Sorption of caffeine onto low-cost sorbent: Application of two and three-parameter isotherm models

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Abstract

The retention capacity of caffeine onto the Zizyphus Mauritiana seeds as adsorbent was investigated. The experimental data were fitted to the Langmuir, Freundlich, Temkin, Sips, Redlich – Peterson and Toth isotherms. The correlation coefficient R^2 between the calculated and the experimental data by the nonlinear regressive analysis was used. For two-parameter isotherms, the Langmuir model showed higher correlation coefficient R^2 compared to Freundlich and Temkin isotherms for the sorption of caffeine onto Zizyphus Mauritiana seeds sorbent. From isotherms’ parameters, the Sips model was found to be the best representative for caffeine adsorption on the studied material. The Zizyphus Mauritiana seeds can be used as low-cost and environmentally friendly sorbent.

Keywords: caffeine, Zizyphus mauritiana seeds, low cost sorbent, isotherms.

1. Introduction

Caffeine is widely used as an adjuvant in analgesic combinations of drugs [1]. Caffeine metabolism in the human body is high and fast, where only a small quantity is excreted. Even so, this component appears in many studies about surface water and wastewater [2; 3].

Some physical, chemical and biological methods have been applied for the elimination of caffeine. These include the coagulation-flocculation [4], the oxidation and ozonation [5], membrane
filtration [6], photocatalytic degradation [7], electrochemical oxidation [8], methanogenesis degradation [9] and microbiological degradation [10].

The adsorption onto activated carbon has attracted many researchers, but its high cost inhibits its application on a large scale [11-12]. The search for alternative and efficient adsorbents at low cost, preferably from the local industrial or agricultural waste has been studied by several researchers [13-15]. The need to design low-cost sorbents for the detoxification of industrial effluents and municipal wastewater has been a growing concern for most environmental researchers. So modeling of experimental data from adsorption processes is an essential means of predicting the mechanisms of various adsorption systems.

In this research, the cheapest and unconventional Zizyphus Mauritiana seeds powder as a low-cost sorbent, without giving it any pre-treatment, have been used to remove caffeine from aqueous solution. The retention capacity of caffeine onto the Zizyphus Mauritiana seeds sorbent is investigated. In this study, we analyzed the non-linear two-parameter equation of Langmuir, Freundlich and Temkin and non-linear three-parameter equation of Sips, Redlich–Peterson and Toth isotherm models by a non-linear regression method.

2. Experimental

2.1. Caffeine solutions

Caffeine, in analytical purity and used in the experiments directly without any further purification. The caffeine solutions were prepared by diluting stocks solution to appropriate concentrations when needed. Their physicochemical properties are shown in Table 1 [11].

<table>
<thead>
<tr>
<th>Structure</th>
<th>Molecular formulae</th>
<th>Molecular weight (g mol⁻¹)</th>
<th>Water solubility (mg L⁻¹)</th>
<th>Log Kow</th>
<th>pKa</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Caffeine Structure" /></td>
<td>C₁₈H₁₀N₄O₂</td>
<td>194.2</td>
<td>21600</td>
<td>-0.07</td>
<td>14</td>
</tr>
</tbody>
</table>

2.2. Preparation and characterization of sorbent

The used Zizyphus Mauritiana seeds (Fig. 1) were collected from the south of Mauritania. Before use, the Zizyphus Mauritiana seeds were washed thoroughly with ultrapure water, dried in an oven at 110 °C for 24 h. Then ground, sieved to obtain particle sizes below 100 µm and stored in a desiccator.
The point of zero charge (pHpzc) of the sorbent was carried out [16]. According to [17], proximate analysis is the determination of moisture, volatile matter and ash content by prescribed methods. The determination of cellulose, lignin and hemicellulose in sorbents carried out by the procedure indicated by [18]. Different samples of sorbent were analyzed by the FTIR spectroscopy to determine the surface functional groups. The wavenumber scanning is in the range of 650–4,000 cm$^{-1}$.

2.3. Adsorption study

The sorption isotherms at ambient temperature are obtained by mixing (70 rpm), for 6 hours, 0.5 g of Zizyphus Mauritania seeds sorbent with 50 mL of caffeine solutions with different concentrations varying from 10 to 100 mg L$^{-1}$. At the end of each experiment, the agitated solution mixture was microfiltered using microfilter, and the residual concentration of caffeine was determined by High-Performance Liquid Chromatography (HPLC). Ultrapure water and methanol (70:30 V/V) were used as a mobile phase at a flow rate of 1 mL min$^{-1}$ at a selected wavelength of 254 nm. Ambient temperature (25 °C), pH (7.2) and all experimental parameters are constant throughout the various tests. The caffeine uptake amount $q_e$ (mg of caffeine per g of dried sorbent) was calculated using the equation (1):

$$ q_e = \frac{(C_i - C_e)V}{m} \quad (1) $$

Where $C_i$ is the initial liquid-phase concentrations of caffeine (mg L$^{-1}$), $C_e$ is the liquid-phase concentration of caffeine (mg L$^{-1}$), $V$ is the solution volume (L) and $m$ is the mass of adsorbent used (g). All batch experiments were conducted in triplicate and the mean values are reported.

The isotherm of adsorption is employed to establish the maximum capacity of adsorption of caffeine onto Zizyphus Mauritiana seeds sorbent, which is expressed in terms of quantity of caffeine adsorbed per unit of mass of used sorbent.

Several isotherm equations can explain solid-liquid adsorption systems, such as Langmuir, Freundlich, Temkin, Sips, Redlich-Peterson and Toth. Using the adsorption isotherms the required amount of an adsorbent for the treatment of some wastewater can be calculated.

The Langmuir adsorption isotherm assumes that adsorption takes place at specific homogeneous surface sites within the adsorbent and has found successful application in many sorption processes of monolayer adsorption. The Freundlich isotherm is an empirical equation employed to describe heterogeneous systems [19]. Temkin is considered to have the effect of some indirect
adsorbate/adsorbate interaction on adsorption isotherms, and because of that interaction, the heat of adsorption of all the molecules in the layer would decrease linearly with coverage [20].

The Sips isotherm is a combination of the Langmuir and Freundlich isotherms, which represent systems for which one adsorbed molecule could occupy more than one adsorption site. The Redlich–Peterson isotherm model combines elements from both the Langmuir and Freundlich equation and the mechanism of adsorption is a hybrid one and does not follow ideal monolayer adsorption. It is used as a compromise to improve the fit by Langmuir or Freundlich. The Toth isotherm model combines the characteristics of both the Langmuir and Freundlich isotherm. It approaches the Freundlich model at high concentration and it is in agreement with the low concentration limit of the Langmuir equation [19]. All the used mathematical models for caffeine adsorption isotherm are summarized in Table 2.

**Table 2: Mathematical models for sorption isotherms**

<table>
<thead>
<tr>
<th>Isotherm</th>
<th>Equation</th>
<th>Parameter (dimension)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>( q_e = \frac{q_mKLC_e}{1 + KLC_e} )</td>
<td>( q_m ) (mg g(^{-1})) ( K_L ) (mg L(^{-1})) (^{-1})</td>
</tr>
<tr>
<td>Freundlich</td>
<td>( q_e = K_F C_e^{1/n} )</td>
<td>( K_F ) (mg/g) × (mg/L)(^{-n}) ( n )</td>
</tr>
<tr>
<td>Temkin</td>
<td>( q_e = B_1 LnK_TC_e )</td>
<td>( B_1 = RT/b ); ( b ) (J mol(^{-1})). ( K_T ) (dm(^3) mg(^{-1})) ( q_m ) (mg g(^{-1}))</td>
</tr>
<tr>
<td>Sips</td>
<td>( q_e = q_m \frac{K_SC_e^n}{(1 + K_SC_e^n)} )</td>
<td>( K_S ) constant (L mg(^{-1}))(^{m}) ( n )</td>
</tr>
<tr>
<td>Toth</td>
<td>( q_e = q_m \frac{C_e}{(1 + \alpha TC_e)^{1/n}} )</td>
<td>( q_m ) (mg g(^{-1})) ( \alpha_T ) ( n )</td>
</tr>
<tr>
<td>Redlich-Peterson</td>
<td>( q_e = \frac{K_{RP}C_e}{1 + \alpha_{RP}C_e^n} )</td>
<td>( K_{RP} ) (mg/g)×(mg/L)(^{r-1}) ( \alpha_{RP} ) ( n )</td>
</tr>
</tbody>
</table>

To optimize the design of an adsorption system for the removal of caffeine, it is crucial to establish the most appropriate correlation for the equilibrium data. The relative parameters of each equation are obtained using the coefficient of determination \( R^2 \) between the calculated and the experimental data by nonlinear regressive analysis using the solver Excel. The coefficient of determination \( R^2 \) value is determined by the following equation (2):

\[
R^2 = 100 \left( 1 - \frac{\|q_{exp} - q_{mod}\|^2}{\|q_{exp} - q_{avr}\|^2} \right) \quad (2)
\]
Where $q_{\text{exp}}$ (mg g$^{-1}$) is equilibrium capacity from the experimental data, $q_{\text{avr}}$ is equilibrium average capacity from the experimental data and $q_{\text{mod}}$ is equilibrium from the model. So that $R^2 \leq 100$ – the closer the value is to 100, the more perfect is the fit.

3. Results and discussion

3.1. Characterization of sorbent

The results of physicochemical characteristics of the Zizyphus Mauritiana seeds sorbent as obtained in this work are shown in Table 3.

Table 3: Characterization of Zizyphus Mauritiana seeds sorbent

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH$_{\text{pzc}}$</td>
<td>6.9</td>
</tr>
<tr>
<td>Moisture (%)</td>
<td>4.2</td>
</tr>
<tr>
<td>Ash (%)</td>
<td>7.5</td>
</tr>
<tr>
<td>Volatile matter (%)</td>
<td>76.20</td>
</tr>
<tr>
<td>Cellulose (%)</td>
<td>11.5</td>
</tr>
<tr>
<td>Hemicellulose (%)</td>
<td>4.6</td>
</tr>
<tr>
<td>Lignin (%)</td>
<td>7.5</td>
</tr>
</tbody>
</table>

The pH$_{\text{pzc}}$ of the Zizyphus Mauritiana seeds sorbent was found to be 6.9. From the proximate analysis, it was observed that moisture, ash and volatile matter was slightly high, which may be due to its plant origin [21]. From the chemical composition, the cellulose, hemicellulose and lignin values of the Ziziphus Mauritiana seeds are higher 11.5 %, 4.6 % and 7.5 %, respectively.

The FTIR spectroscopy analyses of the Ziziphus Mauritiana seeds are given in Fig. 2. The central peak at 3281.48 and 3005.99 cm$^{-1}$ in the spectra of Ziziphus Mauritiana seeds was due to the presence of bounded hydroxyl (–OH) or amine (–NH) groups. The peak at 2922.45 cm$^{-1}$ is attributed to the symmetric and asymmetric C–H stretching vibration of aliphatic acids. The peak observed at 1741 cm$^{-1}$ is the stretching vibration of bond due to carboxyl groups (–COOH, –COOCH$_3$). The bands 1622.41 cm$^{-1}$ indicate functional group region of C=O, C–O, and O–H groups that exist as functional groups of Ziziphus Mauritiana seeds. The peak lying in the area of 1032.21 cm$^{-1}$ shows the presence of Si-O-Si linkages and which is associated with C-O is mainly associated with the lignin present in the Ziziphus Mauritiana seeds.
This influential band, only present in Ziziphus Mauritiana seeds, could be attributed to Si-O stretching vibration of mineral matter contained in the Ziziphus Mauritiana seeds (silicates). This result is in agreement with the high ash content found in Ziziphus Mauritiana seeds (Table 3).

**Fig. 2:** FTIR Spectrum of Ziziphus Mauritania seeds

Hydroxyl and carbonyl groups content in Ziziphus Mauritiana seeds can act as a proton donor, and consequently, coordination is possible with the positively charged caffeine.

### 3.2. Adsorption equilibrium isotherms determination

Equilibrium times between 2 and 4 h are reported for caffeine adsorption onto activated carbon [22-24]. Even so, [24] highlight most of the adsorption process occurs in the first 5 min. Equilibrium time of 60 min is reported for caffeine adsorption onto Grape stalk, grape stalk modified by phosphoric acid and grape stalk activated carbon [14]. In our study, residence time selected was 6 h for Ziziphus Mauritiana seeds sorbent to optimize experiments duration without significant losses in adsorption capacities.

The resulting curves and two-isotherm parameters are compared to the experimental data at Ziziphus Mauritiana seeds sorbent for caffeine removal in Fig. 3 and Table 4.

**Fig. 3:** Two-parameters isotherms for the sorption of caffeine onto Ziziphus Mauritana seeds
Table 4: Isotherm parameters for caffeine onto zizyphus mauritiana seeds sorbent (two-parameter isotherms)

<table>
<thead>
<tr>
<th></th>
<th>Langmuir</th>
<th>Freundlich</th>
<th>Temkin</th>
</tr>
</thead>
<tbody>
<tr>
<td>$q_m$</td>
<td>2.38</td>
<td>1/n=0.81</td>
<td>$B_1=0.29$</td>
</tr>
<tr>
<td>$K_L$</td>
<td>0.005</td>
<td>$K_F=0.020$</td>
<td>$K_T=0.13$</td>
</tr>
<tr>
<td>$R^2$ (%)</td>
<td>99.43</td>
<td>99.01</td>
<td>96.73</td>
</tr>
</tbody>
</table>

The results show that the Langmuir model fitted very well to the experimental data, showing the highest $R^2$ value compared to Freundlich and Temkin isotherms. The Langmuir model estimated that the monolayer adsorption capacity for caffeine-Zizyphus Mauritiana seeds system, herein investigated was of 2.38 mg g$^{-1}$. The values of $K_L$ and $1/n$ are in between zero and one. This confirms that the adsorption of caffeine onto Zizyphus Mauritiana seeds sorbent is favorable.

The abilities of the three-parameter equations, Sips, Redlich–Peterson and Toth, to model the equilibrium adsorption data were examined. According to Table 5 and Fig. 4, the highest coefficient of determination $R^2$ for Sips isotherm suggests that it is the best curve model of experimental data for the sorption of caffeine onto Zizyphus Mauritiana seeds sorbent.

Table 5: Isotherm parameters for caffeine onto Zizyphus Mauritiana seeds sorbent (three-parameter isotherms)

<table>
<thead>
<tr>
<th></th>
<th>Sips</th>
<th>Redlich-Peterson</th>
<th>Toth</th>
</tr>
</thead>
<tbody>
<tr>
<td>$q_m$</td>
<td>0.70</td>
<td>$K_{RP}=0.0126$</td>
<td>$q_{in}=1.22$</td>
</tr>
<tr>
<td>$K_S$</td>
<td>0.031</td>
<td>$a_{RP}=0.0062$</td>
<td>$a_t=0.2$</td>
</tr>
<tr>
<td>$n$</td>
<td>1.41</td>
<td>$n=0.97$</td>
<td>$n=0.044$</td>
</tr>
<tr>
<td>$R^2$ (%)</td>
<td>99.61</td>
<td>99.41</td>
<td>99.04</td>
</tr>
</tbody>
</table>

Fig. 4: Three-parameters isotherms for the sorption of caffeine onto Zizyphus Mauritiana seeds
The results obtained using the three-parameter equations show that the best-fitted adsorption isotherm models were determined to be in the order: Sips > Redlich–Peterson > Toth.

The Sips isotherm suggests that the sorption capacity of Ziziphus Mauritian seeds to uptake caffeine to be 0.70 mg g\(^{-1}\). The maximum adsorption capacity predicted by the Sips isotherm was lower than Langmuir isotherm. The values of Sips model exponent \(n\) (1.41) (table 5) and the values of Redlich–Peterson model exponent \(n\) (0.97) (table 5), indicated that the sorption data were more of Langmuir form rather than that of Freundlich isotherm. It can be concluded that the surface of Ziziphus Mauritian seeds is homogenous for caffeine adsorption.

Best adsorption capacity obtained for Ziziphus Mauritian seeds corresponding to 2.38 mg g\(^{-1}\). This result is inferior to that reported by [25] and [12] respectively, for caffeine removal onto commercial activated carbon and activated carbon fibres from pineapple plant leave.

Likewise, this result is very low compared to the adsorption capacity reached by [26] who reported a capacity removal of 214 and 145 mg g\(^{-1}\) of commercial powdered activated carbon (PAC) and commercial Granular Activated Carbon (GAC), respectively. These comparisons show that for to improve the retention capacity of caffeine, the setting up of activation processes of the Ziziphus Mauritian seeds is necessary.

On the other hand, the value of capacity of caffeine adsorption onto Ziziphus Mauritian seeds is inferior to that reported by [12; 14; 23; 27], where caffeine was removed more efficiently through adsorption at acidic medium. However, the neutral medium in municipal and industrial effluents has been reported by many researchers [28-31].

Also, compounds with low Log \(K_{ow}\) (less than 2.5), have a negligible adsorption rate in solid supports and, therefore, they remain in the aquatic environment [32]. Caffeine is characterized by its high hydrophilicity (log \(K_{ow} = -0.07\)) (table 1) which makes its retention difficult from the Waste Water Treatment Plant (WWTP).

4. Conclusion
In this study, equilibrium isotherm data obtained during sorption of caffeine onto Ziziphus Mauritiana seeds were fitted using different two-parameter and three-parameter models. From the results obtained, the following comments can be made:

-Among two-parameter models, the Langmuir model better described the isotherm data for Ziziphus Mauritiana seeds sorbent.

-In the case of three-parameter models, the Sips model was found to provide the closest fit to the equilibrium experimental data for all the Ziziphus Mauritiana seeds material.

The present study showed that the powdered Ziziphus Mauritiana seed is a promising and alternative sorbent for the removal of caffeine from aqueous solution.
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