

# Batch and Column Studies of Phenol Adsorption by an Activated Carbon Based on Acid Treatment of Corn Cobs

Pablo D. Rocha, Adriana S. Franca, and Leandro S. Oliveira

**Abstract**—Corn cobs were evaluated as raw material in the production of an adsorbent for phenol removal from aqueous solutions. Adsorption kinetics and equilibrium were satisfactorily described by the pseudo second-order and Freundlich models, respectively. Fixed bed adsorption (breakthrough curve) was satisfactorily described by Bohart-Adams, Yoon-Nelson and Dose-Response models. Adsorption tests showed that the prepared adsorbent presented higher adsorption capacity than activated carbons produced from other agricultural residues, confirming that this type of waste material is a suitable candidate for use in the production of adsorbents.

**Index Terms**—Adsorption, agricultural residues, corn cobs, phenol removal.

## I. INTRODUCTION

Phenols are considered to be priority pollutants, because they are harmful to living organisms even at low concentrations due to their toxicity and carcinogenicity properties [1]. Also, the appreciable solubility of this compound in water, combined with its high reactivity and resistance to biodegradation, make it an important toxic material to be monitored in the aquatic environment. The US Environmental Protection Agency (EPA) regulations call for lowering phenol content in wastewater to less than 1 mg/L [2].

Industrial wastes and agricultural by-products are classes of materials evaluated as promising precursors for the production of low-cost adsorbents, because they are renewable, locally available in large quantities and inexpensive [3]. 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 corn cobs present great potential for use as raw materials in the production of adsorbents [4]-[6].

Wastewater treatment by adsorption using activated carbons (AC) is quite very effective and has been cited by EPA as being one of the best available environmental control technologies [7]. However, the widespread use of AC adsorption is still restricted because of the high costs of commercial carbons. Thus, many recent studies have focused on the use of renewable and cheaper precursors, mainly agricultural wastes and by-products, as raw materials in the

production of activated carbons [3], [8].

The basic processes of turning lignocelluloses materials (e.g. agricultural wastes and by-products) into an activated carbon can be divided into physical or chemical activation. Physical activation consists of heat treatment of the material in a stream of gases, usually carried out in a two-step process: i) carbonization in an inert atmosphere to produce the charcoal, followed by ii) activation or a second heat treatment in the presence of CO<sub>2</sub> or steam to increase the porosity of the material [9]. Chemical activation is carried out by means of the impregnation of the carbon structure with an activating agent (either an acid or base) followed by heat treatment, so both the carbonization and activation steps are carried out simultaneously. This process is considered to be more advantageous in comparison to physical activation, because usually occurs at lower temperatures, leads to higher carbon yields, and allows better control of the development of microporosity.

Acidactivation is generally employed in order to oxidize the porous carbon surface. It increases the acidic characteristic, removes the mineral elements and improves the hydrophilic nature of surface [10]. Previous studies have shown that activation of lignocellulosic residues such as rice husks and cherry stones with phosphoric acid provides effective adsorbents for phenol removal [11], [12]. Thus, the objective of this study was to evaluate the potential of acid activated corn cobs as adsorbents. Given that adsorption processes for purification of wastewaters can be carried out either discontinuously, in batch reactors, or continuously, in fixed-bed columns, the performance of the adsorbent was evaluated in both batch and column tests.

## II. METHODOLOGY

### A. Adsorbent Preparation

The corn cobs were ground (particle size < 0.85mm), treated with phosphoric acid 85% (1:1 mL acid/g material) and submitted to 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. The solids were dried at 110 °C for 12 h and ground to particle diameters ranging from 0.15 to 0.43 mm.

### B. 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 concentrations 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

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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  $C$  ( $\text{mg} \cdot \text{L}^{-1}$ ) 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.

Continuous flow adsorption experiments were conducted in a cylindrical stainless steel column (2.5 cm internal diameter and 10 cm height). At the bottom of the column, a 0.5 mm stainless steel sieve was attached followed by glass wool. Known quantities of adsorbent (12 g) were placed into the column, yielding bed heights of 5 cm. Phenol solutions of known concentrations were pumped downward through the column bed. Samples were collected at the column outlet at different time intervals and were analyzed for phenol concentration by a UV-Vis spectrophotometer (Hitachi U-2010) at 269 nm. The inlet concentration was varied from 200 to 500 mg/L and the flow rate was varied from 18 to 33 mL/min at a fixed inlet concentration (500 mg/L).

### III. RESULTS AND DISCUSSION

#### A. Effect of Contact Time

The batch adsorption data shown in Fig. 1 indicate that a contact time of 6 hours assured attainment of equilibrium conditions for initial phenol concentrations below 500  $\text{mg} \cdot \text{L}^{-1}$ . 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 behavior was also observed for phenol removal by other types of adsorbents [13], [14].

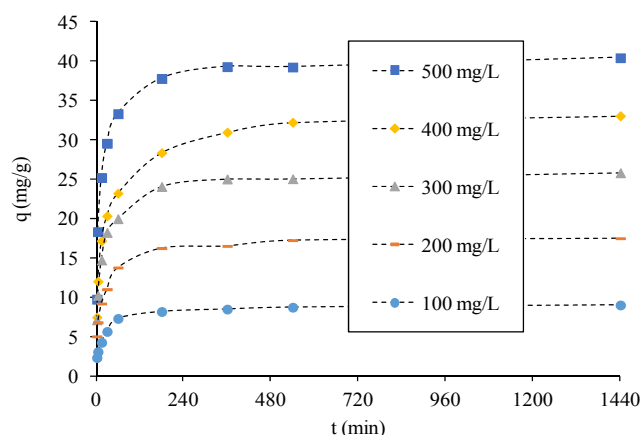


Fig. 1. Adsorption capacity vs. time for different values of initial phenol concentration.

#### B. Adsorption Kinetics

The controlling mechanisms of the adsorption processes are usually investigated by fitting pseudo first and

second-order kinetic models to the experimental data [15] generically represented by the following equation:

$$\frac{dq_t}{dt} = k_n (q_e - q_t)^n \quad (1)$$

where  $q_e$  and  $q_t$  correspond to the amount adsorbed per unit mass of adsorbent ( $\text{mg} \cdot \text{g}^{-1}$ ) 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 ( $n=1$ ):

$$q_t = q_e (1 - e^{-k_1 t}) \quad (2)$$

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

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (3)$$

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:

$$RMS(\%) = 100 \sqrt{\sum \left[ \frac{(q_{t,est} - q_{t,exp})}{q_{t,exp}} \right]^2} / N \quad (4)$$

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 I. 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 all evaluated temperatures. This model has been successfully applied for description of adsorption kinetics of several adsorbates, describing both chemisorption and ion exchange [15]. It was also the more adequate model for description of removal of phenolic aminoacids for adsorbents based on the same residue [5], [16] and also for phenol removal by other types of adsorbents such as zeolites [1] and activated carbon based on tobacco leaves [17].

The effect of diffusion as the rate controlling step in the adsorption was evaluated according to the intra-particle diffusion model [18]:

$$q_t = k_p t^{1/2} + C \quad (5)$$

where  $k_p$  is the intra-particle diffusion rate constant, evaluated as the slope of the linear portion of the curve  $q_t$  vs.  $t^{1/2}$ . Results are displayed in Fig. 2. In theory, the intra-particle diffusion plots can present up to four linear regions, representing boundary-layer diffusion, followed by intraparticle diffusion in macro, meso, and micro pores. These four regions should then be followed by a horizontal line representing the system at equilibrium [16]. The plots presented in Fig. 2 show two regions followed by a plateau for more diluted solutions, indicating that boundary-layer

diffusion seems to be the rate-controlling step. However, for more concentrated solutions ( $C_i > 300 \text{ mg L}^{-1}$ ) we can observe three regions, with the first line crossing the origin, thus indicating that pore diffusion is becoming more important.

TABLE I: KINETIC PARAMETERS FOR PHENOL ADSORPTION.

	Phenol initial concentration ( $\text{mg L}^{-1}$ )				
	100	200	300	400	500
$q_e$ (experimental)	8.991	17.468	25.794	33.03	40.401
Pseudo first-order					
$k_1$ ( $\text{h}^{-1}$ )	0.0454	0.0524	0.0401	0.0488	0.0872
$q_e$ (estimated) ( $\text{mg g}^{-1}$ )	8.537	16.551	25.189	30.414	37.641
$r^2$	0.901	0.844	0.972	0.853	0.893
RMS (%)	8.271	8.39	7.0422	8.345	5.358
Pseudo second-order					
$k_2$ ( $\text{g mg}^{-1}\text{h}^{-1}$ )	0.00862	0.00539	0.00443	0.00252	0.00348
$q_e$ (estimated) ( $\text{mg g}^{-1}$ )	8.874	17.101	25.169	31.772	39.36
$r^2$	0.961	0.941	0.964	0.949	0.981
RMS (%)	5.516	5.375	3.988	5.147	2.121

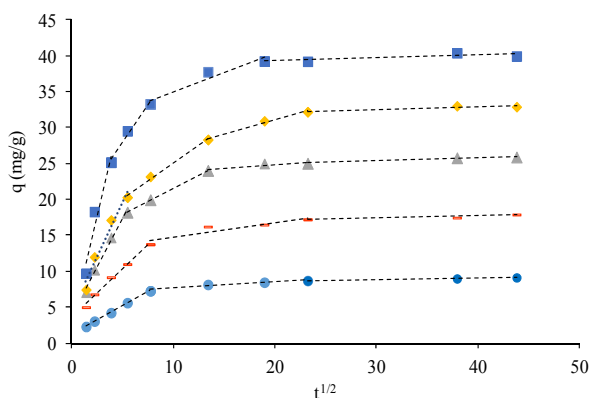


Fig. 2. Fitting of intra-particle diffusion model for phenol adsorption.

### C. Adsorption Equilibrium

The adsorption isotherm is presented in Fig. 3. The shape of the curve indicates favorable adsorption. Although there are many models for description of adsorption isotherms in the literature, the most widely employed are Freundlich and Langmuir. Freundlich's equation is an empirical model that does not account for adsorbent saturation and has been associated to both heterogeneous and multilayer adsorption, being described by the following equation:

$$q_e = K_F C_e^{1/n} \quad (6)$$

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. Langmuir isotherm, on the other hand, is based on a theoretical model assuming monolayer adsorption over an energetically and structurally homogeneous adsorbent surface and takes into account adsorbent saturation, being represented by the following equation:

$$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e} \quad (7)$$

where  $q_e$  ( $\text{mg g}^{-1}$ ) and  $C_e$  ( $\text{mg L}^{-1}$ ) correspond to the amount adsorbed per gram of adsorbent and to the solute

concentration ( $\text{mg L}^{-1}$ ) in the aqueous solution, respectively, after equilibrium was reached.  $q_{max}$  and  $K_L$  are constants related to the maximum adsorption capacity ( $\text{mg g}^{-1}$ ) and the adsorption energy ( $\text{L mg}^{-1}$ ), respectively.

Model selection 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:

$$RMS_e = \sqrt{\sum [(q_{e,est} - q_{e,exp}) / q_{e,exp}]^2 / N} \quad (8)$$

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. Evaluated model parameters are displayed on Table II. An evaluation of both  $R^2$  and  $RM S_e$  values show that phenol adsorption was better described by the Freundlich model, indicating heterogeneous and multilayer adsorption. This model was also the one that provided the best description for phenol removal by zeolites [1].

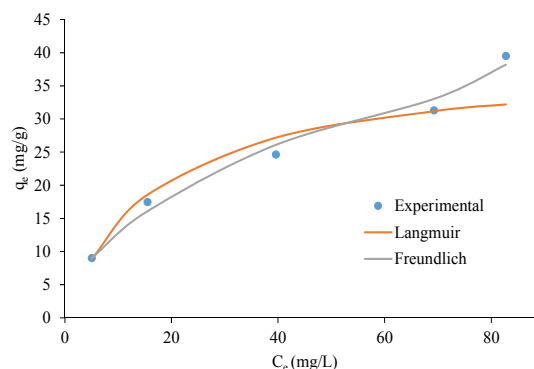


Fig. 3. Equilibrium isotherm (25°C).

TABLE II: EQUILIBRIUM PARAMETERS FOR PHENOL ADSORPTION.

Model	Parameter values	$R^2$	RMS
Langmuir	$K_L = 0.029$ $q_{max} = 52.3$	0.9516	0.1446
Freundlich	$K_F = 3.91$ $n = 1.94$	0.9878	0.0616

### D. Column Studies

The effects of adsorbate solution inlet concentrations on a fixed bed of adsorbents are presented in the breakthrough curves depicted in Fig. 4. Notice from Fig. 4 that the breakthrough curves somewhat follow the ideal "S" shape profile that is characteristic of adsorbates of small molecular sizes and also of adsorbents comprised of small sized particles [19].

An increase in the inlet concentration (Fig. 4a) lead to a shortening of both the breakthrough time and the bed service time, i.e., the adsorbent was more quickly saturated. The increase in inlet adsorbate concentration also led to a steepening of the slope of the breakthrough curve or a shortening of the mass transfer zone. This is attributed to a higher concentration gradient causing a faster transport and more effective intra-particle diffusion [19]. This corroborates the batch results for intra-particle diffusion models, confirming the increased effect of pore diffusion for more concentrated solutions.

The effects observed on the breakthrough behavior when varying the adsorbate solution flow rate (Fig. 4b)) were a decrease in both the volume treated and the breakthrough time as the flow rate was increased. The breakthrough occurred faster at higher flow rates and, thus, the bed service time was shortened. The breakthrough curve became steeper when the flow rate was increased, i.e., the mass transfer zone was shortened, indicating more effective intra-particle diffusion effects [20]. Other studies on fixed bed adsorption

[21] have reported that an increase of the flow rate beyond a certain value will cause the rate of adsorption to decrease because of the decrease in the residence time of the adsorbate in the column. Even though the flow rate in this work has not been increased beyond such value, it is clearly seen from Fig. 4(b) that increasing the flow rate above 33 mL/min would probably not improve the adsorption performance, given that there was not much difference between the breakthrough curves for 25.6 and 33.0 mL/min.

TABLE III: BOHART-ADAMS, YOON-NELSON, AND DOSE-RESPONSE MODEL PARAMETERS AT DIFFERENT ADSORBATE SOLUTION INLET CONCENTRATIONS AND FLOW RATES

Model		$C_i$ (mg/L)				$Q$ (mL/min)		
		200	300	400	500	18.3	25.6	33.0
Bohart-Adams	$K_{BA} \times 10^4$ (L mg <sup>-1</sup> min <sup>-1</sup> )	1.8	1.6	1.57	1.35	1.57	1.35	1.57
	$q_0$ (mg g <sup>-1</sup> )	52.79	63.31	67.48	68.00	37.49	52.48	67.47
	$R^2$	0.9880	0.9970	0.9950	0.9780	0.9935	0.9941	0.9946
Yoon-Nelson	$K_{YN}$ (min <sup>-1</sup> )	0.036	0.0492	0.0544	0.08	0.028	0.046	0.0544
	$q_0$ (mg g <sup>-1</sup> )	52.30	62.87	66.73	67.64	37.07	51.90	66.73
	$t_{50}$ (min)	95.2	78.7	60.3	45.8	114.5	65.9	60.3
	$R^2$	0.9999	0.9998	0.9998	1	0.9935	0.9941	0.9946
Dose-Response	$a$ (-)	2.541	3.0442	2.498	2.54	3.549	2.4984	1.86
	$q_0$ (mg g <sup>-1</sup> )	45.772	57.828	60.95115	61.2549	32.1264	44.977	60.9515
	$R^2$	0.9979	0.9963	0.9982	0.993	0.9795	0.9896	0.9879
Experimental	$q_0$ (mg g <sup>-1</sup> )	47.7472	59.3406	61.7785	64.4230	35.980	47.275	63.218
	$t_{50}$ (min)	86.9	72.0	55.8	46.9	104.5	54.9	57.1

Bohart-Adams, Yoon-Nelson and Dose-Response breakthrough models were fitted to the experimental data and their respective parameters were estimated using nonlinear (Statistica 8.0 program) regressions. Details on estimated models kinetic parameters and the adsorption capacity are presented in Table III together with the respective experimentally determined values.

Bohart-Adams model [22] is based on the assumption that the adsorption rate is proportional to both the residual capacity of the solid and the concentration of the adsorbing species, and can be represented by:

$$\frac{C}{C_i} = \frac{\exp(K_{BA} C_i t)}{\exp(K_{BA} C_i t) + \exp(K_{BA} N_o z / U_o) - 1} \quad (9)$$

$$q_0 = N_o z S / m \quad (10)$$

$$\frac{C}{C_i} = \frac{1}{1 + \exp[k_{YN} (t_{50} - t)]} \quad (11)$$

$$q_0 = \frac{C_i Q t_{50}}{m} \quad (12)$$

where  $C$  (mg L<sup>-1</sup>) is the adsorbate concentration in the fluid at the column outlet at time  $t$  (s),  $C_i$  (mg L<sup>-1</sup>) is the adsorbate concentration in the fluid at the inlet of the column,  $N_o$  (mg L<sup>-1</sup>) is the sorption capacity per unit volume of fixed bed,  $z$  (cm) corresponds to bed depth,  $U_o$  (cm min<sup>-1</sup>) is the superficial velocity,  $S$  (cm<sup>2</sup>) is the bed cross section area,  $m$  (g) is the adsorbent mass and  $q_0$  is the adsorption capacity.

Yoon and Nelson's model [23] considers that the probability of adsorption for each adsorbate molecule decreases at a rate that is proportional to both the adsorbate adsorption and adsorbate breakthrough probabilities. It can

be represented by:

where  $t_{50}$  is the time required for 50% breakthrough and  $Q$  (L min<sup>-1</sup>) is the volumetric flow rate through the column.

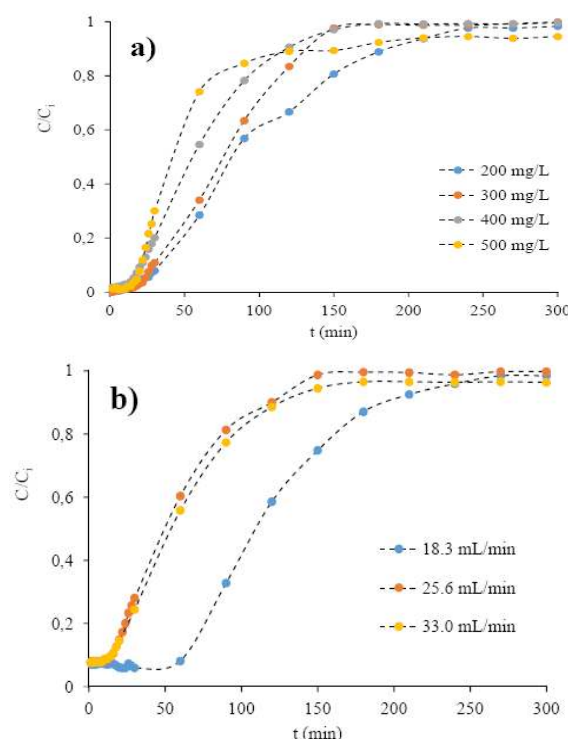


Fig. 4. Experimental breakthrough curves for the produced adsorbent at different values of a) inlet phenol concentration and b) flow rate.

The Dose response model was proposed for the description of heavy metal biosorption in columns [24]. It can be represented by the following equations:

$$\frac{C}{C_i} = 1 - \frac{1}{1 + (Qt/b)^2} \quad (13)$$

$$q_0 = \frac{C_i b}{m} \quad (14)$$

As seen from the data presented in Table III, the rate constant ( $k_{BA}$ ) estimated from the nonlinear fitting of Bohart-Adams model decreased slightly with an increase in adsorbate inlet concentration, and did not vary significantly with flow rate. The opposite behavior was observed for the rate constants of the Yoon-Nelson model, that increased with increases in inlet concentration and flow rates. All models presented satisfactory fits to the experimental data, both in terms of  $r^2$  values and estimation of adsorption capacity.

The adsorption capacity for the prepared adsorbents, ranging from 36 to 64 mg/L can be considered significant when compared to fixed bed capacity data for other low-cost adsorbents such as sugarcane bagasse, ~12 mg/L [25], pinus bark, ~0.4 mg/L [26], as well as adsorbents produced by phosphoric acid activation of other residues such as spent coffee grounds and Raphanussativus press cake, ~28-34 mg/L [27]. Column adsorption capacity was higher in comparison to batch systems under the same initial phenol concentration, 39.5 mg/g. The lack of correspondence between batch and column data is usually attributed to the fact that (i) adsorption in fixed-bed columns does not necessarily operate under equilibrium conditions since the contact time is not sufficiently long for the attainment of equilibrium; (ii) granular adsorbents rarely become totally exhausted in commercial processes, and (iii) chemical or biological changes that occur in the adsorbent cannot be predicted by the isotherms [28].

#### IV. CONCLUSIONS

Experiments were conducted to investigate the potential of acid activated corn cobs, as adsorbents for phenol removal. Equilibrium data demonstrated favorable adsorption. Fixed-bed breakthrough curves presented the "S" profile characteristic of adsorbates of small molecular sizes and also of adsorbents comprised of relatively small sized particles. Breakthrough models fitted well to the experimental data with the Dose-response model presenting a better fit than the others. The maximum value of uptake capacity for this system was higher in comparison to adsorbents obtained by thermal and/or chemical treatment of other residues, confirming the adsorption potential of the material.

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