Adsorption Kinetics and Isotherm of Methylene Blue Dye Removal from Aqueous Solution using Low Cost Adsorbent

Ghada Heikal*

Dr. Ghada El Sayed Heikal, Environmental Engineering Department, Faculty of Engineering, Zagazig University, Postal code 44519, Egypt


Abstract

Dye is difficult to remove from aqueous solution due to its large molecular size. This study aims at describing the removal of methylene blue from aqueous solution using carbonized phragmites australis as an adsorbent. Batch experiments are carried out by observing the effect of pH (4-9), amount of adsorbents (0.25-1.5 g/mL), contact time (30-180 min) and initial concentration of dye (10-50 ppm) at agitation speed 120 rpm. The study results showed that the carbonized P. australis achieve the highest removal of MB dye at optimum conditions of pH=7, adsorbent dose=1.0 g/mL, contact time=150 min and initial dye concentration 10 ppm had the removal efficiency of 97.1%. The study showed that the kinetic data obtained are obeying best to the pseudo-second-order kinetic model (R²=0.993) and adsorption isotherm study results indicated that MB dye adsorption followed Langmuir isotherm (R²=0.9906).

Keywords: Phragmites, Adsorption, Methylene blue, Dye removal

1. Introduction

Dyes in industrial wastewater are visible pollutants that are complicated to treat due to its large molecular bulk and synthetic source, and common treatment techniques of wastewater have demonstrated to be ineffective for the substance. Synthetic dyes are widely used in many industries to colorize substances such as in textiles, leather, paper, wool, printing and cosmetics. Discharge of wastewater containing dye compounds into water sources has caused serious environmental impact because dying effluent will deplete the dissolved oxygen content in water and also inhibit sunlight from reaching to the water sources. Some of the dye wastewater is usually poisonous, carcinogenic, and teratogenic to human beings (Bhattacharyya and Sharma 2005).

Activated carbon is commonly used in water treatment because of its large capacity and wide applicability of adsorption and ready availability. However, the adsorption capacity is significantly affected by the pore size and structure of the carbon and the molecular size and chemical nature of adsorbates.

Methyleneblue (MB) is a thiamine cationic dye and is used extensively in coloring cottons, wools, silk, dying paper and temporary hair colorant. It can cause some harmful effects, for example eye burn, inhalation problems, heartbeat increase, nausea, vomiting, shock, mental confusion (Vijayaraghavan et al. 2008).

On the other hand, large molecules, such as dye, are not treated with the common activated carbon due to its pore characteristics. Because the large molecular size and stability of dye prevent from applying conventional removal techniques from water, various alternative methods have been proposed and tested for the dye removal. Using a simple adsorption treatment, food and wood wastes have been utilized for the dye treatment (Hamdaoui, 2006; Arami, 2006; R. Jain, S. Varshney and S. Sikarwa 2006).

Phragmites australis, commonly known as reed, was used in this study. It is a large perennial grass found in wetlands throughout temperate and tropical regions of the world. It can grow up to 6 m high and is long-lived (Aysu 2014) and contains high amounts of lignin and cellulose (Lenssen et al. 1999). Properties of P. australis not only provide a potentially inexpensive material for wastewater treatment, but also help surface modification by means of great numbers of hydroxyl groups (OH) on its surface. P. australis has thus been used for years for the removal of heavy metals and metalloids from aquatic systems and waste water (Kumari and Tripathi 2015). However, the studies carried out regarding the removal of textile dyes are limited. (Chen et al. 2010) studied the adsorption of methyl orange and methyl violet from aqueous solutions with activated carbon derived from P. australis.

The aim of the present research was place to investigate effectiveness carbonized P. australis as an adsorbent for the removal of the widely used dye MB. The impact of input operational parameters such as
pH, adsorbent dose, contact time and initial concentration of MB on adsorption of MB by carbonized P. australis was experienced to optimize the adsorption process in a batch mode.

2. Material and Methods

2.1 Preparation of raw materials

The phtagmites australis were collected from El Aaoga Canal Branch from Moase Canal. They were cleaned, cut into small size (2 cm long) for both the leaves and the stems. The cut parts were washed with hydrochloric acid (1% conc.), then washed with distilled water to remove any residuals of the acid. Washed parts were carbonized in furnace at 120˚ C for 2 days. The carbonized phagmites was crushed and sieved to particle size < 100 mm. The used carbonized phragmites as an adsorbent in this research set as ratio 1:1 from both leaves and stems.

Table 1 Physical properties and lignocellulosic composition of the carbonized phragmites australis prepared by this method in (wt %)

<table>
<thead>
<tr>
<th></th>
<th>Ash</th>
<th>2.8%</th>
<th>Cellulose</th>
<th>35.9%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Moisture</td>
<td>7.3%</td>
<td>Lignin</td>
<td>26.4%</td>
</tr>
<tr>
<td></td>
<td>Volatile</td>
<td>9.8%</td>
<td>Hemicellulose</td>
<td>18.5%</td>
</tr>
<tr>
<td></td>
<td>Fixed Carbon</td>
<td>80.0%</td>
<td>Extractives</td>
<td>8.9%</td>
</tr>
</tbody>
</table>

2.2 Chemicals

The dye used for the research was Methelyene Blue (MB) (C₁₆H₁₈CIN₃S). The color densities of the dye were scanned using Spectrophotometry started at wavelength 450 nm and ended at wave length 800 nm. The dye solutions were prepared to make a stock solution of MB 100% by dissolving (0.0375 gm in 1 liter of distilled water). MB solutions of different concentrations (10-80) mg/l were prepared by dilution of the stock solution. The pH of aqueous solution was adjusted to the desired value by addition of NaOH (0.1 M) or HCl (0.1 M).

Table 2 Basic properties of methylene blue (MB)

<table>
<thead>
<tr>
<th>Molecular Structure</th>
<th>Molecular Weight (gm/mol)</th>
<th>λ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Methylene Blue Structure" /></td>
<td>319.85</td>
<td>664</td>
</tr>
</tbody>
</table>

The calibration plot for methylene blue at 664 nm was obtained as follows in figure (1).

2.3 Batch Experiments

The study of the ability of carbonized P. australis biomass to remove MB was tested in batch experiments conducted at room temperature. The experimental work consisted of two sets of experiments. The first set included, the studied parameters were pH (4-9), adsorbent dose were (0.25 - 1.50) gm/l, and contact time (10-180 min) at an initial dye concentration of 20 mg/l. The adsorption was carried out by agitation the absorbent (carbonized p. australis) with 100 ml of MB dye solution using water bath kottermann shaker at 120 rpm. The initial pH of dye solution was previously adjusted with 0.1 M NaOH or 0.1 M HCl solutions.

In all experiments, the difference between the initial dye concentration (Co) and the equilibrium concentration (Ce) was calculated and used to calculate the adsorptive capacity (q) and percentage removal as follows: (1) and (2)

\[ q = \frac{[(C_0 - C_e)^*V]}{m} \]  
\[ \% \text{ Removal Eff.} = \frac{[(C_0 - C_e)]}{C_0} * 100 \]
2.3.1 Effect of solution initial pH

To study the effect of solution pH on MB adsorption, 20 mg/L initial concentration of MB at different pH values (4.0–9.0) was agitated with 1.0 g of carbonized phragmites australis in a water bath shaker at room temperature with agitation speed = 120 rpm. Contact time was taken = 30 min. The pH was adjusted with 0.1 M NaOH and 0.1 M HCl solutions.

2.3.2 Effect of adsorbent dose

The adsorption process was carried out for 20 mg/L of MB initial concentration solution in different adsorbent doses of 0.25, 0.5, 0.75, 1, 1.25, and 1.5 gm with agitation speed = 120 rpm and Contact time was taken = 30 min at the optimum value found for pH.

2.3.3 Effect of contact time

The effect of contact time on adsorption process was carried out for 20 mg/L of MB initial concentration solution in different contact time of 30, 60, 90, 120, 150 and 180 min with agitation speed = 120 rpm at the optimum value found for pH and adsorbent dose from previous work.

2.3.4 Effect of the initial MB concentration

The effects of initial concentration of MB on the adsorption process were evaluated for different MB concentrations of 10, 20, 30, 40, and 50 mg/L at the optimum values of pH, adsorbent dosages, and contact time achieved from the first set.

2.4 Isotherm studies

To determine the mechanistic parameters associated with studied dye, the results obtained by the adsorption experiments were analyzed by the well-known models of Langmuir and Freundlich.

2.4.1 Langmuir Isotherm

The Langmuir model assumes uniform energies of adsorption onto the surface and no transmigration of the adsorbate in the plane of the surface. The linear form of the Langmuir isotherm is given by the following equation:

\[ \frac{C_e}{q_e} = \frac{(C_0 - C_e)V}{m} + \frac{1}{bQ_0} \]

(3)

Where \( Q_e \) is the amount adsorbed (mg/g), \( C_e \) is the equilibrium concentration of the adsorbate (mg/L), and \( Q_0 \) and \( b \) are the Langmuir constants related to the maximum adsorption capacity and energy change in adsorption, respectively. Experimental results were used at the pH, adsorbent dose, and contact time where maximum adsorption was achieved.

2.4.2 Freundlich Isotherm

The adsorption data for the MB dye was also analyzed by the Freundlich model. The logarithmic form of the Freundlich model is given by the following equation:

\[ \ln q_e = \ln k_f + \frac{1}{n} \ln C_e \]

(5)

Where \( q_e \) is the amount adsorbed (mg/g), \( C_e \) is the equilibrium concentration of MB (mg/L), and \( K_f \) and \( n \) are Freundlich constants related to the adsorption capacity and adsorption intensity, respectively. Experimental results at the same optimum pH, adsorbent dose, and contact time where maximum adsorption was achieved as that in the previous paragraph are used.

2.5 Kinetic studies

The adsorption rate of MB dye was studied at different time intervals for 180 min using 20 mg/L initial concentrations and at the optimum value of pH. The modeling of MB adsorption kinetics for P. australis were checked by 2 common models using the pseudo-first-order (Lagergren 1898) and pseudo-second-order (Ho and McKay 1999), Eqs. (6) – (7), as explained below:

Pseudo-first-order equation:

\[ \ln (q_e - q_t) = \ln q_e - k_1 t \]

(6)

Pseudo-second-order equation:

\[ \frac{t}{q_t} = \frac{1}{(k_2 q_e^2)} + \frac{t}{q_e} \]

(7)

Where \( q_t \) is the amount of MB dye adsorbed during time \( t \) (mg/g), \( q_e \) is the amount of MB adsorbed at equilibrium state, and \( k_1 \) and \( k_2 \) are constants. Pseudo-first-order and second-order kinetic models were based on the assumption of physisorption and chemisorption process, respectively.

3. Results and Discussion

3.1 Effect of pH solution

The initial pH of a solution is known as an important parameter, which can significantly affect adsorption phenomena (Toor and Jin 2012). pH affects surface binding sites of materials and the ionization process of dye molecules (Ncibi et al. 2007). In adsorption experiments, the effect of the initial solution of pH was evaluated at pH range 4.0–9.0. From Fig. (2) shows the relationship between pH versus the dye concentration on the adsorbent at equilibrium, it is clear that the pH of solution acts an important responsibility in the adsorption of MB in carbonized p. australis biomass. When the pH was increased, dye adsorption capacity of p. australis biomasses increased. This increase was
from 1.65 to 3.25 mg/gm for p. australis biomass as pH increased from 4 to 7 respectively and then decreased to 3.1 mg/gm at pH 8. The highest dye concentration on the adsorbent at equilibrium achieved at pH = 7 was 3.25 mg/gm. This can be explained with the electrostatic interaction of MB (because of its cationic structure) with the negatively charged surface of carbonized P. australis. The cationic dyes give positively charged ions when dissolved in water. Thus, in acidic conditions (at lower pH), the positively charged surface of adsorbent tends to resist the adsorption of cationic dye molecules (Peydayesh and Rahbar-Kelishami 2015). As the pH of dye solution is increased, the surface gains a negative charge that results in an increase in the adsorption capacity of biomass. It was also observed that the results at pH 8–9 were very close. Similar findings with regard to the MB adsorption, by using different adsorbents were reported by various researchers (Low et al. 1995; Hamdaoui 2006; Dogan et al. 2004; Cengiz and Cavas 2008).

3.2 Effect of Adsorbent Dose

It is necessary that the effects of adsorbent dose are analyzed for the optimization of the best required dose of p. australis for the achievement of the highest MB concentration removal. Fig. (3) describes the relationship the adsorbent dose represented in amount of p. australis in grams and the effluent MB concentration represented in % adsorption of MB dye at the optimum pH value achieved from the previous subsection. In this research, variation of adsorbent dose showed that although an increase of adsorbent dose in aqueous solution can result in the improvement of MB concentration removal ratio. The highest % adsorption of MB achieved at the adsorbent dose = 1 gm was 65%. The uptake increased by 20% when the quantity of adsorbent used was doubled, i.e., from 0.5 to 1.0 gm. As the amount of carbonized p. australis was further increased to 1.25 g, the uptake increased by only 1%. As such, 1.0 g of adsorbent was considered to be quite appropriate amount for the removal of MB dye, and this dose was used in all subsequent experiments performed.

This result implies that although the mass elevation of an adsorbent can provide a large available surface area for the adsorption pattern of the pollutant represented in MB concentration. A further increase in p. australis biomass concentration over optimum dose does not lead to appreciable improvement in adsorption of MB removal due to the saturation of the adsorbent surface with dye ions and the establishment of equilibrium between the ions remaining nonadsorbed in the solution and which bound to the adsorbent (Sulak MT, Demirbas E., Kobya M. 2007; Ong ST, Lee CK, Zainal ZI 2007).

3.3 Effect of Contact Time and Kinetics of MB Adsorption

The dependence of adsorption on contact time was studied using fixed amount (1.00gm) of adsorbent (carbonized p. australis) on 20 ppm methylene blue solution in a fixed volume (100 ml). Fig. (4) shows the relationship between The contact time and the % removal ratio occurred in MB concentration.

Fig. 3 The effect of adsorbent dose on the % adsorption of MB concentration at pH = 7

It was observed that % removal of MB concentration increases with increase in contact time. Initially within first 30 min exponential increase in adsorption was reflected till maximum slope reached in next 30 min.
Thereafter a steady state equilibrium was obtained after a very long time. The rapid adsorption at the initial contact time is due to rapid attachment of MB molecules to the surface of the adsorbent and the later slow rate of adsorption is probably due to adsorption taking place in the polymer network of the carbonized p. australis. The optimum % removal of MB concentration takes place at contact time = 150 min, which was 95.3%.

It is obvious that the % adsorption of MB the carbonized p. australis biomass is rapid at first 30 min and equilibrium contact time for carbonized P. australis was 150 and 180 min, respectively. The decrease in the adsorption rate toward the end of experiment is due to a decrease in the number of available sites of adsorbent and dye concentrations, inferring the possible monolayer formation of dye on the adsorbent surface (Peydayesh and Rahbar-Kelishami 2015).

In order to investigate the mechanism of adsorption, particularly potential rate-controlling step, the transient behavior of the MB adsorption process was analyzed using the pseudo-first-order (Lagergren 1898) and pseudo-second-order (Ho and McKay 1999) which are explained previously in eq. (6), (7).

![Fig.5](image1.png)  
**Fig.5** Pseudo-first order kinetic plot for the removal of MB by carbonized P. australis; Co = 20 mg/l

![Fig.6](image2.png)  
**Fig.6** Pseudo-second order kinetic plot for the removal of MB by carbonized P. australis; Co = 20 mg/l

The kinetic constants and correlation coefficients were calculated from the slope and intercept of pseudo-first-order adsorption model and pseudo-second-order adsorption model (Fig. 5 and 6). As seen in Table 3, the higher regression coefficients ($R^2$) with respect to fitted pseudo first-order reaction model suggest that adsorption of MB on carbonized P. australis follows pseudo-second-order kinetics (Fig. 6). The calculated values of adsorption capacity ($q_{e,cal}$) obtained from the pseudo-second-order model also agreed with the experimental adsorption capacity ($q_{e,exp}$). Therefore, the adsorption of MB from aqueous solutions, using carbonized biomass, followed the pseudo second-order model well.

**Table 3** Calculated kinetic parameters for pseudo first-order and pseudo second-order models for the removal of MB using carbonized P. australis as an adsorbent ($Co = 20$ ppm; sorbent dosage: $1.00$ gm for carbonized biomass)

<table>
<thead>
<tr>
<th>Biomass</th>
<th>$q_{e,exp}$ (mg/gm)</th>
<th>$q_{e,cal}$ (mg/gm)</th>
<th>$K_1$ (min$^{-1}$)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carb. p. australis</td>
<td>3.29</td>
<td>2.14</td>
<td>0.0027</td>
<td>0.964</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Biomass</th>
<th>$q_{e,exp}$ (mg/gm)</th>
<th>$q_{e,cal}$ (mg/gm)</th>
<th>$K_2$ (g/mg min)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carb. p. australis</td>
<td>3.29</td>
<td>2.19</td>
<td>0.0171</td>
<td>0.993</td>
</tr>
</tbody>
</table>

3.4 Effect of Initial Dye Concentration and Adsorption Equilibrium Study

The effect of the initial MB concentration on adsorption was shown in fig. (7).

![Fig.7](image3.png)  
**Fig.7** The effect of initial MB concentration on the % adsorption of MB concentration at pH = 7, adsorbent dose = 1 gm

The experiment was conducted at optimum condition 1.0 gm adsorbent dosage of carbonized p. australis and pH 7 for contact time of 150 min. Maximum dye removal occurred for low initial concentration of...
methylene blue that showed gradual reduction when initial concentration of Methylene blue was raised. It could be recognized to fixed concentration of adsorbent dosage. With increase in initial dye concentration the adsorption sites were fixed and achieved saturation at low dye concentration. Hence with increase in dye concentration no further adsorption could be achieved and resulted in reduced adsorption of dye with increase in dye concentration. The highest % adsorption of MB achieved was 97.1% at initial MB concentration was 10 ppm.

Adsorption isotherms are vital for designing the adsorption systems. A variety of adsorption isotherm models are in use, some of which have a theoretical base and some being exclusively of an empirical nature (Armanag et al. 2004; Gupta and Babu 2009). Several isotherm models have been used to fit experimental data such as Langmuir and Freundlich isotherms expression formulas which are given in equations (4) and (5). The isotherm constants calculated from isotherm equations were listed in Table 4.

**Table 4** Isotherm model parameters for the removal of MB by raw and modified P. australis (pH: 7, sorbent dosage: 1.0 gm, initial dye concentration: 10–50 mg/l).

<table>
<thead>
<tr>
<th>Langmuir formula</th>
<th>Freundlich formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Q_0=4.065 \text{ mg/gm}, b=0.8176)</td>
<td>(1/n=0.3528, K=1.6986)</td>
</tr>
<tr>
<td>(l/mg, R^2=0.9906)</td>
<td>(mg/gm(l/mg)^{1/n}, R^2=0.9589)</td>
</tr>
</tbody>
</table>

Fig. (8) and (9) show the conformity of adsorption data to isotherm models for carbonized P. australis. In terms of regression coefficient (R²) values, the applicability of above two models for experimental data obtained from carbonized P. australis approximately followed the order: Langmuir > Freundlich. Thus, the sorption behavior of MB onto carbonized P. australis is considered to be representative of sorption onto a monolayer. The experimental MB uptake is lower than the theoretical maximum adsorption capacity. It may be attributed to the incomplete contact of MB and the carbonized P. australis biomass.

**Fig.9** The conformity of adsorption data to Freundlich isotherm model for carbonized P. australis

**Acknowledgement**

The author expresses gratitude to the staff of employees of Environmental Engineering Laboratory - Faculty of engineering - Zagazig university.

**Conclusions**

In the present study, carbonized leaves and stems of P. australis were used as an adsorbent to remove MB from aqueous solution. The results showed the following:

1) The adsorption capacity of MB by carbonized P. australis increased with increases in pH, adsorbent dosage and contact time.

2) For pH, % removal of MB remains lowest in both acidic & basic medium & it occurs maximum in neutral medium. This can be accounted because in acidic medium due to high H⁺ concentration, there is a repulsion of H⁺ ion with cationic charge of dye for which the adsorption can’t takes place suitably as in comparison to neutral medium. The highest MB removal achieved particularly at pH value = 7 meant that pH adjustments might not be much of need.

3) For adsorbent dose, it was seen that % removal of MB increases with increase in adsorbent dosage. This trend can be attributed because of more doses, the surface area exposed to dye solutions gets more so that more dye can be absorbed into the pores of the adsorbent hence more is the % removal of MB.

4) For contact time, it was seen that % removal of MB increases with increase in contact time. The slope gets further increase at the first 60 min and finally attains a steady value after 150 min. This trend can be attributed to the fact that as the contact time increases more is the adsorbate-adsorbent interaction & thus leads to more adsorption & hence % removal of MB also gets raised with respect to increase in contact time.
5) From the studied kinetics adsorption models, the pseudo-second-order model was the best for describing the kinetics of MB for using the carbonized biomass with $R^2=0.993$.

6) For initial MB concentration, the % removal of MB started decreasing with respect to increase in concentration of MB. This happens due to fixed amount of adsorbent in increasing MB concentration.

7) For adsorption isotherm, the plotted figures for both Langmuir & Freundlich models were observed that regression coefficient came close to 1. Biosorption equilibrium of MB was well fitted by the Langmuir isotherm, exhibited the highest value of regression coefficients (0.9906).

8) Studying through different graphs of pH, adsorbent dose, contact time and initial MB concentration, We got optimum values for each case as

9) pH= 7, Adsorbent dose= 1.0 gm, Contact time = 150 min and initial MB concentration= 10 mg/l.

10) Hence after carrying out precise experiments we finally came to conclusion that carbon prepared from phragmites australis can be effectively used for the removal of methylene blue effectively conducted at the optimum process condition.

References


