

# Comparison of Acid and Basic Thermo-Chemical Treatments in the Production of Adsorbents Based on Corncobs. I: Kinetics Study and Adsorbent Characterization

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**Abstract.** Corncobs were evaluated as a 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 physical characteristics and adsorption performance depending on the activating agent used. Acid activation provided an adsorbent with higher porosity and that was faster and more efficient in terms of phenol removal than that from basic activation. The pseudo second-order model, regardless of the adsorbent, satisfactorily described adsorption kinetics. Adsorption tests showed that both the prepared adsorbents presented satisfactory adsorption performance, confirming that this type of waste material is a suitable candidate for use in the production of adsorbents, with acid activation providing a more efficient adsorbent for phenol removal than basic activation.

**Keywords:** adsorption, corncobs, phenol removal.

## 1. Introduction

Phenols are known pollutants that must be monitored in the aquatic environment, because they are (i) harmful to living organisms even at low concentrations, (ii) highly soluble in water, and (iii) highly reactive and resistant to biodegradation [1]. The US Environmental Protection Agency (EPA) regulations call for lowering phenol contents in wastewater to less than 1 mg/L [2]. This substance is the base structure unit of a variety of synthetic organic compounds and thus can be present in wastewaters from several industries such as gas and coke, paper, pulp, resin, tanning, textile, plastic, rubber, pharmaceutical, petroleum and others [3].

There are many methods available for removal of phenolic compounds from wastewaters. Examples include oxidation, precipitation, ion exchange and solvent extraction [4]. Among these, adsorption using activated carbon (AC) has been shown to be quite effective, especially when such pollutants are present at low concentrations [5]. However, the widespread use of AC adsorption is still restricted due to the high cost of conventional and commercial carbons. Thus, in recent years, many studies have focused on the production of ACs using renewable and cheaper precursors, mostly industrial and agricultural by-products (lignocellulosic materials) [5]-[12]. The basic processes involved in transforming lignocellulosic or any carbon-based material into ACs can be classified into physical and chemical activation [13]. The most popular agents used in chemical activation of lignocellulosic materials are dehydrating agents such as  $H_3PO_4$  or metal hydroxides such as KOH [13].

Brazil is the third largest corn producer in the world, with a production of 55 million tons in 2012. Solid residues from corn production such as corncobs present great potential for use as raw materials in the production of adsorbents [14]-[16].

In view of the aforementioned, the objective of this study was to compare acid ( $H_3PO_4$ ) and basic (KOH) activation procedures in the production of activated carbons with corncobs being employed as raw materials.

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The study was divided into two parts. This is the first part in which we compare the prepared adsorbents in a batch kinetics study, in order to verify their performance and efficiency for phenol removal from aqueous solutions. A comparative evaluation of their physical and chemical surface characteristics is also presented.

## 2. Methodology

### 2.1. Adsorbent preparation

The corncobs were ground (particle size < 0.85 mm). 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. 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 (N<sub>2</sub> 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<sup>-1</sup> at a fixed adsorbent concentration (10 g L<sup>-1</sup>). All tests were performed in two replicates. 2 mL aliquots were taken from the Erlenmeyer flasks at pre-specified time intervals 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<sup>-1</sup>) 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

Adsorbent porosity was evaluated according to iodine number, based on the sodium thiosulfate volumetric method [17]. Surface functional groups determination was based on the Boehm titration method [18].

## 3. Results and Discussion

### 3.1. Effect of contact time

The batch adsorption data shown in Fig. 1 indicate that a contact time of 5 hours assured attainment of equilibrium conditions for initial phenol concentrations below 500 mg L<sup>-1</sup>. Adsorption can be viewed as a two-stage process, with a rapid initial adsorption, followed afterwards by a much slower rate. This is attributed to the high values of concentration gradient in the beginning of the adsorption processes, representing a significant driving force for phenol transfer between the solution and the adsorbent surface. Such qualitative behaviour has been reported for phenol removal by other types of adsorbents [19], [20]. After equilibrium was reached, ACA adsorption efficiency ranged from 95 to 85% as the initial phenol concentration was increased from 100 to 500 mg/L. The decrease in adsorption efficiency for more concentrated solutions is attributed to the smaller number of available adsorption sites in comparison to more diluted solutions. In the case of ACB, adsorption efficiency ranged from 57 to 40% as the initial phenol concentration was increased from 100 to 500 mg/L. An evaluation of the plots presented in Fig. 1 indicates that ACA provided faster and more efficient adsorption in comparison to ACB. This could be an indication that acid activation provided an adsorbent with higher porosity and a more adequate surface chemistry makeup, thus favouring adsorption both at the surface and inside the pores.

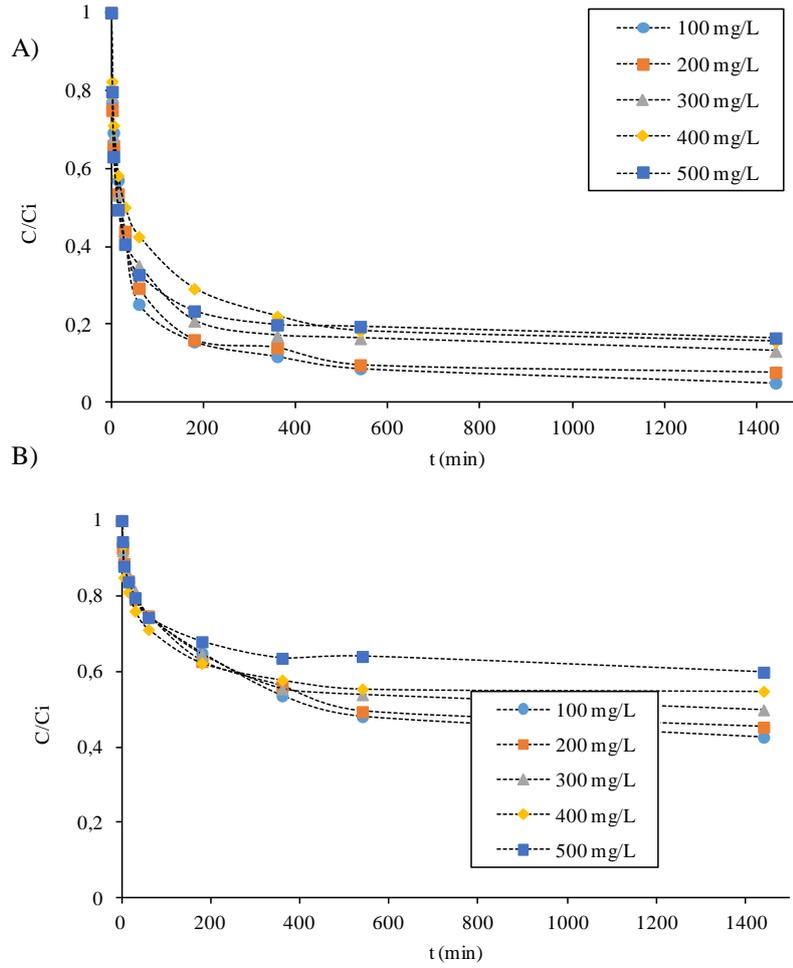


Fig. 1: Variation of phenol concentration with adsorption time for A) ACA and B) ACB.

### 3.3. Adsorption kinetics

Adsorption kinetics was investigated by fitting pseudo first- and second-order kinetic models to the experimental data generically represented by the following equation [21]:

$$\frac{dq_t}{dt} = k_n (q_e - q_t)^n \quad (2)$$

where  $q_e$  and  $q_t$  correspond to the amount adsorbed per unit mass of adsorbent ( $\text{mg g}^{-1}$ ) at equilibrium and at time  $t$ , respectively,  $k_n$  corresponds to the rate constant for  $n^{\text{th}}$  order adsorption. The integrated forms of the equations are:

First-order kinetics ( $n=1$ ):

$$q_t = q_e (1 - e^{-k_1 t}) \quad (3)$$

Second-order kinetics ( $n=2$ ):

$$q_t = \frac{k_2 q_e^2}{1 + k_2 q_e t} \quad (4)$$

Evaluation of each model's ability to predict the experimental data was based on both regression correlation coefficient values ( $r^2$ ) and difference between experimental ( $q_{t,exp}$ ) and model-estimated ( $q_{t,est}$ ) values, evaluated by means of the error measure:

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

where  $N$  is the number of experimental points in each  $q_t$  vs.  $t$  curve.

Results for the non-linear fits of the kinetic models and their estimates for equilibrium adsorption capacity are shown in Table 1. The pseudo-second order model provided higher  $r^2$  values and lower values of

RMS error in comparison to the pseudo-first order model, thus being considered more adequate for description of the adsorption data, for both ACA and ACB. This model has been successfully applied for description of adsorption kinetics of several adsorbates, in association with both chemisorption and ion exchange mechanisms [21]. It was also the more adequate model for description of removal of phenolic aminoacids for adsorbents based on the same residue [15]-[22]. Although the first order model did not provide a good fit, a comparative analysis of  $k_1$  values obtained for ACA and ACB confirms the faster adsorption rate of phenol by ACA (higher  $k_1$  values).

Table 1: Kinetic parameters for phenol adsorption.

	Phenol initial concentration (mg L <sup>-1</sup> )				
	100	200	300	400	500
<b>ACA</b>					
$q_e$ (experimental)	8.991	17.468	25.794	33.03	40.401
Pseudo first-order					
$k_1$ (h <sup>-1</sup> )	0.0454	0.0524	0.0401	0.0488	0.0872
$q_e$ (estimated) (mg g <sup>-1</sup> )	8.537	16.551	25.189	30.414	37.641
$r^2$	0.901	0.844	0.972	0.853	0.893
RMS	0.0827	0.0839	0.0704	0.0835	0.0536
Pseudo second-order					
$k_2$ (g mg <sup>-1</sup> h <sup>-1</sup> )	0.00862	0.00539	0.00443	0.00252	0.00348
$q_e$ (estimated) (mg g <sup>-1</sup> )	8.874	17.101	25.169	31.772	39.36
$r^2$	0.961	0.941	0.964	0.949	0.981
RMS	0.0552	0.0538	0.0399	0.0515	0.0212
<b>ACB</b>					
$q_e$ (experimental)	5.43	10.36	14.23	17.12	19.02
Pseudo first-order					
$k_1$ (h <sup>-1</sup> )	0.0144	0.0168	0.0174	0.0339	0.0275
$q_e$ (estimated) (mg g <sup>-1</sup> )	4.715	9.064	12.819	15.856	17.823
$r^2$	0.8762	0.8806	0.8863	0.8749	0.8904
RMS	0.3978	0.384	0.3834	0.3008	0.2988
Pseudo second-order					
$k_2$ (g mg <sup>-1</sup> h <sup>-1</sup> )	0.0036	0.0022	0.0017	0.0032	0.0029
$q_e$ (estimated) (mg g <sup>-1</sup> )	5.24	9.98	14.02	16.75	18.49
$r^2$	0.939	0.940	0.938	0.947	0.950
RMS	0.3263	0.3185	0.3223	0.1978	0.2019

### 3.4. Adsorbent characterization

The iodine number (IN) is a technique commonly employed to evaluate the structure of activated carbons and can be employed as an approximation for surface area and microporosity with reasonable precision [14]. The results obtained for ACA and ACB were 640 and 470 mg/g, respectively. The higher value obtained for ACA confirms that it presents higher surface area and porosity compared to ACB. These results are in agreement with the expected effects of these activating agents, given that KOH will only increase the number

of micropores while  $H_3PO_4$  should form additional micro and mesopores. Such differences are also evidenced in the adsorption performance (Fig. 1).

Table 2: Chemical characterization of the produced adsorbents based on Boehm titration.

	Acid (mmol.g <sup>-1</sup> )						Basic (mmol.g <sup>-1</sup> )	
	Phenolic		Carboxylic		Lactones			
ACA	2.9259	(38.36)	2.1232	(27.84)	2.3045	(30.22)	0.2733	(3.58)
ACB	0.7705	(16.18)	0.1102	(2.32)	0.4513	(9.48)	3.4291	(72.02)

(numbers in parenthesis refer to corresponding percentage values)

The functional groups at the surface of the adsorbent, characterized by the Boehm titration method, are presented in Table 2. As expected, ACA's surface is predominantly acid (96%) whereas ACB's surface is predominantly basic (72%). Phenol is considered as a weak acid, thus phenol adsorption should be enhanced in activated carbons with surfaces with predominantly basic functional groups [23]. However, phenol adsorption will be affected not only by the presence of surface groups but also by the porosity of the adsorbent and by the extent of graphite-type of structures in the carbon internal surfaces, because hydrophobic interactions of the  $\pi$ - $\pi$  type between the phenol molecule and this type of structure are mostly likely to occur, since they are fairly independent of the solution pH.

#### 4. Conclusions

Activated carbons were successfully prepared by thermo-chemical treatment of corncobs using acid and basic activating agents and the prepared carbons were successfully used as adsorbents for phenol removal from aqueous solutions. Adsorption tests demonstrated both the prepared adsorbents to present satisfactory performance, with the acid activated carbons presenting better adsorption performance than the basic ones. The acid activated carbon was also more porous in comparison to the basic one. Adsorption kinetics models were fitted to the obtained experimental data and the pseudo second-order model satisfactorily described adsorption kinetics, regardless of the type of adsorbent (acid or basic activated). Results for adsorptive removal of phenol by the prepared adsorbents confirmed that waste corncobs are suitable candidates for use in the production of adsorbents.

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