

수용액으로부터 양이온 염료 흡수에 대한 pH 및 온도 효과

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Effects of pH and Temperature on the Adsorption of Cationic Dyes from Aqueous Suspension by Maghnia Montmorillonite

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요 약. Maghnia montmorillonite clay를 이용하여, 두 가지 염료(neutral red; NR과 malachite green oxalates; MG)에 대한 pH 및 온도 효과를 측정하였다. 수용액 속에서 MG는 pH 3-9에서 흡수가 나타나는 반면에, 양이온 NR은 pH 3-5에서 red shift 흡수피크가 나타났으며, 중성 NR은 pH 8-12에서 흡수피크가 얻어졌다. NR에 대해서는 465.13 mg/g, MG에 대해서는 459.89 mg/g의 최대 흡수 피크가 각각 298와 318 K에서 얻어졌으며, 자유에너지 E_a 값은 각각 4.472-5.559 kJ/mol과 2.000-2.886 kJ/mol로 얻어졌다. 또한, ΔH° , ΔS° , ΔG° and E_a 과 같은 다양한 열역학적인 변수들을 계산했으며, 전체적인 반응의 흡수과정은 자발적이고, 흡열반응으로 진행됨을 알 수 있었다.

주제어: Maghnia clay, 흡수, 양이온 염료, isotherm, Langmuir, Freundlich, D-R, NR, MG

ABSTRACT. The effects of pH and temperature on the removal of two dyes (neutral red; NR and malachite green oxalates; MG) from aqueous effluents using Maghnia montmorillonite clay in a batch adsorption process were investigated. The results showed the stability of the optical properties of MG in aqueous solution and adsorbed onto clay under wide range of pH 3-9. However, the interaction of NR dye with clay is accompanied by a red shift of the main absorption bands of monomer cations under pH range of 3-5, whereas, those of neutral form remains nearly constant over the pH range of 8-12. The optimal pH for favorable adsorption of the dyes, i.e. $\geq 90\%$ has been achieved in aqueous solutions at 6 and 7 for NR and VM respectively. The most suitable adsorption temperatures were 298 and 318 K with maximum adsorption capacities of 465.13mg/g for NR and 459.89 mg/g for MG. The adsorption equilibrium results for both dyes follow Langmuir, Freundlich isotherms. The numerical values of the mean free energy E_a of 4.472-5.559 kJ/mol and 2.000-2.886 kJ/mol for NR and MG respectively indicated physical adsorption. Various thermodynamic parameters, such as ΔH° , ΔS° , ΔG° and E_a have been calculated. The data showed that the adsorption process is spontaneous and endothermic. The sticking probability model was further used to assess the potential feasibility of the clay mineral as an alternative adsorbent for organic ion pollutants in aqueous solution.

Keywords: Maghnia clay, Adsorption, Cationic dye, Isotherm, Langmuir, Freundlich, D-R, NR, MG

INTRODUCTION

Clay minerals, the most available, low cost and chemically active surface minerals world, are of great interest, practically because of their extensive uses in many scientific areas such as soil science (stoppage for fertilisers,¹ photostabilizers of pesticides²), industrial technology (heterogeneous catalysis³), colloidal science (decontamination

of water,⁴ pharmaceutical and paint industries⁵) and photochemistry (guide for photo-redox reactions⁶).

Adsorption of cationic organic dyes in smectite clays has been extensively studied, mainly in aqueous solution. This clay is a dioctahedral smectite with isomorphous substitutions of Al^{+3} by Mg^{+2} with structural formula unit:



Where $x=0.5-0.9$.

However for Maghnia montmorillonite, part of the negative charge around 15-50% is due to tetrahedral substitutions of Si^{+4} by Al^{+3} . This clay has an appreciable content of iron.

The great interest of clay minerals for wastewater treatment in recent decade as a result of their catalytic properties and high capacity in the removal contaminants too stable and resistant for conventional methods such as the oxide-reduction and the exchanging resins of ions,⁷ coagulation/flocculation,⁸ membrane separation,⁹ adsorption,¹⁰ the biological methods,¹¹ and more recently the advanced processes of oxidation.¹²

The adsorption of cationic dyes in general is performed via an ionic exchange mechanism, but other interactions, such a hydrophobic effect between guest molecules on the clay surface¹³ and/or H-bonding¹⁴ can contribute to the adsorption of organic dye on clay surface, favouring the dye agglomeration.

Dye adsorption was found to be sensitive to many parameters, such as the dye load rate, surface properties of the clay, exchangeable cations, and the age of dye-clay suspension, pH solution and temperature.¹⁵ It is commonly accepted that in clay-aqueous systems the potential of the layer surface charge is determined by the activity of ions (e.g. H^+ or pH). A convenient index of the tendency of a surface to become either positively or negatively charged as a function of pH is the value of the pH required to give zero point charge (pH_{ZPC}).¹⁶ pH_{ZPC} is a critical value for determining the sign and magnitude of the net charge carried on the clay mineral surface during adsorption of reactive dyes. Temperature is an essential parameter in adsorption reactions. According to the adsorption theory, enthalpies of adsorption are in most cases exothermic,¹⁷ but for smectite-type clay minerals, a different trend is observed where increasing thermal motion allows the uptake of molecules, causing adsorption to increase as temperature rises.

The aim of this study was to assess the effect of pH and temperature on the stability of the absorption band maxima and the adsorption capacities of neutral red and malachite green oxalates dyes from aqueous Na-saturated clay suspension. The Langmuir, Freundlich and Dubini-Radushkevich (D-R) isotherm models were used to the isotherm data for their applicability. Various thermodynamic parameters, such as ΔH° , ΔS° , ΔG° and E_a have been calculated. The sticking probability model was further used to evaluate the applicability of the Na-saturated clay as an alternative adsorbent for organic ion pollutants in aqueous solution.

MATERIALS AND METHODS

A phenazin group cation, Neutral red dye, NR (MW=288.8 $\text{g}\cdot\text{mol}^{-1}$, $\lambda_{\text{max}}=520$ nm, $\epsilon=25000$ $\text{cm}^{-1}\text{mole}^{-1}\text{dm}^3$) and BB9 dyes (MW=319,5 $\text{g}\cdot\text{mol}^{-1}$, $\lambda_{\text{max}}=665$ nm, $\epsilon=95000$ $\text{cm}^{-1}\text{mole}^{-1}\text{dm}^3$) and triphenylmethane dye, Malachite green oxalate (MW=507.51 $\text{g}\cdot\text{mol}^{-1}$, $\lambda_{\text{max}}=617$ nm, $\epsilon=42000$ $\text{cm}^{-1}\text{mole}^{-1}\text{dm}^3$), from Across product for microbiological analysis and were used without any further purification. Molecular structures of Neutral red and Malachite green oxalate dyes were shown in Fig. 1.

Aqueous dye solution stock was prepared by dissolving accurately weighed neat dye in distilled water to the concentration of 1g/L. Experimental solutions were obtained by successive dilutions.

Natural clay was supplied by the Ceramics Society of Maghnia (west of Algeria). The sodium form of clay with a particle size < 0.2 μm was prepared in order to obtain good clay colloidal dispersions, as follows: clay was saturated with Na^+ by repeated exchange with NaCl (1M) aqueous solution. The < 0.2 particle size fraction was separated by centrifugation and it was washed several times with distilled water until free Cl^- was not detected in the suspension (AgNO_3 test). The < 0.2 fraction was collected by centrifugation and freeze dried at 60°C for 24 h and is crushed. The material resulting from different treatments will be indicated by clay-Na.

X-ray fluorescence was performed on a spectrometer of mark (Oxford). The sample is powder tiny room and prepared (pearl borated) is subjected to a source of X-radiation of fluorescence characteristic of its chemical composition.

Adsorption experiments were carried out as a single-stage batch test using a magnetically stirrer. A suspension containing 0.1 g of adsorbent sample was mixed with a

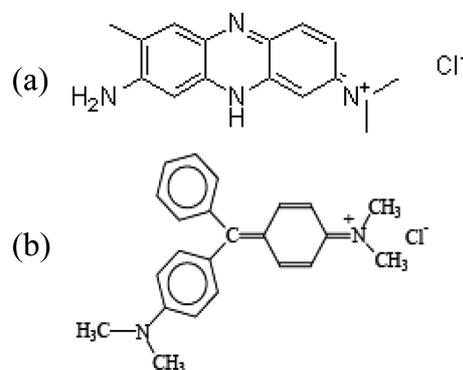


Fig. 1. Molecular structures of basic dyes: (a) Neutral red (NR); (b) Malachite green oxalates (MG).

100 ml aqueous solution of dye at a known initial concentration and initial pH in a flask at constant temperature of 298 K. The initial pH values of the solutions were previously adjusted with 0.1 M HCl or NaOH using digital pH-meter (WTN: WISSENSCHAFTLICH TECHNISECHE WERKSTÄTTEN; weilehein Allemagne pH-330) pH-meter. Aliquot of the solution were withdrawn at a pre-determined time intervals and were centrifuged (EBA-Hetlich) at 3500 rpm for 15 min to remove any adsorbent particles. Dye concentrations in the supernatant solutions were subsequently estimated by measuring absorbance at maximum wavelengths of dyes (UV-2401 (PC) SHIMADZU-corporation spectrometer). The adsorption tests were continued until the equilibrium concentration was reached. The effect of initial pH on the adsorption percentage of MG were researched over a range of pH values from 3 to 12. The experiments were also performed by varying the temperature from 283 to 318 K.

The data obtained from the adsorption experiments were then used to calculate the adsorption capacity, Q_e (mg/g), of the adsorbent by a mass-balance relationship, which represents the amount of adsorbed dye per the amount of dry adsorbent Eq. (1):

$$Q_e \text{ (mg/g)} = \{(C_o - C_e) V\} / m \quad (1)$$

where C_o and C_e are the initial and equilibrium solution concentrations (mg/L) respectively. V is volume of the solution (L), and m is the weight of the dry adsorbent used (g).

The removal rate $A(\%)$ of adsorbed dye was calculated based on following equation Eq. (2):

$$A(\%) = \{(C_o - C_e) 100\} / C_o \quad (2)$$

RESULTS AND DISCUSSION

Table 1 displays the results of chemical composition in the clay-Na sample. The major elements of the clay-Na, expressed in terms of oxide, are primarily of silica, and alumina with appreciable iron content. The CaO and Na₂O (K₂O) reflect the contents of interlayer cationic in clay. The other oxides present in traces amounts such. In the perfect montmorillonite, the total theoretical content of SiO₂ and Al₂O₃ is 92%¹⁸ and the content ratio of SiO₂ to Al₂O₃ is 2.6. In the Magnesia clay, the total content of SiO₂ and Al₂O₃ is 84.90% and the corresponding ratio of SiO₂ to Al₂O₃ is 2.52, so this type of clay belongs to the Na-montmorillonite category. The cation capacity of exchange and total specific surface of the clay-Na sample were estimated by the methylene blue (MB) method¹⁹ are of 101.72

Table 1. XRF analysis of the of the clay-Na sample

Element	Percentage by weight/unit
SiO ₂	60.75
Al ₂ O ₃	24.15
Fe ₂ O ₃	2.51
CaO	1.56
MgO	2.54
Na ₂ O	3.63
K ₂ O	0.65
SiO ₂ /Al ₂ O ₃	2.52
LIO	5.21

LOI : Loss on ignition

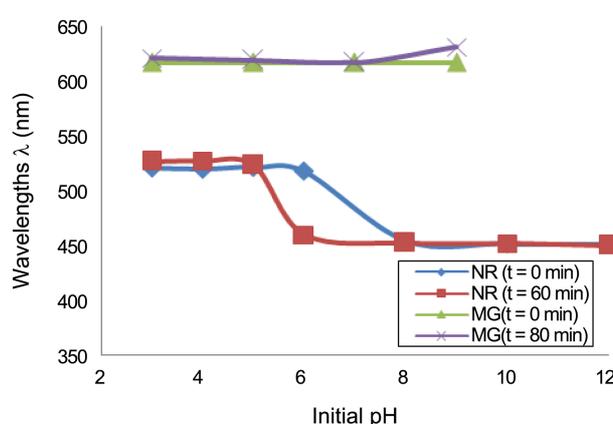


Fig. 2. The position of absorption bands maxima of NR and MG dyes in aqueous solution and adsorbed onto clay-Na as a function of pH for [NR]=[MG]=50 mg/L, [Clay-Na]=0.1g/L, T=298K and contact time of 60 min (NR) and 80 min (MG).

meq/100 gr of clay-Na and 673.93 m²/g respectively.

Fig. 2 and Table 2 represent the evolution of the main absorption bands of dyes in aqueous solution and adsorbed onto clay-Na at various pH values.

Neutral red, in aqueous solution at various pH values, exhibits two forms: NR⁺H and NR, which are in equilibrium with each other. NR, which has absorption bands in the range of 451-454 nm under neutral and alkali conditions (pH>6), whereas NR⁺H, is found to lie between 518 and 521.5 nm under acidic medium (pH≤6) However, the pH has no effect on the absorption bands (at around 617 nm is attributed to the absorption of monomer cations, MG⁺ and near 425 nm is assigned to the protonated cations, MG²⁺H) of MG dye, thus affirming their high stability over the pH range of 3-9. At high alkaline medium (pH>9) the colorless carbinol base is formed. Such an effect was observed for the similar malachite green,²⁰ methyl green²¹ and crystal violet.²²

As seen in Fig. 2, the adsorption of NR onto clay-Na is

Table 2. The position absorption bands and adsorption percentage of NR and MG dyes in aqueous solution and adsorbed onto clay-Na as a function of pH for [NR]=[MG]=50 mg/L, [Clay-Na]=0.1 g/L, T=298 K and contact time=60 min (NR) and 80 min (MG)

Initial pH	NR					MG				
	In aqueous solution		Adsorbed on clay-Na		Percentage Adsorption (%)	In aqueous solution		Adsorbed on clay-Na		Percentage Adsorption (%)
	Species / λ (nm)		Species / λ (nm)			Species / λ (nm)		Species / λ (nm)		
NR ⁺ H	NR	NR ⁺ H	NR	MG ⁺	MG ²⁺ H	MG ⁺	MG ²⁺ H			
3	520.5	-	527	-	62.52	617	424	621	426	59.84
4	519.5	-	527.5	-	69.09	-	-	-	-	-
5/5.4	521.5	-	523.5	-	82.35	617	425	619	-	72.41
6.5/7	518	-	-	460	87.19	617	424	617	426	80.40
8/9	-	454	-	452.5	63.91	617	423	631 / 596	-	81.01
10	-	451.5	-	452	66.66	Col.	Col.	Col.	Col.	-
12	-	451	-	450.5	52.39	Col.	Col.	Col.	Col.	-

R²: Regression coefficient

NR⁺H and MG⁺: monomer cations of neutral red and malachite green dyes, NR: conjugate base form of neutral red, MG²⁺H: protonated cation of malachite green, Col.: colorless.

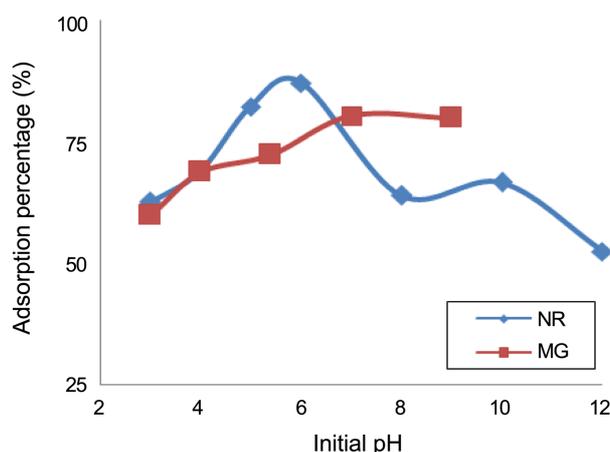
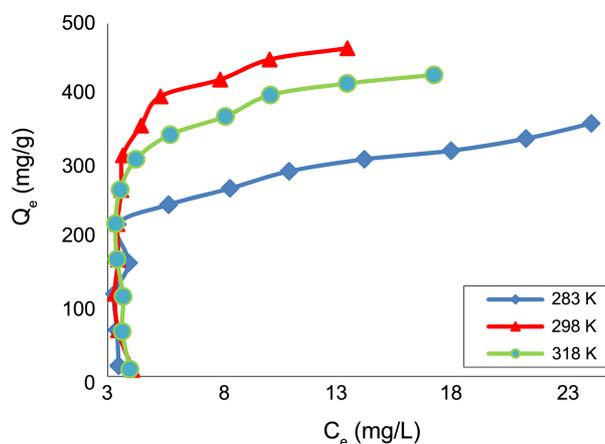
accompanied by a red shift of the main absorption bands to longer wavelengths under pH range of 3-5, whereas, the NR (conjugate base) form has a nearly constant absorption bands over the pH range of 8-12. At pH 6, the band maximum shifts from 518 nm (in aqueous solution) to shorter wavelengths, almost reaching 460 nm (in clay-Na suspension). These results are consistent with externally and internally adsorbed monomer cations (pH<6), monomer cation-conjugate base equilibrium at pH=6 and shifting the monomer cation-conjugate base equilibrium to the conjugate base form (pH>6) respectively.

However, for MG, the results (Table 2) show a slight stability of the main bands of both forms (MG⁺ and MG²⁺H) in clay-Na suspension under pH values in the range of 3-7, while, the absorption band attributed to MG⁺ shifted to longer wavelengths at pH 9, almost reaching 631 nm with respect to that in aqueous solution. The shift did not exceed 10 nm over the pH range of 3-5 and 3-7 for NR and MG respectively, but is significantly higher for NR at pH 6 and MG at pH 9, being 14 and 58 nm respectively.

Shift to higher wavelengths of ≈ 10 nm are always observed for dye monomers adsorbed at the clay surface. The observed shift can be attributed to the change in the environmental polarity/acidity of negatively-charged clay surface with respect to water surrounding, suggesting that the adsorption process is instantaneous.²³

In addition, this change is accompanied by the appearance of new band at 596 nm placed in shorter wavelengths assigned to an influence on π -orbital. Such influence might be caused by an adjacent platelet, indication flocculation or by the formation of dimers on the surface of the clay-Na.^{24,25}

The pH significantly affected the adsorption capacities of both dyes. As shown in Fig. 3 and Table 2, for NR, the

**Fig. 3.** Adsorption percentage of NR and MG dyes onto clay-Na as a function of pH for [MB]=[MG]=50 mg/L, [Clay-Na]=0.1 g/L, T=298 K and contact time of 60 min (NR) and 80 min (MG).**Fig. 4.** Adsorption isotherm of NR dye onto clay-Na for [NR]=5-60 mg/L, [Clay-Na]=0.1 g/L, pH=6 and contact time of 60 min.

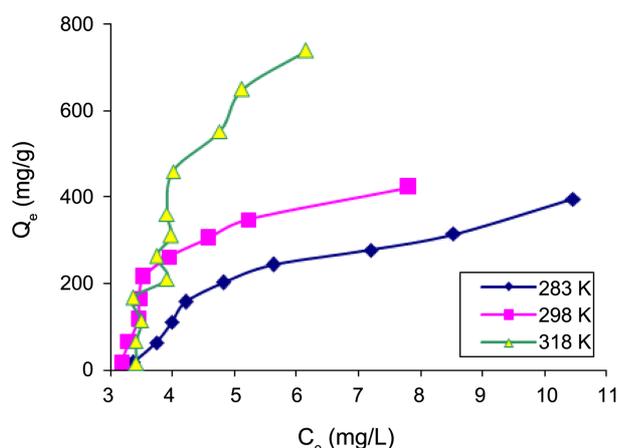


Fig. 5. Adsorption isotherm of MG dye onto clay-Na for [MG]=5-60 mg/L, [Clay-Na]=0.1 g/L, pH=7 and contact time of 80 min.

dye adsorption increases from 62.52% to 87.19% with an increase in pH from 3 to 6.5 and then decreases to 52.39% at pH=12, whereas, for MG, the adsorption increases from 59.84 to 80.40% as the pH value rises from 3 to 7 then it remains constant beyond pH=7. The maxima adsorption of NR (87.19%) and MG (80.40%) are achieved at pH 6 and 7 respectively. For this reason, the pH 6 for NR and 7 for MG are selected for subsequent experiments.

Fig. 4 and 5 display the results of the adsorption isotherms of dyes. The adsorption of both dyes forms a typical Langmuir-type isotherm according to Giles classification system.²⁶ The maximum adsorption capacities of dyes were 465.13 and 459.89 mg/g for NR and MG at 298 and 318 K respectively. It indicates that the adsorption seems to favor the dye NR slightly than MG. This behavior of preferential adsorption can be explained in point of view of structures and molecular weight of dyes (NR=288.8 g/mole and MG=507.51 g/mole). The NR with one weaker size and molecular weight will compete with faster for the actives sites than MG.

Langmuir²⁷ and Freundlich²⁸ and Dubini-Radushkevich (D-R)²⁹ isotherms were applied to assess the performance of the adsorption process of NR and MG dyes onto clay-Na. Parameters of Langmuir, Freundlich and D-R plots of dyes adsorption onto clay-Na were shown in Table 3.

The Langmuir adsorption isotherm assumes that adsorption takes place at specific homogenous sites within the adsorbent and has found successful application in many adsorption processes of monolayer adsorption. The linear form of the Langmuir isotherm equation is represented by the following equation Eq. (3):

$$C_e/Q_e = 1/(K_L Q_{max}) + C_e/Q_{max} \quad (3)$$

where Q_{max} (mg/g) is the maximum amount of the dye per unit weight of clay-Na to form a complete monolayer coverage on the surface bound at high equilibrium dye concentration C_e (mg/L), and K_L is the Langmuir constant related to the free energy of adsorption (L/g). The plots of C_e/Q_e versus C_e for the adsorption of NR and MG onto

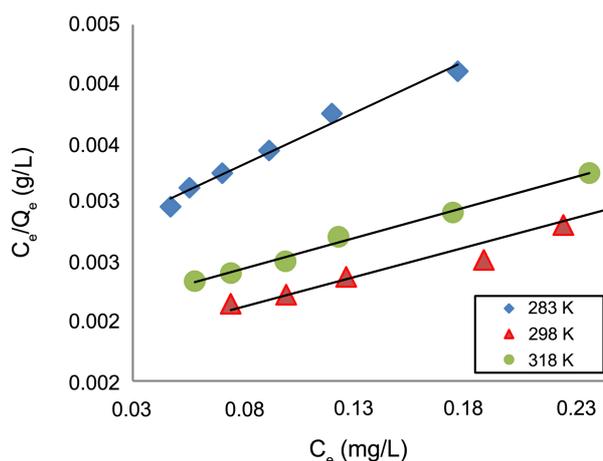


Fig. 6. Langmuir isotherm of NR dye onto clay-Na for [NR]=5-60 mg/L, [Clay-Na]=0.1 g/L, pH=6 and contact time of 60 min.

Table 3. Isotherm parameters of NR and MG dyes adsorbed onto clay-Na for [NR]=[MG]=5-70 mg/L, [Clay-Na]=0.1 g/L, pH=6(NR) and 7 (MG), T=298 K and contact time of 60 min (NR) and 80 min (MG)

Experimental results		Langmuir model $C_e/Q_e = 1/(K_L Q_{max}) + C_e/Q_{max}$			Freundlich model $\text{Ln}Q_e = \text{Ln}K_F + (1/n)\text{Ln}C_e$			Dubini-Radushkevich model $\text{Ln}Q_e = \text{Ln}X_m - K_{DR}E^2$				
System	T (K)	Q_{exp} (mg/g)	Q_{max} (mg/g)	K_L (L/g)	R^2	K_F (L/g)	1/n	R^2	X_m (mg/g)	K_{DR} (mol ² /kJ ²)	Ea (kJ/mol)	R^2
NR/clay-Na	283	358.51	370.37	0.325	0.987	159.940	0.243	0.999	364.672	0.050	4.472	0.981
	298	465.13	588.24	0.320	0.946	262.066	0.227	0.934	625.155	0.038	5.129	0.853
	318	427.25	500.00	0.384	0.994	213.983	0.261	0.982	518.531	0.032	5.590	0.979
MG/clay-Na	283	395.33	500.00	0.053	0.986	188.858	0.327	0.955	31.785	0.125	2.000	0.985
	298	421.79	500.00	0.200	0.97	106.911	0.679	0.954	38.939	0.076	2.564	0.982
	318	459.89	500.00	0.077	0.866	7.591	2.732	0.955	43.684	0.060	2.886	0.982

R^2 : Regression coefficient

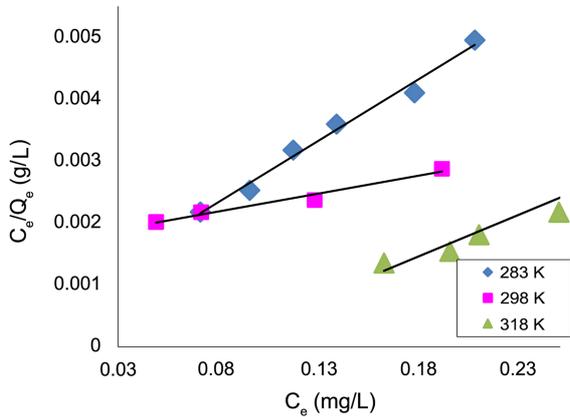


Fig. 7. Langmuir isotherm of MG dye onto clay-Na for [MG]=5-60 mg/L, [Clay-Na]=0.1 g/L, pH=7 and contact time of 80 min.

clay-Na (Fig. 6 and 7) give a straight line of slope of $1/Q_{\max}$ and intercept $1/Q_{\max}K_L$.

The Freundlich isotherm is an empiric equation employed to describe heterogeneous systems. The logarithmic form of the Freundlich equation Eq. (4) is:

$$\ln Q_e = \ln K_F + (1/n) \ln C_e \quad (4)$$

where K_F and n are Freundlich adsorption isotherm constants (L/mg), being indicative of the extent of the adsorption and the degree of nonlinearity between solution concentration and adsorption, respectively. The values of Freundlich constants (K_F and n) were calculated from the plots (Fig. 8 and 9) of $\ln Q_e$ against $\ln C_e$.

The regression coefficients, R^2 (given in Table 3) of the Langmuir and Freundlich are high (0.946-0.994) and (0.934-0.999) for NR (0.866-0.986) and (0.954-0.955) for MG at 283, 298 and 318 K respectively. The calculated Q_{\max} values also agree very well with the experimental data, suggesting that the adsorption of MB as well as MG

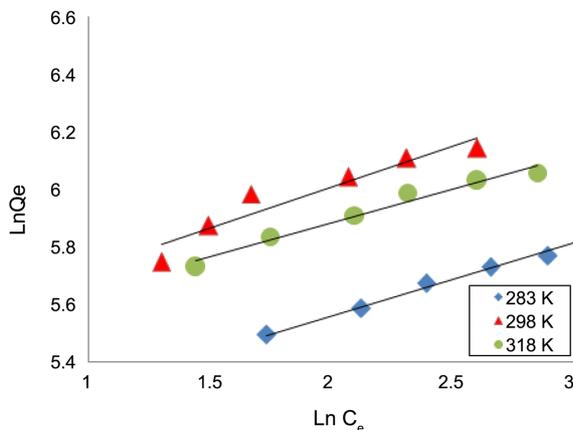


Fig. 8. Freundlich isotherm of NR dye onto clay-Na for [NR]=5-60 mg/L, [Clay-Na]=0.1 g/L, pH=6 and contact time of 60 min.

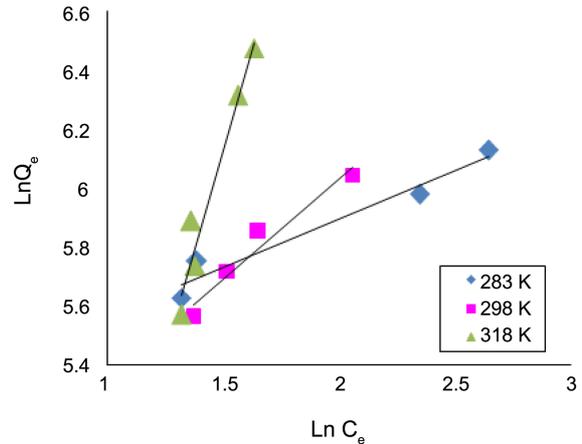


Fig. 9. Freundlich isotherm of MG dye onto clay-Na for [MG]=5-60 mg/L, [Clay-Na]=0.1 g/L, pH=7 and contact time of 80 min.

onto clay-Na is well described by Langmuir than Freundlich isotherm. The high fit to the Langmuir model for both dyes suggests that the adsorption is limited with monolayer coverage.

The Dubini-Radushkevich (D-R) isotherm is more general than the Langmuir isotherm because it does not assume a homogenous surface or constant adsorption potential. It was applied to distinguish between the physical and chemical adsorption of dye. The linear D-R isotherm can be represented in the form Eq. (5):

$$\ln Q_e = \ln Q_m - K_{DR} \varepsilon^2 \quad (5)$$

where K_{DR} (the porosity factor) is related to the mean free energy of adsorption per mole of the adsorbate (mol^2/kJ^2), Q_m is the theoretical saturation capacity (mg/g), and ε is the Polanyi potential, which is defined by Eq. (6):

$$\varepsilon = RT \ln(C_o/C_e) \quad (6)$$

where R is the gas constant (J/mol.k) and T is the absolute temperature (K). Hence the D-R plots (Fig. 10 and 11) $\ln Q_e$ against ε^2 indicates a straight line with a high regression coefficient (R^2).

The values of K_{DR} and Q_m evaluated from the slopes and intercepts of these plots are listed in Table 3.

The adsorption affinities Q_m of clay-Na for NR are 364.672, 625.155 and 525.531 mg/g at 283, 298 and 318 K respectively, indicating that the clay-Na has a greater affinity at 298 K. The calculated Q_m values also agree very well with the experimental data. The porosity factors K_{DR} are found to be less than unity, suggesting that the adsorption of NR can be a significant process.

The constant K_R gives an idea about the mean free energy of adsorption (E_a) when one mole of the ion is transferred

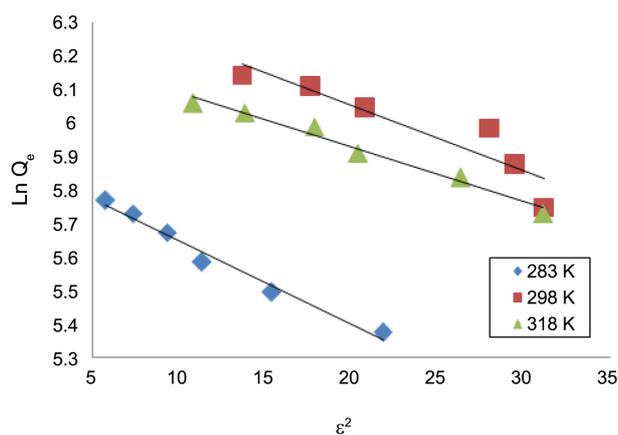


Fig. 10. D-R isotherm of NR dye onto clay-Na for [NR]=5-60 mg/L, [Clay-Na]=0.1 g/L, pH=6 and contact time of 60 min.

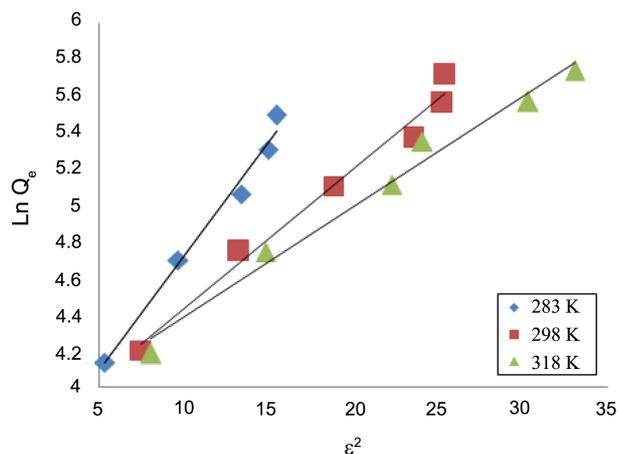


Fig. 11. D-R isotherm of MG dye onto clay-Na for [MG]=5-60 mg/L, [Clay-Na]=0.1 g/L, pH=7 and contact time of 80 min.

to the surface of the adsorbent from the infinity in the solution and it can be computed using the following relationship³⁰ Eq. (7):

$$E_a = (-2K_{DR})^{-1/2} \quad (7)$$

The mean energy provides information about adsorption mechanism is physical adsorption ($0 < E_a < 8$ kJ/mol) or chemisorptions³¹ ($20 < E_a < 40$ kJ/mol).

The numerical value of the apparent free energies E_a from the D-R model for NR are determined at different temperatures and found to lie between 4.472 and 5.590 kJ/mol corresponding to physical adsorption.

On the other hand, as listed in *Table 3*, the calculated Q_m values obtained from the D-R model do not give reasonable values, which are too low compared with experimental data. This finding suggests that the adsorption process of MG onto clay-Na does not follow the D-R model.

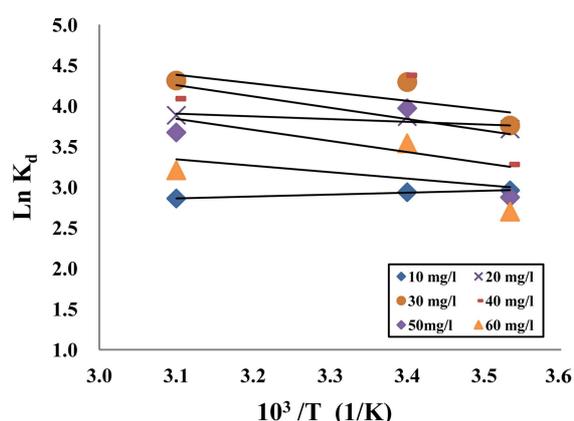


Fig. 12. Plot of $\text{Ln} K_d$ against reciprocal temperature ($1/T$) for NR adsorption onto clay-Na for [Clay-Na]=0.1 g/L, pH=6, [NR]=10-60 mg/L, $T=283-318\text{K}$ and contact time of 60 min.

Table 4. The potential sticking probability relationship between adsorbate and adsorbent

Values of S^* Potential sticking probability	
$S^* > 1$	Adsorbate unsticking to adsorbent - no adsorption
$S^* = 1$	Linear sticking relationship between adsorbate and adsorbent - possible mixture of physisorption and chemisorptions mechanism.
$S^* = 0$	Indefinite sticking of adsorbate to adsorbent chemisorptions mechanism predominant.
$0 < S^* < 1$	Favourable sticking of adsorbate to adsorbent - physisorption mechanism predominant.

S^* : Sticking probability

The influence of temperature on the dye adsorption was investigated over the range of temperature between 283 and 318 K. Thermodynamic parameters were determined using the following equations Eq. (8 and 9):

$$K_d = Q_e/C_e \quad (8)$$

$$\text{Ln} K_d = G^\circ/RT = S^\circ/R - H^\circ/RT \quad (9)$$

where K_d is the distribution coefficient (ml/g^{-1}), C_e and Q_e (mg/g) are the dye concentration and the adsorption capacity at equilibrium respectively. ΔH° , ΔS° , and T are the enthalpy, entropy, and temperature in kelvin, respectively, R is the gas constant. The ΔH° and ΔS° values obtained from the slope and intercept of Van't Hoff plots of $\text{Ln} K_d$ versus $1/T$ for different initial concentration was presented in *Fig. 12* and *13*. Gibbs free energy ΔG was calculated using the equation (Eq. 10):

$$G^\circ = H^\circ - TS^\circ \quad (10)$$

The values of the thermodynamic parameters for the sorption of dyes onto clay-Na are given in *Table 5*. The values

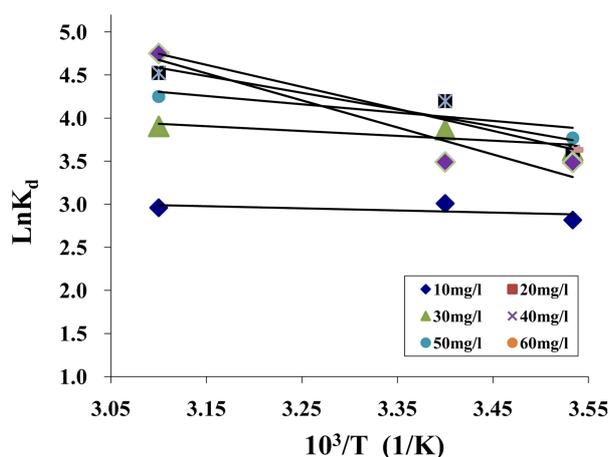


Fig. 13. Plot of $\text{Ln}K_d$ against reciprocal temperature ($1/T$) for MG adsorption onto clay-Na for $[\text{Clay-Na}] = 0.1 \text{ g/L}$, $\text{pH} = 7$, $[\text{MG}] = 10\text{--}60 \text{ mg/L}$, $T = 283\text{--}318 \text{ K}$ and contact time of 80 min.

ΔH° in the range of 2.785 to 11.565 kJ/mol and 2.036 to 26.089 kJ/mol for NR and MG, indicate the physisorption³² of both dyes onto clay-Na for all studied concentrations at different temperatures.

The positive values of ΔH° show the endothermic nature of adsorption. The negative values of free energy ΔG° showed that the adsorption is highly favorable and spontaneous. It is of note that ΔG° up to -20 kJ/mol are consistent with electrostatic interaction between sorption sites and the organic ion (physical adsorption) while $\Delta G^\circ = -40 \text{ kJ/mol}$ involve charge sharing or transfer from de clay-Na surface to the organic ion to form a coordinate bond (chemical adsorption). The ΔG° values obtained in this investigation are $< -12 \text{ kJ/mol}$, indicative that physical adsorption is predominant mechanism in the sorption pro-

cess.³³⁻³⁵

The positive value of ΔS° indicated that the sorption process was irreversible and random at the solid/liquid interface during the sorption of neutral red and malachite green onto clay-Na adsorbent.

In order to additional support the assertion that physical adsorption is the predominant mechanism, the values of activation energy (E_a) and sticking probability (S^*) were estimated from the experimental data. They were calculated using a modified Arrhenius type equation related to surface coverage (θ) as expressed in equation Eq. (11):

$$\text{Ln}(1-\theta) = \text{Ln}S^* + E_a/RT \quad (11)$$

The surface coverage (θ) for studying the sticking probability was calculated from the relation Eq. (12):

$$\theta = (1-C_e/C_0) \quad (12)$$

where C_0 and C_e are the initial and equilibrium dye concentration (mg/L) respectively.

The sticking probability (S^*) is function of the adsorbate/adsorbent and the temperature of the system under consideration. The parameter S^* indicates the measure of the potential of an adsorbate to remain on the adsorbent indefinitely. For favourable sticking of adsorbate to adsorbent, the value of S^* (*Table 4*) must lie in the range $0 < S^* < 1$ which corresponds to physisorption mechanism. The Plot of $\text{Ln}(1-\theta)$ against $1/T$ (*Fig. 14 and 15*) indicates a straight line a slope of E_a/R and an intercept of $\text{Ln}(S^*)$. The apparent activation energy (E_a) and the sticking probability (S^*) are estimated from the plot with a high regression coefficient.

The results (shown in *Table 4*) indicate that the adsorp-

Table 5. Thermodynamic parameters for the adsorption of NR and MG dyes onto clay-Na for $[\text{Clay-Na}] = 0.1 \text{ g/L}$, $[\text{NR}] = [\text{MG}] = 10\text{--}60 \text{ mg/L}$, $\text{pH} = 6$ (NR) and 7 (MG) $T = 283\text{--}318 \text{ K}$ and contact time of 60 min (NR) and 80 min (MG).

system	[Dye] (mg/L)	ΔH (kJ/mol)	ΔS (kJ/mol.K)	ΔG (kJ/mol)			E_a (kJ/mol)	S^* (10^{-1})
				283 K	298 K	318 K		
NR / clay-Na	10	-1.954	0.018	-6.970	-7.236	-7.590	1.978	1.707
	20	2.785	0.041	-8.850	-9.466	-10.289	2.194	0.553
	30	8.879	0.064	-9.226	-10.186	-11.465	-0.515	0.111
	40	11.565	0.071	-8.595	-9.663	-11.088	-10.126	0.002
	50	11.315	0.067	-7.651	-8.656	-9.997	-6.875	0.012
	60	6.576	0.048	-7.058	-7.781	-8.745	-5.927	0.024
MG / clay-Na	10	2.036	0.031	-6.786	-7.254	-7.877	-1.31	2.06
	20	4.664	0.047	-8.688	-9.396	-10.339	-3.79	0.398
	30	7.981	0.060	-9.145	-10.052	-11.263	-6.75	0.096
	40	16.145	0.088	-8.794	-10.116	-11.879	-13.79	0.0054
	50	21.225	0.105	-8.561	-10.140	-12.245	-18.40	0.000084
	60	26.089	0.119	-7.791	-9.5877	-11.982	-22.29	0.000021

S^* : Sticking probability

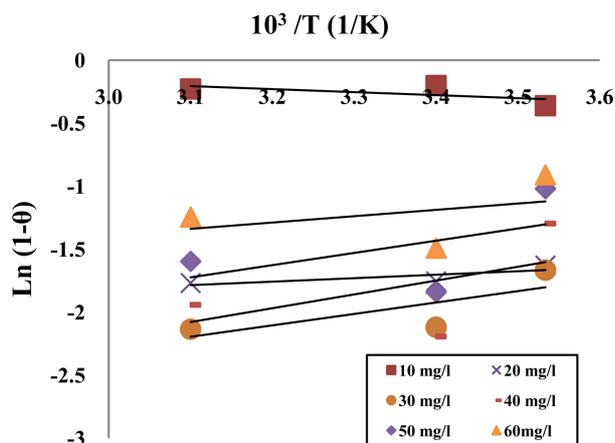


Fig. 14. Plot of $\ln(1-\theta)$ against reciprocal temperature ($1/T$) for the NR adsorption onto clay-Na for $[\text{Clay-Na}] = 0.1 \text{ g/L}$, $\text{pH} = 6$, $[\text{NR}] = 10\text{-}60 \text{ mg/L}$, $T = 283\text{-}318 \text{ K}$ and contact time of 60 min.

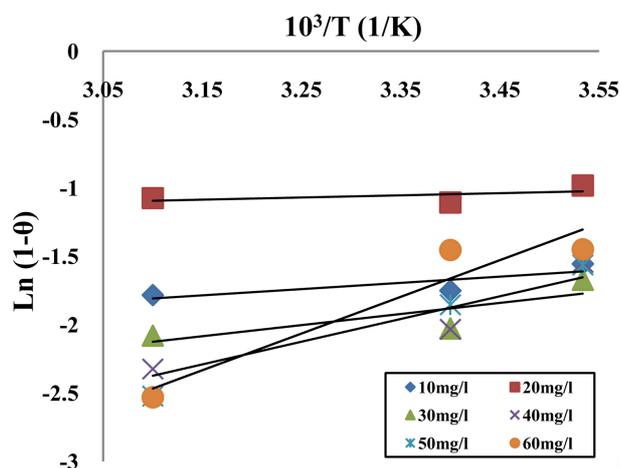


Fig. 15. Plot of $\ln(1-\theta)$ against reciprocal temperature ($1/T$) for the MG adsorption onto clay-Na for $[\text{Clay-Na}] = 0.1 \text{ g/L}$, $\text{pH} = 7$, $[\text{MG}] = 10\text{-}60 \text{ mg/L}$, $T = 283\text{-}318 \text{ K}$ and contact time of 80 min.

tion reaction of MG is exothermic, whereas that of NR is endothermic up to 20 mg/L of NR, while at higher dye concentration the adsorption reaction becomes exothermic. The apparent activated energy, E_a , lie in the range of 1.978 and 2.194 kJ/mol ($\leq 20 \text{ mg/L}$ of NR) and found to be -0.155 and -10.126 kJ/mol when the NR concentration increases above 20 mg/L. However, for MG, the E_a values are found to lie between -1.31 to -22.29 kJ/mol for all dye concentrations.

The negative values of E_a indicate that lower solution temperatures favor dye removal by adsorption onto clay-Na, suggesting that the probability of organic ion sticking to the clay-Na is very high as $S^* \ll 1$ for both dyes. These values confirm that the adsorption process is physisorption.

CONCLUSION

Maghnia clay deposits was selected as a local, cheaper and readily available adsorbent for the removal of Neutral red and Malachite green oxalate dyes from the aqueous effluents. The stability of the main absorption bands and the adsorption capacities of dyes onto clay suspension were assessed as function of pH and temperature. Maximum adsorption of dyes, i.e. $\approx 90\%$ has been achieved at a pH of 6 for NR and 7 for MG. The most proper adsorption temperatures were 298 and 318 K with maximum adsorption capacities of 465.13 and 459.89 mg/g for NR and MG respectively. The adsorption equilibrium results for both dyes follow Langmuir, Freundlich isotherms, whereas the experimental data of NR seem to fit the D-R model very well than that of MG. The values of the mean free energy E_a of 4.472-5.559 kJ/mol for NR indicated physical adsorption. The data showed that the adsorption process is spontaneous and endothermic. The negative values of the apparent activated energy, E_a , indicate that lower solution temperatures favor dye removal by adsorption onto clay-Na, suggesting that the probability of organic ion sticking to the clay-Na is very high as $S^* \ll 1$ for both dyes. These values confirm that the adsorption process is physical adsorption.

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