Adsorption of Paracetamol Using Activated Carbon of Dende and Babassu Coconut Mesocarp


Abstract—Removal of the widespread used drug paracetamol from water was investigated using activated carbon originated from dende coconut mesocarp and babassu coconut mesocarp. Kinetic and equilibrium data were obtained at different values of pH. Both activated carbons showed high efficiency when pH ≤ pH_{PZC} as the carbonil group of paracetamol molecule are adsorbed due to positively charged carbon surface. Microporosity also played an important role in such process. Pseudo-second order model was better adjusted to the kinetic results. Equilibrium data may be represented by Langmuir equation.

Keywords—Adsorption, activated carbon, babassu, dende.

I. INTRODUCTION

THE production of pharmaceuticals has increased rapidly during the last decades as they are used for the health of humans and animals. After their use, large amount of pharmaceuticals are discharged into the water environment, and they have been detected in wastewater and surface water at ng/L to µg/L levels [1], [2]. It has been demonstrated that conventional wastewater treatments are not effective to eliminate or at least degrade most of these compounds. Therefore, residual quantities remain in treated water and have been accumulating in drinking water [3], [4]. As water is an essential resource for life in all ecosystems, a great effort has been made in the past decades to improve the water treatment. One of the technologies is adsorption. Among the most promising biosorbent materials for aquatic environments the use of black tea residue [5], sawdust [6], sugar cane bagasse [7], cork powder, peach stones [8], eggshell waste [9], olive stones [10], aquatic plants [11], mango peel [12], coconut mesocarp [13], banana peel [14], bamboo stem and coconut shells [15], stand out. Nevertheless, activated carbons are always one of the best choices, as they involve a well-established and effective technology widely used. Their adsorption properties are due the large accessible surface area and pore volume as well as possibility of regeneration [8], [16], [17]. Activated carbons may be obtained from a large number of residues of vegetal species. The ones related to native species aggregate advantages related to feasibility and low costs as well. Particularly, babassu and dende are Brazilian palm trees that produce vegetal oil. After extraction, the shells are burned to obtain the activated carbon. Their efficiency in the adsorption of medicines presented in wastewater has been already reported [18]. Then, the objective of this paper was to study the activated carbon of dende coconut mesocarp and babassu coconut mesocarp in the adsorption of paracetamol. Kinetic and equilibrium data were obtained at different values of pH.

II. MATERIALS AND METHODS

A. Materials

The activated carbon of dende coconut mesocarp (DD) was provided by the Bahiacarbon Agro Ind. (Bahia, Brazil) whereas babassu coconut mesocarp (BB) was donated by Tobasa Agro Ind. (Tocantins, Brazil). The samples were previously washed, dried for 24 h at 60°C and sieved. Particles with average diameter of 0.180 mm (70-100 mesh) were selected for the adsorption experiments.

Nanotexture of the carbon materials was characterized by N₂ adsorption at 196 and 0°C, respectively, in conventional volumetric apparatus (ASAP 2000, from Micromeritics). Before the experiments, the samples were outgassed under vacuum at 300°C. The isotherms were used to calculate the specific surface area (S_{BET}), total pore volume, \( V_{\text{TOTAL}} \), and pore size distribution. The S_{BET} was assessed applying the BET equation (in the range 0.05 < p / p_0 < 0.15). The microporous volume \( (V_{\alpha_{\text{total}} - 6 \text{ Å} < \text{pore diameter} < 20 \text{ Å}} \) and ultramicroporous volume \( (V_{\alpha_{\text{Ultra}} - related to pores < 6 \text{ Å}} \) were calculated using the α method [19]. The total pore volume was determined by the quantity adsorbed at p / p_0 = 0.95. The \( V_{\text{Total}} \) (microporous total volume) and \( V_{\alpha_{\text{Ultra}}} \) (ultramicroporous volume) were calculated using the method of the demanding [19]. The volume of supermicropores \( (V_{\alpha_{\text{Super}}} \) was obtained by the difference: \( V_{\alpha_{\text{Total}}} - V_{\alpha_{\text{Ultra}}} \). The mesoporous volume \( (V_{\text{Mesol}} \) was calculated by \( V_{\text{Total}} - V_{\alpha_{\text{Total}}} \) difference.

The pH of the point of zero charge (\( \text{pH}_{PZC} \)) was also estimated in both adsorbents using the mass titration procedure [20].

Paracetamol (acetaminophen or N-acetil-p-aminophenol) molecule is shown in Fig. 1. Paracetamol powder was added
to 10% (v/v) of methanol (Anidrol) diluted in Milli-Q water in order to obtain 50 mg dm$^{-3}$. pH of paracetamol solutions were corrected to pH 2, pH pHPZC of DD and BB samples as well as pH 11 using NaOH or HCl 0.1 mol dm$^{-3}$ solutions.

\[ q_t = q_{0} \left( 1 - e^{-kt} \right) \]  
(3)

The pseudo-second order kinetic model equation is expressed as:

\[ \frac{dq_t}{dt} = k_{2} (q_{e} - q_{t})^{2} \]  
(4)

Integration (4) for the initial conditions $t = 0$ and $q_{t} = 0$ gives the pseudo-second order rate equation as:

\[ q_{t} = \frac{q_{e}^{2} k_{2} t}{1 + k_{2} q_{e} t} \]  
(5)

C. Equilibrium Data

Equilibrium adsorption studies were carried out adding different amount of adsorbent (0.07-60 mg) to 20 cm$^{3}$. After reaching equilibrium, the solution was filtered and concentration of paracetamol in the solid phase ($q_{e}$) was obtained through (1). In this case $t$ refers to the equilibrium time, which was obtained in the kinetic experiments.

In this study Langmuir and Freundlich isotherm models were fitted to the equilibrium data.

The Langmuir adsorption isotherm equation, expressed as follows requires for its applicability a mono-layered coverage on the surface of adsorbent [24]:

\[ q_{e} = \frac{q_{max} k_{L} C_{e}}{1 + k_{L} C_{e}} \]  
(6)

where $k_{L}$ is the Langmuir constant related to the adsorption energy (L mg$^{-1}$), $q_{max}$ is the maximum amount of paracetamol retained in the solid phase and $C_{e}$ (mg L$^{-1}$) stands for paracetamol concentration in the fluid phase that is in equilibrium with $q_{e}$.

The empirical Freundlich isotherm is expressed by [25]:

\[ q_{e} = k_{F} C_{e}^{1/n} \]  
(7)

where $k_{F}$ and $n$ are the Freundlich constants.

The Freundlich equation was successfully used to fit the experimental data for many fluid-solid systems, but one of the main drawbacks of this equation is that it doesn’t tend to a limiting value whereas the equilibrium concentration increases. Generally, Freundlich equation is used to model multilayer adsorption.

III. RESULTS AND DISCUSSION

A. Characterization of the Adsorbent

The nitrogen adsorption-desorption isotherms are presented in Fig. 2. DD and BB were typical microporous–mesoporous adsorbents (type I in the IUPAC classification) with a hysteresis loop (H4 types) in the desorption branch at relative pressures above 0.5. The adsorption-desorption hysteresis on activated carbon isotherm showed clearly that liquid nitrogen was condensed in slit-shaped mesopores [26].
Fig. 2. N₂ adsorption–desorption isotherms at 77 K of DD (●) adsorption and (○) desorption and BB; (▲) adsorption and (Δ) desorption

For low relative pressure a sharp knee is observed followed by an almost horizontal plateau over a wide range of high relative pressures. This shape is related to a predominant microporous structure.

Fig. 3 depicts the pore size distribution. In agreement with the N₂ isotherm shape, DD and BB had a huge contribution of micropores although some mesoporosity was also presented, mainly in the DD sample, where a pronounced pick close to 40 Å was observed. Actually, the average pore diameter was estimated as 34.5 Å for DD whereas BB had an average pore diameter of 11.5 Å.

As shown in Table I, DD had higher specific surface area (672 m² g⁻¹). However, micropores contributed to 78% of the total volume of pores, less than the 88% seen in the BB sample. Probably it was a consequence of the pick near 40 Å already discussed.

It was also noteworthy that, according to pH_PZC, BB had a more acidic behavior probably due to acid superficial groups. Nevertheless, DD had almost a neutral surface. Such differences may be significant when investigating the adsorption mechanism.

B. Preferred Conformation of Paracetamol

Paracetamol is a weak acid with pKa values between 9.0 and 9.50 [27]. At this pH half of molecules is in the neutral form whereas the other 50% is in the anionic form. Therefore, solutions with 2.0 < pH < 9.0 present neutral paracetamol molecules. In solutions with pH > 10 the anionic form predominates.

Fig. 4 shows the optimised structure and the electrostatic potential maps for both forms: neutral (a) obtained at pH 2 and anionic (b) at pH 11.

It can be seen that at pH 2 the paracetamol molecule is neutral with low electronic density. Actually, a significant electronic density can be attributed only to the carbonil group. At pH 11 the most important and clearly more pronounced region of high electronic density is located in the phenolic group, due to the acid dissociation.

C. Kinetic Studies of Paracetamol

Results with acid paracetamol solution with pH 2, pH_PZC and basic solution with pH 11 is seen in Fig. 5 for DD and BB samples.

According to the kinetic results it can be seen that the system reached equilibrium in 240 minutes. Moreover, a rapid initial adsorption occurred due to a large number of surface sites available for adsorption.

According to Fig. 5, it can be also observed that in both systems, the acid solution (pH 2) and solution in the pH_PZC promoted significant removal of paracetamol. Possibly the positively charged surface of the adsorbent may attract the highest electronic charges of the neutral paracetamol molecule located in the C=O group. Then, chemisorption may have some contribution. As already discussed, under these conditions paracetamol was predominantly in its molecular...
form (the anionic form accounts for less than 0.1 mol%) whereas the carbon surface sites are positively charged (pH_{PZC} > solution pH).

When adsorption occurs in the zero point charge, the carbon surface is neutral and the paracetamol charges may be weakly attracted to some superficial groups although physisorption seems to have a huge contribution due to the high microporosity of the activated carbons. On the other hand, in basic solutions, the paracetamol molecules have much higher density charge that was repelled by the negatively charges of the solid sample. In such case, physisorption may be more significant.

This phenomenon can be verified in Table II where the maximum amount of paracetamol experimentally retained in equilibrium is shown. At pH 2 the maximum removal in DD samples occurred. Nevertheless, paracetamol removal suffered a slightly decrease when DD was in contact with solution in the zero point charge of 6.5. In such case the carbonil groups may induce some chemisorption although physisorption should have the greatest contribution, mainly in the micropores, where the molecule may be better retained, as already discussed. In basic solutions where pH > pKa, the amount retained suffered a drastically decrease due to the anionic charges involved.

**Table II**

<table>
<thead>
<tr>
<th>Activated carbon</th>
<th>pH  2</th>
<th>pH PCZ</th>
<th>pH 11</th>
</tr>
</thead>
<tbody>
<tr>
<td>DD</td>
<td>65.57</td>
<td>64.85</td>
<td>44.12</td>
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<tr>
<td>BB</td>
<td>57.29</td>
<td>67.51</td>
<td>49.03</td>
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**Table III**

<table>
<thead>
<tr>
<th>Sample</th>
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<th>pH PCZ</th>
<th>pH 11</th>
</tr>
</thead>
<tbody>
<tr>
<td>DD</td>
<td>Pseudo-first order</td>
<td>59.11±1.892</td>
<td>58.31±1.756</td>
<td>43.07±0.797</td>
</tr>
<tr>
<td></td>
<td>k_1</td>
<td>0.092±0.016</td>
<td>0.08±0.013</td>
<td>0.055±0.005</td>
</tr>
<tr>
<td></td>
<td>R^2</td>
<td>0.911</td>
<td>0.928</td>
<td>0.979</td>
</tr>
<tr>
<td></td>
<td>Pseudo-second order</td>
<td>63.11±1.244</td>
<td>62.91±0.929</td>
<td>46.81±0.804</td>
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<tr>
<td></td>
<td>k_2</td>
<td>0.002±0</td>
<td>0.002±0</td>
<td>0.002±0</td>
</tr>
<tr>
<td></td>
<td>R^2</td>
<td>0.976</td>
<td>0.988</td>
<td>0.978</td>
</tr>
<tr>
<td>BB</td>
<td>Pseudo-first order</td>
<td>54.91±0.878</td>
<td>62.37±1.004</td>
<td>47.69±1.142</td>
</tr>
<tr>
<td></td>
<td>k_1</td>
<td>0.039±0.003</td>
<td>0.036±0.002</td>
<td>0.037±0.004</td>
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<tr>
<td></td>
<td>R^2</td>
<td>0.988</td>
<td>0.998</td>
<td>0.972</td>
</tr>
</tbody>
</table>

**Table IV**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Kinetic model</th>
<th>pH  2</th>
<th>pH PCZ</th>
<th>pH 11</th>
</tr>
</thead>
<tbody>
<tr>
<td>DD</td>
<td>Pseudo-first order</td>
<td>60.73±1.175</td>
<td>69.31±0.888</td>
<td>52.53±0.756</td>
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<tr>
<td></td>
<td>k_2</td>
<td>8.7x10^-3</td>
<td>6.8x10^-3</td>
<td>0.004±0</td>
</tr>
<tr>
<td></td>
<td>R^2</td>
<td>0.988</td>
<td>0.995</td>
<td>0.993</td>
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In both cases the pseudo-second order equation seemed to represent the experimental data as it showed higher R^2 and close to one. Moreover, parameters presented low deviation and the amount retained in equilibrium was similar to the experimental ones presented in Table II. Such model has been successfully applied to the adsorption of organic molecules such as dyes, herbicides, oils, and organic substances from aqueous solutions [30]. In all values of pH studied herein differences could be seen as a consequence of the small electrostatic attraction in acid solutions or electrostatic repulsion in basic solutions. This is in agreement with the fact that in pseudo-second order kinetics, chemisorption involves valence forces [30]. In fact, adsorption of organic molecules
from dilute aqueous solutions on carbon materials is a complex interplay between electrostatic and non-electrostatic interactions and that both interactions depend on the characteristics of the adsorbent and adsorbate, as well as the solution chemical properties [31].

**D. Adsorption Isotherms**

Fig. 6 illustrates the paracetamol adsorption isotherms on the studied carbons and Langmuir model that originated the best fit.

The activated carbon was classified as type L [32], showing a steep initial rise and a concave curvature at low equilibrium concentrations followed by a plateau or saturation limit. This is characteristic of systems where the adsorbate presented high affinity towards the adsorbent, and therefore indicated that no strong competition of the solvent took place for the active sites of adsorption. Acid pH provided again more concavely upward curvature indicating higher adsorption energy, which was in agreement with the electrostatic interaction of the carbonil group with the positively charged surface already explained.

![Graph](image)

**Fig. 6 Experimental adsorption isotherms of paracetamol with different values of pH (a) dende carbon (b) babassu carbon fitted by the Langmuir model**

Table IV presents the maximum experimental retention of both activated carbon whereas Table V shows the quantitative values of Freundlich and Langmuir adjustments. It may be seen that Langmuir adjustment originated the best fit with higher R² and low parameter deviation. Comparing values shown in Table IV and the qmax from Langmuir, it may be seen that the estimated maximum amount was not experimentally reached. Then, only values of kL should be discussed. As expected values of Table IV are similar do the ones shown in Table II obtained when kinetic data reached equilibrium.

### Table IV

<table>
<thead>
<tr>
<th>Activated carbon</th>
<th>pH 2</th>
<th>pH PCZ</th>
<th>pH 11</th>
</tr>
</thead>
<tbody>
<tr>
<td>DD</td>
<td>qmax</td>
<td>70.62</td>
<td>90.813</td>
</tr>
<tr>
<td></td>
<td>kL</td>
<td>0.280±0.026</td>
<td>0.187±0.019</td>
</tr>
<tr>
<td></td>
<td>R²</td>
<td>0.980</td>
<td>0.984</td>
</tr>
<tr>
<td>BB</td>
<td>qmax</td>
<td>71.39</td>
<td>80.87±2.668</td>
</tr>
<tr>
<td></td>
<td>kL</td>
<td>0.293±0.052</td>
<td>0.189±0.016</td>
</tr>
<tr>
<td></td>
<td>R²</td>
<td>0.961</td>
<td>0.992</td>
</tr>
</tbody>
</table>

### Table V

<table>
<thead>
<tr>
<th>Sample</th>
<th>Isot. model</th>
<th>pH</th>
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<tr>
<td>DD</td>
<td>Lang.</td>
<td>kL</td>
<td>0.280±0.026</td>
<td>0.187±0.019</td>
</tr>
<tr>
<td></td>
<td>R²</td>
<td>0.980</td>
<td>0.984</td>
<td>0.925</td>
</tr>
<tr>
<td></td>
<td>qmax</td>
<td>70.62±1.599</td>
<td>90.81±3.073</td>
<td>62.91±5.875</td>
</tr>
<tr>
<td>BB</td>
<td>Lang.</td>
<td>kL</td>
<td>0.293±0.052</td>
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<tr>
<td></td>
<td>R²</td>
<td>0.961</td>
<td>0.992</td>
<td>0.967</td>
</tr>
<tr>
<td></td>
<td>qmax</td>
<td>71.39±3.568</td>
<td>80.87±2.668</td>
<td>56.67±2.492</td>
</tr>
</tbody>
</table>

qmax = mg g⁻¹; kL = L g⁻¹

In all cases kL for BB samples were higher than the ones obtained for DD. Such results were already expected since BB was more acid, with high amount of acid groups in the surface, than DD. Moreover, BB had higher contribution of micropores, where paracetamol may be better accommodated. It must be also emphasized such results are a consequence of the electrostatic attraction of the carbonil group.

IV. Conclusion

The potentialities of low-cost high-value activated carbons, obtained from dende and babassu coconut mesocarp for the removal of a widespread used drug (paracetamol) was investigated. Results show that the two activated carbons are suitable for paracetamol removal. Microporosity and mainly solutions with pH ≤ pH PZC are of quite importance. Paracetamol easily diffuses into micropores and acid solutions promote paracetamol removal due to the attraction of the carbonil group to the positively charged carbon surface. Pseudo-second order model and Langmuir equation may represent the kinetic and equilibrium data, respectively.
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REFERENCES


