Sorption Study of a Basic Dye “Gentian Violet” from Aqueous Solutions Using Activated Bentonite

K. Bellir*, I. Sadok Bouziane, Z. Boutamine, M. Bencheikh Lehocine, A-H. Meniai,

Laboratoire de l’Ingénierie des Procédés de l’Environnement, Département de Chimie Industrielle,
Université Mentouri, Constantine 25000, Algérie.

Abstract

Various industries like textiles, papers, food, plastics, leather, etc are great water and organic colorant users. Hence, the resulting effluents could be an important source of environmental problems, since they may contain stable and non biodegradable contaminants, like organic dyes. The treatment of which is the main scope of the present study. Different ways of dye removal from these effluents do exist, such as flotation, reverse osmosis, chemical flocculation and adsorption etc. Adsorption is used in this work for the removal of a particular basic dye, known as Gentian violet (GV) from an aqueous solution, by means of a natural clay material.

The influence of various key parameters like contact time, temperature, ionic strength, etc. on the adsorbed amount of the dye was investigated, for batch conditions. A kinetic study was also carried out, the obtained experimental results were tested against the pseudo first order and the pseudo second order equations. An analysis of the obtained equilibrium data showed that the dye adsorption is best described by the Langmuir model. The obtained results showed that temperature did enhance the Gentian violet dye retention process onto the considered bentonite whereas the obtained thermodynamic parameters indicated that the adsorption process is spontaneous and endothermic. The simultaneous presence of methylene blue, which is another colorant compound, with the Gentian violet was also considered. The clay materials showed a better affinity for the first one i.e. methylene blue.

In conclusion and according to the obtained results, the clay material may be recommended as an industrial adsorbent for the treatment of effluents containing Gentian violet (GV).

© 2012 Published by Elsevier Ltd. Selection and/or peer review under responsibility of The TerraGreen Society.

Open access under CC BY-NC-ND license.

Keywords: Pollution; Gentian violet; Adsorption; Bentonite; Methylene blue

* Corresponding author. Tel.: +213-31-81-88-80; fax: +213-81-88-80
E-mail address: bellir_k@yahoo.fr
1. Introduction

The rise of dyeing wastewater effluents can be considered as a direct result of dyes production as well as a consequence of their use in many industries [1, 2]. Dyes are usually of synthetic origin with complex aromatic molecular structures, which make them very stable, resistant to fading and difficult to biodegrade [3, 4]. Due to the toxic nature of most dyes to plants and micro-organisms, coloured wastewaters cannot be discharged without adequate treatment. Even if they are non-toxic, such wastewaters obstruct light penetration, decrease the photo-synthesis’ efficiency in aquatic plants and raises the COD [5]. Dyes can cause allergic dermatitis, skin irritation, cancer, and mutations [6].

To remove dyes and other contaminants from wastewaters, several physical, chemical, and biological methods have been developed, such us, adsorption, nanofiltration, ion exchange, coagulation-flocculation, precipitation, ozonation, and aerobic or anaerobic treatment. Few of these processes are effective when the concentration of dye in the effluent is small. Some of them produce large quantity of sludge causing disposal problems, thus increasing operational costs. However Adsorption techniques for wastewater treatment have become more popular in recent years owing to their efficiency and stability in comparison to biological methods [1, 5, 7]. The most common adsorbent used for dye removal is activated carbon, which has a good adsorption capacity for organic molecules. In spite of this, it suffers from a number of disadvantages, its high cost has prevented its application, at least in developing countries. This has led many workers to search for cheaper substitutes. A number of low cost adsorbents are reported in the literature, like fly ash, peat, sawdust, lignite, rice husk, banana pith... [8, 9, 10]. Natural phyllosilicates, such as bentonite, montmorillonite, and smectite, have the potential to act as alternative low cost adsorbent. The abundance of bentonite in most countries, and its high stability and important surface area makes it a suitable adsorbent for the removal of many pollutants from wastewaters especially dyes [1, 9].

In the present work, the ability of an Algerian bentonite to remove a basic dye, namely Gentian Violet, by adsorption, has been studied. The effects of various experimental conditions, such as, contact time, initial dye concentration, temperature, and ionic strength on the amount of dye removal have been investigated. The kinetic parameters were also calculated to determine rate constants. The monolayer equilibrium adsorption capacity was estimated using the adsorption isotherm technique. The simultaneous presence of another dye, methylene blue, on the mixture has also been examined.

2. Experimental materials and methods

2.1. Adsorbent

The mineral clay used in this study is Bentonite, which is originating from Maghnia (North-West of Algeria). The acid activated bentonite was prepared by heating and stirring, at 60°C for two hours, a mixture of natural clay and concentrated sulfuric acid in clay/acid ratio of 1 (V/w). After heating, the suspension was air cooled, filtered and then washed several times with distilled water until the conductivity of the supernatant solution was below 4 μS/cm. Finally the resulting product was dried at 105°C for 24 h to constant weight and stored in desiccators for further use.

2.2. Adsorbate

The basic dye used in this work was Gentian Violet. It was supplied by Fluka and used as received without further purification. Some properties and molecular structure of this dye are listed in Table1. The
dye stock solution was prepared by dissolving an accurately weighted dye in a known volume of distilled water. The serial dilutions were made by diluting the dye stock solution in accurate proportions to the desired concentrations. The pH of each solution was adjusted with 0.1M HCl or 0.1M NaOH.

Table 1. Physical properties and molecular structure of Gentian Violet

<table>
<thead>
<tr>
<th>Dye name</th>
<th>Gentian Violet</th>
</tr>
</thead>
<tbody>
<tr>
<td>Colour Index number</td>
<td>CI 48770</td>
</tr>
<tr>
<td>Chemical formula</td>
<td>C_{25}H_{30}ClN_{3}</td>
</tr>
<tr>
<td>IUPAC name</td>
<td>methanaminium,N-[4-[bis[4-dimethylamino]phenyl]methylene]-2,5-cyclohexadien-1-ylidene]-N-methyl-chloride</td>
</tr>
<tr>
<td>Aspect</td>
<td>Greenish crystalline powder</td>
</tr>
<tr>
<td>Molecular Weight (g/l)</td>
<td>407.79 g·mol^{-1}</td>
</tr>
</tbody>
</table>

2.3. Batch mode adsorption

Adsorption experiments were carried out in a rotary shaker, using round bottom glass flasks containing dye solutions of different concentrations at adjusted pH values. Various fixed amounts of adsorbent were added to each flask and then were sealed. After shaking the flasks for predetermined time intervals, the dye solutions were separated from the sorbent by filtration with Millipore membrane filter 0.2 μm. The concentrations of dye samples were measured at the maximum wavelength (λ_{max}=583nm), using a 160-A UV-VIS Spectrophotometer (Shimadzu) and via standard calibration curve. All determinations were performed in triplicate per experiment. The amount of GV adsorbed onto bentonite and the removal efficiency \( R_e \) are respectively calculated using the following equations:

\[
q_t = \frac{(C_0 - C_t)}{m} \times V \tag{1}
\]

\[
R_e = \frac{C_0 - C_t}{C_0} \times 100 \tag{2}
\]

Where \( C_0 \) is the initial GV concentration (mg/l), \( C_t \) is the concentration of GV at time (mg/L), \( V \) is the volume of dye solution (L) and \( m \) is the mass (g) of the adsorbent.

3. Results and discussion

3.1. Effect of operating parameters

3.1.1. Effect of contact time and initial dye concentration

In order to determine the rate of adsorption, experiments were conducted with different initial concentrations of dye ranging from 10 to 120 mg/l. All other factors were kept constant.
Fig. 1. Effect of contact time and initial dye concentration on the adsorption of GV onto bentonite; Conditions: V=500 rpm, r = 1g/l, T =20 ± 2°C, pH ≈ 3.49, d≤2μm

Fig. 1 reveals that the removal of dye by adsorption onto bentonite is rapid at the beginning and then slows down until reaching to saturation. Moreover, the amount of dye adsorbed increased as the initial dye concentration increased as well. The raise in initial concentration increases the number of collisions and provides an important driving force to overcome all mass transfer resistances of the dye between the aqueous and solid phases, which enhances the adsorption process. Similar results were reported for various dye adsorptions onto other adsorbents “Kannan et al” [10, 11].

3.1.2. Effect of ionic strength

Since large amounts of salts are generally utilized in the dyeing process, the effect of ionic strength on adsorption has been investigated in this work. It was studied by the addition of sodium chloride in the solution at different concentrations 10^{-3}, 10^{-1} and 1M. The increase in adsorption with ionic strength may be due to the compression of the thickness of the diffused double layer. Such compression may help the adsorbent particle and adsorbate species to approach each other more closely, by then the attractive forces become significant, leading to increased adsorption.

The high adsorption capacity of dye after salt addition can be attributed to the aggregation of dye molecules induced by the action of salt ions, i.e., salt ions force dye molecules to aggregate, increasing the extent of adsorption of dyes onto clay. Other possible explanation can be related to the decreasing of
aqueous solubility due to presence of salt. As a result, GV molecules being more attracted to the adsorbent particles [15, 16, 17].

3.2. Adsorption kinetic models

The kinetic study is helpful in the prediction of the adsorption rate and provides important information for designing and modelling the processes. The kinetic data corresponding to 50 mg/l of GV initial concentration were analyzed using pseudo-first order and pseudo-second order kinetic models:

### 3.2.1. Pseudo-first order model

Lagergren in 1898 presented a pseudo-first-order rate equation to describe the kinetic process of liquid-solid phase adsorption of oxalic acid onto charcoal, which is believed to be the earliest model pertaining to the adsorption rate based on the adsorption capacity. It is expressed as follows [19, 20]:

\[
\frac{dq_t}{dt} = k_1(q_e - q_t)
\]

(3)

where \(q_e\) (mg/g) and \(q_t\) (mg/g) are the amounts of GV dye adsorbed at equilibrium and at time \(t\), respectively and \(k_1\) (min\(^{-1}\)) is the rate constant of pseudo first-order adsorption. The integration of Eq.3 after application of the initial conditions \(q_t=0\) at \(t=0\), yields the linear form Eq. 4:

\[
\ln(q_e - q_t) = \ln q_e - k_1t
\]

(4)

The plot of \(\ln(q_e - q_t)\) versus \(t\) as shown in Fig.3 gave the slope \(k_1\) and the intercept \(\ln q_e\). The values of \(k_1\), \(q_e\) and \(R^2\) obtained from the linear plot, are calculated and listed in Table 2. As the difference between \(q_{e,\text{experimental}}\) and \(q_{e,\text{calculated}}\) is considerable and the correlation coefficient values obtained are relatively small, consequently the adsorption of Gentian Violet onto bentonite is not a first-order reaction.

### 3.2.2. Pseudo-second order model

Since the introduction of pseudo-second-order model for the description of adsorption kinetics in 1999, it has been widely applied in liquid-phase adsorption systems. This model is proposed by Ho and McKay [23, 24] and has the following form:

\[
\frac{dq_t}{dt} = k_2(q_e - q_t)^2
\]

(5)

where \(k_2\) is the second order adsorption constant (g.mg\(^{-1}\).min\(^{-1}\)). Taking in the account the boundary conditions, \(t=0\) to \(t\) and \(q_t=0\) to \(q_e\), and after rearrangement, the integrated equation which have the linear form is given by:

\[
\frac{t}{q_t} = \frac{1}{h} + \left(\frac{1}{q_e}\right)t
\]

(6)

where, \(h=k_2q_e^2\) (mg g\(^{-1}\).min\(^{-1}\)), is the initial sorption rate as \(t \rightarrow 0\). Under such circumstances, the plot of \(t/q_t\) versus \(t\) should give a linear relationship, which allows the computation of \(q_e\) and \(k_2\).
Due to the non-applicability of the pseudo-first order model to experimental data, they have been tested with the 2nd order kinetic model by plotting $t/q_t$ versus $t$. As given in Fig. 4 and Table 2, the rate constant of GV uptake was found to decrease from 2.78 to $0.768 \times 10^{-3}$ with the increase of initial dye concentration from 10 to 120 mg/l. Moreover, plot correlation coefficients are closer to unity and higher than those of the first order. It implies that GV adsorption is well described by the pseudo-second order kinetic model. This suggests that the adsorption system may be of chemical or chemisorptions nature.

Table 2: Kinetic parameters for pseudo-first order and pseudo-second order models of GV adsorption using bentonite

<table>
<thead>
<tr>
<th>$C_0$ (mg/l)</th>
<th>$q_{e,\text{exp}}$ (mg/g)</th>
<th>Pseudo-first-order kinetic</th>
<th></th>
<th>Pseudo-second order kinetic</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$k_1$ (min$^{-1}$)</td>
<td>$q_e$ (mg/g)</td>
<td>$R^2$</td>
<td>$k_2 \times 10^3$ (g/mg.min)</td>
</tr>
<tr>
<td>10</td>
<td>0.028</td>
<td>0.093</td>
<td>0.214</td>
<td>2785</td>
</tr>
<tr>
<td>30</td>
<td>0.039</td>
<td>5.592</td>
<td>0.858</td>
<td>26.30</td>
</tr>
<tr>
<td>50</td>
<td>0.047</td>
<td>27.074</td>
<td>0.990</td>
<td>4.404</td>
</tr>
<tr>
<td>90</td>
<td>0.039</td>
<td>55.175</td>
<td>0.985</td>
<td>1.574</td>
</tr>
<tr>
<td>120</td>
<td>0.021</td>
<td>70.891</td>
<td>0.964</td>
<td>0.768</td>
</tr>
</tbody>
</table>

3.3. Isotherm analysis

Several models have been published in the literature to describe the equilibrium adsorption systems.

3.3.1. Langmuir isotherm

The Langmuir isotherm assumes monolayer adsorption on a uniform surface with a finite number of adsorption sites. Once a site is filled, no further sorption can take place at that site. As such the surface will eventually reach a saturation point where the maximum adsorption of the surface will be achieved. The Langmuir isotherm model is given as follow [23, 24]:

$$q_e = \frac{q_{max} \cdot b \cdot C_e}{1 + b \cdot C_e}$$  \hspace{1cm} (7)

where $b$ is the Langmuir constant (1.mg$^{-1}$) and $q_{max}$ is the maximum adsorption capacity (mg.g$^{-1}$).
3.3.2. Freundlich isotherm

The Freundlich isotherm is an empirical model equation used to describe the heterogeneous systems. For adsorption from solution, the Freundlich isotherm is expressed by [23, 25]:

\[
q_e = K_F C_e^{1/n}
\]

(8)

where the Freundlich constant \( K_F \) is an indication of the multilayer adsorption capacity and \( 1/n \) of the adsorption Intensity.

\[
R_L = \frac{1}{1+bC_0}
\]

(9)

where \( C_0 \) is the initial concentration (mg/l) and \( b \) is the Langmuir constant. The value of \( R_L \) indicates the shape of the isotherms to be either unfavorable (\( R_L > 1 \)), linear (\( R_L = 1 \)), favourable (\( 0 < R_L < 1 \)) or irreversible (\( R_L = 0 \)). Also the smaller \( R_L \) value indicates a highly favourable adsorption. The result reveals that Langmuir isotherm best-fit the equilibrium data of GV adsorption onto clay, proving monolayer and homogenous surface of adsorbent (i.e., \( q_{max} = 108.56 \) mg/g). According to the obtained values of \( R_L \), it is well observed that this adsorption is favorable. Moreover, the value of \( n \) was more than 1, which further proved the favorable adsorptive character of the adsorption isotherm. Similar conclusion was also reported by the studies of Patel et al and Bulut et al.
3.3.3. Effect of temperature

The effect of temperature on the adsorption of GV onto clay was studied from 20 to 60°C. An increase in the dye adsorption rate resulted when temperature increased of (Fig. 6). This may be due to the higher rate of diffusion of GV onto the clay surface particle at higher temperatures. The equilibrium dye adsorption was however relatively insensitive to temperature increase even after 120 min of contact time.

![Graph showing temperature effect on GV adsorption onto clay](image)

Fig. 6. (a) Effect of temperature on the GV adsorption onto bentonite; (b) linear plot of thermodynamic parameters

The thermodynamic parameters of the adsorption process were determined from the experimental data obtained at various temperatures in section by employing the following equations:

\[ K_d = \frac{q_e}{C_e} \]  
(10)

\[ \Delta G = -RT \ln K_d \]  
(11)

\[ \ln K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \]  
(12)

where \( K_d \) is the equilibrium constant for the adsorption, \( T \) is the absolute temperature (K), \( R \) is the universal gas constant, \( \Delta G \), \( \Delta H \) and \( \Delta S \) are Gibbs free energy change, enthalpy change and entropy change of the process, respectively [26, 27]. The values of \( \Delta H \) and \( \Delta S \) changes are computed from the slope and intercept of the plot of \( \ln K_d \) versus \( 1/T \) (Fig. 6). The thermodynamic parameters thus calculated are listed in Table 4.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>( \Delta G ) (kJ mol(^{-1}))</th>
<th>( \Delta H ) (kJ mol(^{-1}))</th>
<th>( \Delta S ) (J mol(^{-1}) K(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>-13.3731</td>
<td></td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>-20.2346</td>
<td>64.956</td>
<td>268.8</td>
</tr>
<tr>
<td>60</td>
<td>-24.0646</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The negative values of \( \Delta G \) indicate the feasibility and the spontaneous nature of the process. The change in enthalpy \( \Delta H \) was found to be positive confirming the endothermic nature of dye adsorption.
The positive value of $\Delta S$ reflects the increased randomness of the solid-solution interface and suggests some structural changes in both adsorbate and adsorbent during adsorption process.

3.4. Competition study

Till now all the adsorption results discussed above were obtained by taking a single adsorbate (GV). However, in reality the contaminated water contains more than one adsorbate which can affect the adsorption of the considered dye. Therefore, it was worthwhile examining the effect of the simultaneous presence of another dye in the solution. Adsorption experiments of the binary system of Gentian Violet and Methylene Blue dyes onto bentonite were carried out using the same procedure to that in single dye experiments. The obtained results have been plotted in Fig. 7.

![Fig. 7. Effect of competition on the removal efficiency of MB and GV onto bentonite at different contact time](image)

The activated bentonite exhibits very high adsorption capacities to remove the basic dyes with percentage removal of MB and GV in single dyes at 30min of 98.74 and 87.53 % respectively. However, in the competitive adsorption of the tow dyes from mixture solutions, the percentage uptake of each dye in the mixtures was reduced to 83.41% for MB and 69.6% for GV. Whether it was single or mixed, MB was better adsorbed than GV. Since the bentonite seems to favour MB slightly than GV, this behaviour of preferential and selective adsorption can be explained from the point of view of molecular weight of the dyes (MB = 319.82 g/mole and GV = 497.98 g/mole). The MB with one weaker molecular weight will compete faster for the actives sites than GV. The similar phenomena have been observed by Elaziouti et al. [27]

4. Conclusion

In this work, Algerian activated bentonite has been tested for the removal of Gentian violet from aqueous solutions. In batch mode adsorption, this clay showed clearly a great uptake capacity. The GV adsorption capacity was found to increase with an increase in contact time, initial concentration, temperature and ionic strength. The kinetics data of the GV adsorption onto clay were well described by the pseudo-second order model with a good correlation. The equilibrium results were evaluated according to the Langmuir and Freundlich isotherms, both models fit the empirical data but the Langmuir is the best one. The dimensionless separation factor obtained via Langmuir constant confirms that adsorption process of GV was favourable. The thermodynamic calculations showed that the process was spontaneous and endothermic in nature. Whether it is single or mixed, MB is better adsorbed than GV. This clay has proven to be a promising economic material for the removal of dyes and could be successfully when applied in industrial wastewater treatments.
References


[17] Ho Y.S. Citation review of Lagergreen kinetic rate equation on adsorption reaction, Scientometrics, 2004; 59: 171-177.


