Kinetic and calorimetric study of the adsorption of dyes on mesoporous activated carbon prepared from coconut coir dust

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Abstract

Mesoporous activated carbon has been prepared from coconut coir dust as support for adsorption of some model dye molecules from aqueous solutions. The methylene blue (MB) and remazol yellow (RY) molecules were chosen for study of the adsorption capacity of cationic and anionic dyes onto prepared activated carbon. The adsorption kinetics was studied with the Lagergren first- and pseudo-second-order kinetic models as well as the intraparticle diffusion model. The results for both dyes suggested a multimechanism sorption process. The adsorption mechanisms in the systems dyes/AC follow pseudo-second-order kinetics with a significant contribution of intraparticle diffusion. The samples simultaneously present acidic and basic sites able to act as anchoring sites for basic and acidic dyes, respectively. Calorimetric studies reveal that dyes/AC interaction forces are correlated with the pH of the solution, which can be related to the charge distribution on the AC surface. These AC samples also exhibited very short equilibrium times for the adsorption of both dyes, which is an economically favorable requisite for the activated carbon described in this work, in addition to the local abundance of the raw material.
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1. Introduction

Many economic activities generate a large volume of residues, such as those from agriculture, and in this context coconut shell is a very common residue in tropical countries. When coconut shell is processed, industrially valuable long fibers are removed, leaving a considerable fraction of dust composed of short- to medium-length fibers, known as coir dust [1]. Although the estimated costs of these materials are U.S. $0.80/10 kg, the coir remains available as a waste product for which no important industrial uses have been developed and is normally disposed of or incinerated. To overcome this problem, one option is to develop a chemical industry based on the use of this kind of abundant raw material [2]. Biomass is widely used as an alternative energy source [3–6], but its use as a precursor of several different products has also been described elsewhere [7].

An alternative route for the exploitation of agricultural wastes relies on preparation of activated carbon (AC) as described in previous papers [8–10]. Activated carbon is the most commonly used support in processes of water separation and purification, owing mainly to its highly porous structure and high surface area [11]. These physicochemical properties of activated carbons are essentially dependent on the preparation conditions, which can be based on physical or chemical processes, both occurring at high temperatures [12,13]. The activation process promotes conversion of already existing micro- to mesopores as well as formation of new micropores [13]. This enlargement of pore diameters upon activation makes activated carbons effective for adsorption of dyes from aqueous solu-
tion, as described in several papers [14–16]. Most commercially available activated carbons are predominantly microporous, being especially suitable for the adsorption of small species on the pore surface. As the fraction of mesopores can be increased by activation treatments, the obtained activated carbons are expected to be very efficient as adsorbents of large molecules. The adsorption capacity of activated carbons is generally evaluated under equilibrium conditions. On the other hand, the adsorption mechanisms are best understood through kinetic models, which describe process dynamics. For instance, some very common models are the Lagergren pseudo-second-order kinetic model [17] and the intraparticle diffusion equations [18], which are used in the present study.

This work describes the evaluation of a mesoporous activated carbon prepared from coconut coir dust as support for adsorption of some model dye molecules from aqueous solutions. The model dye molecules chosen for studying the adsorption capacity of the prepared activated carbon were methylene blue (MB) and remazol yellow (RY). Fig. 1 shows the molecular structures and sizes calculated with the molecular modeling system CAChe.

2. Materials and methods

All chemicals were reagent grade and used without further purification. ZnCl₂ was purchased from Vetec (Brazil); the coconut coir dust employed as AC precursor was kindly provided by DILIMP—a local fiber processing industry. The dyes, commercially available as Reactive Yellow GR (reactive yellow 15) and Methylene Blue (C.I. 52015), were free gifts from the Santista Textiles Industries (Sergipe/Brazil), provided by the Dystar Dyes Company and used without purification. For adsorption studies 10⁻⁴ mol L⁻¹ stock solutions of MB and RY were prepared prior to dilution to the required concentrations. Dye solutions were prepared and the initial pH was adjusted with biphtalate/NaOH to the following pH values: 4.0, 6.0, 7.0, and 8.0. The pH variation was followed during all adsorption experiments.

2.1. Preparation of the activated carbons

Prior to use, the coconut coir dust was dried in an oven for 12 h at 100°C and sifted through a 100-mesh sieve.

Zinc chloride (ZnCl₂), used as activating agent, was mixed with coir dust prior to the activation step in the solid state in the mass proportion 3 ZnCl₂:1 coir dust. The activation process was carried out in the following steps: coir dust impregnated with ZnCl₂ was heated in a furnace under N₂ at 10°C/min up to 800°C. In the sequence the atmosphere was changed to CO₂ and the conditions were kept for 2 h following by cooling to room temperature under N₂ [19]. After cooling, the samples were stirred for 3 h in 0.1 mol L⁻¹ HCl, filtered, washed with distilled water until a negative Cl⁻ test result was obtained, and dried for 12 h at 100°C. Characterization was accomplished by the techniques described below.
2.2. Nitrogen isotherms

Textural characterization of AC samples was carried out by N₂ adsorption–desorption isotherm measurements at 77 K using a Quantachrome Instruments Autosorb-1C. Prior to the measurements, the samples were outgassed under vacuum at 473 K.

2.3. Adsorption studies

In a typical adsorption experiment, 5 mg of AC was added to 20 ml of 10⁻⁵ mol L⁻¹ methylene blue solution of a given pH value in 100 ml polyethylene centrifuge tubes. The samples were subjected to rotation at 200 rpm at room temperature (25 ± 3°C). Increasing dye–support contact times ranging from 0 to 120 min were studied. The residual adsorbate solution concentration was determined by the absorbance at 664 nm for methylene blue and at 420 nm for remazol yellow using UV/vis calibration curves. UV/vis measurements were performed with a FEMTO 800 XI spectrophotometer, using buffer solutions containing 5 mg of activated carbon as blank, in each pH value.

2.4. Calorimetric determinations

Calorimetric measurements were performed at 298.15 K in a SETARAM C80 mixing calorimeter. The calorimeter’s performance and details of operation have been described previously [20]. Samples of approximately 50 mg of AC were put into the lower part of the mixing cell, closed by a thin circular membrane of PTFE. Into the upper part of the mixing cell, a volume of 3.0 ml of a specific dye solution was added. After complete stabilization of the baseline, a movable rod enables the dye solution to be pushed into the container with the AC. Each individual experiment yields a thermal effect, \( Q_r \), which was corrected by subtracting the corresponding wetting effect, \( Q_w \), of the activated carbon in the pure solvent, i.e., the buffer solution. The thermal effect of membrane breaking for the empty cell was found to be negligible compared to the \( Q_r \) and \( Q_w \) values. All obtained results are averages of two parallel experiments.

3. Results and discussion

3.1. AC textural characterization

Fig. 2 shows a N₂ adsorption isotherm onto activated carbon prepared from coconut coir dust, where a progressive increment in adsorbed nitrogen is observed at all pressure ranges. The hysteresis loop at high \( P/P_0 \) values is associated with the filling of mesopores by capillary condensation, with the assumption that the pores have been filled with the condensed molecules. This suggests a type IV isotherm, typical of mesoporous solids [21].

The pore-size distribution curve of activated carbon, calculated by the BJH method [22], strongly supports the evidence for mesoporosity proposed on the basis of the shape of N₂ adsorption isotherms. A dramatic increase in surface area from 4 to 1884 m²/g is verified as compared to the raw material.

The pore diameter range of AC was found to lie between 20 and 40 Å (see Fig. 3). Those results suggest that the prepared AC sample can be practically effective for removing methylene blue (MB) and remazol yellow (RY) from water solution, because the molecular sizes are 13.82 and 15.66 Å, respectively, as calculated by the AM1 method [23]. These data are presented in Table 1.

Changes in the chemical nature of the lignocellulosic precursor are expected to occur upon carbonization and activation. These possible modifications were studied by infrared spectroscopy, as presented in Fig. 4.

Before the carbonization, the material has a typical lignocellulosic composition, presenting bands at 3413 cm⁻¹, assigned to \( \nu(O–H) \), at 2923 cm⁻¹, assigned to \( \nu(C–H) \) from methyl and methylene groups, at 1620 cm⁻¹, assigned to \( \nu(C=O) \) from carboxylate groups and at 1377 cm⁻¹, assigned to \( \delta(C–H) \) from methyl groups [12]. After carbonization and activation, which are followed by fixation of carbon and elimination of other elements in the form of water and other species, some changes can be observed, such as the presence of a very broad band centered at 3388 cm⁻¹ (\( \nu(C–H) \)) and at 2352 cm⁻¹ (\( \nu(C≡C) \)), along with the disappearance of the band at 1620 cm⁻¹ and the presence of a band at 1558 cm⁻¹ (\( \nu(C=C) \) from aromatics). Terminal aliphatic groups remain, such as CH₃, as evidenced
by the band at 1379 cm\(^{-1}\), and by continuous absorption in the region of 2900 cm\(^{-1}\) [12]. These changes evidence the formation of structures containing multiple carbon–carbon bonds such as aromatic rings and C≡C units, as well as the elimination of originally present oxygen and hydrogen atoms. It is worth mentioning that the material is noncrystalline, as evidenced by absence of diffraction peaks in the XRD measurements (not shown).

### 3.2. Effect of contact time

Fig. 5 shows the UV/vis absorption spectra before and after treatment with the AC for both dye solutions. The decrease in absorption intensity with increased contact time reveals the AC efficiency in removal of MB and RY from aqueous solutions and also suggests that a large adsorption extent takes place at short time intervals, close to 20 min for both dyes.

A series of experiments have been performed to evaluate the adsorption capacity \(q_t\) of the activated carbons as a function of contact time. The adsorption capacity was calculated from the difference between the initial and final MB concentration after a contact time of 120 min, as follows,

\[
q_t = (C_i - C_f)V/m, \tag{1}
\]

where \(q_t\) is the adsorption capacity (mass MB (mg)/mass AC (g)), \(C_i\) and \(C_f\) are initial and final concentrations, respectively, \(V\) is the volume (L) of the dye solution, and \(m\) is the AC mass (g). Each experimental result was obtained by averaging the data from two parallel experiments.

For this study the initial concentrations of dye solutions were \(1.0 \times 10^{-5}\) mol L\(^{-1}\) for MB and \(7.0 \times 10^{-5}\) mol L\(^{-1}\) for RY. The plot of adsorption capacity \(q_t\), obtained from Eq. (1), versus contact time \(t\) can be observed in Fig. 6. The time required for maximum adsorption of the dye is known as the equilibrium time and was found in this study to be close to 120 min for both dyes. This equilibrium time can be considered very short, which is an economically favorable condition for the activated carbon described here.

For both dyes, the plots show two distinct adsorption profiles, which suggest a multimechanism sorption process as it has been discussed in previous works [24–26]. The regime observed in the first region, between 0 and 20 min, can be related to an external diffusion process, in which the dye molecules migrate to reach the AC external surface (surface layer diffusion). Due to the absence of mechanical barriers in this step, the removal of dyes by adsorption on AC is a fast process. The adsorption profile observed in the second region of the curves starts from 20 min and can be related to an internal diffusion process in which the dye molecules penetrate into the porous AC structure (intraparticle diffusion). The equilibrium of the adsorption process is reached thus at contact times above 20 min. Also the smooth and continuous feature of the curves is a common behavior and it has been related in previous studies with monolayer coverage of dye on the surface the adsorbent [27].
To evaluate the mechanism of the adsorption process, a first-order and a pseudo-second-order kinetic model and a diffusion model were applied to the experimental data.

### 3.3. Intraparticle diffusion model

The possibility of intraparticle diffusion was examined using the intraparticle diffusion model [28], taking into account that during the course of adsorption the adsorbed amount is proportional to the square root of the contact time,

\[
q_t = K_d t^{1/2},
\]

where \( K_d \) is the intraparticle diffusion constant.

Equation (2) was applied to the adsorption data with contact times changing from 20 to 120 min, corresponding to the linear portion of the curves. The rate constant for intraparticle diffusion \( K_d \) was calculated from the slope of linear portion. The resulting plots of \( q_t \) versus \( t^{1/2} \) can be found in Fig. 7.

The curves presented \( R \)-values close to 0.99, indicating the significant contribution of the intraparticle diffusion process. The linear regression and \( K_d \) values are presented in Table 2.

### 3.4. First-order and pseudo-second-order models

For the determination of adsorption constants, kinetic data obtained from batch studies were evaluated using the Lagergren

![Fig. 6. Adsorption capacity curves of AC from aqueous dye solutions: (a) MB, initial concentration \(1.0 \times 10^{-5}\) mol L\(^{-1}\); (b) RY, initial concentration \(7.0 \times 10^{-5}\) mol L\(^{-1}\). Experiments were performed at 25 °C.](image)

![Fig. 7. \(q_t\) versus \(t^{1/2}\) plots from intraparticle diffusion model: (a) MB, initial concentration \(1.0 \times 10^{-5}\) mol L\(^{-1}\); (b) RY, initial concentration \(7.0 \times 10^{-5}\) mol L\(^{-1}\). Experiments were performed at 25 °C.](image)

**Table 2**

Kinetic values calculated agreement with intraparticle diffusion model for methylene blue and remazol yellow on AC

<table>
<thead>
<tr>
<th>pH</th>
<th>(K_d) (MB cationic)—(1.0 \times 10^{-5}) mol L(^{-1})</th>
<th>(R)</th>
<th>(K_d) (RY anionic)—(7.0 \times 10^{-5}) mol L(^{-1})</th>
<th>(R)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.0</td>
<td>(3.69 \times 10^{-2})</td>
<td>0.9879</td>
<td>(4.72 \times 10^{-1})</td>
<td>0.9852</td>
</tr>
<tr>
<td>7.0</td>
<td>(2.91 \times 10^{-2})</td>
<td>0.9396</td>
<td>(4.28 \times 10^{-1})</td>
<td>0.9932</td>
</tr>
<tr>
<td>6.0</td>
<td>(3.52 \times 10^{-2})</td>
<td>0.9612</td>
<td>(6.28 \times 10^{-1})</td>
<td>0.9924</td>
</tr>
<tr>
<td>4.0</td>
<td>(3.42 \times 10^{-2})</td>
<td>0.9604</td>
<td>(8.16 \times 10^{-1})</td>
<td>0.9912</td>
</tr>
</tbody>
</table>
first- and pseudo-second-order equations as modified by Ho, which has been widely used for adsorption evaluation of dyes from aqueous solutions [29,30]. The first-order and pseudo-second-order equation are expressed respectively as

\[ q_t = q_e (1 - e^{-k_{ads}t}), \]
\[ t/q_t = (1/K_{ads}q_e^2) + (1/q_e)t, \]

where \( q_e \) and \( q_t \) are the amount of dye adsorbed (in mg dye per g activated carbon) at equilibrium, \( t \) is the contact time, and \( K_{ads} \) are the first- and pseudo-second-order kinetic constant.

\( K_{ads} \) and \( q_e \) values for application of first- and pseudo-second-order kinetic models, presented in Tables 3 and 4, were determined respectively by the linear regression \( qt vs t \) and \( t/qt vs t \). Figs. 8 and 9 illustrate the resulting first- and pseudo-second-order kinetic plots for MB and RY, respectively. The values of correlation coefficients for the application of the pseudo-second-order model indicate that this model fits the experimental data more accurately than the first-order model. The influence of the pH on the values of rate constants is not clear from these data but can be verified in the calorimetric data, presented in Section 3.5.

The AC samples were found to be efficient in the removal of both cationic and anionic dyes. This can be explained by the presence of different groups containing oxygen on the surface of the activated carbon. As a consequence, the AC samples present simultaneously acidic and basic sites able to act as anchoring sites for basic and acidic dyes, respectively, as a result of electrostatic interactions [30].

Another possible and probably relevant adsorption mechanism that may occur in the case of solutes containing conjugated systems—such as the dye molecules studied here—corresponds to \( \pi-\pi \) dispersive interactions. This mode of interaction can take place between the aromatic rings and \( \text{–N}=\text{C–C–C} \) for MB and also aromatic rings, \( \text{–N}=\text{N–} \) and \( \text{–N}=\text{C–C–C} \) for RY. This situation has been reported in previous studies [31,32].

The adsorption capacity of methylene blue for the adsorbent studied in this work, along with data of other adsorbents, is presented in Table 5 [33–36]. It can be observed that the adsorption capacity found here is comparable to those described for activated carbons prepared from different raw materials. The adsorption capacity of a certain carbon is known to be a function not only of the porous structure but also of the chemical nature of the surface and of the pH of the aqueous solution.
The thermal wetting effect values were found to be higher than can be observed for the MB/AC interaction at pH 4.0 and 6.0, as using the software SETSOFT Version 1.54f (SETARAM). As curves of the detectable calorimeter signals (power versus time) the other hand, opposite behavior is observed for the processes which shows the adsorption of the dyes on AC can be calculated from the ex-

\[ Q_{ads} = \frac{q_e}{K_{ads}} \]

where both \( q_e \) and \( K_{ads} \) were integrated, joining two extreme points selected on the curves of the detectable calorimeter signals (power versus time) using the software SETSOFT Version 1.54f (SETARAM). As can be observed for the MB/AC interaction at pH 4.0 and 6.0, as the thermal wetting effect values were found to be higher than the \( Q_{ads} \) values the process can be considered endothermic. On the other hand, opposite behavior is observed for the processes RY/AC. This feature can be most clearly observed in Fig. 10 which shows the \( Q_r \), \( Q_w \), and \( Q_{int} \) values as functions of pH.

The influence of pH on the adsorption processes is clear. From Fig. 10b it is observed that a conversion of endothermic to exothermic interactions takes place for the adsorption of MB onto the AC samples. The positive \( Q_{int} \) values at pH 4.0 and 6.0 can be understood by taking into account the energy necessary to overcome electrostatic repulsion between the cationic MB molecules and positive sites resulting from protonation of surfaces basic groups on AC surface. On the other hand, surface negative charges are developed at increasing pH from dissociation of the surfaces acidic groups. This enhances the electrostatic attraction between carbon surface and the cationic dye.

3.5. Calorimetric studies

The use of calorimetric data to characterize energetic aspects of dyes adsorption process on mesoporous carbons is becoming attractive, allowing a comparative analysis of structural and interaction properties of activated carbons. From calorimetric measurements the interaction heat (\( Q_{int} \)) originated from the adsorption of the dyes on AC can be calculated from the expression

\[ Q_{int} = Q_r - Q_w, \]  

(5)

where both \( Q_r \) and \( Q_w \) were normalized for 1 g of AC and are presented in Table 6. The areas of the thermal effects \( Q_r \) and \( Q_w \) were integrated, joining two extreme points selected on the curves of the detectable calorimeter signals (power versus time) using the software SETSOFT Version 1.54f (SETARAM). As can be observed for the MB/AC interaction at pH 4.0 and 6.0, as the thermal wetting effect values were found to be higher than the \( Q_r \) values the process can be considered endothermic. On the other hand, opposite behavior is observed for the processes RY/AC. This feature can be most clearly observed in Fig. 10 which shows the \( Q_r \), \( Q_w \), and \( Q_{int} \) values as functions of pH.

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<table>
<thead>
<tr>
<th>pH</th>
<th>MB (cationic)—1.0 × 10⁻⁵ molL⁻¹</th>
<th>RY (anionic)—7.0 × 10⁻⁵ molL⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.0</td>
<td>12.89 ± 0.22 2.90 × 10⁻³ 0.9645</td>
<td>138.94 ± 4.55 1.37 × 10⁻³ 0.9462</td>
</tr>
<tr>
<td>6.0</td>
<td>12.78 ± 0.19 2.51 × 10⁻³ 0.9809</td>
<td>132.07 ± 4.33 1.58 × 10⁻³ 0.9379</td>
</tr>
<tr>
<td>7.0</td>
<td>13.41 ± 0.21 2.87 × 10⁻³ 0.9713</td>
<td>143.48 ± 3.49 1.97 × 10⁻³ 0.9535</td>
</tr>
<tr>
<td>8.0</td>
<td>13.75 ± 0.42 2.41 × 10⁻³ 0.9213</td>
<td>158.03 ± 3.74 2.11 × 10⁻³ 0.9534</td>
</tr>
</tbody>
</table>

Table 4
Kinetic values calculated agreement with Lagergren pseudo-second-order model for methylene blue and remazol yellow on AC.

<table>
<thead>
<tr>
<th>pH</th>
<th>MB (cationic)—1.0 × 10⁻⁵ molL⁻¹</th>
<th>RY (anionic)—7.0 × 10⁻⁵ molL⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.0</td>
<td>13.75 ± 0.92 3.84 × 10⁻⁴ 0.9996</td>
<td>161.35 ± 7.14 1.07 × 10⁻⁵ 0.9984</td>
</tr>
<tr>
<td>6.0</td>
<td>13.95 ± 0.21 2.50 × 10⁻⁴ 0.9994</td>
<td>153.20 ± 3.79 1.22 × 10⁻⁵ 0.9978</td>
</tr>
<tr>
<td>7.0</td>
<td>14.55 ± 0.28 3.03 × 10⁻⁴ 0.9998</td>
<td>160.30 ± 3.96 1.67 × 10⁻⁵ 0.9964</td>
</tr>
<tr>
<td>8.0</td>
<td>15.25 ± 0.07 2.00 × 10⁻⁴ 0.9992</td>
<td>176.10 ± 3.54 1.62 × 10⁻⁵ 0.9996</td>
</tr>
</tbody>
</table>

Table 5
Comparison of adsorption capacity of various adsorbents for MB.
Table 6
Results of thermal effects of reaction, $Q_r$, of wetting, $Q_w$, and of interaction, $Q_{int}$, corresponding to the interactions process dyes/AC, at 298.15 K

<table>
<thead>
<tr>
<th>pH</th>
<th>MB/AC $Q_r$ (J g$^{-1}$)</th>
<th>RY/AC $Q_r$ (J g$^{-1}$)</th>
<th>Buffer/AC $Q_r$ (J g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.0</td>
<td>71.47 ± 0.14</td>
<td>116.05 ± 0.72</td>
<td>97.64 ± 0.19</td>
</tr>
<tr>
<td>6.0</td>
<td>52.57 ± 0.12</td>
<td>65.62 ± 0.52</td>
<td>74.84 ± 0.27</td>
</tr>
<tr>
<td>7.0</td>
<td>68.84 ± 0.10</td>
<td>54.87 ± 0.10</td>
<td>66.57 ± 0.17</td>
</tr>
<tr>
<td>8.0</td>
<td>93.89 ± 0.21</td>
<td>51.67 ± 0.72</td>
<td>65.67 ± 0.49</td>
</tr>
</tbody>
</table>

molecules, resulting in negative interaction energy values. For the anionic RY species the observed opposite behavior is obviously explained on the basis of the same statements.

It was discussed in previous works that in general the internal diffusion process has an endothermic contribution to the energetics of the adsorption of organic solutes on mesoporous carbons [24]. In addition to this fact, it is generally expected that the adsorption processes have an exothermic nature due to overall decrease in the system entropy. However, an endothermic effect can be indicative of an entropy increase if adsorption of each dye molecule causes the displacement of more than one adsorbed water molecule. These are general statements discussed by Khraisheh and co-workers and in the present work can be considered plausible, as indicated by the calorimetric results.

4. Conclusions

The mesoporous AC employed in the adsorption processes is efficient in removing anionic and cationic model dye molecules from aqueous solutions. The adsorption capacity of AC is barely influenced by the pH of the solution for both dyes. The results demonstrate that adsorption mechanisms in the system dyes/AC follow a pseudo-second-order kinetics with a significant contribution of intraparticle diffusion. Calorimetric studies reveal that dye/AC interaction forces are correlated with pH of the solution probably due to the particle charges. The increase of pH promotes an endothermic process for RY and exothermic for MB. The AC samples also exhibited a very short equilibrium time for the adsorption of both dyes.

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