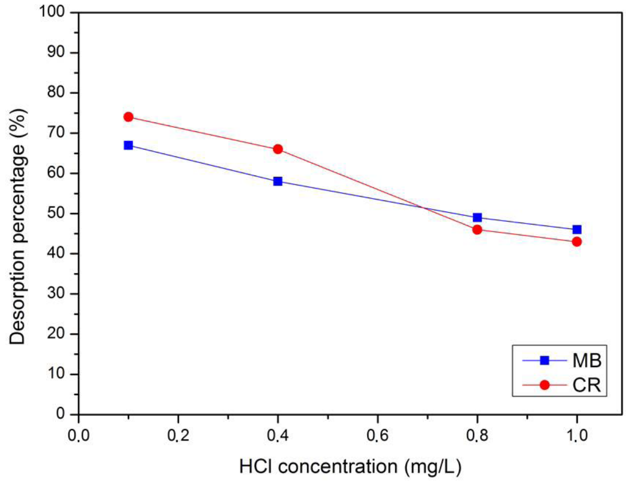

Fig. 17. Desorption of MB and CR from pozzolan by using HCl as desorbing agent.

3.4. Desorption study

The regeneration and reuse of adsorbent is an important factor for possible industrial applications from the viewpoint of minimization of amount adsorbent and reduction of industrial waste. It is worth noting that Bensalah and coworker reported that HCl solution is the best desorbing agent for cationic and anionic dyes in comparison with NaOH, H_2SO_4 and ethanol solutions [11]. Fig. 17 displays desorption percentage of MB and CR as a function of HCl concentration. As revealed by the figure, the maximum desorption is observed for using HCl with concentration of 0.1 M. It could desorb up to 67 and 74% respectively for MB and CR. Furthermore, the more HCl concentration increases the more dyes desorption decreases. This decrease could be explained by deterioration of the active sites on the pozzolan [48]. Regeneration results clearly demonstrate that the pozzolan could be reused again and its recyclability could relatively reduce the cost of wastewater treatment.

4. Conclusions

The adsorption of MB and CR onto natural pozzolan was studied in adsorption batch experiment. The adsorption results show that the optimum pozzolan dose is equal to 15 and 20 mg/L for the adsorption of MB and CR respectively. Furthermore, the adsorption of the MB is favorable in neutral and basic medium however CR adsorption is favorable in acidic medium. Adsorption isotherms show that adsorption of dyes follows Langmuir model and allows estimating maximum capacity which are equal to 4.14 and 106.38 mg/g respectively for MB and CR. In addition, the adsorption kinetics reveals that the

MB and CR adsorption were respectively modulated by pseudo-second-order and pseudo-first-order. They also rapidly reach their equilibrium in 60 and 90 min respectively. Thermodynamic parameters in terms of ΔG°, ΔH° and ΔS° were calculated for both dyes and indicated that adsorption is spontaneous and favorable, then, the MB adsorption is exothermic as well as disorder of MB-pozzolan system is decreased. Whereas, the CR adsorption is endothermic with a strong affinity of CR-pozzolan system. As application, natural pozzolan was used for treatment of simulated textile wastewater by adding NaCl with concentration varied from 0 to 50 mg/L to MB and CR solutions. The results demonstrated that salinity has low influence on the adsorption of MB and CR. Additionally, desorption study using HCl as eluent showed that pozzolan is a regenerative and reusable material. Summing up the findings, it can be concluded that natural pozzolan (cheaper geomaterials) as alternative adsorbent could be successfully used for treatment of industrial wastewater especially that charged with anionic dyes.

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List of symbols

AARE — Average absolute value of relative error (%)
C — Intercept constant (mg/g)
C_i — Initial dye concentration (mg/L)
C_e — Equilibrium dye concentration (mg/L)
k_i — Intraparticle diffusion rate constant (mg/g/min$^{1/2}$)
K_L — Langmuir constant (L/mg)
K_f — isotherm constants of Freundlich isotherm related to the adsorption capacity
K_d — Distribution coefficient
k_1 — Lagergren rate constant of adsorption (min^{-1})
k_2 — Rate constant of pseudo-second-order adsorption (g/mg/min)
m — Mass of adsorbent (g)
n — isotherm constants of Freundlich isotherm related to the adsorption intensity
NDP — Number of data points
q — Amount of adsorbed dye (mg/g)
q_e — Amount of adsorbed dye at equilibrium (mg/g)
q_m — Monolayer capacity of adsorbent (mg/g)
q_t — Amount of adsorbed dye at time (mg/g)
R — Universal gas constant (8.314 J/mol K)
R_L — Separation factor
T — Temperature (K)
t — Time (min)
V — Volume of solution (L)
ΔG° — Gibbs free energy (J/mol)
ΔH° — Enthalpy (J/mol)
ΔS° — Entropy (J/mol/K)

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