ADSorption OF PHENOL ONTO BIOCHAR FROM BLACK WATTLE SHELL WASTE

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ABSTRACT: In this work, biochar was produced from black wattle shell waste, characterized and applied as adsorbent for removal of phenol from aqueous solution. The biochar was prepared by chemical activation using zinc chloride as activating reagent. The adsorption of phenol was studied at different stirring rates and temperatures. The adsorption kinetics follows the pseudo-second order model in all stirring rates. The Weber and Morris model shown that the adsorption occurred by film and intra-particle diffusion. The increase in stirring rate leads to an increase in film diffusion. The Freundlich isotherm was the more suitable to represent the equilibrium data. Thermodynamic study indicated that the adsorption of phenol onto biochar was spontaneous, favorable, endothermic and entropy-controlled process.

KEYWORDS: adsorption; phenol; biochar; black wattle.

1. INTRODUCTION

The tannin extraction from black wattle shell, for biocoagulants production, generates a large amount of solid waste. This material consists mainly of cellulose, hemicellulose and lignin (Linhares et al., 2016). Due to this high carbon content, the use of the black wattle shell waste as a precursor material for the production of activated carbon is a possibility. Besides, commercially activated carbons available are derived from expensive precursor materials (Chen et al., 2010). In this way, the reutilization of wastes for the production of activated carbon can be a potentially viable alternative (Zazycki et al., 2018).

Activated carbon presents good surface characteristics, such as high surface area, high pore volume and presence of functional groups. These features make it a good material to be used in adsorption operation, being widely applied for the removal of contaminants from wastewater (Bhatnagar et al., 2013).

In this field, wastewaters contaminated with phenol can be treated by adsorption. Phenol is found in effluents disposed from many industries, such as petrochemical industry, oil refineries, pharmaceutical, nylon, dyes, pesticides industries, among others (Busca et al., 2008). This organic compound is generally considered one of the most hazardous contaminants (El-Naas et al., 2010). Thus, phenol must be removed from wastewaters. Several methods has been used for treatment of effluents contaminated with phenol, such as, liquid-liquid extraction (Franck and Stadelhofer, 1989), membrane extraction (Xiao et al., 2006), oxidation (Hussain et al., 2013), ozonation (Chedeville et al., 2007) and adsorption (Dotto et al., 2013). Adsorption, compared to these other methods, has advantages, such as, ease of implementation and operation, high efficiency, low cost and regeneration capacity (Zazyckiet al., 2018).

In this context, the aim of this work was to evaluate the potential of the biochar from black wattle shell waste for the removal of phenol from
aqueous solution. First, the biochar was prepared and characterized. Then, adsorptions studies were carried out. Kinetics investigation were performed using the pseudo-first order, pseudo-second order and Elovich models. The stirring effect was investigated using the Weber and Morris model. The equilibrium isotherms were evaluated using Langmuir and Freundlich models and after thermodynamic parameters were estimated.

2. MATERIAL AND METHODS

2.1. Material

The black wattle shell waste, used as precursor material, was supplied by TANAC/RS. ZnCl₂ (136.30 g mol⁻¹, purity of 97.0%) was obtained from Dinamica (Brazil). Phenol (94.11 g mol⁻¹, purity of 99.0%) was obtained from Synth (Brazil).

2.2. Pretreatment of Precursor Material

The black wattle shell was ground in a Willey mill. Then, was washed with warm water and with warm ethanol to remove impurities. After, the waste was filtered, dried at 40 °C for 24 h and sieved. The fraction with diameter between 300 and 425 µm was used in the preparation of biochar.

2.3. Biochar Preparation

The biochar was prepared by chemical activation using zinc chloride. For impregnation of the precursor material, 10 g of black wattle shell waste was added into 200 mL of ZnCl₂ solution in a ratio of 20% w/w (ZnCl₂/precursor material) and stirred at room temperature for 12 h. After, the material was filtered and dried at 110 °C for 24 h. The carbonization was conducted in a muffle furnace at 700 °C for 2 h. The impregnation and carbonization conditions were defined by factorial design developed in previous works (Lütkeet al., 2017). The resultant material was washed with HCl 0.5 mol L⁻¹ at 95 °C for 30 to remove Zn²⁺ and subsequently washed with warm water until the solution pH reached 6. After, was dried at 110 °C for 24 h (Dural et al., 2011).

2.4. Characterization

The textural properties of the biochar prepared was determined using a gas sorption analyzer (Quantachrome Instruments, Nova 4200e, USA). Before the analysis, samples were out gassed at 573 K for 12 h. The nitrogen adsorption/desorption isotherms were obtained at 77 K. The Brunauer-Emmett-Teller (BET) equation was used to calculate de specific surface area (As) and the Barret-Joyner-Haleda (BJH) method was used to calculate the pore size distribution.

The mean particle diameter (Dp) was determined by sieving, the sphericity (ϕ) by permeametry and density (ρ) by picnometry.

2.5. Batch Adsorption Experiments

The adsorption were conducted in kinetic and equilibrium assays. The kinetic assays were carried out in 100, 150 and 200 rpm (Nova Etica, 109-1, Brazil), at 298 K, with pH 6.5, adsorbent dosage of 1 g L⁻¹ and phenol concentration of 500 mg L⁻¹. Aliquots were removed at set time intervals (5-120 min). The equilibrium studies were carried out in a thermostatic agitator (Fanem, 315 SE, Brazil) at 100 rpm, with pH 6.5, adsorbent dosage of 1 g L⁻¹ until the equilibrium. The temperatures were 308, 318 and 328 K, and the phenol concentration from 50 to 500 mg L⁻¹.

The phenol concentration remaining in the liquid phase was measured by spectrophotometry (Shimadzu, UV240, Japan) at 270 nm. The adsorption capacity at time t (qₜ) and equilibrium adsorption capacity (qₑ) were determined by Equations 01 and 02, respectively:

\[ qₜ = \left( \frac{C₀ - Cₜ}{m} \right) V \]  
\[ qₑ = \left( \frac{C₀ - Cₑ}{m} \right) V \]  

where \( C₀ \) is the initial phenol concentration in liquid phase (mg L⁻¹), \( Cₑ \) is the equilibrium phenol concentration in liquid phase (mg L⁻¹), \( Cₜ \) is the phenol concentration in liquid phase at time \( t \) (mg L⁻¹), \( m \) is amount of adsorbent (g), and \( V \) is the volume of solution (L).
2.6. Kinetic Models

The kinetic data were evaluated by pseudo-first order (Equation 03), pseudo-second order (Equation 04) and Elovich (Equation 05) models (Ruthven, 1984):

\[ q_t = q_f (1 - \exp(-k_1t)) \]  

(03)

\[ q_t = \frac{t}{(1/k_2q_i^2) + (t/q_i)} \]  

(04)

\[ q_t = \frac{1}{a} \ln(1 + abt) \]  

(05)

where \( k_1 \) and \( k_2 \) are the rate constants of pseudo-first order (min\(^{-1}\)) and pseudo-second order (g mg\(^{-1}\) min\(^{-1}\)) models, respectively, \( q_t \) and \( q_i \) are the theoretical values for the adsorption capacity (mg g\(^{-1}\)), \( a \) is the initial sorption rate due to \( dq/dt \) with \( qt = 0 \) (mg g\(^{-1}\) min\(^{-1}\)) and \( b \) is the desorption constant of the Elovich model (g mg\(^{-1}\)).

2.7. Weber-Morris Model

The stirring effect was investigated using the Weber and Morris model, shown in Equation 06 (Weber and Morris, 1963):

\[ q_i = k_{WB} t^{1/2} + C_i \]  

(06)

where \( k_{WB} \) is the diffusion constant (mg g\(^{-1}\) t\(^{1/2}\)) and \( C_i \) is a parameter that indicates the resistance of interfacial film (mg g\(^{-1}\)). To investigate the stirring effect, adsorption capacities were plotted as function of square root of time.

According to Weber and Morris (1963), the plot of \( q_t \) versus \( t^{1/2} \) shows multi linearity. Each linear portion represents a particular mass transfer mechanism. The first portion is relative to external mass transfer (film diffusion), the second is relative to intra-particle diffusion and the third represents the final equilibrium.

2.8. Equilibrium Models

The adsorption equilibrium isotherms were adjusted using the Langmuir (Equation 07) and Freundlich (Equation 08) models (Ruthven, 1984):

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

(07)

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

(08)

where \( q_m \) is the maximum adsorption capacity (mg g\(^{-1}\)), \( k_e \) is the Langmuir constant (L mg\(^{-1}\)), \( k_F \) is the Freundlich constant ((mg g\(^{-1}\))(mg L\(^{-1}\))\(^{-1/n}\)) and \( 1/n \) is the heterogeneity factor.

2.9. Thermodynamic Parameters

The thermodynamic parameters, Gibbs free energy change (\( \Delta G^0 \)) (kJ mol\(^{-1}\)), enthalpy change (\( \Delta H^0 \)) (kJ mol\(^{-1}\)) and entropy change (\( \Delta S^0 \)) (J K\(^{-1}\) mol\(^{-1}\)) were determined by Equations 09 and 10 (Liu, 2009):

\[ \Delta G^0 = -RT\ln(\rho_w k_D) \]  

(09)

\[ \ln(\rho_w k_D) = \frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \]  

(10)

where \( k_D \) is the thermodynamic equilibrium constant (L g\(^{-1}\)), \( \rho_w \) is the solution density (g L\(^{-1}\)), \( T \) is the temperature (K), and \( R \) is the universal gas constant (8.314 J mol\(^{-1}\) K\(^{-1}\)). The \( k_D \) value were obtained by the ratio \( q_e/C_e \).

2.10. Statistical Analysis

The models were fitted to experimental data through nonlinear regression using Quasi-Newton method by the Statistic 7.0 software (StatSoft, USA). The fit quality was obtained through determination coefficient (\( R^2 \)) and average relative error (ARE), showed in Equation 11:

\[ ARE = \frac{100}{n} \sum_{i=1}^{n} \left| \frac{q_{i,model} - q_{i,exp}}{q_{i,exp}} \right| \]  

(11)

where \( q_{i,model} \) is the each value of \( q \) predicted by the adjusted model, \( q_{i,exp} \) is the each value of \( q \) experimentally measured and \( n \) is the number of experimental points.
3. RESULTS AND DISCUSSION

3.1. Characterization of Biochar

Table 1 shown the specific surface area, pore size distribution, total pore volume, mean particle diameter, sphericity and density of the biochar.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>As (m² g⁻¹)</td>
<td>305.51</td>
</tr>
<tr>
<td>Pore size distribution (Å)</td>
<td>13.29</td>
</tr>
<tr>
<td>Total pore volume (cm³ g⁻¹)</td>
<td>0.2031</td>
</tr>
<tr>
<td>Dp (μm)*</td>
<td>180.54 ± 10.12</td>
</tr>
<tr>
<td>ø*</td>
<td>0.67 ± 0.07</td>
</tr>
<tr>
<td>ρ (kg m⁻³)*</td>
<td>1100 ± 20</td>
</tr>
</tbody>
</table>

* mean ± standard deviation (n = 3).

3.2. Adsorption Kinetics

Figure 1 shows the adsorption kinetic curves obtained in all stirring rates studied.

![Figure 1. Kinetic curves for adsorption of phenol onto biochar with different stirring rate.](image_url)

The kinetic parameters are shown in Table 2. Based on the higher values of determination coefficient and the lower values of average relative error, it can be conclude that the pseudo-second order model was the more suitable to represent the kinetic adsorption of phenol onto biochar.

<table>
<thead>
<tr>
<th>Stirring rate (rpm)</th>
<th>100</th>
<th>150</th>
<th>200</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFO</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>q₁ (mg g⁻¹)</td>
<td>63.69</td>
<td>65.39</td>
<td>79.73</td>
</tr>
<tr>
<td>k₁ (min⁻¹)</td>
<td>0.056</td>
<td>0.063</td>
<td>0.048</td>
</tr>
<tr>
<td>R²</td>
<td>0.985</td>
<td>0.990</td>
<td>0.995</td>
</tr>
<tr>
<td>ARE (%)</td>
<td>5.60</td>
<td>5.52</td>
<td>2.16</td>
</tr>
<tr>
<td>PSO</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>q₂ (mg g⁻¹)</td>
<td>75.07</td>
<td>76.74</td>
<td>95.24</td>
</tr>
<tr>
<td>k₂ (g mg⁻¹ min⁻¹)</td>
<td>0.0009</td>
<td>0.0010</td>
<td>0.0006</td>
</tr>
<tr>
<td>R²</td>
<td>0.998</td>
<td>0.999</td>
<td>0.990</td>
</tr>
<tr>
<td>ARE (%)</td>
<td>2.05</td>
<td>1.61</td>
<td>3.44</td>
</tr>
<tr>
<td>Elovich</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a (mg g⁻¹ min⁻¹)</td>
<td>0.060</td>
<td>0.058</td>
<td>0.048</td>
</tr>
<tr>
<td>b (mg g⁻¹)</td>
<td>9.14</td>
<td>10.53</td>
<td>10.52</td>
</tr>
<tr>
<td>R²</td>
<td>0.995</td>
<td>0.994</td>
<td>0.990</td>
</tr>
<tr>
<td>ARE (%)</td>
<td>3.05</td>
<td>3.39</td>
<td>5.25</td>
</tr>
</tbody>
</table>
3.3. Stirring Effect

Figure 2 shows the Weber and Morris plot in all stirring rates studied. It can be observed that the plot has multi linearity with two distinct phases. This shows that both film diffusion and intra-particle diffusion occurs in the adsorption operation of phenol onto biochar. In all stirring rates studied, the adsorption occurs by film diffusion until 30 min.

![Figure 2. Stirring rate effect in adsorption of phenol onto biochar.](image)

Table 3 shows the slope obtained by fitting the Weber and Morris model with the first portion \(k_{WB1}\) and second portion \(k_{WB2}\) of the adsorption capacities plot versus square root of time, in all stirring rates studied. It can be observed that the increase in stirring rate leads to an increase in \(k_{WB1}\). This increase indicate the facilitates of phenol molecules diffusion of phenol molecules to the adsorbent surface. The similarity in \(k_{WB2}\) values showed that the intra-particle diffusion was independent of stirring rate (Ruthven, 1984).

**Table 3.** Slope of Weber and Morris model, in all stirring rates studied.

<table>
<thead>
<tr>
<th>Stirring rate (rpm)</th>
<th>(k_{WB1}) (mg g(^{-1}) t(^{1/2}))</th>
<th>(k_{WB2}) (mg g(^{-1}) t(^{1/2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>9.51</td>
<td>2.92</td>
</tr>
<tr>
<td>150</td>
<td>10.09</td>
<td>2.96</td>
</tr>
<tr>
<td>200</td>
<td>10.72</td>
<td>3.10</td>
</tr>
</tbody>
</table>

3.4. Adsorption Isotherms

The adsorption isotherms, in all temperatures studied, are shown in Figure 3. It was verified that the increase in temperature causes an increase in equilibrium adsorption capacity.

![Figure 3. Equilibrium curves for adsorption of phenol onto biochar.](image)

The equilibrium parameters are shown in Table 4. The higher values of the determination coefficient and the lower values of average relative error showed that the Freundlich model was the more suitable to fit the equilibrium data. The \(k_F\) value increased with the temperature increase.

3.5. Adsorption Thermodynamics

Table 5 shows the thermodynamic parameters, Gibbs free energy change \(\Delta G^0\), enthalpy change \(\Delta H^0\) and entropy change \(\Delta S^0\). The negative \(\Delta G^0\) values indicate that the adsorption of phenol onto biochar was a
spontaneous and favorable process. Besides, the $\Delta G^0$ values were more negative at 328 K, confirming that the adsorption was favored by the temperature increase. The negative $\Delta H^0$ value indicates an endothermic operation. The magnitude of $\Delta H^0$ value suggested that physisorption occurs in the adsorption of phenol onto biochar. The positive $\Delta S^0$ value indicates that disorder in solid–liquid interface increased after the adsorption. It was observed that only the entropy change contributed to obtain negative values of $\Delta G^0$ (Table 5). This shows that the adsorption of phenol onto biochar was an entropy-controlled phenomenon.

Table 4. Equilibrium parameters adsorption of phenol onto biochar.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Langmuir</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$q_m$ (mg g$^{-1}$)</td>
<td>$k_L$ (L mg$^{-1}$)</td>
<td>$R^2$</td>
<td>ARE (%)</td>
</tr>
<tr>
<td>308</td>
<td>91.48</td>
<td>0.0218</td>
<td>0.967</td>
<td>7.99</td>
</tr>
<tr>
<td>318</td>
<td>96.6</td>
<td>0.0244</td>
<td>0.976</td>
<td>7.32</td>
</tr>
<tr>
<td>328</td>
<td>98.57</td>
<td>0.0372</td>
<td>0.932</td>
<td>12.14</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Freundsich</th>
<th>$k_F$((mg g$^{-1}$)(L mg$^{-1}$)$^{1/n}$)</th>
<th>$1/n$</th>
<th>$R^2$</th>
<th>ARE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>308</td>
<td>13.45</td>
<td>3.20</td>
<td>0.998</td>
<td>8.31</td>
</tr>
<tr>
<td>318</td>
<td>13.87</td>
<td>3.12</td>
<td>0.998</td>
<td>1.42</td>
</tr>
<tr>
<td>328</td>
<td>20.14</td>
<td>3.71</td>
<td>0.993</td>
<td>3.87</td>
</tr>
</tbody>
</table>

Table 5. Thermodynamic parameters for adsorption of phenol onto biochar.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$\Delta G^0$ (kJ mol$^{-1}$)*</th>
<th>$\Delta H^0$ (kJ mol$^{-1}$)</th>
<th>$\Delta S^0$ (kJ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>308</td>
<td>-13.72 ± 0.08</td>
<td></td>
<td></td>
</tr>
<tr>
<td>318</td>
<td>-14.42 ± 0.05</td>
<td>8.47</td>
<td>0.072</td>
</tr>
<tr>
<td>328</td>
<td>-15.17 ± 0.03</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* mean ± standard deviation (n = 3).
4. CONCLUSIONS

In this work, black wattle shell waste was used as precursor material to produce a new biochar. The biochar presented surface area of 305.51 $\text{mg cm}^{-3}$, pore size distribution of 13.29 Å, total pore volume of 0.2031 $\text{cm}^3\text{g}^{-1}$, sphericity of 0.67, mean particle diameter of 180.54 µm and density of 1100 $\text{kg m}^{-3}$. The potential of the biochar in the phenol removal from aqueous solutions was investigated under different stirring rates and temperatures. The pseudo-second order model was the more suitable to represent the adsorption kinetic. The Weber and Morris analysis shown that the adsorption operation occurs through film and intra-particle diffusion. The increase in stirring rate leads to an increase in film diffusion. The increase in temperature causes an increase in equilibrium adsorption capacity. The higher adsorption capacity, at 328 K, was around 100 mg $\text{g}^{-1}$. The Freundlich isotherm model presented the best fit to the equilibrium data. According to the thermodynamic study, the adsorption of phenol onto biochar was spontaneous, favorable, endothermic. The entropy controlled the operation, and the energy involved suggest that a physisorption occurred. Overall, black wattle shell waste can be used as a precursor material of low-cost adsorbent, being a way of aggregate value to this material.

5. REFERENCES


