ADSORPTIVE REMOVAL OF CARBAMAZEPINE FROM WASTEWATERS BY ACTIVATED CHARCOALS

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ABSTRACT

The capacity of activated charcoals for the adsorption of Carbamazepine, an antiepileptic drug, from aqueous solutions was studied. The charcoals were activated with water steam at different temperatures prior to adsorption experiments. Langmuir and Freundlich models were used for the description of the adsorption equilibrium of Carbamazepine on different activated beech-charcoals. The uptake of the adsorbents was directly proportional to their specific surface area. The adsorbents, activated at higher temperatures (480 - 740°C; 360 - 630°C and 650 - 700°C) had a higher adsorption capacity for Carbamazepine (14.49 mg g⁻¹; 13.97 mg g⁻¹ and 11.81 mg g⁻¹, respectively) than those activated at lower temperatures (220 - 655°C and 7,45 mg g⁻¹; 185 - 450°C and 4.46 mg g⁻¹, respectively). All adsorbents showed quick and full adsorption at the lower concentration range.

Keywords: carbamazepine, adsorption, low-cost adsorbents, beech-charcoal.

INTRODUCTION

During the last years trace pollutants increasingly gather scientific attention. Newly included in this group are the pharmaceutically active compounds (PhACs) and the endocrine disrupting compounds (EDCs). Many studies report their presence in wastewater effluents, surface- and groundwater [1-6]. Pharmaceuticals are also found in soils [2, 7] and wastewaters from the drug industry [8]. The reason is that they can not be degraded completely in the wastewater treatment plants [3, 9]. Antibiotics from hospital effluents are detected in surface waters [10]. 30 - 90 % of the applied drug dose is not degraded in the human or animal body and is excreted as still active compound. This leads to ecotoxicological effect over some algae and other lower organisms, persistence in the environment and bacterial resistance in long terms [11]. Current technologies, used in the wastewater and drinking water treatment plants need to be optimized and improved in order to be able to eliminate the pharmaceuticals.

Many methods are known for the removal of organic pollutants, among which adsorption, membrane processes, chemical oxidation, biological degradation, etc. Adsorption on activated carbons is one of the most popular methods. Though the benefits of their high adsorption capacities, the use of activated carbons has also a negative side – the high costs and the necessity of regeneration. That is why researchers investigate other, low-cost adsorbents as an alternative [12-14].

Activated charcoals are described in the literature mostly as very good adsorbent for prevention of drug poisoning [15, 16]. They have been also used as a low-cost adsorbent for the removal of Cr (VI) and dyes [17, 18].
In this study the adsorption capacity of activated by steam at different temperatures beech charcoals for the removal of Carbamazepine from aqueous solutions was evaluated, as a cheap alternative of the activated carbon. The experimental equilibrium isotherms were modeled by the Langmuir and Freundlich equations.

EXPERIMENTAL

Target Pharmaceuticals

The target substance in this study was Carbamazepine. It was obtained from Sigma-Aldrich. Its molecular structure is shown on Fig. 1. Carbamazepine is an anticonvulsant and mood-stabilizing drug used primarily in the treatment of epilepsy and bipolar disorders.

![Structural formula of Carbamazepine](image)

Fig. 1. Structural formula of Carbamazepine.

Adsorbents

The adsorbents, used in this study, were made from beech-charcoal, activated with steam at different temperatures. The activation temperatures and the resulting physicochemical characteristics of the 5 adsorbents and the physicochemical characteristics of the untreated beech-charcoal are presented in Table 1. The specific surface area was determined on the basis of the Brunauer, Emmet und Teller (BET) method.

Analytical measurements

The concentrations of Carbamazepine were measured with a High performance liquid chromatography (HPLC). The used HPLC device was Hewlett Packard Series 1100 Pump, Autosampler and Detector. The column was Chromolith Flash RP 18e. The HPLC eluent was 45 % acetonitrile. The wavelength corresponding to maximum absorbance was 210 nm.

Adsorption equilibrium studies

The equilibrium experiments were performed with model solutions of Carbamazepine in distilled water and 3 ml acetonitrile. The experiments were carried out at 20±2°C. Various Carbamazepine solutions with different initial concentrations in range of 1,0 – 20,0 mg l\(^{-1}\) were used. Adsorbent mass of 0,05 g was added to 50 ml of model solutions in Erlenmeyer flasks with caps. The flasks were sealed and agitated on a platform shaker. After the equilibrium was reached, each sample was filtered through a membrane filter with pore size 0,45 µm. The residual Carbamazepine concentrations (Ce, mg l\(^{-1}\)) were determined by the HPLC.

The data obtained from the adsorption tests were used to calculate the adsorption capacity (q, mg g\(^{-1}\)) of each of the used charcoals:

\[
q_e = \frac{(C_0 - C_e) \cdot V}{w}, \text{ mg g}^{-1}
\]  

(1)

where

- \(C_0\), mg l\(^{-1}\), is the initial pollutant concentration in the liquid phase,
- \(w\), g, is the adsorbent mass,
- \(V\), ml, is the sample volume.

Equilibrium modeling

Equilibrium is expressed by adsorption isotherms. The Langmuir isotherm model assumes monolayer coverage of the adsorbent surface by the adsorbate at homogenous, energetically identical sites within the adsorbent [19]. According to this model:

\[
q_e = \frac{K_L \cdot C_e}{1 + a_L \cdot C_e},
\]  

(2)

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Material</th>
<th>Activation Method</th>
<th>T (°C)</th>
<th>BET Surface (m(^2)/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>V10</td>
<td>Beech-charcoal</td>
<td>Steam-Activation</td>
<td>480-740</td>
<td>447,1</td>
</tr>
<tr>
<td>V11</td>
<td>Beech-charcoal</td>
<td>Steam-Activation</td>
<td>360-630</td>
<td>452,4</td>
</tr>
<tr>
<td>V12</td>
<td>Beech-charcoal</td>
<td>Steam-Activation</td>
<td>220-655</td>
<td>375,7</td>
</tr>
<tr>
<td>V13</td>
<td>Beech-charcoal</td>
<td>Steam-Activation</td>
<td>185-450</td>
<td>267,2</td>
</tr>
<tr>
<td>V14</td>
<td>Beech-charcoal</td>
<td>Steam-Activation</td>
<td>650-700</td>
<td>415,5</td>
</tr>
<tr>
<td>BHK5</td>
<td>Beech-charcoal</td>
<td>Grinded</td>
<td>-</td>
<td>65,1</td>
</tr>
</tbody>
</table>
where
\[ q_e, \text{ mg g}^{-1}, \text{ is the adsorption capacity at equilibrium;} \]
\[ C_e, \text{ mg l}^{-1}, \text{ is the equilibrium pollutant concentration in the liquid phase;} \]
\[ a_L, 1 \text{ mg}^{-1} \text{ and } K_L, 1 \text{ g}^{-1}, \text{ are the Langmuir isotherm constants. They are evaluated through the linear form of the Langmuir equation} \]
\[
\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{a_L}{K_L} C_e
\]  

(3)

The Freundlich isotherm model describes a multilayer adsorption on heterogeneous surfaces [19]. According to it:
\[
q_e = K_F . C_e^{n_F}
\]

(4)

where \( K_F, 1 \text{ g}^{-1} \) and \( n_F \) (heterogeneity factor) are the Freundlich constants, which can be determined from the linear form of the equation:
\[
\log q_e = \log K_F + n_F . \log C_e
\]

(5)

RESULTS AND DISCUSSION

The activation experiments showed that the most suitable temperatures for steam activation of the beech charcoals, resulting in highest specific surfaces, were in the range of 360°C-740°C. These were for samples V10 and V11, respectively. Good results were found also with sample V14, activated at 650-700°C. Experiments showed that the activation at lower start temperature (sample V12) or lower start/lower end temperature (sample V13) lead to lower specific surface. The dependence of the activation temperature on the specific surface of the adsorbents is shown in Fig. 2.

In this study the Langmuir and Freundlich equilibrium models were used to describe the adsorption results. The calculated values of the model parameters and the regression coefficients are given in Table 2. According to the literature, \( K_F \) of the Freundlich isotherm expresses the adsorbent capacity and the larger the value, the higher is the capacity. On the other hand \( n_F \) represents the heterogeneity of the adsorbent’s surface. \( n_F \)'s values range between 0 and 1 and the closer \( n_F \) is to 0, the more heterogeneous is the surface [19]. From the six studied adsorbents, three of them (V10, V11 and V14) had higher \( K_F \) values than the others, which corresponds to the higher adsorption capacity values calculated for them. Respectively their \( n_F \) values were closer to 0 than those of the other adsorbents, suggesting that they have more heterogeneous surfaces. These three adsorbents had also the highest specific surfaces (Table 1).

According to the results of the equilibrium experiments, both Langmuir and Freundlich models proved to fit well all systems (Fig. 3), except the BHK5/Carbamazepine system. For this system the Freundlich isotherm was found better. These conclusions are drawn from the corresponding values of the regression coefficients (R2) (Table 2).

The maximum adsorption capacities \( q_e \) of the studied adsorbents were 14.49; 13.97; 7.45; 4.46; 11.81 and 6.94 mg g\(^{-1}\), for adsorbents V10, V11, V12, V13, V14 and BHK5, respectively. According to this equilibrium

<table>
<thead>
<tr>
<th>Model</th>
<th>Coefficients</th>
<th>V10</th>
<th>V11</th>
<th>V12</th>
<th>V13</th>
<th>V14</th>
<th>BHK5</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( a_L )</td>
<td>1.9785</td>
<td>2.1285</td>
<td>0.7381</td>
<td>0.5956</td>
<td>1.6205</td>
<td>0.1524</td>
</tr>
<tr>
<td></td>
<td>( R^2 )</td>
<td>0.992</td>
<td>0.9924</td>
<td>0.9737</td>
<td>0.937</td>
<td>0.9913</td>
<td>0.6105</td>
</tr>
<tr>
<td>Freundlich</td>
<td>( K_F )</td>
<td>10.5148</td>
<td>10.3205</td>
<td>3.5002</td>
<td>2.1149</td>
<td>8.1377</td>
<td>2.7378</td>
</tr>
<tr>
<td></td>
<td>( n_F )</td>
<td>0.1711</td>
<td>0.1522</td>
<td>0.3374</td>
<td>0.2126</td>
<td>0.1625</td>
<td>0.1804</td>
</tr>
<tr>
<td></td>
<td>( R^2 )</td>
<td>0.9708</td>
<td>0.9701</td>
<td>0.9471</td>
<td>0.9421</td>
<td>0.9662</td>
<td>0.8769</td>
</tr>
</tbody>
</table>

Table 2. Values of the calculated constants in the Langmuir and Freundlich models.
data, the adsorption capacity follows the order: BHK5 < V13 < V12 < V14 < V10 and V11. As shown on Fig. 4, the same trend follows the specific surface area, which the charcoals had. Thus, as expected, their uptake was directly proportional to their specific surface area.

Samples V10 and V11 adsorbed 100% of the Carbamazepine at lower concentrations, almost 100% at medium concentrations and around 70% at the higher concentration range. V14 adsorbed 100% at lower concentration and then gradually started saturating, but still adsorbed 60% of the Carbamazepine at higher concentrations. V12 and V13 also adsorbed 100% at the lower concentrations range, but then V12 kept slowly adsorbing, while V13 almost reached saturation. BHK5 started with good adsorption percents, but quickly reached saturation (Fig. 5).

The experimental points of adsorbent samples V10, V11 and V14 had a distinct vertical section in the low to medium concentration range, where a sharp increase of the solid phase concentration from 0 to 9 mg g⁻¹ was identified (Fig. 3). Similar, but yet not so sharp leap was detected for sample V12, reaching from 0 to 5,8 mg g⁻¹. Therefore, higher rate of adsorption in the initial stages of the process could be expected. This applies for all five steam-activated beech charcoals. This trend was not noticed by the non-activated beech charcoal. The leap of Carbamazepine solid phase concentration on BHK5 was more gradual in the whole concentration range. This indicates slower adsorption process. BHK5 demonstrated the lowest energy of adsorption $a_0, 0,151$ mg⁻¹ (Table 2) and due to the lower specific area of this adsorbent poor adsorption is to be expected.
Additionally, microscope pictures were made to show the surface changes that adsorbents undergo after steam activation (Figs. 6 and 7). They clearly demonstrate the increased amount of pores and active sites after steam activation.

**CONCLUSIONS**

The equilibrium adsorption behavior of Carbamazepine on 5 activated with water steam at different temperatures and one untreated beech charcoals was investigated. Both, Langmuir and Freundlich isotherm models proved suitable. The uptake of the adsorbents was directly proportional to their specific surface area. The adsorbents, activated at higher temperatures, had a higher adsorption capacity for Carbamazepine than the ones, activated at lower temperatures.

All adsorbents showed quick and full adsorption in the lower concentration range. These with higher surface area kept the higher adsorption trend also at the next stages. This proved again their high adsorption capacity. Therefore, since pharmaceuticals are discharged in lower concentrations in the environment, the studied adsorbents can be considered as good replacement of the active carbon.

**REFERENCES**


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