Comparative Evaluation of Activated Carbons Prepared by Thermo-Chemical Activation of Lignocellulosic Residues in Fixed Bed Column Studies

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Abstract—**This paper presents a comparative evaluation of two activated carbons produced from different lignocellulosic residues (spent coffee grounds and *Raphanus Sativus* press cake), as adsorbents for removal of phenol from aqueous solutions in fixed-bed column studies. Both the prepared adsorbents presented outstanding adsorption capacities when compared to other low-cost adsorbents presented in the literature. Breakthrough curves were produced and several breakthrough models were evaluated for adequate description of the adsorption process in the column, with the Dose-Response model presenting the best fit to the experimental data.**

Index Terms—**Adsorption, agricultural residues, fixed bed, phenol removal.**

I. INTRODUCTION

Agricultural by-products and wastes are materials that are being evaluated as promising precursors for the production of low-cost activated carbons, given that they are renewable, locally available in large quantities and inexpensive [1]. Coffee is the most important agricultural product in Brazil, and this crop generates large amounts of solid residues, including spent coffee grounds (SC) [2]. Recent studies have demonstrated the potential of non-edible oils for biodiesel production, employing *Raphanussativus L.* seeds (RS) [3]. However, thisprocess generates an extensive amount of solid residues, e.g., pressed seed cakes. Both the previously mentioned solid residues present environmental problems in terms of adequate disposal, given their limited applications as animal feed, silage or energy source, thus reinforcing the need for alternative uses [2].

Phenol is the base structure unit of a variety of synthetic organic compounds. It usually enters water sources from various chemicals, pesticides, paper, pulp and dye manufacturing industries, wastewaters from industries such as gas, resin, tanning, textile, plastic, rubber, pharmaceutical and petroleum [4]. The appreciable solubility of this compound in water, combined with its high reactivity and resistance to biodegradation, make it an important toxic material listed as a priority pollutant to be monitored in the aquatic environment [5]. Adsorption using activated carbon (AC) has proved to be very effective in treating effluents and has been cited by the United States Environmental Protect Agency (EPA) as being one of the best available environmental control technologies [6]. However, the widespread use of AC adsorption is restricted because of the high cost of conventional and commercial carbons. Therefore, in recent years, many researchers have tried to produce ACs using renewable and cheaper precursors which are mainly industrial and agricultural by-products (lignocellulosics) [1], [7], [8].

In a previous study [1] we evaluated the aforementioned lignocellulosic residues, spent coffee grounds and *Raphanussativus L.* seeds pressed cake, in the preparation of activated carbons by thermo-chemical activation. The produced ACspresented adsorption capacities that were similar or even higher than those of commercial ACs and other residue-based adsorbents, and were found to be adequate for phenol removal in batch studies. However, 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 adsorbents was herein further evaluated in column tests.

II. METHODOLOGY

A. Adsorbent Preparation

The raw materials were treated with phosphoric acid 85% (1.7 mL acid/g material) and submitted to 2 h carbonization in a muffle oven at 500 ℃. Afterwards, the produced adsorbents were washed until pH 7 to remove the excess acid. The solids were dried at 110 ℃ for 12 h and ground to particle diameters ranging grom 0.15 to 0.43 mm [1]. The produced adsorbents are denominated: SC (based on spent coffee grounds) and RS (based on Raphanus sativus press cake). The surface morphology of the samples was examined using a scanning electron microscope (JEOL JSM-5510).

B. Adsorption Tests

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 4.68 and 5.28 cm of adsorbent for SC and RC, respectively. 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 300 to 500 mg/L at a flow rate of 33.3 mL/min.

Phenol adsorption mechanism was evaluated in terms of fitting classical mathematic models. Model selection was based on highest R^2 values coupled with the lowest difference between calculated and experimental C/C_i (y) values, evaluated according to the following root mean square error measure:

$$RMS = \sqrt{\sum \left[\left(y_{,est} - y_{,exp} \right) / q_{e,exp} \right]^2 / N} \qquad (1)$$

where $y_{,exp}$ and $y_{,est}$ are the experimental and calculated equilibrium adsorbent amounts, respectively, and N corresponds to the number of experimental isotherm points.
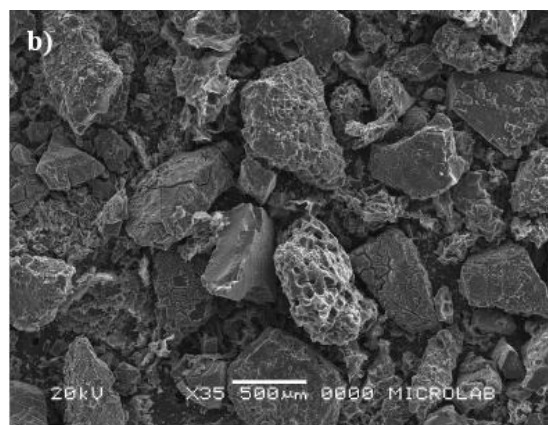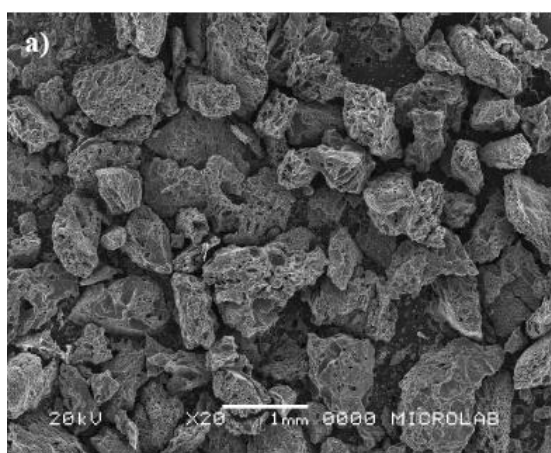

Fig. 1. Scanning electron micrograph (SEM) of activated carbons: a) SC - based on spent coffee grounds and b) RC - based on raphanussativus pressed cake.

III. RESULTS AND DISCUSSION

A. Adsorbent Characterization

SEM images of the prepared activated carbons are shown in Fig. 1. It can be seen from the micrographs that the produced adsorbents present different pore sizes, and it seems that RS is more microporous. These results are in agreement with iodine number results from our previous study [1]. The iodine number (IN) can be directly correlated to the

micropore volume, since the micropores are accessed preferentially by the iodine molecules due to their size. IN values were 25% higher for RS in comparison to SC [1].

B. Adsorption Tests

The effects of adsorb ate solution inlet concentrations on a fixed bed of adsorbents are presented in the breakthrough curves depicted in Fig. 2. Notice from Fig. 2 that the breakthrough curves do not follow the ideal "S" shape profile that is characteristic of adsorb ates of small molecular sizes and also of adsorbents comprised of relatively small sized particles. Phenol is a substance considered of small molecular size when compared to other common pollutants that are commonly removed from aqueous solutions by adsorption onto activated carbon-type of materials. Thus, the explanation for the deviation from the ideal "S" shape profile in this case can be attributed both to the adsorbents particle sizes and to their respective texture characteristics (e.g., pore size). The intrinsic low porosity of the adsorbent particles seems to be introducing a rather high resistance to the adsorb ateintraparticle diffusion, which, in turn, allows for axial dispersion to dominate the process. Not only it explains the deviation from the S-shaped profile, but also explains the rather short breakthrough times and rather steep mass transfer zones of the breakthrough curves for both the Sc and RC adsorbents. Notice that an increase in the inlet adsorb ate concentration did not significantly affect the breakthrough times. However, as expected, the slope of the mass transfer zone became steeper and the bed service time shortened with an increase in inlet concentration [9], [10].
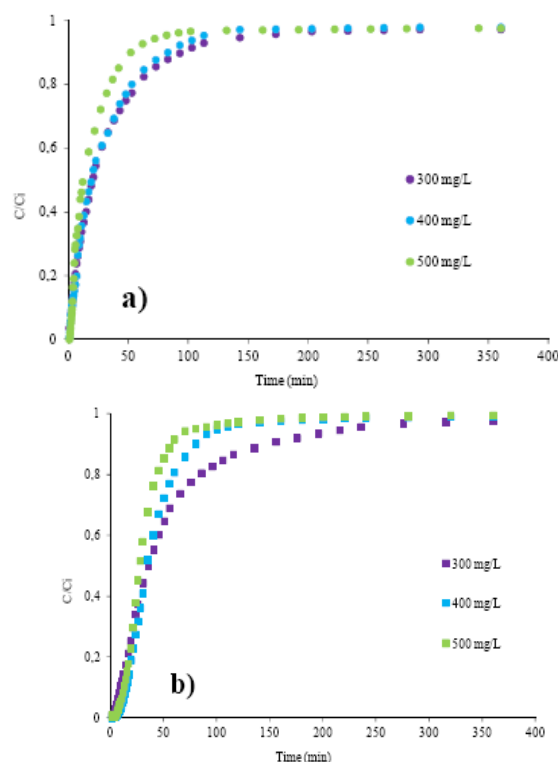

Fig. 2. Experimental breakthrough curves for the produced adsorbents at different values of inlet flow concentrations: a) SC - based on spent coffee grounds and b) RC - based on *Raphanussativus*pressed cake.

The differences in the curves in Fig. 2(a) and 2(b), not only can be explained by the differences in textural properties of

the adsorbents and their respective beds (porosities of 0.39 and 0.44 for the SC and RC beds, respectively), but also by the difference in bed heights. Lower bed heights promote faster breakthrough times and steeper mass transfer zones, as it is clearly seen when the curves for the SC adsorbent are compared to those for the RC adsorbent, with the latter presenting a slightly deeper bed. Lower bed porosities will lead to higher resistance to antiparticle diffusion with consequent higher axial dispersion and faster breakthrough times.

Bohart-Adams, Yoon-Nelson, Thomas 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 I together with the respective experimentally determined values.

Bohart-Adams model [11] assumes that the adsorption rate is proportional to both the residual capacity of the solid and the concentration of the adsorbing species. It can be represented by the following equations:

$$\frac{C}{C_i} = \frac{exp(K_{BA}C_i t)}{exp(K_{BA}C_i t) + exp(K_{BA}N_o z / U_o) - 1} \quad (2)$$

$$q_0 = N_0 z S / m$$

$$\frac{C}{C_i} = 1 - \frac{1}{1 + (Qt/b)^a} \quad (3)$$

$$q_0 = \frac{C_i b}{m}$$

where C (mg L^{-1}) is the adsorbate concentration in the fluid at the column outlet at time $t(s)$, C_i (mg L^{-1}) is the adsorbate concentration in the fluid at the inlet of the column, N_o (mg L^{-1}) is the sorption capacity per unit volume of fixed bed, z (cm) corresponds to bed depth, U_o (cm min^{-1}) is the superficial velocity, S (cm^2) is the bed cross section area, m (g) is the adsorbent mass and q$_0$ is the adsorption capacity. As seen from the data presented in Table I, the rate constant (k_{BA}) estimated from the nonlinear fitting of Bohart-Adams model does not vary significantly with variations in adsorbate inlet concentration, which means that the rate controlling mechanism is actually the adsorption kinetics rather than the mass transfer or the intraparticle diffusion. This was confirmed by the parameters obtained for both the Yoon-Nelson [12] and the Thomas [13] model fitting to the breakthrough data. These models presented the same fits, since all of them were developed under the assumption that adsorption kinetics is the controlling mechanism. Yoon and Nelson's model is based on the assumption 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 as [12]:

$$\frac{C}{C_i} = \frac{1}{1 + exp[k_{YN}(t_{50} - t)]} \quad (4)$$

$$q_0 = \frac{C_i Q t_{50}}{m} \quad (5)$$

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

Thomas´ model is frequently applied to estimate the adsorptive capacity of adsorbent and predict breakthrough curves, assuming second-order reversible reaction kinetics and Langmuir isotherm [14]. Theoretically, it is suitable to estimate the adsorption process where external and internal diffusion resistances are extremely small [15]. It can be represented by the following equation:

$$\frac{C}{C_i} = \frac{1}{(1 + exp[(K_T/Q).(q_o.m - C_i.V_{ef})])} \quad (6)$$

where V_{ef} (L) is the volume of the effluent. According to the RMS values, it was observed that RC presented the best fits, which may be an indication that the chemical interactions in SC were more pronounced when compared to RS. Similar results were also found in batch experiments. The best fits for the RC adsorbent also corroborates the experimental observations that axial dispersion is less pronounced in that case when compared to the results for the SC adsorbent.

The best fit to the experimental data was presented by the Dose-Response model. This model was proposed for the description of heavy metal biosorption in columns [16]. It is has been recently employed in other studies and it is referred as being commonly used to describe different processes in pharmacology. It can be represented by the following equations:

$$\frac{C}{C_i} = 1 - \frac{1}{1 + (Qt/b)^a} \quad (7)$$

$$q_0 = \frac{C_i b}{m} \quad (8)$$

Yan and his co-workers [16] observed that use of this model minimizes the error resulting from the use of the Thomas model, especially at lower or higher time periods of the breakthrough curve. However, the parameters in this model have no physical significance and hence cannot be evaluated accordingly.

The experimental fixed-bed adsorption capacities are presented in Table II, together with data for other adsorbents from the literature. The experimental fixed-bed adsorption capacities ($q_{0, exp}$) were calculated according to equations:

$$q_{o,exp} = \frac{BC}{m} \quad (9)$$

$$BC = Q \int_0^T (C_i - C) dt \quad (10)$$

where BC is the bed capacity and represents the area below the breakthrough curve (mg), G is the solution rate (L/min), C_i and C are the inlet phenol concentration and outlet phenol

concentration (mg/L) at time t, respectively, and T is the actual time required for full bed exhaustion.

TABLE I: Bohart-Adams, Yoon-Nelson, Thomas and Dose-Response Model Parameters at Different Adsorbate Solution Inlet Concentrations

Model	Parameters	C_i (mg L^{-1}) [Q = 33.3 mL min^{-1}]					
		300		400		500	
		SC	RS	SC	RS	SC	RS
Bohart-Adams	$K_{BA} \times 10^5$ (L mg^{-1} min^{-1})	23.504	19.929	19.192	22.997	20.892	25.297
	q_0 (mg g^{-1})	22.457	31.215	28.172	36.670	30.763	35.571
	R^2	0.954	0.960	0.958	0.989	0.977	0.993
	RMS	0.083	0.343	0.242	0.586	0.151	0.268
Yoon-Nelson	K_{YN} (min^{-1})	0.070	0.060	0.077	0.092	0.129	0.125
	q_0 (mg g^{-1})	20.376	33.778	25.737	40.629	29.139	39.510
	t_{50} (min)	24.698	40.943	23.397	36.935	21.192	28.735
	R^2	0.954	0.960	0.956	0.989	0.977	0.993
	RMS	0.161	0.506	0.438	0.957	0.306	0.472
Thomas	$K_T \times 10^5$ (min^{-1})	23.717	19.891	18.201	22.866	20.465	24.919
	q_0 (mg g^{-1})	20.564	34.083	25.971	40.997	29.030	39.869
	R^2	0.954	0.960	0.956	0.990	0.977	0.993
	RMS	0.164	0.517	0.444	0.985	0.311	0.487
Dose-Response	a (-)	1.197	1.670	1.269	2.613	1.580	2.930
	b (L)	0.614	1.176	0.589	1.144	0.583	0.909
	q_0 (mg g^{-1})	15.371	29.416	19.652	38.140	24.325	37.885
	R^2	0.997	0.999	0.996	0.999	0.995	0.999
	RMS	0.022	0.026	0.024	0.036	0.050	0.043
Experimental	q_0 (mg g^{-1})	16.611	18.435	22.544	31.550	26.269	34.675

TABLE II: Experimental Fixed-Bed Adsorption Capacities ($Q_{0,EXP}$) for Phenol Removal by Adsorbents Based on Agricultural Residues

Precursor material	m (g)	C_0 (mg/L)	Q (mL/min)	$q_{0,exp}$ (mg/g)	Ref.
Spent coffee grounds	12	500	33.3	27.65	This study
Raphanussativus	12	500	33.3	34.67	This study
Sugarcane bagasse	5	20	33.3	12.02	[17]
Sugarcane bagasse	10	20	33.3	12.34	[17]
Pinuspinaster bark	16	100	30.0	0.38	[18]

The adsorption capacity for the activated carbons (SC and RS), in fixed bed adsorption process, can be considered significant when compared to capacity data for other low-cost adsorbents. Column adsorption capacity was lower in comparison to batch systems under the same initial phenol concentration, 40.1 and 39.7 mg/g for SC and RC, reespectively [1]. The lower adsorption capacities observed in fixed bed systems in comparison to batch systems is usually attributed to the fact that the influent continuously meets a fresh part of adsorbent when it passes through the column and tends to establish a new equilibrium of adsorption, which is never attained, because the contact time in column systems is limited, thus reducing the adsorption capacity of adsorbents [19]. Also, a comparison between the experimentaly determined capacities and those calculated for each model demonstrates that the models consistently overestimated the fixed-bed adsorption capacities for both adsorbents, with the exception of the Dose-Response model fit of SC data. This can be explained by the fact that the assumptions made in the development of the models regarding adsorption mechanisms do not necessarily represent the actual mechanisms occurring during the experiments.

IV. Conclusions

Fixed-bed column adsorption studies were conducted for the removal of phenol from aqueous solutions, using activated carbons prepared from spent coffee grounds and press-cake of Raphanussativus seeds as adsorbents. Both carbons were demonstrated to be adequate for such task and presented higher adsorption capacities for phenol than other low-cost adsorbents from the literature. Breakthrough models fitted well to the experimental data with the Dose-response model presenting a better fit than the others.

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