Effect of nitric acid treatment on the paracetamol adsorption of activated adsorbents from groundnut shells

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Received 06 Aug 2019, Revised 15 Sep 2019, Accepted 24 Sep 2019

Abstract

Two adsorbents were obtained by thermal activation (TA) and thermal and chemical activation (TCA) on groundnut shells. For to characterize the surface charges and functional groups on the TA and TCA adsorbents, the pH to point of zero charge (pH\text{PZC}) and Fourier transform Infra-Red (FTIR) Spectroscopy were used. Four isotherm models (Langmuir, Freundlich, Jovanovic and Temkin) were tested for modeling the adsorption isotherms by nonlinear method. The model of Langmuir described best the adsorption on TA and TCA with the maximal quantities adsorbed were 3.19 and 13.85 mg g$^{-1}$, respectively. This study has demonstrated that TCA can be used as a novel adsorbent for the treatment of water contaminated with pharmaceutical products.

Keywords: pharmaceutical products, paracetamol, nitric acid, Groundnut shell.

1. Introduction

The production of pharmaceuticals has increased rapidly, providing better health quality for living beings. Upon their use, large amounts of pharmaceutical products are discharged into the water bodies and are thus detected in aquatic media [1-3]. In addition, the conventional wastewater treatments for pharmaceuticals are ineffective in eliminating most of these compounds. Therefore, residual quantities remain in the treated water and have been found in drinking water [4; 5].

Paracetamol is one of the most commonly prescribed pharmaceutical drugs. Unfortunately, its presence in recycled water and drinking water has already been detected [6; 7].

The removal of these classes of pollutants is thus an impelling environmental issue. Among the numerous techniques used to this end, adsorption has been found an effective method for scavenging organic pollutants from wastewater and activated carbon is surely the most valuable
sorbent thanks to its high sorption capacity, though its relatively high cost limits large-scale applications. The adsorption of different pharmaceuticals has become one of the aims of the researchers in the world [8-12].

The aim of this study was to use groundnut shells an agricultural waste, to produce activated adsorbents and to determine the adsorption isotherms of paracetamol from aqueous solution using these activated adsorbents and to model the corresponding data. The principle of our study was based on the preparation of materials an economic time, energy and reagents.

2. Experimental

2.1. Adsorbate

All the solutions are prepared using pure paracetamol and ultra-pure water. The stock solution is prepared by adding 1 g of the sorbate to 1L of ultrapure water. The experimental solutions of desired concentration were prepared by diluting the stock solution with ultrapure water [12].

2.2. Adsorbents

The groundnut shell was collected from the local market of Nouakchott City in Mauritania. Before use, the groundnut shell was washed thoroughly with ultra pure water and sundried for 8 h. The dried shell was ground to powder, sieved to obtain particle sizes below 100 µm, dried in an oven at 80 °C for 24 h [12].

The powdered groundnut shell was carried out in a closed furnace at 300 °C for 2 h. The thermally activated groundnut shell (TA) was stored in a desiccator and used for further studies. The powdered groundnut shell was carried out in a closed furnace at 300 °C for 2 h. This thermally activated powdered groundnut shell (100 g) was treated by nitric acid activation (0.1N HNO₃ in a ratio of 200 mL acid solution/100 g of thermally activated powdered groundnut shell) for 24 h and again drying (80 °C) for 24 h.

The thermally and chemically activated groundnut shell (TCA) was stored in a desiccator before use. Functional groups on the TA and TCA adsorbents were investigated by a Fourier transform Infra-Red (FTIR) Spectroscopy in the scanned range of 650–4,000 cm⁻¹. The pH to point of zero charge (pHₚₑ𝑍𝑪) of the TA and TCA adsorbents was carried out [13].

2.3. Adsorption isotherms

The adsorption isotherms are obtained by mixing (70 rpm), for 12 h, 0.5 g of adsorbent with 25 mL of paracetamol solutions with different concentrations varying from 1 to 100 mg L⁻¹. At the end of each experiment the agitated solution mixture was micofiltered and the residual concentration of paracetamol was determined by High Performance Liquid Chromatography (HPLC) according to [12]. The adsorbed quantity at equilibrium (qₑ) is calculated according to the following equation (1):
where

- \( q_e \): quantity of paracetamol per g of adsorbent (mg g\(^{-1}\))
- \( C_i \): initial solution concentration of paracetamol (mg L\(^{-1}\)),
- \( C_e \): equilibrium solution concentration of paracetamol (mg L\(^{-1}\)),
- \( m \): the adsorbent weight (g),
- \( V \): Volume of the solution (L).

Adsorption isotherms are normally developed to evaluate the capacity of adsorbent for the adsorption of a particular molecule. Four isotherm models (Langmuir, Freundlich, Jovanovic and Temkin) were tested for modeling the adsorption isotherm by nonlinear method. The Langmuir adsorption isotherm assumes that the adsorption takes place at specific homogeneous surface sites. The Freundlich isotherm describes heterogeneous systems. The model of Jovanovic is essentially the same as that considered by Langmuir. The Temkin isotherm assumes that the fall in the heat of adsorption is linear rather than logarithmic [14-18].

The nonlinear Langmuir, Freundlich, Jovanovic and Temkin models can be expressed by equations (2), (3), (4) and (5), respectively:

\[
q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (2)
\]

\[
q_e = K_F C_e^{1/n} \quad (3)
\]

\[
q_e = q_m \left(1 - e^{-K_J C_e}\right) \quad (4)
\]

\[
q_e = B_T \ln K_T C_e \quad (5)
\]

- \( q_e \) is the amount of paracetamol adsorbed per unit mass of adsorbent (mg g\(^{-1}\)), \( K_L \) is the Langmuir constant related to the adsorption capacity (L g\(^{-1}\)), \( C_e \) is the concentration of paracetamol in the solution at equilibrium (mg L\(^{-1}\)) and \( q_m \) is the maximum uptake per unit mass of adsorbent (mg g\(^{-1}\)).
- \( K_F \) (mg g\(^{-1}\)) (L mg\(^{-1}\))\(^n\) and \( 1/n \) are the Freundlich constants related to adsorption capacity and adsorption intensity, respectively.
- \( q_m \) (mg g\(^{-1}\)) and \( K_J \) (L mg\(^{-1}\)) are Jovanovitch constants related to the adsorption capacity and the rate of adsorption, respectively.
- \( B_T = RT/b \) is a constant related to heat of sorption and \( b \) shows the variation of adsorption energy (J mol\(^{-1}\)). \( K_T \) is a Temkin constant which take onto account the interactions paracetamol/adsorbent (dm\(^3\) mg\(^{-1}\)).
The relative parameters of each equation are obtained using the correlation coefficient $R^2$ by nonlinear regressive analysis using the solver Excel. The $R^2$ values are determined by following equation (6):

$$
R^2 = 100 \left( 1 - \left| \frac{q_{\text{mod}} - q_{\text{avr}}}{q_{\text{exp}} - q_{\text{avr}}} \right| \right)
$$

(6)

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 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. FTIR analysis

The FTIR spectroscopy analyses of the TA adsorbent before and after paracetamol adsorption are given in Figures 1 and 2, respectively. The FTIR spectra of the sorbent before paracetamol retention are used as a reference. The peak at 3335.52 cm$^{-1}$ representing surface bonded O-H group or a stretching N-H group was shifted to 3340 cm$^{-1}$ after paracetamol adsorption. The peak at 1604.41 cm$^{-1}$ assigned to CO of carboxyl groups was shifted to 1624.19 cm$^{-1}$. The peak at 1260.99 cm$^{-1}$ can be attributed to the presence of C–O stretching. After adsorption this peak was shifted to 1259.11 cm$^{-1}$. The peak observed at 1026.99 cm$^{-1}$ shows the presence of O-Si-O linkage. This peak shifted to 1030.70 cm$^{-1}$ after paracetamol adsorption. The shifts in the absorption peaks generally observed indicate the existence of a paracetamol binding process taking place on the surface of TA adsorbent.

![Figure 1: FTIR Spectrum of TA before paracetamol adsorption](image-url)
The FTIR spectroscopy analyses of the TCA before and after paracetamol adsorption are given in Figures 3 and 4, respectively. The FTIR spectra of the sorbent before paracetamol retention are used as a reference. The presence of a peak at 3335.92 cm$^{-1}$ representing surface bonded O-H groups or a stretching N-H group which was shifted to 3340.88 cm$^{-1}$ after paracetamol sorption. The peak at 1617.54 cm$^{-1}$ assigned to CO of carboxyl groups was shifted to 1624.19 cm$^{-1}$. The absorption peaks at 1232.11 cm$^{-1}$ can be attributed to the presence of–C–O stretching. After adsorption this peak was shifted to 1259.11 cm$^{-1}$. The peak observed at 1028.52 cm$^{-1}$ shows the presence of O-Si-O linkage was shifted to 1030.70 cm$^{-1}$ after paracetamol adsorption. The shifts in the absorption peaks generally observed indicate the existence of a paracetamol binding process taking place on the surface of TCA.
3.2. Adsorption isotherms

The isotherm parameters obtained using non-linear forms are given in table 1 for both materials. The Langmuir isotherm showed slightly high correlation coefficients $R^2$ compared to Freundlich, Jovanovic and Temkin isotherms for the adsorption of paracetamol onto TA and TCA. The figures 5 and 6 confirmed that the suitable isotherms models for our experimental equilibrium curves.

Table 1: Parameters isotherm models for paracetamol retention on the TA and TCA adsorbents

<table>
<thead>
<tr>
<th>Models</th>
<th>Parameters</th>
<th>TA</th>
<th>TCA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>$q_m$</td>
<td>3.19</td>
<td>13.85</td>
</tr>
<tr>
<td></td>
<td>$K_L$</td>
<td>0.0086</td>
<td>0.0014</td>
</tr>
<tr>
<td></td>
<td>$R^2$ (%)</td>
<td>99.3</td>
<td>99.6</td>
</tr>
<tr>
<td>Freundlich</td>
<td>$1/n$</td>
<td>0.77</td>
<td>0.85</td>
</tr>
<tr>
<td></td>
<td>$K_F$</td>
<td>0.045</td>
<td>0.033</td>
</tr>
<tr>
<td></td>
<td>$R^2$ (%)</td>
<td>98.5</td>
<td>99.1</td>
</tr>
<tr>
<td>Jovanovic</td>
<td>$q_m$</td>
<td>1.90</td>
<td>7.61</td>
</tr>
<tr>
<td></td>
<td>$K_J$</td>
<td>0.014</td>
<td>0.0026</td>
</tr>
<tr>
<td></td>
<td>$R^2$ (%)</td>
<td>99.4</td>
<td>99.5</td>
</tr>
<tr>
<td>Temkin</td>
<td>$K_T$</td>
<td>0.59</td>
<td>0.53</td>
</tr>
<tr>
<td></td>
<td>$B_T$</td>
<td>0.26</td>
<td>0.27</td>
</tr>
<tr>
<td></td>
<td>$R^2$ (%)</td>
<td>85.5</td>
<td>84.2</td>
</tr>
</tbody>
</table>
The results obtained show that the best-fitted adsorption isotherm models were determined to be in the order: Langmuir> Jovanovic> Freundlich> Temkin.

The adsorption capacities obtained for TA and TCA, corresponding to 3.19 and 13.85 mg g\(^{-1}\). From these values, the adsorption capacity of TCA for paracetamol is higher than that obtained by TA, suggesting the higher effectiveness of TCA for the adsorption removal of paracetamol.

This high adsorption value obtained by TCA could be due to the effect of HNO\(_3\) treatment. The HNO\(_3\) is a responsible for adding oxygenated surface groups, increasing the material hydrophilicity and favoring sorption of paracetamol. This is similar to the one reported by [19]. Many researchers report that the HNO\(_3\) is the reagent frequently used to enhanced oxygen content on the surface [20-23]. It is interesting to note that the carboxyl, lactone, phenolic hydroxyl, quinone and carboxylic anhydride groups are the oxygen containing functional groups commonly located on the surface of the adsorbent.
The $pH_{PZC}$ is an important parameter for adsorbent to characterize the sensitivity to the pH and their surface charges. The $pH_{PZC}$ values of the TA and TCA were found to be 6.8 and 4.6, respectively. According to [20], the thermal activation may cause considerable reduction on the surface in terms of oxygen containing species and the HNO$_3$ treatment reduces some of basic species from the surface.

As regards the surface chemistry, the values of the $pH_{PZC}$ revealed that the TCA possess predominantly acidic nature than the TA. In addition, the FTIR spectrum of TCA did not differ significantly from that of the TA, suggesting that the HNO$_3$ treatment process did not change the lignocellulose structure of groundnut shell, however, changed surface charge of the adsorbent. This is similar to the one reported by [24].

A comparison of the adsorption capacity of different sorbents for paracetamol was given in table 3. It is clear from the table 2, that the adsorption capacity of TCA is found substantially superior or comparable with many reported adsorbents.

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>$q_m$ (mg g$^{-1}$)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grape stalk</td>
<td>1.74</td>
<td>[25]</td>
</tr>
<tr>
<td>Yohimbe bark</td>
<td>0.77</td>
<td></td>
</tr>
<tr>
<td>Cork bark</td>
<td>0.99</td>
<td></td>
</tr>
<tr>
<td>P. Oceanica</td>
<td>1.638</td>
<td>[9]</td>
</tr>
<tr>
<td>Dehydrated sewage sludge</td>
<td>0.956</td>
<td></td>
</tr>
<tr>
<td>Activated Carbon (CANa1)</td>
<td>20.964</td>
<td>[26]</td>
</tr>
<tr>
<td>Activated Carbon (CANa2)</td>
<td>14.881</td>
<td></td>
</tr>
<tr>
<td>Groundnut Shell</td>
<td>3.02</td>
<td>[12]</td>
</tr>
<tr>
<td>TA</td>
<td>3.19</td>
<td>Present study</td>
</tr>
<tr>
<td>TCA</td>
<td>13.85</td>
<td>Present study</td>
</tr>
</tbody>
</table>

4. Conclusion

In this study, the potential of two activated adsorbents, obtained from groundnut shells, for the adsorption of paracetamol from aqueous solutions was established. As for the equilibrium study, isotherm of Langmuir described better the adsorption of paracetamol on TA and TCA. The maximum adsorption capacities of TA and TCA were found to be 3.19 and 13.85 mg g$^{-1}$. The maximum adsorption capacity of TCA compared with the adsorption capacities obtained by activated carbons and others materials for adsorption of paracetamol show that the TCA adsorbent are cheap and economically suitable for removal of paracetamol from wastewater.
References