

Comparison of Acid and Basic Thermo-Chemical Treatments in the Production of Adsorbents Based on Corncobs. II: Equilibrium Study and FTIR Analysis

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Abstract. Corncobs were evaluated as raw material in the production of adsorbents for phenol removal from aqueous solutions. A comparative evaluation of acid and basic activating agents is presented. There were differences in both surface chemistry makeup and adsorption performance depending on the activating agent. Acid activation provided an adsorbent with better adsorption capacity for phenol. Adsorption tests showed that both the prepared adsorbents presented adsorption capacities that were higher or similar to those of commercially available activated carbons as well as other adsorbents produced from agricultural residues, confirming that this type of waste material is a suitable candidate for use in the production of adsorbents.

Keywords: adsorption, corncobs, phenol removal.

1. Introduction

There are many methods available for removal of phenolic compounds from wastewaters, with adsorption being one of the most effective, especially when these types of pollutants are present at low concentrations [1]. Many recent studies have focused on the production of activated carbons (ACs) using agricultural by-products, mainly lignocellulosic materials [1]-[9]. The basic processes involved in transforming lignocellulosic or any carbon-based material into ACs can be divided into (i) physical and (ii) chemical activation [10]. Physical activation is based solely on thermal treatment of the material, usually carried out in a two-step process: (i) carbonization in an inert atmosphere to produce the charcoal, followed by (ii) activation or second heat treatment, in the presence of CO₂ or steam, in order to increase the porosity of the material. Chemical activation is carried out by means of the impregnation of the carbon structure with an activating agent followed by heat treatment. In this case, both the carbonization and activation steps can be carried out in a single step. This process is thus considered more advantageous in comparison to physical activation, given that it usually occurs at lower temperatures, leads to higher carbon yields, and allows better control of the development of microporosity [11].

The general action of an activating chemical agent during the impregnation step includes promotion of hydrolysis and simultaneous swelling of the carbon structure, while occupying a volume that inhibits the shrinking of the structure during heat treatment. The most common agents used in chemical activation of lignocellulosic materials include dehydrating agents such as inorganic acids (e.g., H₃PO₄ and H₂SO₄), metal chlorides (e.g., ZnCl₂, FeCl₃ and CaCl₂) and metal hydroxides (e.g., KOH and NaOH), with the most popular among them being H₃PO₄, ZnCl₂ and KOH [10]. Different activating mechanisms are proposed for each of these chemical agents during carbonization. The major effect of the agents on the activated carbon structure can be generalized as KOH promoting a widening of the micropores produced by the carbonization of the precursor, ZnCl₂ further developing small mesoporosity, and H₃PO₄ leading to a more heterogeneous pore size distribution, including micro, meso and macropores [11].

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In view of the aforementioned, the objective of this study was to compare acid (H₃PO₄) and basic (KOH) activation procedures in the production of activated carbons targeting phenol removal, with corncobs being employed as raw materials. The study was divided into two parts. In the first part, we compared the prepared adsorbents in a batch adsorption kinetics study as well as their physical and chemical surface characteristics [12]. In this part, we compare the adsorption capacity of the prepared adsorbents as well as their surface chemistry characteristics based on FTIR analysis.

2. Methodology

2.1. Adsorbent preparation

The corncobs were ground (particle size < 0.85mm). The acid activation procedure consisted of treatment with phosphoric acid 85% (1:1 mL acid/g material) followed by 2 h carbonization in a muffle oven at 500 °C. Afterwards, the produced adsorbents were washed with NaOH until pH 7 to remove the excess acid. Basic activation consisted of treatment with KOH (1:1 mL acid/g material) followed by 30 min carbonization in a muffle oven at 400 °C. Afterwards, the produced adsorbents were washed with HCl and distilled water until pH 7. In both cases, carbonization was performed under inert atmosphere (N₂ stream). After both acid and basic activation procedures, the solids were dried at 110°C for 12 h and ground to particle diameters ranging from 0.15 to 0.43 mm. The produced adsorbents will be herein denominated ACA (acid activation) and ACB (basic activation).

2.2. Adsorption tests

Batch experiments of adsorption were performed in 250 mL Erlenmeyer flasks, with the flasks being agitated on an orbital shaker at 100 rpm. In all sets of experiments, the adsorbent was thoroughly mixed with 100 mL phenol (Phe). Initial Phe concentration ranged from 100 to 500 mg L⁻¹ at a fixed adsorbent concentration (10 g L⁻¹). All tests were performed in two replicates. 2 mL aliquots were taken from the Erlenmeyer flasks after equilibrium was reached and phenol concentration was determined by a UV–Vis spectrophotometer (Hitachi U-2010) at 269 nm. The amount of phenol adsorbed, q (mg/g) was calculated by:

$$q = \frac{(C_o - C)V}{W} \quad (1)$$

where C_o and C (mg.L⁻¹) are the liquid-phase concentrations of phenol at initial and sampling times, respectively; V is the volume of the solution and W is the mass of dry adsorbent used.

2.3. Adsorbent characterization

The surface structure of the prepared adsorbents was also investigated using Fourier Transform Infrared (FTIR) spectroscopy. The FTIR spectra were obtained and recorded on a FTIR spectrometer (IRAffinity-1, Shimadzu, Japan) operating in the range of 600–4000 cm⁻¹, 4 cm⁻¹ resolution. Diffuse reflectance (DR) measurements were performed in diffuse reflection mode with a Shimadzu sampling accessory (DRS8000A).

3. Results and Discussion

3.1. Adsorption equilibrium

The adsorption isotherms obtained at 25°C are presented in Fig. 1. The shape of the curves indicates favorable adsorption and clearly show that ACA presented better performance. Although there are many models for description of adsorption isotherms in the literature, the simpler and most widely employed are two-parameter models. Langmuir isotherm [13] is based on a theoretical model assuming monolayer adsorption over an energetically and structurally homogeneous adsorbent surface, being represented by the following equation:

$$q_e = \frac{q_{max}K_L C_e}{1 + K_L C_e} \quad (2)$$

where q_e (mg g⁻¹) and C_e (mg L⁻¹) correspond to the amount adsorbed per gram of adsorbent and to the solute concentration (mg L⁻¹) in the aqueous solution, respectively, after equilibrium was reached. q_{max} and K_L are constants related to the maximum adsorption capacity (mg g⁻¹) and the adsorption energy (L mg⁻¹),

respectively. Freundlich's equation [14] is an empirical model that has been associated to both heterogeneous and multilayer adsorption, being described by the following equation:

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

where K_F is a constant that indicates the relative adsorption capacity ($\text{mg}^{1-(1/n)}\text{L}^{1/n}\text{g}^{-1}$) and n is related to the intensity of adsorption. Temkin's model [15] is based on the assumption that the heat of adsorption of all the molecules in the layer decrease linearly with surface coverage due to adsorbent-adsorbate interactions. Adsorption is thus characterized by a uniform distribution of binding energies, up to a maximum value. The Temkin isotherm can be described by the following equation:

$$q_e = RT / b \ln(K_T C_e) \quad (4)$$

where b is the Temkin constant related to the heat of sorption (J mol^{-1}), K_T is the Temkin isotherm constant (L g^{-1}), R is the universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$) and T is the absolute temperature (K).

Selection of the best-fit model was based on highest R^2 values coupled with the lowest difference between calculated and experimental q_e values, evaluated according to the following root mean square error measure:

$$RMS_e = \sqrt{\sum [(q_{e,est} - q_{e,exp}) / q_{e,exp}]^2} / N \quad (5)$$

where $q_{e,exp}$ and $q_{e,est}$ are the experimental and model estimated equilibrium adsorbent amounts, respectively, and N corresponds to the number of experimental isotherm points.

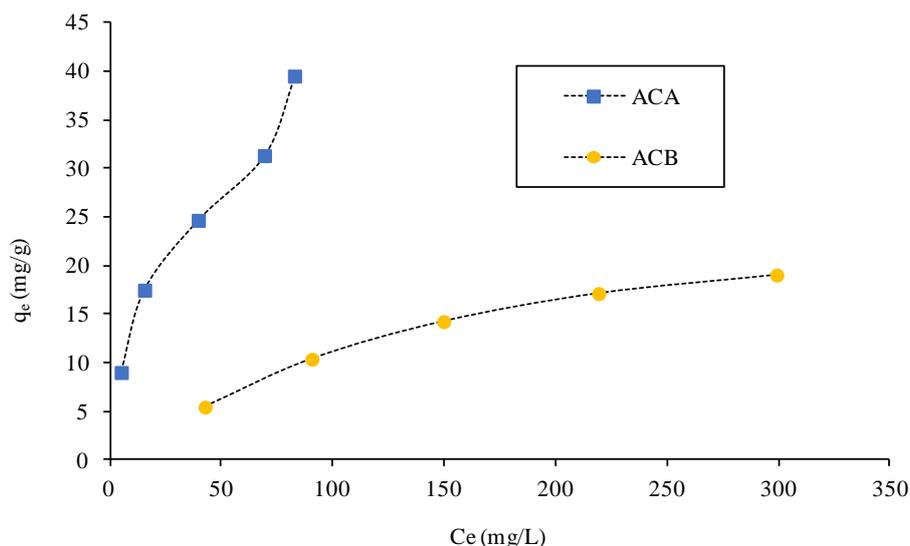


Fig. 1: Equilibrium isotherms (25°C).

Evaluated model parameters are displayed on Table 1. An evaluation of both R^2 and RMS values show that phenol adsorption was better described by the Freundlich model, in the case of ACA, suggesting heterogeneous and multilayer adsorption given the change in slope in the ACA equilibrium isotherm. This model was also the one that provided the best description for phenol removal by zeolites [16]. In the case of ACB, however, Temkin and Langmuir models provided a better fit, pointing towards homogeneous adsorption. In a previous study [17] with other types of residues treated with NaOH, we also observed a better fit of Langmuir model for adsorbents based on spent coffee grounds and coffee husks, indicating an adsorption behaviour typical of microporous materials and consistent with the basic treatment.

A comparison of the maximum adsorption capacities of the prepared adsorbents with literature data is shown in Table 2, indicating that the prepared ACs are adequate for phenol removal, given that they presented adsorption capacities similar or even higher than those of commercial ACs and of other residue-based adsorbents submitted to thermo-chemical activation. Notice that, in general, H_3PO_4 was a better activating agent in comparison to NaOH and KOH. However, NaOH was a better activating agent than H_3PO_4 for spent coffee grounds. In that study, carbonization was performed in a microwave oven, indicating

that variations in the thermal treatment (temperature, time of exposure to heat and type of heating source and mechanism) could improve the performance of the produced adsorbents.

Table 1: Equilibrium parameters for phenol adsorption.

Model	Parameter values	R ²	RMS
ACA			
Langmuir	K _L = 0.029 q _{max} = 52.3	0.9516	0.1446
Freundlich	K _F = 3.91 n = 1.94	0.9878	0.0236
Temkin	K _T = 0.43 b = 252	0.9340	0.0514
ACB			
Langmuir	K _L = 0.00559 q _{max} = 30.8	0.9970	0.0368
Freundlich	K _F = 0.78 n = 1.77	0.9780	0.0965
Temkin	K _T = 0.50 b = 350	0.9990	0.0077

Table 2: Maximum adsorption capacity for phenol.

Precursor material/activating agent	q _{max} (mg.g ⁻¹)	Reference
Corn cobs/H ₃ PO ₄	52.3	This study
Corn cobs/KOH	30.8	This study
Raphanus sativus press cake/H ₃ PO ₄	35.7	[18]
Spent coffee grounds/H ₃ PO ₄	41.8	[18]
Spent coffee grounds/NaOH	45.8	[17]
Coffee husk/NaOH	34.1	[17]
Commercial activated carbon	33.8	[19]
Rice husks/H ₃ PO ₄	22.1	[20]
Vegetable cords/NaOH	5.07	[21]

3.2. Adsorbent characterization

Fig. 2 shows the FTIR spectra of the produced adsorbents. In general, the spectra for the prepared adsorbents are similar to those reported in the literature for chemical activation of other lignocellulosic materials with H₃PO₄ and KOH [22]. Both adsorbents present a large band in the 3200–3600 cm⁻¹ range, associated to O-H stretching [22] in hydroxyl (ACB) and phenol (ACA) groups. Another common band is the one at the 1570–1580 cm⁻¹ range, attributed to C=C bonds. In the case of ACA, the bands in the 1140–1200 cm⁻¹ range are usually seen in adsorbents prepared by H₃PO₄ activation in association to stretching vibrations of P=O, P–O–C and P=OOH [11]. Interaction between adsorbent and adsorbate was evidenced by the reduction of a band at 1068 cm⁻¹, associated to C–O bonds (spectra not shown). In the case of ACB, an intense band around 1400–1300 cm⁻¹ is indicative of potassium associated to the adsorbent surface. Bands at the 600–800 cm⁻¹ range can be attributed to stretching vibrations in the aromatic ring and bands in the 750–900 cm⁻¹ range are associated to C–OH bonds in ethers.

4. Conclusions

Activated carbons were prepared by thermo-chemical treatment of corncobs using acid (H₃PO₄) and basic (KOH) activating agents for use as an adsorbent for phenol removal from aqueous solutions. The chemical functionalities at the adsorbents surfaces were successfully characterized by Fourier transform

infrared spectroscopy, allowing the phenol adsorption mechanism to be inferred. Experimental data showed that both the prepared adsorbents presented higher adsorption capacities for phenol than commercial carbons and other adsorbents prepared from agricultural residues. The acid activated carbon presented better phenol adsorption capacity than the basic one. Adsorption equilibrium models were fitted to the obtained experimental data and the Freundlich model satisfactorily described adsorption capacity for the acid activated carbon, whereas Temkin and Langmuir models better described adsorption capacity for the basic activated carbon. Results for adsorptive removal of phenol by the prepared adsorbents confirmed that waste corncobs are suitable candidates for use in the production of adsorbents.

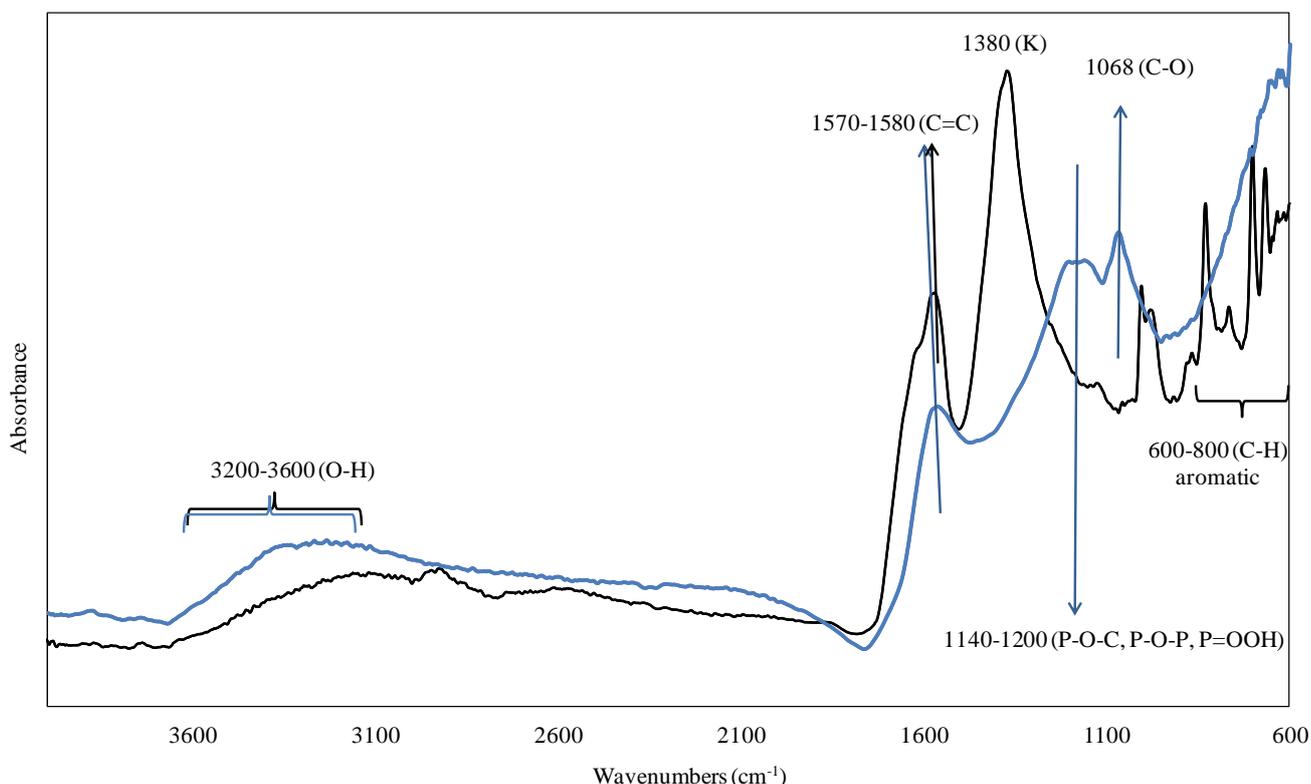


Fig. 2: FTIR spectra of the prepared adsorbents: ACA (blue solid line) and ACB (black dashed line).

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6. References

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