EQUILIBRIUM AND KINETICS STUDY OF ADSORPTION
OF SOME DYES ONTO FELDSPAR

H.A. Awala, M.M. El Jamal

Lebanese University, Faculty of Sciences (I),
Chemistry Department, El Hadath, Lebanon.
E-mail: mjmal@ul.edu.lb

Accepted 20 February 2011

ABSTRACT

Adsorption of three dyes methylene blue, methyl red, and fluoresceine onto feldspar have been investigated in this study. To assess the use of feldspar to remove dyes from aqueous solution, the effect of dye concentrations, pH, mass of adsorbent, temperature, and shaking speed have been evaluated. Methyl red and fluoresceine did not show any adsorption at any pH, however methylene blue showed low adsorption. Pseudo-first and pseudo-second order kinetic models were applied to the adsorption data. Pseudo second order model was well in line with the experimental data. Langmuir, Temkin and Freundlich isotherm models were also investigated. According to Langmuir isotherm, the maximum adsorption capacity was estimated as 0.66 mg/g at 40°C. The positive enthalpy indicated that the adsorption was endothermic. The negative values of Gibbs free energy revealed that adsorption was spontaneous.

Keywords: Methylene blue, feldspar, adsorption isotherms, kinetics.

INTRODUCTION

Water pollution mostly comes from wastewater which contains industrial and environmental pollutants. Dyes manufacturing causes serious problems for wastewaters. They affect biodegradation, light penetration and photosynthesis. Minor releases of colorants impact the aesthetics and health disorders to organisms exposed to them producing imbalances in these ecosystems. Furthermore, some of these dyes on passage to drinking water cause damage to human life. For example methylene blue, organic dye usually used to dye cotton and wool, can cause serious health problems such as vomiting, hard breathing, and mental disorder [1]. Possible treatments such as filtration, oxidation, sedimentation and adsorption for cotton textile wastes and their associated advantages and disadvantages are listed in [2]. Adsorption techniques for wastewater treatment have become more popular in recent years owing to their efficiency. Activated carbon is mainly used to remove dyes from aqueous solutions, but it is very expensive [3]. Many reviews appeared in literature about the low cost adsorbents used [3, 4]. The adsorbent can be from agriculture waste (sugarcane bagasse pith and dates' stones) [5, 6], industrial waste products (fly ash and red mud) [7], natural organic products (algae) [8] and natural inorganic materials [9]. Many researchers studied the ability of some natural inorganic materials such as bentonite [10], gypsum [11], perlite [12], zeolite [13] and kaolin [14] to remove dyes from aqueous solution. The use of natural materials as clays and siliceous materials for waste water treatment is increasing because of their high abundance, availability and low cost. Feldspar is natural clay (belong to this group), the most abundant constituent of igneous rocks in nature. The general formula of alkali feldspar is MA1Si3O8 where M is an alkali metal as Na (Albite), K (orthose). It has a formula of the Si2O5 but up to two of the Si(IV) may be replaced by Al(III) with the charge deficiency balanced by large univalent cation. The tetrahedra (of Si and Al four coordinated by oxygen) are linked together in three dimensions to make a framework. The articles about
feldspar adsorption are rare. There is only one concerning the removal of sulfate, phosphate and colored substances from wastewater effluents, but the study on the dyes adsorption is preliminary [15], so in this work, a full adsorption study on feldspar is undertaken. As there is not universal adsorbent for all types of dyes [14], Methylene Blue (basic dye), Methyl Red (azo dye) and Fluoresceine (xanthene dye) are selected as model compounds in an attempt to use feldspar as an adsorbent.

The effect of pH, contact time, initial concentration and temperature were tested in order to optimize the adsorption process. Besides, equilibrium, kinetic and thermodynamic studies were performed in order to investigate the mechanisms of adsorption onto feldspar.

**EXPERIMENTAL**

**Adsorbent**

The raw feldspar (99.5 % pure) was kindly supplied by Soliver, Lebanese society, and used without any further purification. The feldspar was grinded with MF 10 Basic grinder (IKA WEKE) and sieved at 250 μm. The particle size distribution delay in the range 2-280 μm with an average diameter equal to 84 μm. This was determined by Laser scattering particle size distribution analyzer (Horiba, Partica, LA-950V2). The main chemical composition is: SiO₂ (68.9 %), Al₂O₃ (18.1 %), Na₂O (11.5 %) and CaO (1.2 %). XRD and FTIR analyses have been used for the examination of any variation in the samples’ spectra after adsorption of dye. XRD analysis was carried out with D8 Focus Bruker (CuKα, 1.54 E at 50 kV) and FTIR is done on spectrophotometer Thermo, Nicolet IR 200 (dilution with KBr).

**Dyes**

The dyes are of analytical grade (purchased from BDH or Siegfried society) and their chemical structures are illustrated in Fig. 1. Fluoresceine and Methyl Red have acid - base properties, whereas Methylene Blue, cationic dye, has ox-red properties. Accurately weighted quantities of dyes were dissolved in ultra pure water with conductivity of 18 μS (from Force Chankahy, China) to prepare the stock solutions. The working solutions were prepared by diluting the stock solutions to give the appropriate concentrations.

**Batch adsorption experiments**

All adsorption experiments were carried out by agitating the feldspar powder of required amount with certain volume of dye solution of desired concentration at constant temperature in a water bath shaker at 215 rpm.

Several parameters affects the uptakes on the adsorbent, so preliminary study was undertaken to choose the best conditions. The experiments were carried out for various feldspar mass, at different initial dye concentrations, contact time, temperature and pH. The effect of shaking speed and salinity were also studied. At the end of a preliminary determined period of time, samples were withdrawn from the bath shaker, centrifuged at 5000 rpm for 5 minutes and the supernatant solution was analyzed for residual dye concentration. It was determined at λ max of each dye by double beam UV-Vis, Specord 200, Analytical Jena spectrophotometer. Blank samples without adsorbent were run under similar experimental conditions in order to determine any significant loss of dye on the container walls.

The amount of dye adsorbed per unit mass of feldspar at equilibrium (qₑ, mg/g) or at time t (qₜ) were calculated according to the following relations

\[
qₑ = \frac{(C₀ - Cₑ) V}{m}
\]

(1)

\[
qₜ = \frac{(C₀ - Cₜ) V}{m}
\]

(2)
where \( C_o \) and \( C_e \) are the initial and equilibrium concentrations of dye, mg/L, respectively. \( V \) is the volume of the dye solution, L, and \( m \) is the amount of the adsorbent used, g. The percentage of dye removal was determined using equation:

\[
\% \text{removed} = \left( \frac{C_o - C_e}{C_o} \right) \times 100
\]

(3)

**RESULTS AND DISCUSSION**

The preliminary study showed that methyl red and fluoresceine were not adsorbed onto feldspar at any pH, so only the adsorption of methylene blue (MB) will be presented below. The absence of adsorption of fluoresceine and methyl red onto feldspar is due to the absence of attraction between the feldspar and these dyes. The same behavior was observed with kaolinite where the strongest preference was shown by polyaromatic molecules carrying positively charged amino groups [14].

**Effect of initial pH on the adsorption of MB**

In general the pH of the solution affects the charge of the dye and of the adsorbent. In our case it affects only the adsorbent since MB does not have acid base properties. MB remains positively charged. The visible spectrum of MB does not change in function of pH. According to Beer’s law, the constant \( K = A/[MB] \) corresponds to 0.203 L/mg at \( \lambda_{max} \), 656 nm. The effects of pH were studied in range of pH 1.5 - 11.0. For adjusting pH, diluted solutions of NaOH and HCl were used. In this analysis, initial dye concentration was determined as 14 mg/L and experiment was carried out at 20°C. Fig. 2 pointed out that in the pH range 1.5 - 3, the dye removal increased sharply, and for pH > 3.0, the dye removal remained similar. The increase in MB removal is due to the electrostatic interactions between adsorbent and MB [8a, 14, 17]. The increase in the MB removal onto feldspar (68 % SiO\(_2\)) in acidic medium is related to its low pHzc since the pHzc of pure SiO\(_2\) and kaolin (45 % SiO\(_2\)) is 2 and 4, respectively [14].

**Effect of adsorbent dosage**

The effect of adsorbent dosage for MB adsorption onto feldspar was shown in Fig. 3. The adsorbent amount was taken between 0.2 g - 2.5 g and initial dye concentration was determined as 14 mg/L. The results showed that when the adsorbent dosage increased from 0.2 to 1.15 g the removal of the dye increased from 25 % to 90 %, and then reached a plateau. As Pavan et al. reported [16], the larger adsorption surface causes higher adsorption of dye. Similar result is obtained with brown and Posidonia oceanica algae [8, 17]. Therefore, for convenience the adsorbent dosage in the following experiments was selected as 1.0 g. The volume of dye solution in contact with 1g of feldspar also has been defined. The experimental results show 30 mL of sample is enough.

**Effect of contact time**

The effect of contact time for MB adsorption onto feldspar was shown in Fig. 4. It can be observed that, the rate of adsorption was fast in the first 20 minutes.
then gradually slow down until equilibrium was reached. This may be due to strong attractive forces between the dye molecules and the adsorbent. The results indicated that after 1 h the adsorption reached equilibrium for low initial MB concentration. As the equilibrium time is also function of initial dye concentration [17], 3 h will be sufficient to reach equilibrium for isotherm adsorption study.

Effect of shaking speed

The adsorption of dye was undertaken at several shaking speeds ranging from 0 (soaking) to 250 rpm. The results showed that the % of MB removed increased sharply from 5 % to 75 % with the increase of shaking speed from zero to 150 rpm, and then it increased slightly after 150 rpm. The shaking speed selected for further experiments was 215 rpm (78 %). Similar result was obtained by Cavas [8b].

Matrix effect

The wastewater containing dye has commonly high salt concentration, and matrix effect is of some importance in the study of dye adsorption onto adsorbents. Previous research showed that an increase in salinity or ionic strength (Na+ or Ca++) of the solution could cause a decrease in maximum adsorption capacity of basic dyes on other adsorbents [18, 19]. Fig. 5 shows the effect of NaCl concentration on the amount of MB adsorbed. The increase in the salt concentration in dye solution resulted in a decrease of MB adsorption.

This trend could be attributed to the competition between MB ions and Na+ from the salt for the sites available for the adsorption process or to the compression of electric double layer which propelled away the positive charged dye molecules [19].

Characterization of feldspar

The major peaks of feldspar in the XRD spectra appear at 6.325 Å (20 %), and 3.186 Å (100 %). Other small peaks appear at 20 less than 30°. FTIR spectrum of feldspar showed a small wide band with maximum peak at 3440 cm\(^{-1}\). This band can be assigned to the O-H stretching mode of hydroxyl groups and adsorbed water. The Si-O vibration bands at 1155.27, 1096.48 cm\(^{-1}\) are observed. The peaks at 762.11 and 645.53 cm\(^{-1}\) were attributed to Al-OH and Al-O deformation [20]. The comparison of the XRD or the FTIR spectrum before
and after adsorption of MB at highest initial MB concentration did not show any change in the position or in the intensity of the bands. The similarity in the spectra before and after adsorption can be due to the low value of $q_{\text{max}}$. The crystalline structure of feldspar is demonstrated in Fig. 9 [30].

**Kinetic study**

In this study adsorption data are applied to the pseudo-first order, pseudo-second order kinetic models to find the rate constants of adsorption.

The possibility of adsorption data to follow Lagergren pseudo-first order kinetics [21] is given by

$$\frac{dq}{dt} = K_1 (q_e - q)$$  \hspace{1cm} (4)

By integrating Eq. (4), the kinetic rate expression becomes:

$$\log(q_e - q_l) = \log q_e - \frac{K_1}{2.3} t$$  \hspace{1cm} (5)

The first order rate constant $K_1$ can be obtained from the slope of plot between $\log(q_e - q)$ versus time $t$.

A pseudo-second order model proposed by Ho and McKay [22] can be used to explain the sorption kinetics. This model is based on the assumption that the adsorption follows second order chemisorption [23]. The pseudo-second order model can be expressed as:

$$\frac{dq}{dt} = K_II (q_e - q)^2$$  \hspace{1cm} (6)

Integrating Eq. 7 simplifies it to:

$$\frac{t}{q_l} = \frac{1}{K_{II} q_e^2} + \frac{t}{q_l q_e}$$  \hspace{1cm} (8)

where $t$ is the contact time, $q_l$ and $q_e$ are the amount of dye adsorbed, mg/g, at equilibrium and at any time $t$. A plot between $t/q_l$ versus $t$ gives the value of the constant $K_{II}$, g/mg min, and also $q_e$, mg/g, can be calculated.

From the pseudo first order plots, the rate constants and correlation coefficient values of first order model were found at 293 K. As it can be seen from Table 1, the adsorption did not comply well with the pseudo-first order model because of the absence of linearity between log ($q_e - q$) and $t$. In this study, pseudo-

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**Fig. 7.** Determination of activation energy according to Arrhenius equation.

**Fig. 8.** (a) Linear Langmuir plots at different temperatures; (b) Non-linear regression of $Q$ vs. $C_e$. 

$$R^2 = 0.9317 \text{ (15 mg/L)}$$

$$R^2 = 0.9975 \text{ (295 K)}$$

$$R^2 = 0.979 \text{ (303 K)}$$

$$y = 1.7406x + 10.732$$

$$y = 1.4165x + 7.7677$$

$$R^2 = 0.9974 \text{ (303 K)}$$
second order model fitted better when compared with the first order kinetic model (Table 1). Therefore, the adsorption data in the present study supported the chemisorption. The linearity of the plots also showed the validity of the model (Fig. 6). The adsorption rate \( (k_n) \) decreased with increasing solute concentration and increased with increasing temperature, this trend was also observed by Cavas [8] and Ncibi et al. [17]. The activation energy are 25 KJ/mol and 30.7 KJ/mol for 9 and 13 mg/L of MB according to Arrhenius equation (Fig.7).

**Equilibrium study**

The analysis of the isotherm data is important to develop an equation which accurately represents the results and can be used for design purposes. Several isotherm models are used in literature to find the relationship between \( q_e \) and \( C_e \) [24]. The experimental data were estimated by using Langmuir, Freundlich and Temkin equations. The linear forms of these models were used to find the adsorption isotherms as shown below.

The Langmuir isotherm suggests that MB adsorption is limited with monolayer coverage and there is no significant interaction among adsorbed species. The Langmuir isotherm relationship is of a hyperbolic form [25]:

\[
\theta = \frac{q_e}{q_{max}} = \frac{bC_e}{1 + bC_e} \quad b = \frac{K_{ads}}{K_{des}}
\]

(9)

\[
\frac{C_e}{q_e} = \frac{1}{q_{max}} b + \frac{C_e}{q_{max}}
\]

(10)

The plot of \((C_e/q_e)\) vs. \((C_e)\) gives the Langmuir constants, where:

- \( q_{max} \), mg/g, is the maximum sorbate uptake under the given conditions;
- \( b \), L/mg, is the adsorption equilibrium constant, related to the affinity between the adsorbent and sorbate.

Langmuir isotherm determines whether the adsorption is favorable or unfavorable. To determine the characteristic behavior of the adsorption, dimensionless equilibrium parameter is used:

\[
R_L = \frac{1}{1 + bC_e}
\]

where \( b \) is the Langmuir constant and \( C_e \) is the highest dye concentration. For the favorable adsorption \( R_L \) value must be between 0 and 1.

Freundlich isotherm [26] is exponential:

\[
q = K C_e^{(1/n)}
\]

where: \( K \) and \( n \) \((1/n = n_p)\) are Freundlich constants. The linear form of the Freundlich equation was used to find them:

\[
\log q = \log K_f + n_p \log C_e
\]

(11)

Freundlich isotherm constant of \( n_p \) indicates the heterogeneity factor. In the literature, \( n_p \) values lower

<table>
<thead>
<tr>
<th>[MB]_o (mg/L)</th>
<th>Pseudo-first order</th>
<th>Pseudo-second order</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( q_e ) (mg/g)</td>
<td>( q_e ) (mg/g)</td>
</tr>
<tr>
<td>9 (293 K)</td>
<td>0.218</td>
<td>0.049</td>
</tr>
<tr>
<td>9 (303 K)</td>
<td>0.234</td>
<td>0.031</td>
</tr>
<tr>
<td>9 (313 K)</td>
<td>0.245</td>
<td>0.059</td>
</tr>
<tr>
<td>13 (293 K)</td>
<td>0.225</td>
<td>0.073</td>
</tr>
<tr>
<td>18 (293 K)</td>
<td>0.279</td>
<td>0.074</td>
</tr>
</tbody>
</table>
Table 2. Langmuir, Freundlich and Temkin isotherm constants for the adsorption of MB by feldspar obtained by linear regression (The underlined values are obtained by non-linear regression).

<table>
<thead>
<tr>
<th>T (K)</th>
<th>q_{max, exp}</th>
<th>q_{max}</th>
<th>b</th>
<th>R^2</th>
<th>R_L</th>
<th>K_F</th>
<th>n_F</th>
<th>R^2</th>
<th>B</th>
<th>R^2</th>
</tr>
</thead>
<tbody>
<tr>
<td>295</td>
<td>0.37</td>
<td>0.375</td>
<td>0.21</td>
<td>0.9975</td>
<td>0.045</td>
<td>0.154</td>
<td>0.194</td>
<td>0.835</td>
<td>0.056</td>
<td>0.89</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.37</td>
<td>0.26</td>
<td>0.999</td>
<td>0.037</td>
<td>0.155</td>
<td>0.196</td>
<td>0.90</td>
<td>0.0549</td>
<td>0.94</td>
</tr>
<tr>
<td>303</td>
<td>0.54</td>
<td>0.57</td>
<td>0.16</td>
<td>0.9974</td>
<td>0.058</td>
<td>0.185</td>
<td>0.255</td>
<td>0.968</td>
<td>0.097</td>
<td>0.990</td>
</tr>
<tr>
<td>313</td>
<td>0.66</td>
<td>0.706</td>
<td>0.18</td>
<td>0.9953</td>
<td>0.053</td>
<td>0.251</td>
<td>0.23</td>
<td>0.962</td>
<td>0.1044</td>
<td>0.938</td>
</tr>
</tbody>
</table>

than 1 interpret the strong adsorption between adsorbent and sorbate [27].

Temkin isotherm [28] is:

\[ q = \frac{RT}{b} \ln K_T + \frac{RT}{b} \ln C_c = A + B \ln C_c \quad (12) \]

where B - factor related to the heat of adsorption and K_T - Temkin equilibrium constant, L/mg. As seen from Table 2, the adsorption capacity increases with increasing the temperature. In order to know MB adsorption behavior, the experimental data were applied to Langmuir, Freundlich, and Temkin isotherms (Table 2). Fig. 8a and Table 2 show the high fit of the Langmuir model for all three temperatures. The non-linear regression confirmed the compatibility of Langmuir isotherm model (Fig.8b, Table 2). The choice of Langmuir model is confirmed by the low value of \((q_{\text{exp}} - q_{\text{exp}})^2\) (< 0.002).

Feldspar has low adsorption capacity as pure silica (sea sand), so it is not competitive with other inorganic adsorbents such as raw kaolin (15 mg/g) [1], zeolite (20 mg/g) [13] and bentonite (151 mg/g) [29]. The low value of \(q_{\text{max}}\) of MB on feldspar is due probably to its crystalline structure (Fig.9) which let the adsorption occurred only at the surface in contrast to kaolin [14].

Thermal activation of feldspar at 473 and 673 K or NaOH treatments (at 353 K with reflux) did not improve the adsorption of MB onto feldspar as in the case of kaolin [1].

### Thermodynamic study

Thermodynamic considerations of an adsorption process are necessary to conclude whether the process is spontaneous or not. The Gibb's free energy change, \(\Delta G^\circ\), is an indication of spontaneity of a chemical reaction and therefore is an important criterion for spontaneity. Both energy and entropy factors must be considered in order to determine the Gibbs free energy of the process. The thermodynamic parameters are estimated from the equations below:

\[ \ln K_d = -\frac{\Delta H^\circ}{R} \frac{1}{T} + \frac{\Delta S^\circ}{R} \quad (13) \]

(Van’t Hoff Equation)

\[ K_d = \frac{C_s}{C_e} \quad \text{with} \quad C_s = C_e - C_c \quad (14) \]

\[ \Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \quad (15) \]

where \(K_d\) is equilibrium constant for adsorption, \(C_s\) - the amount of the dye adsorbed at equilibrium, mg/L, \(C_c\) - equilibrium concentration of dye, mg/L, \(R\) - ideal gas constant (8.314 J/mol K), and \(T\) - temperature (Kelvin). The value of ln \(K_d\) was plotted versus 1/T. The values of enthalpy and entropy changes were calculated from the graph, and the results for 10 mg/L of MB are summarized in Table 3. The positive values of enthalpy (\(\Delta H^\circ\)) agreed with the endothermic nature of adsorp-

<table>
<thead>
<tr>
<th><a href="mg/L">MB</a></th>
<th>K_d (295 K)</th>
<th>K_d (303 K)</th>
<th>K_d (313 K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>1.487</td>
<td>2.77</td>
<td>9.1</td>
</tr>
</tbody>
</table>

\[
\begin{array}{cccc}
[MB](mg/L) & \Delta H^\circ (KJ/mol) & \Delta S^\circ (KJ/mol.K) & 295 K & 303 K & 313 K \\
10 & 77.85 & 0.286 & 0.70 & 2.83 & 5.5 \\
\end{array}
\]
tion, and the positive values of entropy ($\Delta S^\circ$) imply the increase in randomness. Additionally, the negative values of free energy ($\Delta G^\circ$) imply that the adsorption occurs spontaneously. The $\Delta H^\circ$ value could be used to distinguish physical from chemical adsorption with a borderline at 40 KJ/mol. The $\Delta H^\circ$ value of 77.65 KJ/mol suggested that the adsorption is rather chemisorption. This conclusion is in accordance with the kinetic study where second order condition probably to chemisorption. The adsorption of MB onto bentonite follows the same behavior [29].

CONCLUSIONS

The adsorption was highly dependent on various operating parameters such as adsorbent dose, contact time, pH, initial dye concentration, stirring speed, salt concentration and temperature. Adsorption of MB followed Langmuir isotherm and pseudo second order kinetics. The adsorption process was spontaneous and endothermic. The low adsorption capacity ($q_{max}$) of feldspar let it uncompetitive with other siliceous adsorbent materials.

Acknowledgements

The authors wish to thank the “Ecole Doctorale de Sciences & Technologie” at Lebanese University for its financial support and to Dr. M.H. El Masri, Assistant Professor in Lebanese University, Faculty of Sciences, for her help.

REFERENCES

13. R. Han, J. Zhang, P. Han, Y. Wang, Z. Zhao, M. Tang, Chemical Engineering Journal 145, 2009, 496 –504.
18. R. Han, Y. Wang, P. Han, J. Shi, J. Yang, Y. Lu, J. Hazard Mater, 137, 1, 2006, 550-557.