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. Due to their synthetic origin and complex aromatic molecular structures, which make them more stable, non-biodegradable, conventional wastewater treatment techniques such as oxidation-reduction and exchanging resins of ions, coagulation/flocculation, membrane separation, adsorption, biological methods, and more recently the advanced processes of oxidation, 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, agricultural wastes, microbial biomass, higher plant biomass, tree fern, orange peel, date pits, palm kernel fiber, sawdust, peanut hull, neem leaf, de-oiled soyat, moss Rhytidiadelphus squarrosus, activated carbon, rice husk-based porous carbon, magnetic particles and paper sludge.

Recently, we used clay mineral for the successful adsorption of metal ions, basic dyes 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 $\text{Al}^{3+}$ by $\text{Mg}^{2+}$ with structural formula unit:

$$(\text{Si}_8)^{4+}(\text{Al}_{4-x}\text{Mg}_x)^{6+}\text{O}_{20}(\text{OH})_4$$

where $x = 0.5 - 0.9$.

However, for Maghnia montmorillonite, part of the negative charge around 15 - 50% is due to tetrahedral substitutions of $\text{Si}^{4+}$ by $\text{Al}^{3+}$. 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 as a hydrophobic effect between guest molecules on the clay surface and/or H-bonding 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 ($\text{MW = 319.5 g.mol}^{-1}$, $\lambda_{\text{max}} = 665 \text{ nm}$, $\varepsilon = 95000 \text{ cm}^{-1} \text{ mole}^{-1} \text{ dm}^{3}$), a phenazin group cation, Neutral red dye, NR ($\text{MW = 319.50 g.mol}^{-1}$, $\lambda_{\text{max}} = 520 \text{ nm}$, $\varepsilon = 25000 \text{ cm}^{-1} \text{ mole}^{-1} \text{ dm}^{3}$) and a triphenylemethane group cation, Malachite green oxalates, MG ($\text{MW = 507.51 g/mol}$, $\lambda_{\text{max}} = 617 \text{ nm}$, $\varepsilon = 42000 \text{ dm}^{3}/\text{cm mole}$) 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 $< 0.2 \mu$m 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 $< 0.2 \mu$m 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 at 60 °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 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 SHIMADZU) 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

<table>
<thead>
<tr>
<th>element</th>
<th>percentage by weight/unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>60.75</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>24.15</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>2.51</td>
</tr>
<tr>
<td>CaO</td>
<td>1.56</td>
</tr>
<tr>
<td>MgO</td>
<td>2.54</td>
</tr>
<tr>
<td>Na₂O</td>
<td>3.63</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.65</td>
</tr>
<tr>
<td>SiO₂/Al₂O₃</td>
<td>2.52</td>
</tr>
<tr>
<td>LOI</td>
<td>5.21</td>
</tr>
</tbody>
</table>

LOI: Loss on ignition

\[
A(\%) = \left( \frac{C_o - C_e}{C_o} \right) \times 100 \quad (1)
\]

\[
Q_e (\text{mg/g}) = \left( \frac{C_o - C_e}{V} \right) \div C_o \quad (2)
\]

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 Na₂O (K₂O) 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 SiO₂ and Al₂O₃ is 92%³² and the content ratio of SiO₂ to Al₂O₃ is 2.6. In the Maghnia 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 were estimated by the methylene blue (MB) method³³ are of 101.72 meq/100 gr of clay-Na and 673.93 m²/g respectively.

The effects of initial pH solution on the adsorption percentages of dyes onto clay-Na for \([\text{Clay-Na}] = 0.1 \text{ g/L (NR and MG)}\) and \([\text{MB}] = 0.3 \text{ g/L (MB)}\), \([\text{MB}] = [\text{NR}] = [\text{MG}] = 50 \text{ mg/L, } T = 298 \text{ K, and contact time of 60 min.}\)

![Fig. 2. Effect of initial pH solution on the adsorption percentages of dyes onto clay-Na for \([\text{Clay-Na}] = 0.1 \text{ g/L (NR and MG)}\) and \([\text{MB}] = 0.3 \text{ g/L (MB)}\), \([\text{MB}] = [\text{NR}] = [\text{MG}] = 50 \text{ mg/L, } T = 298 \text{ K, and contact time of 60 min.}\)](image-url)

At low pH the reaction might be:

\[
\text{Si-OH} + H^+ \leftrightarrow \text{Si-OH}^+ \quad (\text{Rec.1})
\]

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.

At high pH the reaction is:

\[
\text{Si-OH} + \text{OH}^- \leftrightarrow \text{Si-O}^- + H_2O \quad (\text{Rec.2})
\]
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):

\[
\text{Si-O}^- + \text{Dye}^+ \leftrightarrow (\text{Si-O}^-, \text{D}^+) \tag{Rec.3}
\]

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.
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 alkaline medium.\textsuperscript{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.

<table>
<thead>
<tr>
<th>System</th>
<th>Dye/clay-Na</th>
<th>[MG] (mg/L)</th>
<th>Qexp (mg/g)</th>
<th>Qe (mg/g)</th>
<th>K1 (min⁻¹)</th>
<th>R²</th>
<th>Qe (mg/g)</th>
<th>K2 (g/mg.min)</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>MB/clay-Na</td>
<td>30</td>
<td>239.223</td>
<td>48.463</td>
<td>0.0514</td>
<td>0.968</td>
<td></td>
<td>256.41</td>
<td>0.001</td>
<td></td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>320.923</td>
<td>89.598</td>
<td>0.0606</td>
<td>0.921</td>
<td></td>
<td>400.00</td>
<td>0.003</td>
<td></td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>440.506</td>
<td>196.743</td>
<td>0.1131</td>
<td>0.938</td>
<td></td>
<td>500.00</td>
<td>0.004</td>
<td></td>
</tr>
<tr>
<td>NR/clay-Na</td>
<td>30</td>
<td>251.71</td>
<td>199.84</td>
<td>0.465</td>
<td>0.988</td>
<td></td>
<td>256.41</td>
<td>0.001</td>
<td></td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>398.09</td>
<td>172.58</td>
<td>0.129</td>
<td>0.979</td>
<td></td>
<td>400.00</td>
<td>0.003</td>
<td></td>
</tr>
<tr>
<td>ME/clay-Na</td>
<td>70</td>
<td>498.13</td>
<td>130.14</td>
<td>0.037</td>
<td>0.968</td>
<td></td>
<td>500.00</td>
<td>0.004</td>
<td></td>
</tr>
</tbody>
</table>

R²: Regression coefficient

The values of K₁ were calculated from the slopes of the respective linear plots of log (Qe - Qt) versus t. The regression coefficients, R² (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, R² (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 Ho⁴⁰ is represented in the form (Eq. (5)):

\[
dQ/dt = K_2 (Qe - Q)^2
\]

where Q and Qe represent the amount of dye adsorbed (mg/g) at any time t; K₂ 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:

\[
dQ/(Qe - Q)^2 = K_2 dt
\]

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)):
order rate equation.

respectively. The adsorption of dyes followed the 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. The calculated $Q_e$ values obtained from pseudo-second-order kinetic model were close to the experimental $Q_{exp}$ 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.

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 $T = 298 K$.

<table>
<thead>
<tr>
<th>System</th>
<th>[MG] (mg/L)</th>
<th>$Q_{exp}$ (mg/g)</th>
<th>$Q_e$ (mg/g)</th>
<th>$K_1$ (min$^{-1}$)</th>
<th>$R^2$</th>
<th>$Q_e$ (mg/g)</th>
<th>$K_2$ (g/mg.min)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MB/clay-Na</td>
<td>0.1</td>
<td>367.515</td>
<td>500.000</td>
<td>0.000</td>
<td>0.999</td>
<td>50.816</td>
<td>0.060</td>
<td>0.539</td>
</tr>
<tr>
<td></td>
<td>0.3</td>
<td>163.810</td>
<td>166.667</td>
<td>0.720</td>
<td>0.999</td>
<td>6.622</td>
<td>0.055</td>
<td>0.539</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>99.631</td>
<td>100.000</td>
<td>0.000</td>
<td>1.000</td>
<td>3.214</td>
<td>0.067</td>
<td>0.402</td>
</tr>
<tr>
<td>NR/clay-Na</td>
<td>0.07</td>
<td>537.010</td>
<td>199.894</td>
<td>0.051</td>
<td>0.836</td>
<td>555.556</td>
<td>0.004</td>
<td>0.999</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>320.924</td>
<td>89.598</td>
<td>0.061</td>
<td>0.921</td>
<td>322.581</td>
<td>0.005</td>
<td>0.998</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>227.217</td>
<td>29.074</td>
<td>0.063</td>
<td>0.867</td>
<td>227.273</td>
<td>0.013</td>
<td>0.999</td>
</tr>
<tr>
<td>MG/clay-Na</td>
<td>0.07</td>
<td>460.44</td>
<td>363.99</td>
<td>0.115</td>
<td>0.941</td>
<td>476.19</td>
<td>0.006</td>
<td>0.999</td>
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<tr>
<td></td>
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<td>398.09</td>
<td>172.58</td>
<td>0.129</td>
<td>0.979</td>
<td>400.00</td>
<td>0.003</td>
<td>0.999</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>230.05</td>
<td>26.90</td>
<td>0.424</td>
<td>0.966</td>
<td>232.56</td>
<td>0.002</td>
<td>0.999</td>
</tr>
</tbody>
</table>

$R^2$: Regression coefficient

$1/(Q_e - Q) = 1/Q_e + K_2t$ (7)

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

$t/Qt = 1/K_2Q_e^2 + t/Qe$ (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. The calculated $Q_e$ values obtained from pseudo-second-order kinetic model were close to the experimental $Q_{exp}$ values for all dyes.

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**REFERENCES**

37. Renmin, Gong; Mei, Li.; Chao, Yang; Yingzhi, Sun; Jian, Chen *Journal of Hazardous Materials B* 2005, 121, 247-250.