Removal of Cationic Dye Methylene Blue from Aqueous Solution by Adsorption on Algerian Clay

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Received date: October 20, 2014, Accepted date: January 21, 2015, Published date: January 27, 2015

Abstract

The objective of this study was to demonstrate the potential of Tiout-Naama (TN) clay for removing a cationic Methylene blue (MB) dye from aqueous solutions which was used for the first time like an adsorbent. For this, the effect of several parameters such as contact time, adsorbent dose, pH and temperature have been reported. Nearly 30 min of contact time are found to be sufficient for the adsorption to reach equilibrium. The residual concentration of the dye is determined using UV/Vis Spectrophotometer at wavelength 664 nm. Langmuir and Freundlich isotherm models were used to describe adsorption data. The result revealed that the adsorptions of MB dye onto TN clay is the best-fit both Langmuir and Freundlich isotherms, further to understand the adsorption kinetics the adsorption data were analyzed by the second-order and the pseudo-second-order. The results show that the methylene blue adsorption follows pseudo-second-order kinetics.

Keywords: Dye; Adsorption; TN clay; Adsorption kinetics; Adsorption isotherms

Introduction

Water and soil pollution is a source of decay of the environment. Among these pollutants are the textile industry rejects which are heavily saturated by organic colorants. These colorants are usually used in excess to make the dye better, and consequently sewage is highly concentrated with colorants. In this objective, several methods are used to eliminate these colorants from industrial wastes. Traditional process; such as chemical-physical treatments based on the addition of coagulant and flocculants (aluminium salts and polymers) [1] and biological process by the use of activation mud with a sufficient aeration [2], nevertheless these methods are not satisfying because of the weak colorant biodegradability [3]. The adsorption on active carbon is efficient but very expensive and has high operating costs due to the high price of the activated carbon and to the high water flow rate always involved [4]. In this way the majority of the processes are very selective according to the colorant categories to treat and some just move the pollution instead of removing it. It is necessary for the process to mineralize the colorant. Research is focussing on process using natural materials such as clay, agriculture waste residues [5] e.g wood, Waste. The different applications of the clay depend on their specific adsorption properties, the ion exchange and the surface nature. Due to these qualities, clay is used in different field, like in medical and pharmaceutical industries, organic molecule polymerization [6], and pollutant retention e.g. Pesticides, organic colorants, heavy metals [7,8]. This paper presents the elimination of Methylene blue, an organic colorant used in textile industries, by adsorption on a natural material that is the clay of Tiout region in Algeria. This kind of clay fulfills all the environment protection conditions, and is very abundant and not expensive [9]. Kinetic and isotherm adsorption models are performed in order to better understand the organic colorant adsorption mechanisms [10].

Materials and Methods

Materials

The clay used in this work is montmorillonite type from Tiout region located south west Algeria. The clay undergoes a pretreatment by stirring it for two hours at room temperature. The obtained suspension is filtered, ground and heated until obtaining a constant weight, then stored in a securely closed flask against the moisture.

In order to show the clay capacity of decoloration, we chose an organic colorant that it has methylene blue taken as a reference for pollutants because of its middle-size molecule and its several uses in tests, has a high solubility in water and it is one of the Thiazine colorants having the chemical formula C18H13N2ClS and molecular weight of 319.89 g/mole. The chemical structure is presented in Figure 1.

Figure 1: Chemical structure of methylene blue dye.

Chemical analysis showed the clay used is composed essentially of silica and alumina approximately 71.5% and of iron oxide 7.30% (Table 1), the presence of ions Na+, Ca2+ and K+ in the clay gives it a swelling type. The ratio SiO2/Al2O3=3.51 reveals its montmorillonite characteristics. The mineralogical composition of the natural clay was determined by X-ray diffraction (XRD) using DRX.D8 ADVANCE BRUKER generator with copper anticathode (λCuKa=1.5406 Å). The Xray spectrum shows that the TN clay is a mixture of montmorillonite and impuretes of calcite and quartz (Figure 2).
Elements | SiO$_2$ | Al$_2$O$_3$ | Fe$_2$O$_3$ | CaO | MgO | Na$_2$O | K$_2$O | SO$_3$ | SO$_3^{gyp}$ | Cl | PF
---|---|---|---|---|---|---|---|---|---|---|
% CCM | 55.72 | 15.85 | 7.30 | 4.11 | 2.26 | 1.30 | 4.08 | 0.43 | 1.11 | 0.01 | 7.66

Table 1: Chemical composition of TN Clay.

Methods

In a series of 100 ml flasks, 80 mg of adsorbent (raw clay) is mixed with each 50 ml volume of Methylene blue aqueous solution having an initial concentration 25.59 mg/l. The adsorption tests are perfumed at natural pH, room temperature and magnetic stirring at 450 rpm at different time intervals. After equilibration, the aqueous phase was separated by centrifugation at 2500 rpm during 15 min. The concentration of the residual dye Cr was determined using SHIMADZU 1240, a spectrophotometer UV/Vis at 664nm of wavelength after 30 min. The equilibrium adsorption capacity $q_e$ (mg/g) was calculated from the following equation:

$$q_t = (C_0 - C_t) \times \frac{V}{m}$$

where $q_e$ is the amount of dye adsorbed at equilibrium (mg/g), $C_0$ and $C_t$ are the initial and equilibrium concentrations of the dye, respectively, computed from the calibration curve (mg/l), $V$: is the volume of the solution (l), $m$: is the mass of the adsorbent (g).

Results and Discussion

Effect of contact time

The influence of time is achieved at natural pH of the solution for an initial concentration of 25.59 mg/l, with a mass of clay of 80 mg/l and at room temperature. The amount of colorant adsorbed $q_t$ at time $t$ was determined by the following expression:

$$q_t = (C_0 - C_t) \times \frac{V}{m}$$

Kinetics order

Adsorption kinetics is literary reviewed in different forms. In this paper kinetic laws of the second order and pseudo-second order are used. The second order kinetic model has the following formula.

$$\frac{dq}{dt} = k(q_e - q)^2$$

Where is the rate constant of second-order adsorption has the following formula.

$$\frac{1}{q} - \frac{1}{q_e} = \frac{k}{q_e} \cdot t$$

For the pseudo-second-order model is given by the following equation.

$$\frac{dq}{dt} = k' \cdot (q_e - q)^2$$

Where is the rate constant of pseudo-second-order adsorption has the following formula.

$$\frac{1}{q} - \frac{1}{q_e} = \frac{k'}{q_e^2} \cdot t$$
The kinetic data obtained using the second order and pseudo-second order is depicted in Figures 4 and 5.

Figure 4: Plot of $t/q$ versus $t$ from the pseudo-second-order model.

Figure 5: Plot $1/(q_e - q)$ versus $t$ from the second-order model.

The $q_e$ value calculated from the pseudo-second-order model is in accordance with the experimental $q_e$ value. The correlation coefficient $R^2$ of the linear plot is very high. The result is shown in Table 2. The value of kinetic constant and $q_e$ indicates that the adsorption follow the pseudo-second order model. Several studies found that the kinetics of adsorption of dyes on clay supports obey to the pseudo-second-order [13-16].

Table 2: The pseudo-second-order parameters of MB adsorption into TN clay.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Pseudo-second-order</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K'$ (g/mg min)</td>
<td>0.092</td>
</tr>
<tr>
<td>$Q_{o-cal}$ (mg/g)</td>
<td>12,229</td>
</tr>
<tr>
<td>$q_{e-pred}$ (mg/g)</td>
<td>12,183</td>
</tr>
</tbody>
</table>

Effect of adsorbent mass

The effect of adsorbent mass on the adsorption capacity was studied using 50 ml of Methylene blue (25.591 mg/l) onto 1-4 g/l of adsorbent with shaking at room temperature for 30 min, the solid particles were removed and the remaining concentration of colorant in the filtrate was measured by using the UV/Vis spectrophotometer at 664 nm.

The effect of sorbent quantity on dye removal is illustrated in Figure 6. From the figure it can be seen that an increase mass of crude clay 1 g/l down to a value of 4 g/l causes a decreases in residual dye concentration. The increase in Methylene blue adsorption with the increase in adsorbent mass is attributed to increase in surface area of micro pores and the increase in availability of vacant adsorption sites. The same results were obtained by other authors [17,18].

Figure 6: The effect of adsorbent mass on the adsorption of MB by TN clay.

Effect of pH

The influence of pH on dye removal was determined by performing the adsorption experiments at different initial pH of the solution (2-11) at room temperature. The pH of the solution was adjusted with HCl (0.1 N) or NaOH (0.1 N) solution by using a HANNA 210 pH-meter equipped with a combined pH electrode. The adsorption of Methylene blue onto clay is highly dependent on pH of the solution. The Figure 7 shows that the adsorption increased with increasing pH. The removal dye is low in the acid pH region because the hydrogen ions neutralize the negatively charged clay surface thereby decreasing the adsorption of the positively charged caution because of reduction in the force of attraction between adsorbate and adsorbent. The removal of dye is more at higher pH, because the surface of used clay is negatively charged. Therefore, the electrostatic attractive force between the colorant dye, which has a positive charge, and the adsorbent surface increases, and consequently, the rate of dye adsorption increases, the highest dye removal was detected in pH 9.

Similar results have been reported for the adsorption of Methylene blue on morocco clay [19,20].

\[ \Delta G = -RT \ln K_c \]  
(7)

\[ K_c = \frac{q_e}{C_e} \]  
(8)

Where:

- \( q_e \): is the amount of dye adsorbed at equilibrium (mg/g)
- \( C_e \): is the equilibrium concentrations of the dye in the solution.

The thermodynamic equation:

\[ \Delta G = \Delta H - T \Delta S \]  
(9)

And the Vant’Hoff formula:

\[ \Delta G = -RT \ln K_c \]  
(10)

Can be deduced the following formula:

\[ \ln K_c = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \]  
(11)

The values and can be obtained by plotting the versus 1/T (Figure 9).

Effect of temperature

The amount of dye adsorbed on Tiout-Naama clay was determined at 20, 30, 40 and 60°C to investigate the effect of temperature. 80 mg of adsorbent was added to 50 ml dye solution with initial concentration of 25.59 mg/l. The contents in the flasks were agitated for 30 min.

The Figure 8 shows that as temperature increases from 20°C to 60°C, the adsorbed amount of dye at the same equilibrium concentration increased. Similar observations have been reported in the literature [21]. When temperature increased, the physical bonding between the organic compounds (including dyes) and the active sites of the adsorbent weakened. Besides, the solubility of Methylene bleu also increased with increase in temperature.

Thermodynamic parameters

The Gibbs energy is calculated from the given equation:

\[ \Delta G = -RT \ln K_c \]  
(7)

\[ K_c \] represented the ability of the retain the adsorbate and extent of movement of it within the solution. The value of \( K_c \) can be deduced from the following formula:

\[ K_c = \frac{q_e}{C_e} \]  
(8)

According to the thermodynamic parameters represented in Table 3, we realized that the \( \Delta H \) enthalpy of the system is positive so the adsorption process on Tiout-Naama clay is endothermic, the low value of this energy (<40 KJ/mole) shows that it is a physical adsorption, the positive value of \( \Delta S \) shows the attraction of the adsorption according to the dye, the negative value of \( \Delta G \) indicates that the adsorption is done through a spontaneous and favourable process [22].
Adsorption isotherm

Several laws have been proposed for the study of adsorption. They express the relation between the amount adsorbed and the concentration of aqueous solution at a specific temperature; the most commonly models used for adsorption are Langmuir and Freundlich isotherms those have been selected in this study.

The Langmuir isotherm is valid for monolayer adsorption onto a surface with a finite number of identical sites. The homogeneous Langmuir adsorption isotherm is represented by the following equation:

\[ q_e = \frac{q_{\text{max}} b C_e}{1 + b C_e} \]  \hspace{1cm} (12)

Where \( q_e \) is the amount adsorbed at equilibrium (mg/g), \( C_e \) the equilibrium concentration (mg/l), \( b \) constant related to the adsorption energy (l/mg), and \( q_{\text{max}} \) the maximum adsorption capacity (mg/g).

The linear form of Langmuir equation may be written as

\[ \frac{1}{q_e} = \frac{1}{q_{\text{max}}} \cdot \frac{1}{b} + \frac{1}{q_{\text{max}} C_e} \]  \hspace{1cm} (13)

By plotting \( (1/q_e) \) versus \( C_e \), \( q_{\text{max}} \) and \( b \) can be determined if a straight line is obtained.

The Freundlich isotherm is an empirical equation assuming that the adsorption process takes place on heterogeneous surfaces, and adsorption capacity is related to the concentration of colorant at equilibrium. The heterogeneous Freundlich adsorption isotherm is represented by the following equation:

\[ q_e = C_e^{1/n} K_F \]  \hspace{1cm} (14)

Where the \( K_F \) is Freundlich constant related to the adsorption capacity (mg/g) and \( 1/n \) shows the adsorption intensity (l/mg).

The linear form of Freundlich equation may be written as

\[ \log q_e = \frac{1}{n} \log C_e + \log K_F \]  \hspace{1cm} (15)

The values of \( n \) and \( K_F \) can be determined by plotting the versus if a straight line is obtained.

In the experiments of equilibrium adsorption isotherm, a fixed amount of 80 mg adsorbent is contacted with 50 ml of aqueous solutions Methyline blue have different concentrations (10–250 mg/l). The adsorption was carried at room temperature while keeping all other parameters constant and the result is shown in Figures 10 and 11. Values for \( q_{\text{max}}, b, n \) and \( K_F \), are summarised in Table 4. It can be seen, the result revealed that the adsorption of Methylene blue dye onto raw clay was the best-fit both Langmuir and Freundlich isotherms. The \( n \) value is greater than 1 which indicates that the adsorption process is favourable [23].
blue dye from aqueous solution. The value of kinetic constant and $q_e$ indicates that the adsorption follow the pseudo-second order model.

Nearly 30 min of contact time are found to be sufficient for the adsorption to reach equilibrium. When the amount of crude clay increases from 1 g/l to a value of 4 g/l causes decreases in residual dye concentration. The results suggested that the adsorption capacity of organic compound colorant on raw clay adsorbent increased with increasing pH, rising the temperature induces a slight growth in the adsorption capacity, the negative value of $\Delta G$ indicates that the adsorption is done through a spontaneous and favourable process, the result revealed that the adsorption of Methylene blue dye onto Tiout-Naama clay was the best-fit both Langmuir and Freundlich isotherms and the maximum adsorption capacity is in the order of 56.85 mg /g.

References