ADSORPTIVE REMOVAL OF MALACHITE GREEN (OXALATE) BY LOW COST ADSORBENT

Subbareddy Y., Jeseentharani V., Jayakumar C., Nagaraja K. S. and Jeyaraj B.*
Department of Chemistry and Loyola Institute of Frontier Energy (LIFE), Loyola College, Chennai, Tamil Nadu (INDIA)

Received July 05, 2012 Accepted September 20, 2012

ABSTRACT
This study investigated the potential use of a low-cost Fuller’s Earth (FE) for removal of Malachite Green oxalate (MG) dye from an aqueous solution. Batch studies were performed to evaluate the influence of various experimental parameters like adsorbent dose, effect of pH, initial dye concentration at different temperature and different contact time and on the removal of MG. The experimental data were analyzed by Langmuir, Freundlich and Dubinin-Radushkevich isotherms. The isothermal adsorption data fitted best to the Langmuir model. The maximum adsorption capacity of FE was found to be 1.96 x 10^-4 mol/g for MG at room temperature according to the Langmuir equation. The mean energy of adsorption (E) values was in the range of 25.828 kJ/mol to 27.317 kJ/mol, indicating that chemisorption might be major mode in the adsorption of MG onto FE. Adsorption kinetics was studied using pseudo first order and pseudo second order models. Adsorption data of MG onto FE was fitted well by the pseudo second order model. Thermodynamic studies were carried out and the parameters suggest that the process of removal of MG by FE is a spontaneous and endothermic nature since ΔG° value was negative and ΔH° value was positive.

Key Words : Adsorption, Fuller’s Earth (FE), Malachite Green (MG), Kinetics, Endothermic nature

INTRODUCTION
Dyes are used extensively by several industries such as textile dyeing, rubber, plastics and paper industry. About 100,000 dyes commercially available and more than 7 x 10^5 tons of these dyes are produced annually worldwide. Malachite green (MG), a triphenylmethane dye is highly soluble in water and used in aquacultures and animal husbandry as an antifungal, anti-bacterial, anti-parasitical therapeutic agent. MG dye is used extensively in silk, wool, jute and leather industries for dyeing process and in the manufacturing of paints and printing inks. MG in high concentration causes harmful effects on liver, kidney, intestine and gonads of aquatic organisms. There are different methods for removal of dyes. These include photo-degradation, chemical oxidation, ozonation and adsorption. Adsorption process is best among all these methods because of its low cost, effectiveness, simple design, easy operation, free from generation of toxic substances and adsorbent can be recycled. The activated carbon is good adsorbent for removal of dyes from industrial effluents but regeneration desorption is difficult under normal conditions and the overall process becomes more expensive.

AIMS AND OBJECTIVES
The present work is aimed to study the adsorption capacity of FE for MG removal from aqueous solutions. For the removal of MG, different parameters such as adsorbent dose, effect of pH, initial dye concentration, contact time and effect of temperature were studied. The adsorption isotherms, kinetics and thermodynamic parameters were investigated.

MATERIAL AND METHODS
The chemicals used were Malachite green (oxalate) obtained from Merck and Fuller’s earth supplied by Loba Chemie. The chemical composition of the FE sample was analyzed by
X-ray fluorescence (XRF) technique; Axios model DY 8. The X-ray diffraction spectrum was taken on the X-ray Diffraction System, XRD 3003GE, Seifert Analyzer. The BET surface area of FE was measured by using ASAP 2020 Micromeritics instrument. Concentration of MG dye solution was determined by finding out the absorbance at $\lambda_{\text{max}}$ of 617nm using UV-Visible spectrophotometer (ELICO, Model SL-159).

**Batch adsorption experiments**

Batch adsorption experiments were carried out to study the effect of pH, adsorbent dosage, initial dye concentration at different temperature and contact time. The pH of the experimental solution was adjusted by adding few drops of HCl or NaOH solutions. In the adsorption experiments, 50ml of a dye solution of known initial concentration was equilibrated with a required amount of adsorbent in 100ml conical flask. The mixtures were shaken in a water bath shaker (Remi) at a constant temperature until the equilibrium reached. The mixture was filtered and the absorbance of the filtrate was determined by UV – visible spectrophotometer at the maximum wavelength of 617nm. The unadsorbed dye concentration in aqueous solution was obtained by comparing absorbance with calibration curve. Kinetics of adsorption was used to investigate the effect of contact time and to determine the kinetic parameters. 0.08 g FE was added to 50 ml of dye solutions with different initial dye concentrations without changing the solution pH. The mixture was mechanically agitated in a water bath shaker (Remi) at constant temperature. At predetermined time intervals (5–120 min), the samples were drawn and analyzed for the concentration of MG. The percentage removal was calculated by the following equation:

$$\text{Percentage removal (\%) } = \frac{c_0 - c_e}{c_0} \times 100$$

where $c_0$ and $c_e$ (mol/l) are the initial and at equilibrium concentrations of the dye solution respectively.

**RESULTS AND DISCUSSION**

**Characterization of adsorbent**

The XRF technique revealed that the chemical composition of FE consists mainly of SiO$_2$ (71.61%), and it has 12.92 %, Al$_2$O$_3$ % 2.87 Fe$_2$O$_3$, % 2.12 MgO % 1.38 CaO and 1.29 % TiO$_2$. The major peaks that appear in the XRD spectrum for the fresh FE (Fig. 1) at 2θ of 26.62° is characteristic of SiO$_2$. Other peaks appearing at 25.34°, 49.55°, and 62.07° correspond to TiO$_2$. The 2θ peaks appearing at 36.81° and 42.99° are characteristics of MgO. The 2θ peaks corresponding to Al$_2$O$_3$ are observed at 37.11° and 42.41°, while those correspond to Fe$_2$O$_3$ is present at the 2θ peaks of 19.84°, and 45.24°. The BET

![Fig. 1 : X-ray diffraction pattern of Fuller’s Earth (FE)](image)
surface area of FE is 233.92 m²/g. The single point total pore volume of mesopores (914.157 Å) is 0.3490 cm³/g. The BJH pore size distribution measurement indicates that the sample has mesoporosity with pore diameter in the range of 4 – 12nm.

**Effect of adsorbent dose**

Fig. 2 shows the effect of FE dose on the removal of MG. The percentage removal of MG has increased from 54.1 to 99.8% as the adsorbent dose increased from 0.02 to 0.18g per 50m ℓ of dye solution. The increase in percent removal of dye with the increasing FE dosage is due to the increase in the surface area and availability of more adsorption sites.

![Graph showing effect of adsorbent dose on the removal of MG](image)

**Fig. 2**: Effect of FE dose on the removal of MG (2.0 to 3.5×10⁻⁴ M), contact time 120 min

**Effect of pH**

The effect of variation of pH on the removal of MG is shown in Fig. 3 and it is clearly indicated that the removal of MG increases from 85.7 to 99.8% when the pH was increased from 2 to 10. It was found that the maximum MG removal by FE is 99.80% at pH 8.0 with initial concentration of 3 x 10⁻⁴ M. At acidic pH, the dissociation of the metal-hydroxide complexes causes the surface to become positively charged. At basic pH, the surface becomes negatively charged. The metal oxides are converted into MO⁻ type of functional sites and as a result, the binding of cationic dyes onto these surfaces become much favorable.

**Effect of contact time**

Fig. 4 shows effect of contact time on adsorption of MG by FE. This that the adsorption increased with the contact time. The percentage removal was found to be very fast in the first few minutes and thereafter the adsorption becomes slow (Fig. 4). The equilibrium time was found to be 120 min for 2.0×10⁻⁴, 2.5×10⁻⁴ and 3.0×10⁻⁴ M dye concentration.

**Effect of concentration at different temperatures**

The removal of MG was studied in its concentration range from 2.0×10⁻⁴ M to 4.0×10⁻⁴ M, at a fixed dose of 0.08 g and different temperatures (305, 315 and 325±1K). The results are given in Fig. 5. The rate of adsorption of MG was lower at higher concentrations this is due to non availability of adsorption sites on the surface of FE and presence of more number of dye molecules. The adsorption of MG dye was found to increase with increasing temperature (Fig.5),
indicating that the adsorption should be endothermic or chemisorptions in nature. As the temperature increased the extent of adsorption increased due to increase in the number of adsorption sites.

**Adsorption isotherms**

The equilibrium adsorption isotherms are used to describe the adsorption mechanism of dye molecule over the surface of adsorbent. There are different isotherm equations and three important isotherms are selected in this study namely, Langmuir, Freundlich and Dubinin – Radushkevich adsorption isotherms.

**Langmuir adsorption isotherm**

The Langmuir adsorption isotherm explains the homogeneous and uniform adsorption on the surface of adsorbent containing number of identical sites. The linear form of the Langmuir adsorption equation is:

\[ \frac{C_e}{q_e} = \frac{1}{Q_m K_L} + \frac{1}{Q_m} C_e \]  

(2)

where \( q_e \) (mol/g) and \( C_e \) (mol/l) are the amount of dye adsorbed per unit weight of adsorbent and the concentration of the dye solution at equilibrium. The constant \( Q_m \) (mol/g) is the adsorption capacity and \( K_L \) (l/mol) is the Langmuir equilibrium constant. The plot of \( C_e/q_e \) vs. \( C_e \) shows that adsorption follows a Langmuir isotherm (Fig. 6 (a)). Values of \( Q_m \) and \( K_L \) were calculated from the intercept and slope of the linear plots and are presented in Table 1.
**Freundlich adsorption isotherm**

Freundlich adsorption isotherm gives an idea about the heterogeneous system and reversible adsorption. The Freundlich adsorption isotherm equation can be expressed as:

\[
\log(q_e) = \log(K_f) + \frac{1}{n} \log(C_e)
\]  

Where \( K_f \) (mol/g) and \( n \) (dimensionless) are the Freundlich constants, indicating adsorption capacity and adsorption intensity, respectively. The plot of \( \log(q_e) \) vs. \( \log(C_e) \) gives a straight line and the Freundlich constants could be obtained from the slope and the intercept of the plot (Fig. 6 (b)).

**Dubinin and Radushkevich (D-R) isotherm**

Dubinin–Radushkevich (D–R) isotherm is used to distinguish the adsorption takes place by physical or chemical processes. The linear form of the isotherm can be expressed as follows:

\[
\ln(q_e) = \ln(Q_m) - K\varepsilon^2
\]  

where \( K \) is constant related to the adsorption constant (mol\(^2\)/KJ\(^2\)), and \( \varepsilon \) is the Polanyi potential that can be calculated from the equation:

\[
\varepsilon = RT \ln \left( 1 + \frac{1}{C_e} \right)
\]  

where \( T \) is the absolute temperature in K and \( R \) is the universal gas constant (8.314 J/mol/K).

**Fig. 6 (c)** shows the plot of \( \ln(q_e) \) vs. \( \varepsilon^2 \) of the experimental data for the adsorption of MG onto FE. The slope gives \( K \) and from intercept \( Q_m \) can be calculated. The mean energy of sorption, \( E \) (kJ/mol), is calculated by the following equation:

\[
E = \frac{1}{\sqrt{(2K)}}
\]  

The adsorption constants and the correlation coefficients obtained from the isotherms are given in Table 1. The value of \( 1/n \) lies between 0.1 to 1.0 and the \( n \) value lying in the range of 1–10 confirm favorable for adsorption of MG onto FE. The calculated mean energy of adsorption (E) values was found to be in the range of 25.828 kJ/mol to 27.317 kJ/mol, indicating that chemisorption play an important role in the adsorption of MG onto FE. The isotherm plots indicated that the Langmuir equation gave better correlation coefficients than Freundlich and D-R isotherms (Table 1). The applicability of the Langmuir isotherm suggests the monolayer coverage of the dye on the surface of the FE.

**Adsorption kinetics**

In order to evaluate the adsorption kinetics, pseudo first order and pseudo second order models were applied to the experimental data. The pseudo first order equation can be expressed as:

\[
\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303} t
\]  

Where \( q_e \) and \( q_t \) are the amounts (mol/g) adsorbed at equilibrium and at time and \( k_1 \) is the pseudo first order rate constant (1/min).
Table 1: Adsorption isotherm parameters

<table>
<thead>
<tr>
<th>Adsorption isotherm</th>
<th>Temperature (K)</th>
<th>305</th>
<th>315</th>
<th>325</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir isotherm</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$Q_m$ (mol/g)</td>
<td></td>
<td>1.96 x 10^{-4}</td>
<td>2.00 x 10^{-4}</td>
<td>2.08 x 10^{-4}</td>
</tr>
<tr>
<td>$K_L$ (l/mol)</td>
<td></td>
<td>4.66 x 10^{4}</td>
<td>5.50 x 10^{4}</td>
<td>8.43 x 10^{4}</td>
</tr>
<tr>
<td>$R^2$</td>
<td></td>
<td>0.998</td>
<td>0.998</td>
<td>0.997</td>
</tr>
<tr>
<td>Freundlich isotherm</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$K_f$ (mol/g)</td>
<td></td>
<td>5.54 x 10^{-4}</td>
<td>5.19 x 10^{-4}</td>
<td>6.19 x 10^{-4}</td>
</tr>
<tr>
<td>$1/n$</td>
<td></td>
<td>0.113</td>
<td>0.103</td>
<td>0.115</td>
</tr>
<tr>
<td>$R^2$</td>
<td></td>
<td>0.974</td>
<td>0.974</td>
<td>0.971</td>
</tr>
<tr>
<td>Dubinin – Radushkevich isotherm</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$Q_m$ (mol/g)</td>
<td></td>
<td>2.91 x 10^{-4}</td>
<td>3.04 x 10^{-4}</td>
<td>3.21 x 10^{-4}</td>
</tr>
<tr>
<td>$K$ (molF/KJ)</td>
<td></td>
<td>0.074 x 10^{-8}</td>
<td>0.070 x 10^{-8}</td>
<td>0.067 x 10^{-8}</td>
</tr>
<tr>
<td>$E$ (kJ/mol)</td>
<td></td>
<td>25.828</td>
<td>26.640</td>
<td>27.156</td>
</tr>
<tr>
<td>$R^2$</td>
<td></td>
<td>0.937</td>
<td>0.974</td>
<td>0.971</td>
</tr>
</tbody>
</table>

Fig. 6(a): Langmuir isotherm plots for MG adsorption on FE
Fig. 6(b): Freundlich isotherm plots for MG adsorption on FE.

Fig. 6(c): D-R isotherm plots for MG adsorption on FE.
The pseudo second order kinetic model can be represented in the following form:

\[
\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{1}{q_e}t
\]  

(8)

where \(k_2\) is the pseudo second order rate constant (g/mol min). Fig. 7(a) and Fig. 7(b) shows the plots for the pseudo first order \([\log (q_e - q_t) \text{ vs. } t]\) and second order \(t/q_t \text{ vs. } t\) kinetic models, respectively. The kinetic parameters \((q_e, k_1\) and \(k_2)\) were calculated from the intercepts and slopes of the plots for the two models are given in Table 2. The data do not fit the Lagergren model as the \(R^2\) values are comparatively low (ranging from 0.764 to 0.922) and the calculated \(q_e\) (calc) values are too low compared with experimental \(q_e\) (exp). This indicates that the adsorption of MG onto FE is not a pseudo first order model (Table 2). For the second order kinetic model, the correlation coefficients for the linear plots are good (0.999). The calculated \(q_e\) (calc) values are nearly equal to the experimental data (Table 2), which indicated that the MG adsorption system obeys the pseudo second order kinetic model.

Adsorption thermodynamics

Thermodynamic parameters such as Gibbs free energy change \((\Delta G^0)\), enthalpy change \((\Delta H^0)\), and entropy change \((\Delta S^0)\) were determined to evaluate the spontaneity and endothermic nature of the adsorption process. These values were calculated by using the following relationships:

\[
\Delta G^0 = RT \ln K_L
\]  

(9)

\[
\ln K_L = \frac{-\Delta G^0}{RT} = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{R} \left( \frac{1}{T} \right)
\]  

(10)

where \(\Delta G^0\) is Gibb’s free energy change, \(\Delta S^0\) is Change in entropy, \(\Delta H^0\) is change in enthalpy, \(K_L\) is Langmuir constant, \(R\) is universal gas constant (8.314 J/mol/K) and \(T\) is temperature. The values \(\Delta H^0\) and \(\Delta S^0\) can be calculated from the slope and intercept of plot of \(\ln K\) vs. \(1/T\). The negative values of \(\Delta G^0\) (34.28 to 36.83 kJ/mol) in the temperature range 305–325 K, indicated that the process was spontaneous. \(\Delta H^0\) and \(\Delta S^0\) were calculated as 24.36kJ/mol and 188.22 J/mol, respectively. The positive value of \(\Delta H^0\) indicates the endothermic nature of the adsorption process.

Fig. 7(a) : Pseudo first order plots for MG adsorption on FE
Fe acts as a good adsorbent for adsorption of MG dye from aqueous solution. The percentage removal of MG dye was found to vary with adsorbent dose, initial dye concentration, pH, contact time and temperature. Equilibrium data best fitted to the Langmuir adsorption isotherm equation, confirming the monolayer coverage of MG onto FE with a monolayer adsorption capacity of $1.96 \times 10^{-4}$ mol/g. The value of mean sorption energy was found to be greater than 16 kJ/mol indicates that adsorption of MG over FE occurred through chemisorption. The rate of adsorption of MG onto FE was very high in the first few minutes. Equilibrium was reached after a long contact time of 120 min. Adsorption kinetics was found to follow a pseudo second order model. Even though the adsorption is endothermic, the $\Delta G^\circ$ being negative will indicate that the process is favorable. This is due to high positive entropy of the process.

**ACKNOWLEDGEMENT**

The authors thank the financial support from Tamil Nadu State Council for Science and Technology (TNSCST/S&T Projects/AR/CHE/2010-2011), Tamil Nadu, India.
REFERENCES


