Maghnia Montmorillonite흡착제에 의한 수용액으로부터 양이온 염료 제거에 관한 반응속도론 연구

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Kinetics on the Removal of Cationic Dyes from Aqueous Solutions over Maghnia Montmorillonite Adsorbent

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요약. 수용액으로부터 3개 양이온 염료(메틸렌 블루 MB, 중성래드 NR, 녹공작석 옥살산염MG)를 제거하는 Maghnia 점토의 흡착제로서의 가능성을 알아보기 위해 접촉시간, pH, 초기 염료 농도, 흡착제 사용량등을 변화시키면서 조사하였다. 적절한 pH는 NR의 경우 6이었고, MB와 MG의 경우 7로 나타났다. 90% 이상의 최대 염료 흡착은 약 60분내에 이루어졌으며, 염료 흡착은 유사 2차반응속도식을 따랐다.

주제어: 점토, 흡착, 반응속도론, 염료, 메틸렌 블루, 중성래드, 녹공작석 옥살산염

ABSTRACT. The potential feasibility of Maghnia clay as adsorbent to remove three cationic dyes (methylene blue (MB), neutral red (NR) and malachite green oxalates (MG)) from aqueous solution was investigated at various operating parameters such as contact time, pH, initial dye concentration and adsorbent dose. Optimum pH values for dyes adsorption were 6 for NR and 7 for MB and MG, respectively. Maximum adsorption of dyes, i.e. $\geq$ 90% has been achieved in aqueous solutions in 60 minutes. The adsorption of dyes followed the pseudo-second-order rate equation.

Keywords: Clay, Adsorption, Kinetic, Dye, Methylene blue, Neutral red, Malachite green oxalates

INTRODUCTION

Dyes effluents released (approximately 7. 10^5 tons) into the environment by technological activities pose a serious threat to the environment. Their presence in water, even at very low concentrations, may significantly affect photosynthetic activity in aquatic life due to reduced light penetration. In addition, some dyes such as azo and triphenylmethanes groups are either toxic or mutagenic and carcinogenic.[1] Due to their synthetic origin and complex aromatic molecular structures, which make them more stable, non- biodegrade, conventional wastewater treatment techniques such as oxidation-reduction and exchanging resins of ions,[2] coagulation/ flocculation,[3] membrane separation,[4] adsorption,[5] biological methods,[6] and more recently the advanced processes of oxidation,[7] are ineffective. Adsorption is one of the effective methods to remove coloured textile contaminants from wastewaters.

Many low-cost adsorbents for dye removal from mineral waste,[9] agricultural wastes, microbial biomass,[10] higher plant biomass,[11] tree fern,[12] orange peel,[13] date pits[14] palm kernel fiber, sawdust,[15] peanut hull,[16] neem leaf,[17] de-oiled soya,[18] moss Rhytidiadelphus squarrosus,[19] activated carbon,[20,21] rice husk-based porous carbon,[22] magnetic particles[23] and paper sludge.[24]

Recently, we used clay mineral for the successful adsorption of metal ions,[25,26,27] basic dyes[28,29] as a result of their catalytic properties and high capacity in the removal con-

taminants too stable and resistant for conventional methods. Adsorption of cationic organic dyes in smectite clays has been extensively studied, mainly in aqueous solution. This clay is a dioctahedral smectite with isomorphic substitutions of Al^{+3} by Mg^{+2} with structural formula unit:

$$(Si_8)^{IV} (Al_{4-x} Mg_x)^{VI} O_{20} (OH)_4$$

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 adsorption of cationic dyes is not exclusively due to the ionic exchange mechanism but other interactions, such a hydrophobic effect between guest molecules on the clay surface[30] and/or H-bonding[31] can contribute to the adsorption of organic dye on clay surface, favouring the dye agglomeration.

The aim of the present study was to assess the potential ability of locally available clay originated of Maghnia montmorillonite deposit (west of Algeria) for removal of three cationic dyes (methylene blue, neutral red and malachite green oxalates) from aqueous solutions. The adsorption of dyes was investigated in solutions of pH 3 - 13. The adsorption kinetics was determined quantitatively by the pseudo-first- and second-order reactions.

MATERIALS AND METHODS

Natural clay from Maghnia (Algeria) was used in a purified form. A thiazin group cation, methylene blue, MB (MW = 319,5 g.mol^{-1}, λ_{max} = 665 nm, ε = 95000 cm^{-1} mole^{-1} dm^3), a phenazin group cation, Neutral red dye, NR (MW = 319.50 g.mol^{-1}, λ_{max} = 520 nm, ε = 25000 cm^{-1} mole^{-1}dm^3) and a triphenylemethane group cation, Malachite green oxalates, MG (MW = 507. 51 g/mol, λ_{max} = 617 nm, ε = 42000 dm^3/cm mole) from Across product for microbiological analysis and used without any further purification. Molecular structures of dyes is shown in *Fig*. 1.

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 (1 M) 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, freeze dried

(a)

(b)

(c)
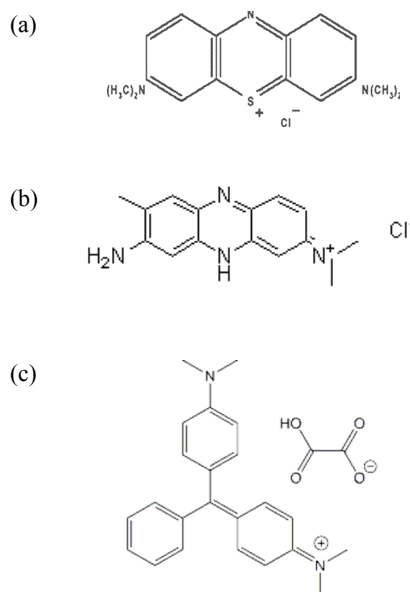
Fig. 1. Molecular structures of dyes (a) Methylene blue (MB) (b) Neutral red (NR) and (c) Malachite green oxalates (MG).

at 60 ^{o}C for 24 h and crushed. The material resulting from different treatments will be indicated by clay-Na.

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

Adsorption kinetics experiments were carried out as a single-stage batch test using a magnetically stirrer at 298 K using 250 mL beaker containing 100 mL different concentrations and initial pH values of dye solutions. The initial pH of dye solutions was adjusted by HCl/NaOH solutions using digital pH-meter (HANNA HI 83141). Different doses of sorbent were added to each beaker. The samples were withdrawn from the beaker at the predetermined time intervals, and adsorbent was separated from the solution by centrifugation (EBA-Hetlich) at 3500 rpm for 15 min. Dye concentrations in the supernatant solutions were subsequently estimated by measuring absorbance at maximum wavelengths of dyes with **UV** mini-1240 spectrophotometer (UV-Vis Spectrometer SHIMAHIDZU) and computing from the calibration curves. The experiments were done by varying the initial pH (3 - 13); amount of adsorbent (0.1 - 0.5 g/L) for MB and (0.07 - 0.2 g/L) for NR and MG respectively and concentration of dye solution (30 - 70 mg/L) at different time intervals.

The efficiency of color removal was expressed as the percentage ratio of decolorized dye concentration to that of initial one (Eq. (1) and (2)):

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

element	percentage by weight/unit
SiO_2	60.75
Al_2O_3	24.15
Fe_2O_3	2.51
CaO	1.56
MgO	2.54
Na_2O	3.63
K_2O	0.65
SiO_2/Al_2O_3	2.52
LIO	5.21

LOI: Loss on ignition

$$A(\%) = \{(C_o - C_e) \times 100\}/C_o \qquad (1)$$

$$Q_e \ (mg/g) = \{(C_o - C_e) \times V\}/C_o \qquad (2)$$

Where C_o and C_e are the initial and equilibrium dye concentrations (mg/L) respectively. V is the volume of the solutions (L), and m is the weight of the clay-Na (g).

RESULTS AND DISCUSSION

Table 1 displays the results of chemical composition (Oxford spectrometer) 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 Na_2O (K_2O) reflect the contents of interlayer cationic in clay. The other oxides present in traces amounts such. In the perfect montmorillonite structure, the total theoretical content of SiO_2 and Al_2O_3 is 92%[32] and the content ratio of SiO_2 to Al_2O_3 is 2.6. In the Maghnia clay, the total content of SiO_2 and Al_2O_3 is 84.90% and the corresponding ratio of SiO_2 to Al_2O_3 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 were estimated by the methylene blue (MB) method[33] are of 101.72 meq/100 gr of clay-Na and 673.93 m^2/g respectively.

The effects of initial pH solution on the adsorption percentages of NR and MB dyes were investigated over a range of pH values from of 3 to 13, but for MG, the experiments were only conducted from pH 3 to 9 for avoiding dye degradation. As shown in *Fig*. 2, when the initial pH for both MB and MG dyes was increased from 3 to 7, the percentage of dyes adsorbed increased from 81.47 to 90. 81% for MB and from 59.84 to 80.40% for MG, then the dye adsorption was unaffected by pH in the range of 7 - 9. At higher pH values of 9 - 13 the dye adsorption decreased to 80. 46 % at pH of 13. However, for NR, the percentage of dye increased from
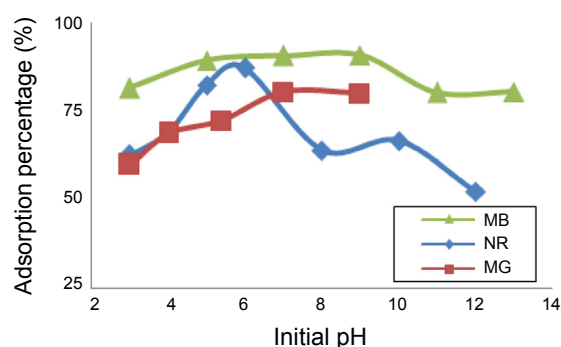
Fig. 2. Effect of initial pH solution on the adsorption percentages of dyes onto clay-Na for [Clay-Na] = 0.1 g/L (NR and MG) and 0.3 g/L (MB), [MB] = [NR] = [MG] = 50 mg/L, T = 298 K, and contact time of 60 min.

62.52 to 87.19% as the pH value was increased from 3 to 6.5, which decreased to 52.39 % at pH of 12. The maximum adsorptions of dyes were 90.81, 87.19 and 80.40 % for MB, NR and MG were achieved at pH 7, 6 and 7 respectively. For this reason, the pH 7 for MG, 6 for NR and 7 for MG are selected for subsequent experiments.

The adsorption of these charged dye groups onto the adsorbent surface is primarily influenced by the surface charge on the adsorbent, which is in turn influenced by the solution.

For clay minerals the potential determining ions are H^+ and OH^- and complex ions formed by bonding with H^+ and OH^-. The broken Si-O bonds and Al-OH bonds along the surfaces of the clay crystals result in hydrolysis, is an amphoteric surface hydroxyl group that can associate (Rec. 1) and dissociate (Rec. 2) proton.

To explain the relationship between the layer charge density and the adsorption, so-colled models of surface complexation (SCM) was developed.[34] In the 2-pK approach we assume two reactions for surface protonation.[35]

At low pH the reaction might be:

$$Si\text{-}OH + H^+ \leftrightarrow Si\text{-}OH_2^+ \qquad (Rec.1)$$

Lower adsorption rate of dyes at low pH is probably due to the presence of excess H^+ ions competing with the cations groups on the dyes for the adsorption sites.

However, the high removal percentage observed for NR at pH 6 (low pH) is attributed to the formation of surface hydrogen bonds between the surface of the hydrogen bonds of the hydroxyl groups on the clay-Na surface and the nitrogen atoms of neutral red cations.[36]

At high pH the reaction is:

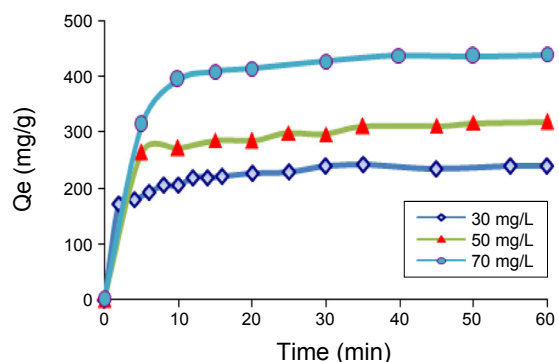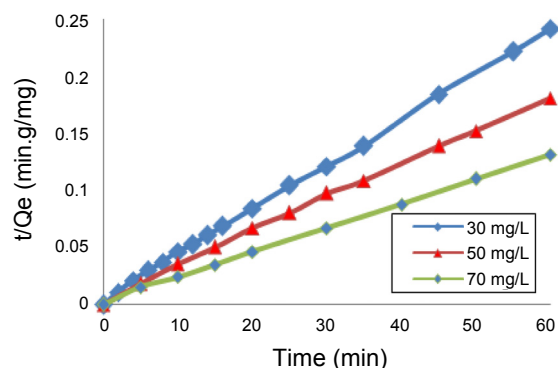$$Si\text{-}OH + OH^- \leftrightarrow Si\text{-}O^- + H_2O \qquad (Rec.2)$$
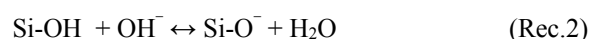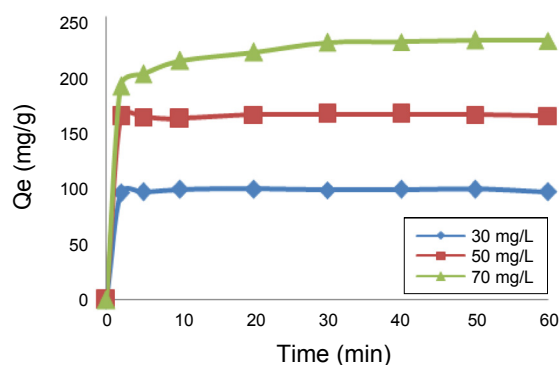
Fig. 3. Adsorption kinetic for MB adsorption at various initial concentrations for [Clay-Na] = 0.3 g/L, pH = 7 and T = 298 K.
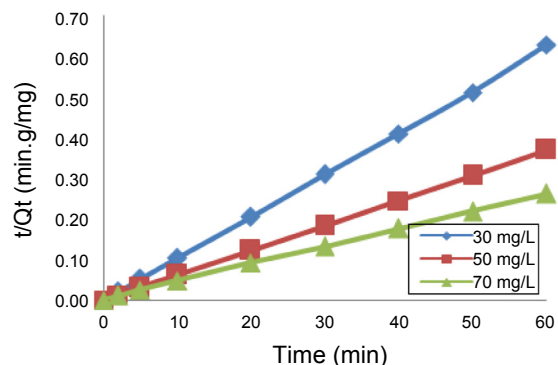
Fig. 6. Pseudo-second order kinetic for MB adsorption at various initial concentrations for [Clay-Na] = 0.3 g/L, pH = 7 and T = 298 K.

Fig. 4. Adsorption kinetic for NR adsorption at various initial concentrations for [Clay-Na] = 0.1 g/L, pH = 6 and T = 298 K.
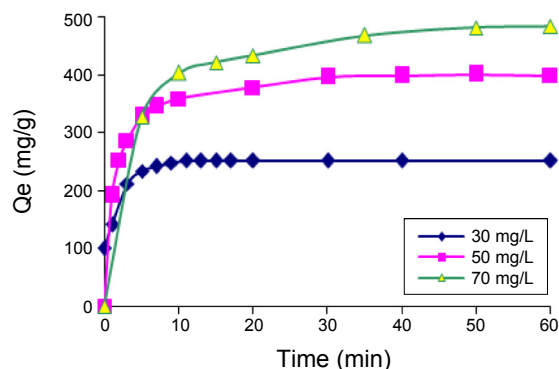

Fig. 7. Pseudo-second order kinetic for NR adsorption at various initial concentrations for [Clay-Na] = 0.1 g/L, pH = 6 and T = 298 K.

Fig. 5. Adsorption kinetic for MG adsorption at various initial concentrations for [Clay-Na] = 0.1 g/L, pH = 7 and T = 298 K.

Fig. 8. Pseudo-second order kinetic for MG adsorption at various initial concentrations for [Clay-Na] = 0.1 g/L, pH = 7 and T = 298 K.
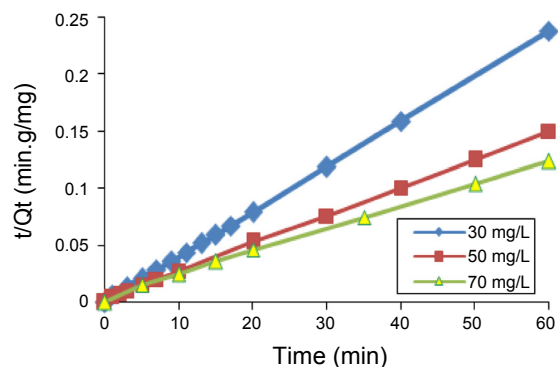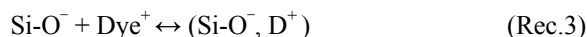
In our studies the adsorption maximum for both MB and MG dyes were achieved at pH 7 respectively. So at neutral and high pH, the solution in contact with the basal oxygen surface of the tetrahedral sheet will contain excess hydroxyls. The surface will then exhibit a cation exchange capacity (Rec. 3):

$$Si\text{-}O^- + Dye^+ \leftrightarrow (Si\text{-}O^-, D^+) \qquad (Rec.3)$$

The adsorption percentage of MB decreased over the pH range of 9 - 13(above pH 9), then remained constant up to pH 13. Such decrease is assigned to the presence of dimers in the clay-Na environment competing with the monomers
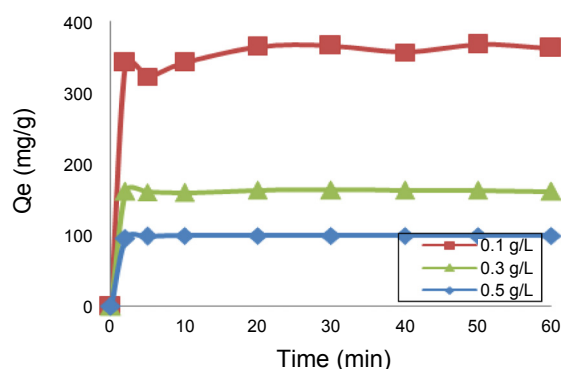
Fig. 9. Adsorption kinetic for MB adsorption at various adsorbent doses for [MB] = 50 mg/L, pH = 7 and T = 298 K.

Fig. 12. Pseudo-second order kinetic for MB adsorption at various adsorbent doses for [MB] = 50 mg/L, pH = 7 and T = 298 K.

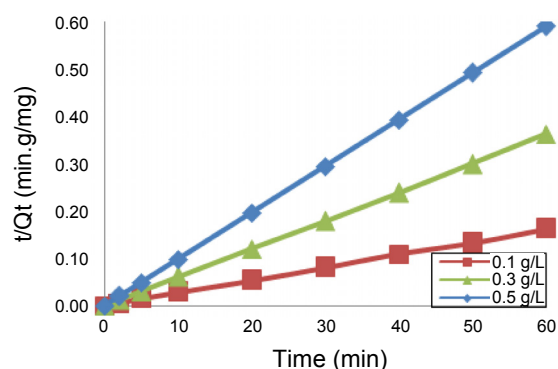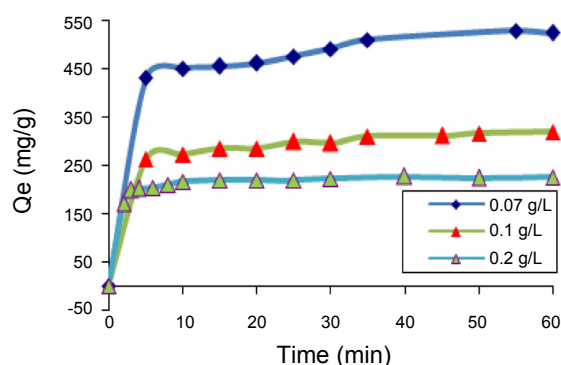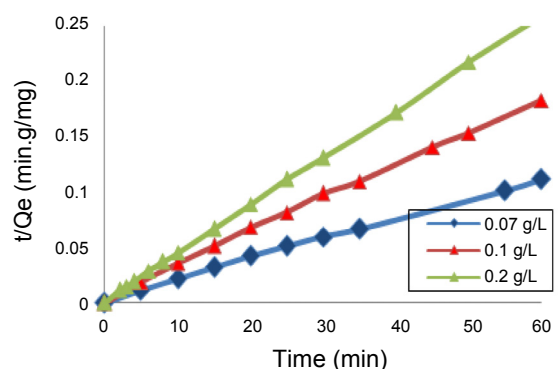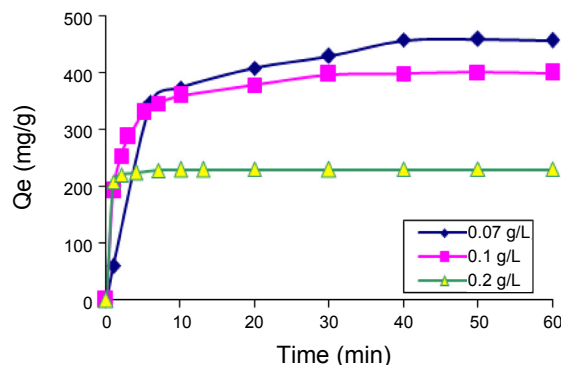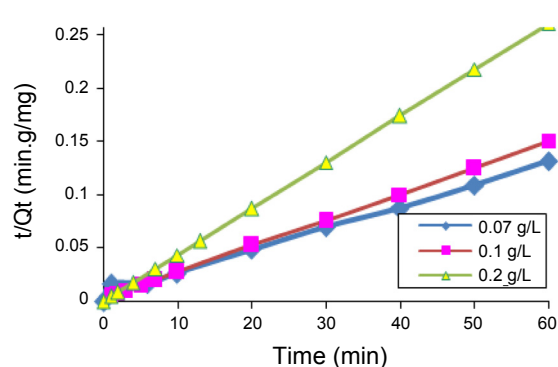**Fig. 10.** Adsorption kinetic for NR adsorption at various adsorbent doses for [NR] = 50 mg/L, [Clay-Na] = 0.1 g/L, pH = 6 and T = 298 K.

Fig. 13. Pseudo-second order kinetic for NR adsorption at various adsorbent doses for [NR] = 50 mg/L, pH = 6 and T = 298 K.

Fig. 11. Adsorption kinetic for MG adsorption onto clay-Na at various adsorbent doses for [NR] = 50 mg/L, pH = 7 and T = 298 K.

Fig. 14. Pseudo-second order kinetic for MG adsorption onto clay-Na at various adsorbent doses for [NR] = 50 mg/L, pH = 7 and T = 298 K.

cations (MB[+]) on the dyes for the active sites (Supporting results).

On the other hand, at neutral and higher pH (above 10), most NR dye occurred in the undissociated form. Due to hydrophobic interactions between aromatic rings of dye molecules, Neutral red tends to aggregate in aqueous solution. This aggregation phenomenon is more noticed at high

alkali medium.[37]

The effects of initial dye concentration (*Figs*. 3, 4 and 5) and adsorbent dose (*Figs*. 9, 10 and 11) as a function of contact time were conducted in the range of 0 to 60 min. The results indicated that the process is found to be very rapid initially, and the equilibrium is achieved within 10 min.

As illustrated in *Figs*. 3, 4 and 5, the adsorption capacity

Table 2. Adsorption kinetic parameters for dyes adsorption onto clay-Na at various initial concentrations for [Clay-Na] = 0.1 g/L (NR and MG), 0.3 g/L (MB), pH = 6 (NR), pH = 7 (MB and MG) and T = 298 K.

Experimental results			Pseudo-first order $\log (Q_e - Q_t) = \log Q_e - (K_1/2.303)t$			Pseudo-second order $t/Q_t = 1/K_2 Q_e^2 + t/Q_e$		
System Dye/clay-Na	[MG] (mg/L)	Qexp (mg/g)	Qe (mg/g)	K_1 (min^{-1})	R^2	Qe (mg/g)	K_2 (g/mg.min)	R^2
MB/clay-Na	30	96.971	3.972	0.032	0.184	100.000	0.000	0.999
	50	163.810	6.622	0.055	0.356	166.667	0.000	0.999
	70	228.900	66.222	0.092	0.925	250.000	0.002	0.999
NR/clay-Na	30	239.223	48.461	0.0514	0.968	243.902	0.006	0.999
	50	320.923	89.598	0.0606	0.921	322.581	0.005	0.998
	70	440.506	196.743	0.1131	0.938	476.190	0.005	0.999
MG/clay-Na	30	251.71	199.84	0.465	0.988	256.41	0.001	0.999
	50	398.09	172.58	0.129	0.979	400.00	0.003	0.999
	70	498.13	130.14	0.037	0.968	500.00	0.004	0.999

R^2: Regression coefficient

increased from 96.971 to 228.900 mg/g for MB, from 239.223 to 440.506 mg/g for NR and from 251.71 to 498.13 mg/g for MG when the initial concentration of dyes was increased from 30 to 70 mg/L respectively. Initial concentration provides an important driving force to overcome all mass transfer resistances of the dye between the aqueous and solid phases. Hence a higher initial concentration of dye may enhance the process.

Fig. 9 showed that the adsorption capacity of MB decreased from 367.515 to 99.631 mg/g when the adsorbent dose was increased from 0.1 to 0.5 g/L. As results showed in *Figs.* 10 and 11, the adsorption capacity of dyes decreased from 537.010 to 227.217 mg/g for NR and from 460.44 to 230.05 mg/g for MG as the adsorbent dose was increased from 0.07 to 0.2 g/L respectively.

This may be attributed to overlapping of adsorption sites as a result of overcrowding of adsorbent.[38]

The adsorption kinetics of dyes at different initial concentration, illustrated in *Figs.* 3, 4 and 5, were treated with a pseudo-first order and pseudo-second order models.

The pseudo-first order equation of Lagergren[39] is generally expressed as follows (Eq. (3)):

$$dQ_t/dt = K_1 (Q_e - Q_t) \qquad (3)$$

where Qe and Qt (both in mg/g) are the amount of dye adsorbed per unit weight of adsorbent at equilibrium and at any time *t*, respectively and K_1 (min^{-1}) is the rate constant for adsorption of dye. At given boundary conditions for t = 0, Qt = 0, the equation Eq. (3) can be integrated to give (Eq. (4)):

$$\log_{10} (Q_e - Q_t) = \log_{10} Q_e - (K_1/2.303) t \qquad (4)$$

The values of K_1 were calculated from the slopes of the respective linear plots of log (Qe - Qt) *versus* t. The regression coefficients, R^2, (given in *Table* 2) for the pseudo-first order model at different initial concentration (30 - 70 mg/L) did not exceed the values of 0.925, 0.968 and 0.988 for MB, NR and MG respectively. The calculated Qe values obtained from pseudo-first order kinetic model for dyes were much different compared with experimental Qexp values. These results suggest that the process does not follow the pseudo-first order rate equation of Lagergren.

The adsorption of dyes onto clay-Na at different adsorbent doses were also analyzed with pseudo-first-order model, the regression coefficients, R^2 (given in *Table* 3) result as 0.539, 0.921 and 0.966 for MB, NR and MG respectively. This finding indicates that the adsorption of dyes onto clay-Na does not follow the pseudo-first order model of Lagergren.

The adsorption kinetics following pseudo-second order model given by Ho[40] is represented in the form (Eq. (5)):

$$dQ/dt = K_2 (Q_e - Q)^2 \qquad (5)$$

where Q and Qe represent the amount of dye adsorbed (mg/g) at any time t; K_2 is the rate of sorption (g/mg.min) and Qe the amount of dye adsorbed onto clay-Na at equilibrium (mg/g). Separating (Eq. (6)) gives:

$$dQ/(Q_e - Q)^2 = K_2 dt \qquad (6)$$

Integrating Eq. (5) with respect to the boundary conditions Q = 0 at t = 0 and Q = Q at t = t, the linearised form of pseudo-second order expression can be obtained as (Eq. (7)):

Table **3.** Adsorption kinetic parameters for dyes adsorption onto clay-Na at various adsorbent doses for [MB] = [NR] = [MG] = 50 mg/L pH = 6 (NR); pH = 7 (MB and MG) and T = 298 K.

System Dye/clay-Na	[MG] (mg/L)	Qexp (mg/g)	Pseudo-first order kinetic $\log(Qe - Qt) = \log Qe - (K_1/2.303)t$			Pseudo-second order kinetic $t/Qt = 1/K_2Qe^2 + t/Qe$		
			Qe (mg/g)	K_1 (min^{-1})	R^2	Qe (mg/g)	K_2 (g/mg.min)	R^2
MB/clay-Na	0.1	367.515	500.000	0.000	0.999	50.816	0.060	0.539
	0.3	163.810	166.667	0.720	0.999	6.622	0.055	0.539
	0.5	99.631	100.000	0.000	1.000	3.214	0.067	0.402
NR/clay-Na	0.07	537.010	199.894	0.051	0.836	555.556	0.004	0.999
	0.1	320.924	89.598	0.061	0.921	322.581	0.005	0.998
	0.2	227.217	29.074	0.063	0.867	227.273	0.013	0.999
MG/clay-Na	0.07	460.44	363.99	0.115	0.941	476.19	0.006	0.999
	0.1	398.09	172.58	0.129	0.979	400.00	0.003	0.999
	0.2	230.05	26.90	0.424	0.966	232.56	0.002	0.999

R^2: Regression coefficient

$$1/(Qe - Q) = 1/Qe + K_2t \qquad (7)$$

Equation (7) can be further linearised to (Eq. (8)):

$$t/Qt = 1/K_2Qe^2 + t/Qe \qquad (8)$$

The linearity of the plots of t/Qt *versus* t for adsorption of dyes onto clay-Na at different initial concentration (*Figs.* 6, 7 and 8, *Table* 2) and various adsorbent dose (*Figs.* 12, 13 and 14, *Table* 3) suggest that all adsorption data of dyes are satisfactorily described by pseudo-second order model with extremely higher regression coefficient ($R^2 > 0.998$), based on the assumption that the rate-limiting step may be chemisorptions involving valency forces through sharing or exchange of electrons between the hydrophilic edge sites of clay-Na and polar dye ions.[41] The calculated Qe values obtained from pseudo-second-order kinetic model were close to the experimental Qexp values for all dyes.

CONCLUSION

The potential ability of Maghnia clay to remove three cationic dyes (methylene blue, neutral red and malachite green oxalates) from aqueous solution was investigated at various parameters (contact time, pH, initial dye concentration and adsorbent dose). Optimum pH values for dyes adsorption were 6 for NR and 7 for MB and MG respectively. Maximum adsorption of dyes, i.e. ≥ 90% has been achieved in aqueous solutions by using 0.1 and 0.3 g/L of clay at pH 7 (for both NR and MG) and 6 for MB respectively. The adsorption of dyes followed the pseudo-second-order rate equation.

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