Research Article

Activated Carbon for Dyes Removal: Modeling and Understanding the Adsorption Process

Y. El maguana, N. Elhadiri, M. Benchanaa, and R. Chikri

Research Laboratory on Materials Reactivity and Process Optimization «REMATOP», Department of Chemistry, Faculty of Science Semlalia, Cadi Ayyad University, B.P. 2390, Marrakech, Morocco

Correspondence should be addressed to Y. El maguana; youssefelmaguana@gmail.com

Received 7 June 2020; Revised 16 August 2020; Accepted 1 September 2020; Published 14 September 2020

Batch adsorption experiments have been conducted to investigate the removal of methyl orange from aqueous solution by an activated carbon prepared from prickly pear seed cake by phosphoric acid activation. The adsorption process has been described by using kinetic and isotherm models. The kinetic of adsorption was examined by pseudo-first-order, pseudo-second-order, and intraparticle diffusion models. Adsorption isotherm was modeled using Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherms. The adsorption process of methyl orange was well explained by the pseudo-second-order model and Freundlich isotherm. Also, pseudo-\( n \)-order model has been applied to estimate the order of adsorption kinetic and it was found equal to 2 which confirm the good accuracy of the pseudo-second order. Moreover, Dubinin–Radushkevich isotherm reveals that the adsorption of methyl orange onto activated carbon was a physisorption process in nature. The adsorption capacity of activated carbon was found to be 336.12 mg/g at temperature 20 °C and pH ∼ 7. These results demonstrated that the prickly pear seed cake is a suitable precursor for the preparation of appropriate activated carbon for dyes removal from aqueous solution.

1. Introduction

Industrial liquid effluents contain a wide variety of chemicals which affect, if discharged without any treatment, rivers, seas, lakes, and groundwater and therefore cause environmental pollution and harmful effects on human and animal health even in low concentrations [1–4]. Among these chemicals, the dyes used in several sectors such as textiles, cosmetics, plastics, pigments units, leather, and paper industries have been considered as the primary pollutant due to their stability and low biodegradability [3]. Indeed, significant quantities of dyes are released into the environment by colored textile wastewater. Approximately, it is estimated that 10 to 15% is lost in the effluent during the dyeing process [5]. Consequently, the scientific community has focused their research on the development effective dyes removal techniques. In recent years, Considerable interest has been focused on the adsorption technique for dyes removal from solutions using various adsorbent such as activated carbon [6–8], clays [9, 10], siliceous material [11, 12], zeolites [13, 14], alumina [15], and hybrid materials [16, 17]. The adsorption is highly effective technique for dyes removal from wastewater. The major advantages of adsorption process are its relative simplicity, low cost, and possible regeneration of the adsorbent [3].

Activated carbon is well known as an adsorbent characterized by its large specific surface, its porous structure, and its thermostability, which is extensively used in a variety of applications such as removal of pollutants and odor from liquid and gaseous phases, medical uses, catalysis, gas storage, electrode materials in electrochemical devices, and removal of organic pollutants from drinking water and in the waste water treatment [7, 18–24]. Adsorption on activated carbon has been found to be a very efficient technique for removal of dyes from wastewater in terms of capability for efficiently adsorbing a broad range of pollutants, fast adsorption kinetics, simplicity of design, and low cost [25–27]. In recent years, there has been increasing interest in the research of the production of activated carbons from the agricultural byproducts and industrial wastes for dyes
removal [8, 28–32]. The utilization of those biomass wastes has a positive impact in environment protection by reducing solid wastes and also the production of low-cost activated carbons with high added value which can reduce contaminants in wastewater at a reasonable cost.

In industrial scale, the adsorbent and liquid effluent are in contact with each other for a given time, therefore, predicking the equilibrium time and the rate of adsorption is of paramount importance. For that, the kinetic and equilibrium properties of the adsorbate/adsorbent system have been investigated to understand the characteristic of the adsorption behavior. The modeling of adsorption processes is usually carried out using well-established adsorption kinetic and isotherm models. Adsorption kinetics models provide invaluable information on the controlling mechanisms of adsorption process. The overall adsorption process may be controlled by either external or film diffusion, pore diffusion and adsorption on the pore surface, or a combination of more than one step. The adsorption isotherm describes the interaction between the adsorbate molecules and the adsorbent when the system reaches the equilibrium. It provides the qualitative information on the nature of adsorbate-adsorbent surface interactions and could be used to evaluate the adsorption capacity.

The aim of this work is to investigate both kinetic and equilibrium adsorption of methyl orange (MO) onto an activated carbon prepared from prickly pear seed cake by phosphoric acid activation. Methyl orange was chosen as an adsorbate to evaluate the adsorption characteristics of activated carbon and also serves as a model compound for adsorption of organic contaminants from aqueous solution.

2. Materials and Methods

2.1. Materials. Activated carbon prepared by El maguana et al. [33] was sieved to obtain particles size less than 100 μm. Methyl orange used as adsorbate in the present study and without further purification was supplied by Merck. A stock solution was prepared by dissolving the weighted quantity of methyl orange in distilled water. Then solutions of desired concentrations were prepared by diluting stock solution with distilled water.

The structure of methyl orange is given by

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{N} \quad \text{N} \quad \text{SO}_3\text{Na} \\
\text{H}_3\text{C} & \quad \text{N} \quad \text{N} \quad \text{SO}_3\text{Na}
\end{align*}
\]

2.2. Adsorption Experiments. Batch adsorption experiments have been conducted to evaluate the efficiency of activated carbon to remove methyl orange dye from aqueous solution. The experiments were performed in flasks containing a defined amount of activated carbon and 100 cm\(^2\) of desired concentration of methyl orange solution. The suspensions were mixed on a shaker at 180 rpm at 20°C during a given time and separated with centrifuge. After adsorption, the residual concentration of methyl orange was determined by spectrophotometric method (UV-3100PC Spectrophotometer) at 462 nm. The amount of adsorption at equilibrium \(q_e\) was defined as the amount of adsorbate per Gram of adsorbent (in mg/g) and was calculated using the following equation:

\[
q_e = \frac{C_0 - C_e \times V}{m}
\]

The percentage removal \(R\%\) of the methyl orange at equilibrium was calculated using the following relationship:

\[
R\% = \frac{C_0 - C_e}{C_0} \times 100,
\]

where \(C_0\) and \(C_e\) (in mg/L) are the initial and equilibrium concentrations in aqueous solution respectively, \(V\) (L) is the volume of the solution, and \(m\) (g) is the mass of the adsorbent.

3. Results and Discussion

Activated carbon used in this study was prepared from prickly pear seed cake by phosphoric acid activation [33]. The authors reported that the obtained activated carbon is effective for removing cationic dyes such as methylene blue from aqueous solution. FTIR analysis indicated the presence of various functional groups (oxygen functions and phosphorus compounds) on the surface of the obtained activated carbon, which gave the adsorbent an acidic surface (\(\text{pH}_{\text{pzc}} = 3.8\)). Moreover, the adsorption process was well described by the pseudo-second-order model and Freundlich isotherm. The adsorption capacity of the prepared activated carbon for methylene blue at temperature 20°C and \(\text{pH} \sim 7\) was found to be 260 mg/g [33]. To test the performance of the prepared activated carbon in the removal of anionic dyes from aqueous solution, methyl orange was chosen as a model adsorbate. The adsorption performance was evaluated by kinetic and isotherm studies.

3.1. Adsorption Kinetic. To investigate the adsorption kinetic, the amount of methyl orange adsorbed by the activated carbon is studied at \(\text{pH} \sim 7\) for an adsorbent dose of 0.2 g/L, and an initial methyl orange concentration of 100 mg/L at 20°C. Figure 1 shows the effect of contact time on the adsorption capacity of the activated carbon prepared from prickly pear seed cake for methyl orange, at room temperature. It reveals that the adsorbed amount increased with contact time at the initial stage of adsorption and reached equilibrium in 120 min. The adsorption process of methyl orange was rapid at the beginning of the process due to the availability of active sites on the exterior surfaces and after the saturation of those active sites, the methyl orange entered to the pores of the adsorbent with a slower rate to reach the equilibrium time [33]. The amount of methyl orange removed by adsorption onto the activated carbon at the equilibrium time was 194 mg/g.

Adsorption kinetics models provide invaluable information on the controlling mechanisms of adsorption
process [34]. The overall adsorption process may be controlled by either external or film diffusion, pore diffusion and adsorption on the pore surface, or a combination of more than one step [34]. In order to predict the mechanism of the adsorption process of methyl orange onto the activated carbon, the experimental data were fitted with different kinetic models. In a first step, the experimental kinetic data were fitted by pseudo-first-order and pseudo-second-order kinetic models. We employed pseudo-first-order and pseudo-second-order models in their nonlinear forms to determine the kinetic parameters because, in this way, the kinetic parameters are predicted better than in the linearized forms of these models [33, 35].

The nonlinear form of pseudo-first-order model [36] is given by the following equation:

\[ q_t = q_e \left(1 - e^{-k_1 t}\right). \] (3)

The nonlinear form of pseudo-second-order model [37] is given as follows:

\[ q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t}, \] (4)

where \( q_e \) (mg/g) is the adsorption amount at equilibrium, \( q_t \) (mg/g) is the adsorption amount at time \( t \) (min), and \( k_1 \) (1/min) and \( k_2 \) (g/mg min) are the adsorption rate constants of pseudo-first-order and pseudo-second-order models, respectively. Kinetic parameters, \( q_e \), \( k_1 \), and \( k_2 \), can be calculated from the plots of \( q_t \) versus \( t \).

The validity of these models was evaluated by the coefficient of regression \( R^2 \) and by the normalized standard deviation \( \Delta q \) (%), which is defined as follows:

\[ \Delta q (\%) = 100 \left\{ \frac{\sum (q_{exp} - q_{cal})^2}{q_{exp}} \right\}^{1/2}. \] (5)

where \( q_{exp} \) and \( q_{cal} \) are the experimental and calculated equilibrium adsorption capacity value, respectively, and \( N \) is the number of data points.

Figure 2 shows the plots for pseudo-first-order and pseudo-second-order models. The calculated values of \( k_1, k_2, q_e \), correlation coefficient \( (R^2) \), and normalized standard deviation \( \Delta q \) are presented in Table 1. It can be seen that both pseudo-first-order and pseudo-second-order models have a good fit to the experimental data \( (R^2 \) greater than 0.99 and \( \Delta q \) lower than 5%). Moreover, the equilibrium adsorption capacities \( (q_{e,cal}) \) calculated by the pseudo-first-order and pseudo-second order are closer to the experimental value \( (q_{e,exp} = 194.08 \text{mg/g}) \). According to these results, we can say that both pseudo-first-order and pseudo-second-order models could be used to describe the adsorption process of methyl orange onto activated carbon. However, \( \Delta q \) for pseudo-second order was lower than that for pseudo-first order, thus suggesting an order kinetic greater than 1. Taking into account that the kinetic order can take a decimal value, the kinetic data were fitted with a pseudo-\( n \)-order kinetic model [38] expressed as follows:

\[ q_t = q_e \left[1 - \left(1 + (n-1)k_n t \right)^{1/(-n)} \right], \] (6)

where \( q_e \) (mg/g) is the adsorption amount at equilibrium, \( q_t \) (mg/g) is the adsorption amount at time \( t \) (min), and \( k_n \) (1/min) is the adsorption rate constant of pseudo-\( n \)-order model.

The plot corresponding to the nonlinear fit of pseudo-\( n \)-order kinetic model for methyl orange adsorption onto activated carbon is presented in Figure 3. The kinetic parameters obtained from the pseudo-\( n \)-order kinetic model are listed in Table 2. The results show that the values of \( R^2 \) and \( \Delta q \) obtained by pseudo-\( n \)-order kinetic model are equal to those for pseudo-second order. Moreover, the equilibrium adsorption capacities \( (q_{e,cal}) \) calculated by pseudo-\( n \)-order and pseudo-second-order kinetic models are similar and the value of \( n \) is almost equal to 2 \( (n = 1.97) \). Therefore, the adsorption process of methyl orange on the activated carbon can be well described by pseudo-second-order model, suggesting that the boundary layer resistance was not the rate-limiting step [33]. So, if the pseudo-first-order kinetic parameters are closer to those for pseudo-second order, then we cannot deduce the kinetic model which can
Experimental data by Weber and Morris [39], expressed as follows: Einstein’s rate of intraparticle diffusion model is not linear and did not pass through the origin, indicating that intraparticle diffusion was not the only rate-limiting step of the adsorption process of methyl orange onto the activated carbon, but also other mechanisms may control the rate of the adsorption, all of which may be operating simultaneously [8, 34, 40]. The possible intraparticle diffusion resistance was explored by using the intraparticle diffusion model proposed by Weber and Morris [39], expressed as follows:

$$q_t = k_{id}t^{1/2} + c,$$  \hspace{1cm} (7)

where $q_t$ (mg/g) is the adsorption amount at time $t$ (min), $k_{id}$ (mg/g/min$^{1/2}$) is the adsorption rate constant of intraparticle diffusion model, and $c$ is a constant related to the thickness of the boundary layer.

If the plot of $q_t$ versus $t^{1/2}$ is linear and passes through the origin, then intraparticle diffusion is the sole rate-limiting step of the adsorption process. Figure 4 shows the plot of the intraparticle diffusion model, which is not linear and did not pass through the origin, indicating that intraparticle diffusion was not the only rate-limiting step of the adsorption process of methyl orange onto the activated carbon, but also other mechanisms may control the rate of the adsorption, all of which may be operating simultaneously [8, 34, 40]. The first portion of the plot is attributed to the transport of solute from bulk solution through liquid film to the adsorbent exterior surface. Thereafter, the second part is ascribed to the intraparticle diffusion as slower process. In fact, the slope of the linear portion indicates the rate of the adsorption process: the lower slope corresponds to a slower adsorption process [34, 41]. Thus, the rate of the diffusion of methyl orange molecules through boundary layer film in the initial stage of the adsorption process was faster than the rate of the intraparticle diffusion because the slope of the first linear portion was higher than of the second linear portion. Initially, the methyl orange molecules are quickly adsorbed onto the surface of the activated carbon, and when saturation is reached, the methyl orange molecules are diffused into the interior of adsorbent particles [34]. Finally, the last portion is attributed to the final equilibrium stage for which the intraparticle diffusion slows down due to the low concentration dye in the aqueous solution [42].

3.2. Equilibrium Adsorption. Adsorption equilibrium is established between the adsorbed molecules and the adsorbent surface when an adsorbate is in contact with the adsorbent. The equilibrium relationship between the adsorbed amount of adsorbate ($q_e$) and the residual adsorbate concentration ($C_e$) at constant temperature is described by the adsorption isotherm. This last is very useful for understanding the adsorption mechanism. In general, adsorption isotherms provide information on the affinity and the binding energy between the adsorbate and the adsorbent, on the adsorption capacity and on the surface phase which may be considered as a monolayer or multilayer. All this information can be extracted from equilibrium isotherms.

<table>
<thead>
<tr>
<th>$q_{exp}$ (mg/g)</th>
<th>$q_{e,cal}$ (mg/g)</th>
<th>$k_1$ (1/min)</th>
<th>$R^2$</th>
<th>$\Delta q$ (%)</th>
<th>$q_{e,cal}$ (mg/g)</th>
<th>$k_2$ (g/mg/min)</th>
<th>$R^2$</th>
<th>$\Delta q$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>194.08</td>
<td>188.42</td>
<td>7.95 $10^{-2}$</td>
<td>0.990</td>
<td>3.83</td>
<td>200.34</td>
<td>7.15 $10^{-3}$</td>
<td>0.998</td>
<td>1.60</td>
</tr>
</tbody>
</table>

**Table 1**: Pseudo-first-order and pseudo-second-order kinetic parameters ($C_0$ = 100 mg/L; adsorbent dose = 0.2 g/L; pH ∼ 7; $T$ = 20°C).

**Table 2**: Pseudo-$n$-order kinetic parameters ($C_0$ = 100 mg/L; adsorbent dose = 0.2 g/L; pH ∼ 7; $T$ = 20°C).

![Figure 3: Nonlinear fit of pseudo-$n$-order kinetic model for MO adsorption onto activated carbon ($C_0$ = 100 mg/L; adsorbent dose = 0.2 g/L; pH ∼ 7; $T$ = 20°C).](image)

![Figure 4: Plot of the intraparticle diffusion model for MO adsorption onto sugar scum ($C_0$ = 100 mg/L; adsorbent dose = 0.2 g/L; pH ∼ 7; $T$ = 20°C).](image)
isotherm models describing the adsorption process. Several isotherm models are presented in the literature, which permit a better understanding of the adsorption phenomenon of chemical species on the adsorbent. The modeling of the adsorption isotherms consists in describing the experimental data using theoretical or empirical mathematical equations and allowing determination of isotherm parameters to compare the efficiency of different adsorbents.

To investigate the adsorption isotherm, the adsorption capacity of the activated carbon prepared from prickly pear seed cake for methyl orange is studied at temperature 20°C and pH \( \sim 7 \) for an adsorbent dose of 1 g/L. Figure 5 shows the adsorption isotherm of methyl orange onto the activated carbon which indicates a significant adsorption at low concentrations. According to Giles classification [43], this isotherm displayed an H curve pattern, indicating that the methyl orange and activated carbon have a high affinity.

In the first step, the experimental data of adsorption isotherm were fitted to the Langmuir and Freundlich models to find which one can be used to describe the adsorption process of methyl orange onto the surface of the activated carbon. Langmuir equation assumes the monolayer adsorption on a homogenous surface without interaction between adsorbates [44], while the Freundlich isotherm was based on the assumption of the multilayer adsorption on heterogeneous surface [45].

The Langmuir isotherm equation is expressed as follows:

\[
q_e = \frac{q_m K_L C_e}{1 + K_L C_e}.
\]  

The Freundlich isotherm equation is given as follows:

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

where \( C_e \) (mg/L) is the equilibrium concentration of adsorbate, \( q_e \) (mg/g) is the amount of adsorption at the equilibrium, \( q_m \) (mg/g) is the monolayer adsorption capacity, \( n \) is the Freundlich intensity constant, and \( K_L \) and \( K_F \) are the Langmuir and Freundlich constants, respectively.

Figure 6 shows the Freundlich and Langmuir curves generated using (8) and (9). It can be seen from this figure that the adsorption isotherm of methyl orange onto the activated carbon was well described by the Freundlich equation. Calculated parameters of Langmuir and Freundlich isotherms along with \( R^2 \) values, obtained by the nonlinear fitting method, are listed in Table 3. Via comparison of the \( R^2 \) values, Freundlich equation represents a better fit of equilibrium experimental data than Langmuir. Therefore, the adsorption process of methyl orange onto the activated carbon can be described more appropriately by the Freundlich isotherm, indicating the multilayer adsorption on the heterogeneous surface with a different energy distribution. Freundlich constant, \( n \), is a measure of adsorption intensity. As seen from Table 3, a value of \( 1/n \) was found between 0 and 1, indicating the favorable adsorption of methyl orange on the activated carbon [33].

The experimental data of the adsorption isotherm were also fitted to Temkin isotherm equation to approach energetic aspects. Temkin isotherm is based on the assumption that the heat of adsorption of all the molecules in the layer decreased linearly with coverage and adsorption is characterized by a uniform distribution of binding energies [46].

The Temkin isotherm equation is expressed as

\[
q_e = \frac{RT}{b} \ln(K_T C_e),
\]

\( C_e \) (mg/L) is the equilibrium concentration of adsorbate, \( q_e \) (mg/g) is the amount of adsorption at the equilibrium, \( q_m \) (mg/g) is the monolayer adsorption capacity, \( n \) is the Freundlich intensity constant, and \( K_L \) and \( K_F \) are the Langmuir and Freundlich constants, respectively.
where \( q_e \) (mg/g) is the amount of adsorption at the equilibrium, \( C_e \) (mg/L) is the equilibrium concentration of adsorbate, \( T \) (K) is the temperature, \( R \) is the universal gas constant, and \( K_T \) is the equilibrium binding constant corresponding to the maximum binding energy. The constant \( b \) (L/mol) is related to the heat of adsorption. The Temkin isotherm parameters were obtained by plotting \( q_e \) versus \( C_e \) shown in Figure 7 and summarized in Table 4. According to the \( R^2 \) value, the Temkin isotherm model did not fit well with the experimental data indicating the energetic heterogeneity of the adsorption sites.

Besides the Langmuir, Freundlich, and Temkin models, the Dubinin–Radushkevich isotherm model was also employed for the estimation of the adsorption energy (\( E \)) and further finding the nature of the adsorption [41, 47]. Its equation is given as follows:

\[
q_e = q_m \exp \left[ -K_{DR} \left( \frac{RT}{C_e} \ln \left( 1 + \frac{1}{C_e} \right) \right)^2 \right], \quad (11)
\]

where \( q_e \) (mg/g) is the amount of adsorption at the equilibrium, \( C_e \) (mg/L) is the equilibrium concentration of adsorbate, \( q_m \) is the monolayer adsorption capacity, \( K_{DR} \) is the D-R constant which gives the adsorption energy (\( E \)), \( T \) (K) is the temperature, and \( R \) is the universal gas constant. The adsorption energy can be computed using the following relationship:

\[
E = \frac{1}{\sqrt{2B}} \quad (12)
\]

The adsorption energy (\( E \)) value gives information about adsorption mechanism and more specifically its physical or chemical nature. When \( E \) is lower than 8 kJ/mol, the type of adsorption can be explained by physisorption and it can be controlled by ion-exchange or chemical adsorption when \( E \) is higher than 8 kJ/mol [48].

Figure 8 shows the fitting curve of Dubinin–Radushkevich isotherm and the obtained parameters are listed in Table 4. The calculated adsorption energy (\( E = 0.57 \) kJ/mol) reveals that the type of adsorption of methyl orange onto activated carbon can be explained by physisorption, indicating that the adsorption is illustrated by the formation of weak physical attraction forces, such as hydrogen-bonding and van der Waals forces, between adsorbate molecules and solid surface, and thus adsorption is reversible. This result indicates that the adsorption of methyl orange onto the surface of the prepared activated carbon is a multilayer adsorption which confirms that this process follows the Freundlich isotherm.

The results of the previous [33] and present study showed that the activated carbon prepared from prickly pear seed cake by phosphoric acid activation is effective for removing cationic and anionic dyes such as methylene blue and methyl orange from aqueous solution. This can be explained by the presence of a variety of functional groups on the adsorbent surface, which have enhanced the adsorption capacity [33]. The activated carbon simultaneously presents acidic and basic sites able to fix cationic and anionic dyes by electrostatic interactions. The adsorption mechanism can also be explained by the interactions between delocalized \( \pi \)-electrons of the activated carbon surface and the free electrons of the dye molecules present in the aromatic rings and multiple bonds [49, 50]. The adsorption capacities of MO onto various materials are given in Table 5.
in order to evaluate the performance of the activated carbon prepared from prickly pear seed cake.

4. Conclusion

In this study, the use of the activated carbon prepared from prickly pear seed cake by thermo chemical process using phosphoric acid for the removal of methyl orange from aqueous solution has been studied. The kinetic of adsorbate-adsorbent interactions can be represented by the pseudo-second-order model. The equilibrium adsorption data are best fitted by the Freundlich model as compared to Langmuir and Temkin models. The adsorption capacity for methyl orange was found to be 336.12 mg/g at temperature 20°C and pH ~ 7 indicating that the activated carbon may be an efficient adsorbent with great adsorptive capacity. Dubinin–Radushkevich isotherm reveals that the adsorption of methyl orange onto the activated carbon was a physisorption process in nature. The results demonstrated that the prickly pear seed cake is a suitable precursor for the preparation of an adequate activated carbon for dyes removal from industrial effluents.

Data Availability

All the data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

The authors are grateful to the Center of Analyses and Charactization (CAC) of University Caddy Ayyad, Morocco. Also, the authors also extend their appreciation to professors of REMATOP, LCOA, and REMINEX Managem Laboratories in Marrakech, Morocco.

References


