Comparison of novel *Ziziphus lotus* adsorbent and industrial carbon on methylene blue removal from aqueous solutions

Asmaa Msaad, Mounir Belbahloul, Samir El Hajjaji and Abdeljalil Zouhri

**ABSTRACT**

In this work, the use of a novel low-cost adsorbent derived from *Ziziphus lotus* (ZL) and industrial carbon (IC) has been successfully applied to the removal of methylene blue (MB) from aqueous solutions. The efficiency of this material was studied through Lagergren pseudo-first-order and pseudo-second-order kinetic models. The process for the novel activated carbon and the IC were best represented by the pseudo-second-order rate model. Langmuir and Freundlich isotherms were used to describe the sorption equilibrium data. The Langmuir model turned out to be the most adequate and maximum capacities were measured to be 833.33 and 142.85 mg g\(^{-1}\) for ZL activated carbon and IC from Sigma Aldrich, respectively. The thermodynamic study revealed that the sorption process is spontaneous and endothermic for the two adsorbents. To explain the effectiveness of MB removal, ZL activated carbon was characterized by scanning electron microscopy, Brunauer–Emmett–Teller surface area, X-ray diffraction and Fourier transform infrared spectroscopy.

**Key words** | activated carbon, adsorption, industrial carbon, methylene blue, *Ziziphus lotus*

**INTRODUCTION**

In modern times, consequences of large-scale urbanization and industrialization have caused serious environmental degradation; one important industrial contributor is the textile industry, which is responsible for the release of toxic effluents containing typically large amounts of pollutants such as colored materials, dyes, organic compounds, and heavy metal ions (Ngah & Hanafiah 2008). These colored materials can affect the physicochemical and biological properties of the sea, drinking water and the ecosystem at large. In addition, some colored dyes may produce carcinogens and toxic products by degradation (Dasgupta et al. 2015). One particular dye of interest commonly utilized in the industry is methylene blue (MB), a cationic dye that is part of the thiazine class of heterocycles, which is considered more toxic than anionic ones (Gao et al. 2016). Effects of the acute exposure to MB on humans are numerous and include irritation of the mouth, throat, esophagus, and stomach, as well as irritation of the skin with redness and itching, nausea, vomiting, dizziness, headache and fever (Shakoor & Nasar 2017). As a result, MB elimination from effluents is highly desirable. To help prevent further deterioration of the quality of surface water, legislation governing the levels of dye concentration discharged from textile industries is getting stricter. Technical solutions have been reported to remove color from wastewater; they include chemical precipitation, chemical oxidation, and reduction, ion-exchange and adsorption (Mahesh & Ahammed 2016). However, most of these methods have significant disadvantages, especially their substantial operational cost. Adsorption is an appealing and low-cost solution in terms of simplicity in design, ease of operation and insensitivity to toxic substances (Hachoumi et al. 2017); furthermore, it provides an attractive alternative treatment, especially if the adsorbent employed is inexpensive, readily available and reusable (Bera et al. 2017). Currently, many kinds of non-conventional adsorbent materials are tested for their adsorption ability to remove dyes, such as cactus (*Opuntia ficus indica*), agricultural wastes, corn cob, activated carbon prepared from the waste of *Manihot esculenta* Crantz and others (Barka et al. 2013; Rangabhashiyam et al. 2013; Miyah et al. 2016; Beakou et al. 2017). Nevertheless, adsorption capacity of these adsorbents is relatively low.

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The goal of the work presented herein is to test the effectiveness of a novel activated carbon, prepared from *Ziziphus lotus* (ZL) leaves, which remains unreported in the literature. Study of this biomaterial was performed by comparing it with a commercial industrial carbon (IC) purchased from Sigma Aldrich. Parameters investigated were the effect of pH, adsorbent dosage, contact time, initial concentration of dye, and temperature. Finally, ZL activated carbon was characterized using scanning electron microscopy (SEM), X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy and Brunauer–Emmett–Teller (BET) specific surface area to explain its effectiveness.

**MATERIALS AND METHODS**

**Materials and reagents**

Acquisition of data and experiments were done by means of a UV-visible spectrophotometer (Hach, Germany) set at 662 nm, a multi-parameter analyzer (Consort, C3040, Germany) for pH measurements and a multi-agitator (WTW OxiTop IS 12, Germany). Adsorption experiments requiring temperature control were performed in a shaken double-jacketed beaker placed in a thermostated bath (JP Selecta Frigiderm, Spain).

XRD was performed using a D2 PHASER-BREKUR diffractometer. The FTIR spectrum was obtained using a Shimadzu FTIR-8400S spectrometer, and BET was measured using a Micromeritics machine, model 3 FLEX 3500. Finally, SEM and energy dispersive X-ray spectroscopy were performed using an environmental scanning electron microscope, FEI Quanta 450 FEG. pH values were adjusted using 0.1 N HCl or 0.1 N NaOH aqueous solutions. MB, C₁₆H₁₈ClN₃S, was obtained from Sigma Aldrich, with a molecular weight of 319.85 g·mol⁻¹ and \( \lambda_{\text{max}} \) of 662 nm.

**Preparation of ZL activated carbon**

ZL leaves were collected from the Casablanca-Settat region, in the central-western part of Morocco, washed several times with distilled water, and oven-dried at 75 °C for 24 h. The biomaterial was then ground prior to chemical activation using optimal conditions. To determine the optimal production conditions of the ZL adsorbent, three factors influencing the synthesis were selected: impregnation ratio of material: \( \text{H}_3\text{PO}_4 \) (1–5), carbonization temperature (200–800 °C), and time of carbonization (30–120 min). The efficiency of MB elimination was the parameter chosen as a ‘response’, in order to optimize the activated carbon synthesis conditions using Box–Behnken model. Optimal conditions of production of ZL activated carbon were found to be a \( \text{H}_3\text{PO}_4 \) impregnation ratio of 2.76 w/w, carbonization temperature of 415 °C, and carbonization time of 73 min. Finally, the activated carbon was neutralized, dried at 60 °C for 6 h and sieved to sizes between 40 and 63 \( \mu \)m.

**Adsorption experiments**

Effects of parameters influencing removal of MB by ZL activated carbon and commercial carbon were investigated. To this end, various pH values, adsorbent dosages, contact times, temperatures, and batch adsorption experiments were carried out. A 100 mL sample of MB solution at 100 ppm concentration was treated by ZL activated carbon and IC. For the pH study, pH of the solution was varied from 2 to 12 using dilute solutions of NaOH and HCl (each 0.1 N); pH at the point of zero charge (pHₚzc) was measured by mixing 50 mL of 0.1 M KNO₃ solution with 0.1 g of ZL activated carbon to form a suspension which was stirred for 48 h at room temperature (25 °C ± 1 °C).

Study of the adsorbent dosage was conducted by varying the dose of adsorbent between 5 and 100 mg at optimal pH and ambient temperature. The kinetic study was achieved by taking a sample every 2 min; finally, the thermodynamic study was done at temperatures ranging from 30 to 60 °C. The dye solution was separated from the adsorbent by centrifugation at 7,500 rpm for 5 min. Absorbance of the supernatant was then measured by spectrophotometry at a maximum wavelength of 662 nm. The amount of MB adsorbed at equilibrium, noted \( q_e \) in mg·g⁻¹, and the performance of adsorption, \( R(\%) \), respectively, were calculated using Equations (1) and (2) below:

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

\[
R(\%) = \frac{(C_0 - C_t)}{C_0} \times 100 \tag{2}
\]

where \( C_0 \) is the MB initial concentration (mg·L⁻¹); \( C_t \) is the MB equilibrium concentration (mg·L⁻¹); \( V \) is the volume of the solution and \( m \) is the mass of the adsorbent (g).

**Kinetic study**

Kinetic experiments were run at optimal pH, optimal adsorbent dosage, and ambient temperature. One hundred
millilitres of MB solution was agitated at a fixed dye concentration of 100 ppm. Agitation time was set from 2 to 120 min. The pseudo-first-order and pseudo-second-order models, given by Equations (3) and (4) respectively (Lagergren 1898), were used to fit the experimental results.

\[
\ln \left( \frac{q_e}{q_t} \right) = \ln q_e - k_1 t
\]  

(3)

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^*} + \frac{t}{q_e}
\]  

(4)

where \( k_1 \) is the rate constant of the pseudo-first-order model (min\(^{-1}\)); \( q_t \) and \( q_e \) are the amounts of dye adsorbed in mg.g\(^{-1}\) at time \( t \) and at equilibrium respectively; \( k_2 \) is the rate constant of the pseudo-second-order model (g.mg\(^{-1}\).min\(^{-1}\)).

Isotherm study

Insight about the adsorption behavior was gained by plotting an adsorption isotherm. The latter was obtained by varying the initial MB concentration from 10 to 100 mg.L\(^{-1}\). Models of Langmuir and Freundlich were used to fit equilibrium experimental data of MB adsorption into ZL activated carbon and IC. The Langmuir model assumes the presence of a limited number of identical sites homogeneously distributed over the adsorbent surface; the linear form of this model is shown in Equation (5).

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

(5)

where \( q_e \) is the equilibrium dye concentration on the adsorbent (mg.g\(^{-1}\)); \( C_e \) is the equilibrium dye concentration in the solution (mg.L\(^{-1}\)); \( q_{max} \) is the maximum adsorption capacity of the adsorbent (mg.g\(^{-1}\)); \( K_L \) is the Langmuir adsorption constant (L.mg\(^{-1}\)). The crucial characteristics and the feasibility of the Langmuir isotherm are expressed in terms of the equilibrium parameter \( R_L \). This dimensionless constant is defined as \( R_L = 1/(1 + C_0K_L) \) where \( C_0 \) is the initial textile dye concentration (mg.L\(^{-1}\)).

The Freundlich model instead proposes the presence of heterogeneous surfaces with an interaction between the adsorbed molecules. The linear equation of the Freundlich model is given in Equation (6).

\[
\log q_e = \log K_F + \left( \frac{1}{n_F} \right) \log C_e
\]  

(6)

where \( q_e \) is the equilibrium dye concentration on the adsorbent (mg.g\(^{-1}\)); \( C_e \) is the equilibrium dye concentration in the solution (mg.L\(^{-1}\)); \( K_F \) is the proportionality constant [(mg.g\(^{-1}\) (L.mg\(^{-1}\))\(^{1/n_F} \)]; \( 1/n_F \) is the adsorption intensity.

Thermodynamic studies

The effect of temperature on MB adsorption using ZL adsorbent and IC was studied at different temperatures (20–60 °C), optimal pH and optimal adsorbent dosage. Next, samples were shaken for the optimum time. Thermodynamic parameters such as change in Gibbs free energy (\( \Delta G^\circ \)), change in enthalpy of adsorption (\( \Delta H^\circ \)), change in entropy (\( \Delta S^\circ \)) and the equilibrium constant \( K_d \) for this adsorption process were determined using Equations (7)–(9) (Tan et al. 2008).

\[
K_d = \frac{q_e}{C_e}
\]  

(7)

\[
\Delta G^\circ = -RT \ln K_d
\]  

(8)

\[
\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}
\]  

(9)

where \( q_e \) is the equilibrium dye concentration on the adsorbent (mg.g\(^{-1}\)); \( C_e \) is the equilibrium dye concentration in the solution (mg.L\(^{-1}\)); \( R \) is the universal gas constant (8.314 J.mol\(^{-1}\).K\(^{-1}\)); \( T \) is the absolute temperature of the solution (K).

Characterization of the ZL sorbent

To explain the efficacy of MB sorption using ZL activated carbon, physicochemical characterization of the sorbent was carried out. Analytical methods used for this process include XRD, FTIR spectroscopy, BET, SEM and energy dispersive X-ray.

RESULTS AND DISCUSSION

Effect of pH

Plots of MB removal percentage versus pH for prepared and ICs are shown in Figure 1(a). It has been demonstrated that the performance of MB removal for these adsorbents increases slightly when pH increases from 2 to 6 and remains constant. To explain this behavior, the pH\(_{pzc}\) was studied (Figure 1(b)). It was found that pH\(_{pzc}\) is 5.86 and 7.7 for IC and ZL activated carbon respectively. When pH\(_{pzc}\) > pH (i.e., adsorbent surface is positive), there is a
significant increase of decolorization, and when pH_{pzc} < pH (i.e., adsorbent surface is negative) (Figure 1(b)), the decolorization increases slightly due to the attractive electrostatic forces (Sivaramakrishna et al. 2014), so pH values higher than these pH_{pzc} are most suitable for the adsorption of the cationic dyes.

**Effect of adsorbent dosage**

The effect of adsorbent dosage on MB removal is presented in Figure 2. As shown in this figure, MB removal increases with an increase in the adsorbent dosage from 0.01 to 0.05 g and from 0.01 to 0.06 g for ZL activated carbon and IC respectively. This result can be explained by the availability of more adsorbent sites as well as greater availability of specific surfaces on the adsorbents. From the results we can see that a dose of 0.3 g.L^{-1} of ZL activated carbon is sufficient to eliminate all of the MB dye, whereas 0.6 g.L^{-1} is required when using IC, i.e., twice as much. El-Sayed et al. (2014) noticed that the dye removal increases from 96.2% to 99.6% when using a dose of corn cob activated carbon (prepared by chemical activation with phosphoric acid) between 1 and 5 g.L^{-1}; comparison of this finding with our results suggests only a minimal quantity of ZL activated carbon is sufficient for MB removal.

**Effect of contact time**

Study of the adsorption process on the sorbents involves the determination of the contact time corresponding to the adsorption equilibrium. Figure 3 shows the effect of contact time on MB adsorption onto IC and ZL activated carbon. MB adsorption is initially rapid for both the industrial and prepared carbons and increases constantly until equilibrium is reached. Maximum MB removal percentages were obtained in the first 10 min with a value of 99% for the two carbons.
Kinetic study

The pseudo-first-order and pseudo-second-order models were used to explain the sorption kinetic behavior of MB onto ZL activated carbon and IC. The pseudo-second-order was selected as the best-fit model considering its higher linear regression correlation coefficients $R^2$ with the two sorbents (Table 1). Results of the pseudo-second-order kinetic model are presented in Figure 4. These results indicate that the kinetic model of the MB adsorption is based on a high driving force making the fast transfer of dye molecules to the surface of adsorbent particles. The availability of the uncovered surface area and the remaining active sites on the adsorbent suggests that the adsorption process is based on a rate-limiting step, being a chemisorption involving valence forces through the sharing or exchange of electrons between adsorbent and adsorbate (Kula et al. 2008). Comparable results have been reported using rice husk (Vadivelan & Kumar 2005) and other products for MB removal.

| Parameters of pseudo-first- and pseudo-second-order models for ZL adsorbent and IC |
|---------------------------------|-----------------|-----------------|------------------|-----------------|
| Pseudo-first-order             | Pseudo-second-order |
| $q_e$ (mg.g)                   | $K_1$ (min$^{-1}$) | $R^2$           | $q_e$ (mg.g)     | $K_2$ (g.mg$^{-1}$.min$^{-1}$) | $R^2$ |
| ZL sorbent                     | 172.43           | 0.010           | 0.98             | 500              | 0.00036         | 0.99 |
| IC                             | 7.61             | 0.05            | 0.67             | 500              | 0.02            | 1    |

Isotherm study

The effect of MB concentration on the sorption by ZL and IC was carried out in the concentration range of 10–1,000 ppm (Figure 5). Freundlich and Langmuir isotherms were used to explain the adsorption of solutes from aqueous solutions. Table 2 lists the parameters of Freundlich and Langmuir models.

The Langmuir model shows a very good fit ($R^2 = 0.99$), thus revealing that the adsorption comes from a monolayer coverage of adsorbate over a homogeneous adsorbent surface containing a finite number of adsorption sites (Langmuir 1916). The maximum Langmuir monolayer adsorption capacity was found to be 833.33 mg.g using ZL activated carbon, and only 142.85 mg.g using IC. Similar results were obtained by Hameed (2009) who reported a maximal adsorption capacity of 555.5 mg.g with papaya seeds.

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>Langmuir isotherm</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_L$ (L.mg$^{-1}$)</td>
<td>$R^2$</td>
</tr>
<tr>
<td>IC</td>
<td>0.16</td>
</tr>
<tr>
<td>ZL sorbent</td>
<td>0.24</td>
</tr>
</tbody>
</table>

Thermodynamic study

A thermodynamic study was also performed to understand the thermodynamic behavior of MB sorption onto ZL sorbent and IC. Experimental results obtained using Equations (7)–(9) are given in Table 3. Values of $\Delta H^\circ$ and $\Delta S^\circ$ can be estimated by plotting $\ln K_d$ versus $1/T$ (Figure 6).
We can notice that $\Delta H^\circ$ and $\Delta S^\circ$ are positive, while $\Delta G^\circ$ values are negative (Table 3); these results show that the adsorption process of MB onto the ZL adsorbent and IC is endothermic, feasible and spontaneous. Also, the positive value of $\Delta S^\circ$ suggests an increase of randomness. Similar thermodynamic results for MB removal using wheat shells were obtained by Bulut & Aydın (2006).

Characterization of ZL activated carbon

The surface area of ZL activated carbon obtained by BET analysis was determined to be 553.39 $m^2.g^{-1}$. Comparatively, this value of $S_{BET}$ is higher than the 377 $m^2.g^{-1}$ reported by Saeidi et al. (2018) for activated carbon made from sewage sludge. It is also slightly lower than the 564 $m^2.g^{-1}$ reported for commercial activated carbon (Cazetta et al. 2011), and much lower than the 966.74 $m^2.g^{-1}$ reported for activated carbon made from Typha orientalis leaves (Hameed & El-khaiary 2008). Generally, adsorption capacity rises with the increase of this parameter, which makes it useful to predict the effectiveness of a given activated carbon. In order to provide more information about the structure of the ZL material, SEM analysis was run. Figure 7(a) shows a SEM image of the adsorbent at 2,400 magnification. This image confirms results of the BET analysis and indicates a large development of pores that are clearly found on the surface of the ZL activated carbon. This is possibly due to the activation process using phosphoric acid ($H_3PO_4$) as a chemical activating agent. Also, we notice the presence of heterogeneous pores which are essential for the adsorption of different types of pollutants. Thus, it can be claimed that the surface of ZL activated carbon has a nanoporous structure. Similar observations were reported by Hameed & Daud (2008) using agricultural waste activated carbon.

The EDX spectrum of the ZL sorbent shows the presence of C (83.98%) and O (14.17%) as the major constituents of the product and the presence of other minor elements such as P (2.23%), Na (1.18%), Ca (0.43%) and Si (0.26%) in the structure (Figure 7(b)). The presence of phosphorus and sodium is due to the $H_3PO_4$ and NaOH used in the activation and neutralization steps in the preparation of activated carbon. The presence of Si and Ca in the activated carbon is normal since these elements are contained naturally in ZL leaves. The high content of carbon indicates a high degree of graphitization as well as a low content of functional groups; on the other hand, the high content of oxygen suggests a high content of acid functional groups (Montoya & Petriciolet 2015). In their study, Van & Thi (2014) obtained almost the same content of C and O (83.04 and 16.96%) with activated carbon derived from rice husk. Adsorption efficacy is related not only to the surface area, but also to the chemical properties on the surface of the adsorbent.

FTIR analysis of ZL carbon was performed to determine the functional groups, and then evaluate the involvement of these functional groups in the adsorption of textile dye onto ZL leaves activated carbon. Figure 8(a) shows the spectrum of the adsorbent; the band located between 3,200 and 3,600 cm$^{-1}$ can be attributed to the hydroxyl groups –OH.

Table 3 | Thermodynamic parameters of MB dye adsorption onto ZL adsorbent and IC

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>T</th>
<th>1/T</th>
<th>Ln $K_d$</th>
<th>$R^2$</th>
<th>$\Delta S^\circ$ (J.mol$^{-1}$)</th>
<th>$\Delta H^\circ$ (J.mol$^{-1}$)</th>
<th>$\Delta G^\circ$ (J.mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IC</td>
<td>20</td>
<td>0.05</td>
<td>3.66</td>
<td>0.989</td>
<td>100.96</td>
<td>20,733.45</td>
<td>−8,927.88</td>
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<tr>
<td></td>
<td>30</td>
<td>0.033</td>
<td>3.92</td>
<td></td>
<td></td>
<td>−9,865.89</td>
<td>−10,662.94</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>0.025</td>
<td>4.10</td>
<td></td>
<td></td>
<td>−12,994.30</td>
<td>−12,836.96</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>0.017</td>
<td>4.69</td>
<td></td>
<td></td>
<td>−14,162.22</td>
<td>−15,274.08</td>
</tr>
<tr>
<td>ZL sorbent</td>
<td>20</td>
<td>0.05</td>
<td>5.17</td>
<td>0.991</td>
<td>146.16</td>
<td>30,264.62</td>
<td>−18,509.07</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>0.033</td>
<td>5.62</td>
<td></td>
<td></td>
<td>−14,162.22</td>
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<td></td>
<td>−18,509.07</td>
<td>−18,509.07</td>
</tr>
</tbody>
</table>

Figure 6 | Plot of Ln $K_d$ versus 1/T for the ZL and industrial activated carbon.
of lignin (Myglowets et al. 2014) and the hydrogen-bonded OH vibration of the cellulosic structure (Weng et al. 2009). Bands observed at around 1,610 cm\(^{-1}\) could be attributed to the stretching of the aromatic rings (C=C) (Chen et al. 2011). The band at 1,223 cm\(^{-1}\) is partly associated with C-O stretching and O-H bending modes in the functional group (Foo & Hameed 2009), and the band at around 1,080 cm\(^{-1}\) can be attributed to the C-OH stretching of phenolic groups (Figueiredo et al. 1999). Also, a band at around 640 cm\(^{-1}\) justifies the presence of the out-of-plane deformation mode of O-H of cellulose (Zheng et al. 2014). The presence of lignin and cellulose suggests a lignocellulosic structure of active and carbonized ZL; this structure is also observed with other types of carbon like the Brazilian coconut shell (Cazetta et al. 2011). The XRD spectrum of ZL activated carbon is shown in Figure 8(b). Presence of a broad diffraction background in that spectrum and the absence of a sharp peak reveals a predominantly amorphous structure (Omri & Benzina 2012). As a matter of fact, this type of structure in activated carbon has also been reported.
CONCLUSION

The adsorption processes of MB onto activated-carbon prepared from ZL on one hand, and onto commercial IC have been studied. Results obtained have enabled us to draw several conclusions. It has been shown that the kinetics of MB adsorption onto ZL activated carbon and IC follows a pseudo-second-order and that its isotherm follows the Langmuir model with a maximum capacity of 833.33 and 142.85 mg·g−1 respectively. The thermodynamic study revealed that the sorption of MB onto these carbons is endothermic and spontaneous. To conclude, ZL activated carbon is a low-cost sorbent that turns out to be very effective and efficient material for MB removal from aqueous solutions.

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