MICROWAVE ASSISTED THERMAL TREATMENT OF BIODIESEL SOLID RESIDUE (COFFEE BEANS PRESS CAKE) FOR THE PRODUCTION OF ACTIVATED CARBONS

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Abstract. *The objective of the present study was to propose an alternative use for coffee beans press cake, a solid residue from coffee oil biodiesel production, as an adsorbent for treatment of dye contaminated waters. Batch adsorption tests were performed using methylene blue (MB), with the adsorbent being obtained by carbonization of the solid residue at 300^oC during 6 min in a household microwave oven. The effects of solution pH, adsorbent dosage and contact time on MB removal were investigated. The adsorption kinetics was determined by fitting first and second-order kinetic models to the experimental data, with the second-order model providing the best description. The experimental adsorption equilibrium data were fitted to both Langmuir and Freundlich adsorption models, with Freundlich providing the best fit. Also, the activated carbon (AC) obtained by microwave activation presented a significantly higher adsorption capacity (3.5 times higher) in comparison the AC obtained by conventional activation of the same type of residue in a muffle furnace during 1 hour at 800^oC. The experimental data obtained in the present study indicated that this type of waste material is a suitable candidate for use in the production of adsorbents for removal of cationic dyes, contributing for the implementation of sustainable development in both the coffee and biodiesel production chains.*

Keywords*: microwave activation, adsorption, wastewater treatment, sustainable development.*

1. INTRODUCTION

Approximately 20% of the Brazilian coffee production consists of defective beans or low quality coffee. These defective beans are physically separated from the non defective ones prior to commercialization in international markets. However, since to coffee producers they represent an investment in growing, harvesting, and handling, these defective beans are commercialized in the internal market in Brazil, where the roasting industry uses them in blends with non defective beans. Thus, the quality of the roasted coffee consumed in Brazil is depreciated since, after separation from the exportable portion, defective beans may be representing more than 50% of the coffee consumed in Brazil. In view of this situation, several studies are currently under development in order to find an alternative use for such defective coffee beans. One of the alternatives being considered is biodiesel production, using the oil extracted from such defective coffee beans. This procedure has proven to be feasible (Oliveira et al., 2008), but it generates a solid processing residue after removal of the oil by pressing, i.e., coffee beans press cake.

A few recent studies have shown that seed press cakes can be employed as adsorbents for cationic dyes, including the ones obtained by pressing sunflower seeds (Karagöz et al. 2008), Raphanus sativus (L. Var.) oilseeds (Lázaro et al., 2008) and defective coffee beans (Nunes et al., 2008). The study by Nunes et al. (2008) demonstrated the potential of this agricultural residue for removal of methylene blue from aqueous solutions. The maximum value of adsorption capacity obtained for the AC based on defective coffee beans was quite high in comparison to other residue based activated carbons such as date pits and apricot stones (Aygun et al., 2003; Banat et al., 2003). However, the adsorption capacity was slightly low in comparison to other seed press cakes (Karagöz et al. 2008; Lázaro et al., 2008). Microwaves have been extensively employed as an alternative heating method (Franca & Oliveira, 2008) and recent studies have demonstrated that this technique can be successfully employed in the production of activated carbons (Hirata et al., 2002; Wang et al., 2005; Li et al., 2008), providing both reduction in processing time and increase in adsorption capacity. Thus, the objective of this study was to evaluate microwave thermal activation as an alternative technique for the production of adsorbents based on defective coffee press cake. The produced AC was tested for MB adsorption.

2. MATERIAL AND METHODS

2.1. Material

Defective coffee beans were acquired from Santo Antonio State Coffee (Santo Antônio do Amparo, MG, Brazil). MB stock solutions were prepared in distilled water. Working solutions (100 to 1000 mg/L) were prepared by diluting the stock solution with distilled water prior to each adsorption test.

2.2. Adsorbent preparation

Defective coffee beans were screw pressed (Ecirtec, Brazil) for oil removal. The coffee press cake (CC) was submitted to preliminary carbonization tests employing a household microwave operating at 2450MHz, based on the studies of Hirata et al. (2002). After 2 min carbonization at a constant power, the samples would burn to ashes. So, several tests were conducted at varying power levels and also employing intermittent heating. The conditions that provided homogeneous carbonization without ash formation are described as follows. The CC sample (15g) was placed in a quartz container (100mL), which was then placed inside the microwave oven. Carbonization occurred for 2 min at 800W and then intermittently in 8 intervals of 30s at 600W followed by 20s cooling. Total processing time was 8.7 min and total microwave heating time was 6 min.

2.3. Adsorption studies

Batch experiments of adsorption were performed in 250 mL Erlenmeyer flasks, with the flasks being agitated on a shaker at 100 rpm for pre-determined time intervals. In all sets of experiments, a pre-determined amount of adsorbent was thoroughly mixed with 100 mL MB solution. Effect of particle size (diameter = D) was evaluated in the following ranges: D < 0.50 mm; 0.50 mm < D < 0.84 mm; D > 0.84 mm. Effect of initial solution pH was evaluated in the range of 3 to 11 and of adsorbent concentration in the range of 5 to 50 g L^{-1} at a fixed initial dye concentration (500 mg L^{-1}). Effect of contact time was evaluated at time periods ranging from 5 min to 6 hours and initial MB concentration ranging from 100 to 1000 mg L^{-1}, employing the best values obtained for initial solution pH, particle size and adsorbent concentration. After the specified time periods, 2 mL aliquots were taken from the Erlenmeyer flasks and the dye concentration was determined by a spectrophotometer (Cole Parmer 1100 RS) at 665 nm. The amount of dye adsorbed was determined by taking the difference between the initial dye concentration and the concentration of the solution at the time of sampling. All determinations were performed in a total of three replicates per experiment.

3. RESULTS AND DISCUSSION

3.1. Adsorption parameters

Results for the effect of particle size and initial solution pH are displayed in Fig.1 (a) and (b), respectively. An evaluation of the results presented in Fig. 1(a) shows that MB uptake increased with the decrease in particle size, due to the corresponding increase in surface area. Similar results on particle size effect have been reported for other residues (Nassar et al., 1995; Banat et al. 2003) and also for the coffee press cake activated carbon (CPAC) obtained by carbonization in a muffle oven (Nunes et al., 2008). An evaluation of Fig. 1 (b) shows that no significant differences in adsorption capacity were observed after equilibrium was attained – 5h adsorption (based on the Tuckey test at 5% probability). Similar results were reported by Kavitha & Namasivayam (2007) and Nunes et al. (2008) for MB adsorption.
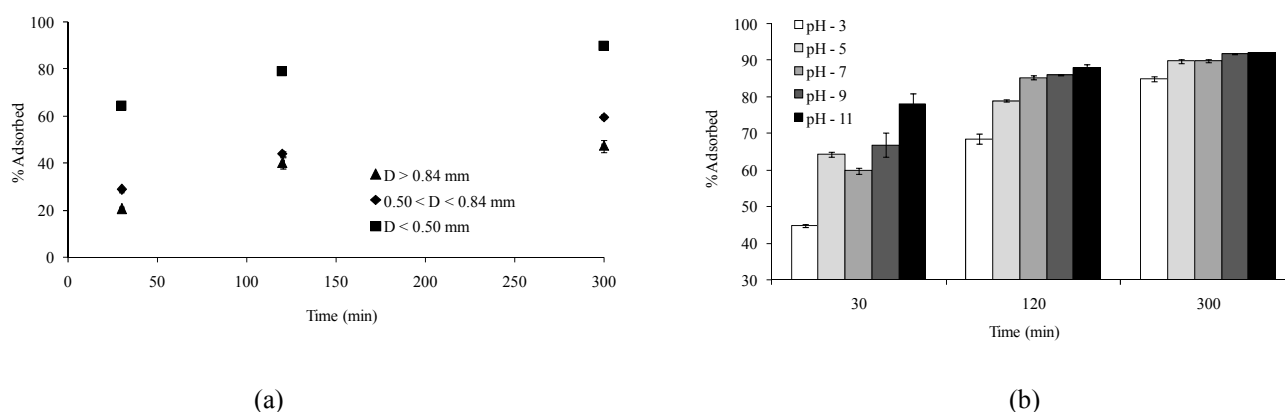

(a)   (b)

Figure 1. Effect of (a) particle size and (b) initial solution pH on MB adsorption (initial MB concentration 500 mg L^{-1}, adsorbent dosage 10 g L^{-1}).

The influence of adsorbent dosage on the efficiency of MB removal can be viewed in Fig. 2. Dye removal efficiency increased with the increase in adsorbent dosage, due to the increase in surface area resulting from the increase in adsorbent mass, and the resulting increase in number of active adsorption sites. However, the amount of dye adsorbed per unit mass of adsorbent decreased with increasing adsorbent mass, given the reduction in effective surface area.

Based on the results presented in Figs 1 and 2, the remaining experiments were conducted employing the following parameters: D < 0.50 mm, initial pH 5 and adsorbent dosage of 10 g L^{-1}.
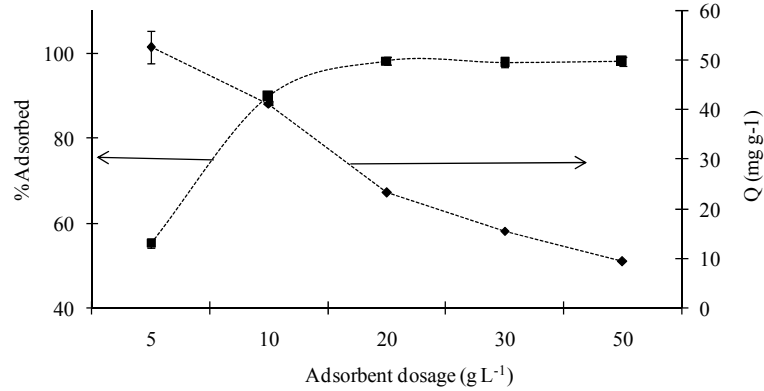

Figure 2. Effect of adsorbent dosage on MB adsorption (initial MB concentration 500 mg L^{-1}, initial pH 5).

3.2. Adsorption kinetics

The kinetics adsorption data showed that a contact time of 2 hours assured attainment of equilibrium conditions for initial dye concentrations below 400 mg L^{-1} (Fig. 3). The adsorption can be described by a two-stage kinetic behavior, with a rapid initial adsorption during the first 30 minutes, followed afterwards by a much slower rate. The MB adsorption efficiency ranged from 46 to 96% after 30 min and from 67 to 98% after 12 hours. The faster adsorption of methylene blue at lower concentrations is as indication that methylene blue adsorption occurs mainly on the surface of the adsorbent as reported by other studies on MB adsorption (Banat et al., 2003). Results presented in Fig. 3 also show that adsorption presents a strong dependency of MB initial concentration. An increase in the initial MB concentration led to an increase in the amount adsorbed, which is attributed to the increase in driving force (concentration gradient) with the increase in the initial dye concentration. The amount of MB adsorbed increased from 9 to 64 mg g^{-1} as the initial concentration was increased from 100 to 1000 mg L^{-1}.
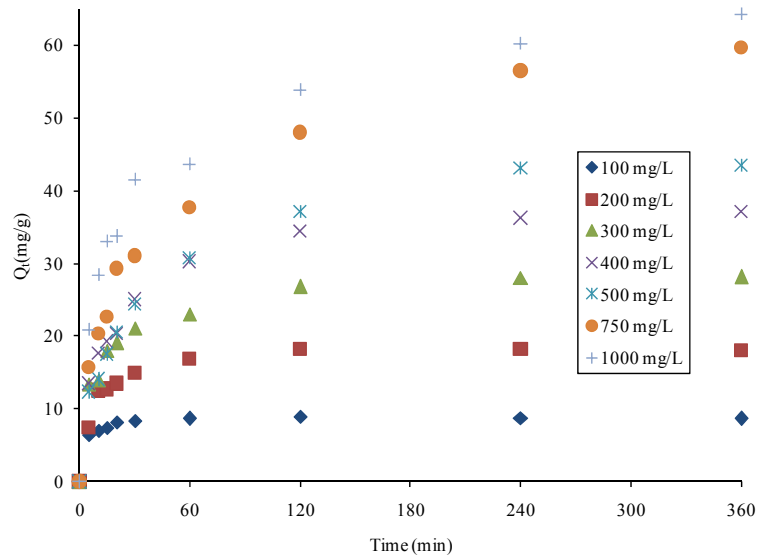

Figure 3. Effect of contact time on MB adsorption.

The controlling mechanisms of the adsorption processes were investigated by fitting first and second-order kinetic models to the experimental data. The kinetics models can be represented by the following equation:

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

where q_e and q_t correspond to the amount of dye adsorbed per unit mass of adsorbent (mg g^{-1}) at equilibrium and at time t, respectively; k_n corresponds to the rate constant for nth order adsorption (k_n units are min^{-1} for n=1 and g mg^{-1}min^{-1} for n=2). The linearized integrated forms of the equations are (Nunes et al., 2008):

First-order kinetics (n=1):

$$\ln(q_e - q_t) = \ln q_e - k_1 t \qquad (2)$$

Second-order kinetics (n=2):

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

The best-fit model selection was based on both linear regression correlation coefficient (R^2) and the difference between estimated and experimental q_e values. Results are displayed in Tab. 1. The first-order model did not provide a good fit, with low R^2 values and q_e values being significantly underestimated (or overestimated in the case of initial MB conc. of 300 mg L^{-1}). An evaluation of both the correlation coefficients and estimated q_e values indicates that MB adsorption can be satisfactorily described by the pseudo second-order model. The values of the rate constant decreased with increasing initial MB concentration.

Table 1. Kinetic parameters for MB adsorption.

Initial dye concentration (mg L⁻¹)	q_e (exp.)*	Pseudo first-order			Pseudo second-order		
		q_e	k_1	R^2	q_e	k_2	R^2
			MB				
100	8.67±0.00	7.56	0.1355	0.981	8.772	0.0100	0.9998
200	18.08±0.00	11.59	0.0399	0.9029	18.51	0.0090	0.9997
300	28.13±0.00	138691.00	0.0606	0.7334	28.985	0.0034	0.9995
400	37.04±0.24	21.94	0.0149	0.9275	38.314	0.0019	0.9996
500	43.39±0.09	36.75	0.0181	0.9828	46.296	0.0009	0.9982
750	59.62±0.34	44.71	0.0111	0.9794	62.893	0.0006	0.9956
1000	64.27±0.31	40.65	0.0101	0.9335	66.225	0.0008	0.9966

3.3. Adsorption equilibrium

The adsorption isotherm at 25°C is presented in Fig. 4. The shape of the curve indicates favorable adsorption. Langmuir and Freundlich adsorption models were evaluated for description of the MB sorption isotherm and coefficients are displayed in Table 2.

Langmuir isotherm, based on a theoretical model assuming monolayer adsorption over an energetically and structurally homogeneous adsorbent surface, has been successfully employed to describe MB adsorption by residue based activated carbons (Banat et al., 2003; Kavitha & Namasivayam, 2007). It can be described by the following equation:

$$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e} \qquad (4)$$

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. A characteristic parameter of the Langmuir isotherm is the dimensionless factor r (separation factor), related to the shape of the isotherm. Its value indicates either unfavorable ($r > 1$), linear ($r = 1$), favorable ($0 < r < 1$) or irreversible ($r = 0$) adsorption and it is evaluated as (Hamdaoui & Naffrechoux, 2007):

$$r = (1 + K_L C_0)^{-1} \qquad (5)$$

where C_0 is the highest value for initial sorbate concentration (mg L^{-1}).

Freundlich´s equation is an empirical model based on heterogeneous adsorption over independent sites. Multilayer adsorption is considered, but the model does not account for saturation. It can be described by the following equation:

$$q_e = K_F C_e^{1/n} \tag{6}$$

where K_F is a constant that indicates the relative adsorption capacity ($mg^{1-(1/n)}L^{1/n}\ g^{-1}$) and n is related to the intensity of adsorption (Hamdaoui & Naffrechoux, 2007). Freundlich isotherm has also been successfully employed to describe MB adsorption by residue based activated carbons (Aygun et al., 2003).

MB adsorption was better described by the Langmuir model, indicating homogeneous and multilayer adsorption. Favorable adsorption is also corroborated by the quite low value of the Langmuir separation parameter (Tab. 2). Maximum MB uptake capacity, based on Langmuir model, was 68.5 mg g^{-1}, a high value to other residue-based adsorbents reported in the literature for MB adsorption at ambient temperature. Examples include sunflower oil cake, 16.4 mg g^{-1} (Karagöz et al. 2008) and date pits, 13 mg g^{-1} (Banat et al., 2003). Furthermore, there was a significant increase in adsorption capacity for the same type of residue submitted to activation in a muffle oven, 14.9 mg g^{-1} (Nunes et al., 2008), indicating that microwave activation provides not only a significant reduction in processing time and energy requirements, but also an increase in adsorption capacity.
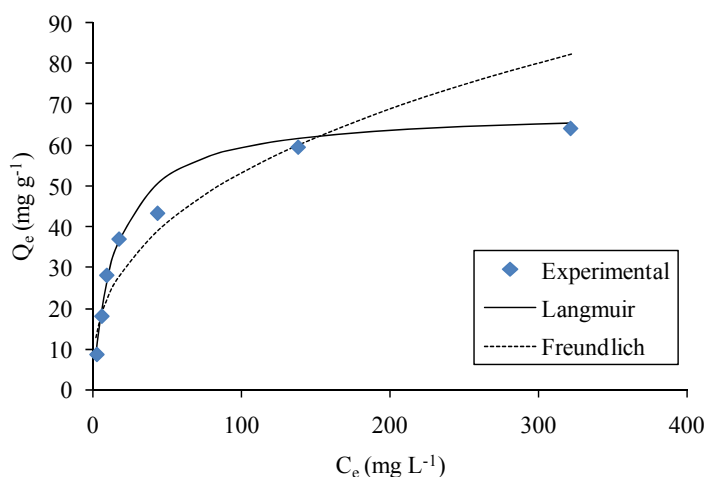

Figure 4. MB adsorption isotherm.

Table 2. Langmuir and Freundlich isotherm constants for adsorption of methylene blue.

Model	Constants
Langmuir	
K_L (L mg^{-1})	0.0642
q_{max} (mg g^{-1})	68.49
r	0.015
R^2	0.9957
Freundlich	
K_F	9.54
n	0.3735
R^2	0.8704

4. CONCLUSIONS

Experiments were conducted to investigate the potential microwave activation for the production of adsorbents employing defective coffee press cake, a residue from coffee oil biodiesel production. Equilibrium data indicated favorable adsorption and were better described by the Freundlich model, in comparison to Langmuir, thus indicating heterogeneus adsorption. Microwave activation provided a significant increase in the maximum uptake capacity (15 →

69 mg g^{-1}) coupled to a significant decrease in processing time (60 $\rightarrow$ 8 min) in comparison to conventional activation in a muffle oven. The results presented in this study show that defective coffee press cake presents great potential as an inexpensive and easily available alternative adsorbent for the removal of cationic dyes in wastewater treatments.

5. ACKNOWLEDGEMENTS

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