

Research Article

Valorization of Agroindustrial Wastes as Biosorbent for the Removal of Textile Dyes from Aqueous Solutions

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The goal is to determinate the technical feasibility of using agroindustrial wastes for adsorption of dyes. The pH_{pzc} of Brewer's spent grains and Orange peel is 5.3 and 3.5, respectively. The equilibrium isotherms of Basic Blue 41, Reactive Black 5, and Acid Black 1 were carried out without pHs control which ranging between 4 and 5.5. The equilibrium concentrations for both adsorbents were fitted by the Freundlich and Langmuir models. The maximum adsorption capacity measured for Basic Blue 41, Reactive Black 5, and Acid Black 1 was 32.4, 22.3, and 19.8 mg g^{-1} for Brewer's spent grains; and 157, 62.6, and 45.5 for orange peel, respectively. The kinetic of process was fitted by the model of pseudo-second order. The constant rate for orange peel decreased to extend the initial concentration of dye increased, obtaining 4.08×10^{-3} – 0.6×10^{-3} (Basic Blue 41), 2.98×10^{-3} – 0.36×10^{-3} (Acid Black 1), and 3.40×10^{-3} – 0.46×10^{-3} $\text{g mg}^{-1} \text{min}^{-1}$ (Reactive Black 5). The best removal efficiency was obtained in orange peel with values started from 63% to 20%. Consequently, according the results obtained there are two positive effects, the reuse of agricultural wastes and its use as low-cost adsorbent of the dyes.

1. Introduction

The discharges of industrial wastewater containing dyes cause serious environmental problems, because their chemical structure gives them a persistent and recalcitrant nature. The released dye in water streams represents a risk of ecotoxicity and a potential danger of bioaccumulation. The transport of these contaminants through the food chain could even affect the human health. In the last two decades, the elimination of dyes from industrial textile waste waters has been one of the major challenges for researchers.

Adsorption has received special attention as a treatment for colored wastewater because it produces an effluent of better quality and comparatively can become more effective and less expensive than conventional treatments. Granular-activated carbon has been designated by the Environmental Protection Agency (EPA) of USA as the best available technology (BAT) for organic chemicals removal. In fact, activated carbon adsorption is an effective treatment for removing varied organic contaminants and, particularly, textile

dyes of different ionic nature [1, 2]. However, the high volume of effluents generated in the textile wet process involves a high cost for regeneration of the activated carbon [3, 4].

On the other hand, as a consequence of industrial development, enormous quantities of agroindustrial wastes are generated annually that can be used like supplies for other processes in order to give added value. An alternative is the application in processes of wastewater treatment, promoting in this way a sustainable and environmentally friendly development. Recently, it has been evaluated the performance of different low-cost adsorbents, which can be used only once to avoid the costly stage of regeneration. These studies have included some types of biomass such as agroindustrial or forest wastes, namely, rice husk [5], coconut [6], spent coffee grounds, a byproducts of instant coffee industry [7], wood bark [8], among others. Although the removal efficiency that is achieved is less than using the activated carbon, the application to industrial scale can be economically attractive [9].

The adsorption capacity of these nonconventional adsorbents is due to the presence of biopolymers such as polysaccharides, lignin, hemicelluloses, and cellulose [9, 10]. Brewers' spent grains, a lignocellulosic residual biomass from the brewing industry, are the major solid waste generated during the production process. The potential use of this waste as raw material in food industry, energy production, and biotechnological processes is currently being investigated [11]. Brewer's spent grains also have showed a significant potential as a biosorbent for application in the remediation of wastewater contaminated with metal and dye [12–14]. Besides other cellulose-based wastes such as banana peel have been used in the removal of dyes by adsorption [15, 16]. The biomass residual of the citrus juice industry, peel, pulp, and seed represents 50% of the processed fruit mass. The efficient management of these agroindustrial wastes should not only promote but diversify its use. The utilization of citrus peel, orange, lemon, mandarin, and grapefruit, as a low-cost adsorbent, has recently been studied [17–20].

The aim of this research is to explore the technical feasibility of use the waste biomass such as Brewer's spent grains and orange peel for the biosorptive removal of textile dyes.

2. Materials and Methods

2.1. Agroindustrial Wastes. Brewer's spent grains (BSG,) were obtained from the local brewery. Orange peel (OP) from fruit purchased from a local market. These residual biomasses were dried at room temperature until they reached the equilibrium moisture content, around 10% (wt). The dry solids were crushed and later the mesh cut $[-18 + 60]$, which corresponds to particles larger than 0.25 mm and smaller than 1 mm, was selected.

2.2. Dyes. The adsorbates evaluated in this study were the cationic dye Basic Blue 41 (C.I. 11105) and the anionic dyes, Acid Black 1 (C.I. 20470) and Reactive Black 5 (C.I. 20505). Methylene Blue (Basic Blue 9, C.I. 52015) was used for the determination of adsorptive properties of the agroindustrial wastes. Dyes are analytical grade supplied by Sigma Aldrich Co. The structure and properties of the dyes are shown in Table 1.

2.3. Physical and Chemical Characterization

Morphologic Characterization. It was realized by a Scanning Electron Microscopy analysis of the agroindustrial wastes, using JSPM-5410 Scanning Probe Microscope (JEOL Ltda) implemented with Anaglyph Maker 1.08 software. The images were obtained with a magnification of 1000x.

Surface Acidity and Basicity. The concentrations of acidic and basic sites in the adsorbents were determined by acid-base titration method proposed by Boehm [21]. 0.5 g of agroindustrial waste was contacted with 50 mL of NaOH 0.01 M (acidity) or 50 mL of 0.1 M HCl (basicity) until the equilibrium was reached. An aliquot of 20 mL filtrate obtained from the contact assay (24 h) was then titrated with 0.01 M HCl or 0.1 M NaOH to neutralize the sodium hydroxide or hydrochloric acid in excess, respectively.

Point of Zero Charge (pH_{pzc}). 10, 7.5, 5, 2.5, and 1.25 mL of 0.1 M HCl were added to 1 g of agroindustrial wastes. Similarly, there was prepared another set of suspensions with 0.1 M NaOH. Next, in all the flasks was added 5 mL of KCl 0.1 M and was then completed with distilled water until 100 mL. The flasks were maintained in a shaker with thermal control (20°C, 150 rpm) for 1 h and pH values (pH_1) were recorded. Subsequently 5 mL of KCl 1 M was added to each sample, maintaining the agitation during 1 h. The final pH of each sample (pH_2) was measured. The pH_{pzc} for each waste was estimated as the final pH value, for which the difference between pH_1 and pH_2 was equal to zero [22].

pH of Adsorbent ($pH_{KCl\ 1\ M}$, $pH_{CaCl_2\ 0.01\ M}$). 50 mL of solution KCl 0.1 M or $CaCl_2$ 0.01 M was added in a flask containing 0.2 g of agroindustrial waste. The flasks were maintained in a shaker with thermal control (25°C, 220 rpm) for 2 h; after that, the pH was measured for each suspension.

2.4. Adsorptive Properties

Methylene Blue Index. There was evaluated the adsorptive power of each waste by the Methylene Blue. Brewer's spent grains and Orange peel were placed in contact with solution of Methylene Blue until equilibrium was reached. Solutions of dyes with an initial concentration between 50 and 500 mg L⁻¹ and a dose of 3 g of Brewer's spent grains or 2 g of Orange peel per liter of solution were used. These suspensions were continuously stirred in a shaker with temperature controlled at 20°C for 24 h. Finally the equilibrium concentration of dye in the solution was determined. The experimental equilibrium concentrations in the liquid and solid phase were correlated using the Langmuir isotherm model.

2.5. Biosorption of Dyes

Adsorption Equilibrium of Dyes. 100 mL of solutions with different initial concentrations in the range 50–500 mg L⁻¹ were placed in contact with 0.2 g of BSG or OP in Erlenmeyer flasks which were kept with agitation and temperature control (200 rpm, 25 ± 2°C) until the equilibrium was achieved. Finally, the equilibrium concentration of dye in the solution was determined.

Adsorption Kinetic of Dyes. 100 mL of dye solution with different initial concentrations (50, 200, and 500 mg L⁻¹) was placed in contact with 0.2 g of agroindustrial waste (BSG and OP), in Erlenmeyer flasks which were agitated and kept with controlled temperature (200 rpm, 25 ± 2°C). The dynamic process was identified through the evolution of residual concentration of dye in solution at different contact times, until the variation between two successive measurements was not significant.

pH of Adsorbent. 50 mL of solution KCl 1 M or of $CaCl_2$ 0.01 M was added to 0.2 g of agroindustrial wastes, and then, the flasks were maintained in a shaker with thermal control (25°C, 220 rpm) for 2 h. Finally the pH of each suspension was measured.

TABLE 1: Structure and properties of dyes.

Dye	Molecular weight g mol ⁻¹	Wavelength of maximum absorption nm	Structure
Basic Blue 41 (BB41)	482.57	617	
Acid Black 1 (AB1)	616.49	620	
Reactive Black 5 (RB5)	991.82	597	
Basic Blue 9 (Methylene Blue)	319.86	665	

2.6. *Parameter Estimation of Equilibrium and Kinetic Model.* The function was fitted by the method of Nonlinear-Least-Squares using the algorithm of Levenberg-Marquardt that minimizes the sum of the squares of the errors between the data points and the function. The statistical indicators used to assess convergence were the determination coefficient (R^2) and the quadratic sum of the residues ($\sum e^2$) by

$$R^2 = \frac{\sum_1^n (q_{\text{exp}} - \bar{q})^2 - \sum_1^n (q_{\text{exp}} - q_{\text{model}})^2}{\sum_1^n (q_{\text{exp}} - \bar{q})^2}, \quad (1)$$

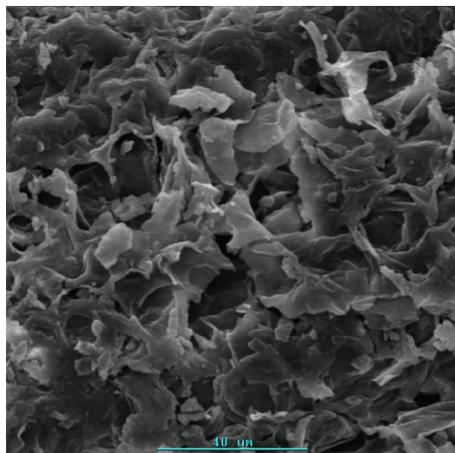
$$\sum e^2 = \sum_1^n (q_{\text{exp}} - q_{\text{model}})^2.$$

The resolution of algorithm was realized by Statistic 7.0 software.

2.7. *Analytical Assays.* The samples were centrifuged and the residual dye concentration in the supernatant was determined by measuring absorbance at maximum wavelength of each dye in a Helios Gamma UV-Vis spectrophotometer (UK).

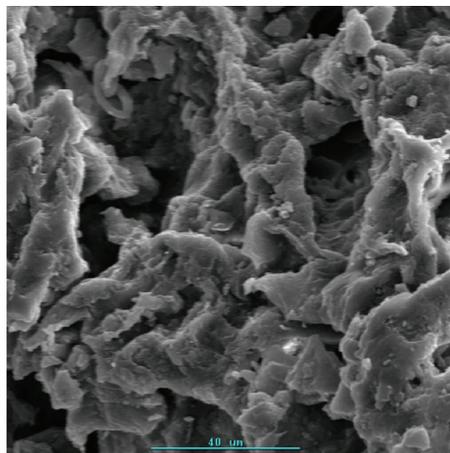
The adsorption capacity was determined using mass balance, applied to solid and liquid phases in accordance with the following:

$$q = \frac{V(C_0 - C)}{m}, \quad (2)$$



Accelerating voltage: 20Kev
Resolution: 1024x1024
Magnification: 1000
Pixel size: 0.118515 microns

(a) Brewer's spent grains



Accelerating voltage: 20Kev
Resolution: 1024x1024
Magnification: 1000
Pixel size: 0.118515 microns

(b) Orange peel

FIGURE 1: Analysis SEM of agroindustrial wastes.

TABLE 2: Chemical and physical characterization of adsorbents.

	Brewer's spent grains	Orange peel
Point of zero charge	5.3	3.5
pH_{water}	—	4.98 ± 0.00
$\text{pH}_{\text{KCl } 1.0\text{M}}$	4.80 ± 0.08	4.21 ± 0.04
$\text{pH}_{\text{CaCl}_2 \text{ 0.01 M}}$	4.55 ± 0.10	4.67 ± 0.01
Surface acidity (NaOH) mmol g^{-1}	3.37 ± 0.02	2.58 ± 0.19
Surface basicity (HCl) mmol g^{-1}	3.16 ± 0.01	0.25 ± 0.07
Methylene Blue Index mg g^{-1}	64.9	178.7

where q is the adsorption capacity (mg g^{-1}), V is the solution volume (L), C_0 is the initial dye concentration (mg L^{-1}), and C is the dye concentration on time (mg L^{-1}).

3. Results and Discussion

3.1. Physical and Chemical Characterization of Adsorbent.

The surface morphology of the particle wastes, Brewer's spent grains (Figure 1(a)) and Orange peel (Figure 1(b)), was analyzed by scanning electron microscopy. The micrographs revealed that the particles of Brewer's spent grains showed a rigid structure and higher density of macropores, while the particles of Orange peel are rather nonporous. The particles of both wastes have irregular shape and the textures of its surface are microrough.

The acid-base behavior of functional groups of the adsorbent surface plays a crucial role in interactions occurring during the process. The surface charge of the agroindustrial waste can be explained in terms of its pH_{pzc} value and of the concentration of acidic and basic sites at the particles surface. The acidic characteristic of activated carbon surface,

for example, is caused by the presence of carboxyl groups, lactones, and of phenolic hydroxyl groups [21]. Similarly the cellulose, one of the major components of agroindustrial waste, has a predominantly acid character because the hydrogen atoms of the hydroxyl groups act as electron acceptors [23]. Furthermore the principal components of the Orange peel, addition of the soluble material (41%) and other minor compounds, are cellulose (16%), hemicellulose (13.8%), pectin (14%), and protein (7.9%) [24, 25]. These components contain carboxyl and hydroxyl groups, causing the acid behavior of its surface. Brewer's spent grains contain principally cellulose (16–25%), hemicellulose (30%), lignin (7–27%), and protein (2.4–24%), its acid character being determined principally by phenolic hydroxyl groups present in the lignin [12]. The basic behavior of BSG is caused by the amine groups present in the protein.

Table 2 shows the value of pH_{pzc} and the basicity and acidity surface of Brewer's spent grains and Orange peel. The magnitude of these properties agrees with the values presented by other authors for this same type of wastes [25]. It can be seen that Orange peel has acid character higher than

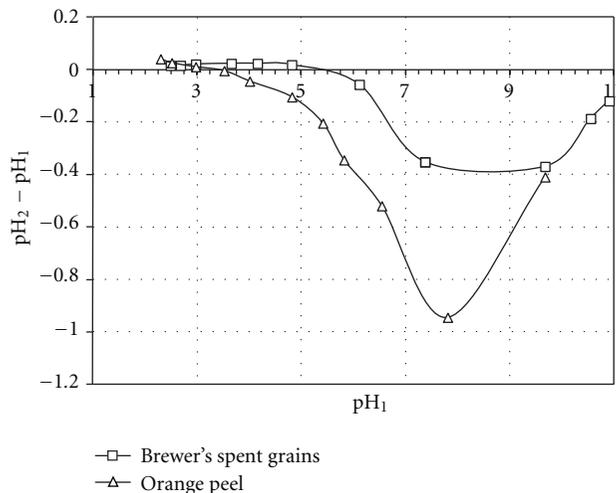


FIGURE 2: Zero charge point of agroindustrial wastes.

Brewer's spent grains. The acidic sites concentration of OP is 10 times higher than the sites with basic behavior while in BSG this relation is scarcely higher than one.

Consequently the zero-charge point of OP is less than BSG and corresponds to pH value of 3.5 (Figure 2). Then OP is classified as a biosorbent of acid type so that, when the pH of a solution is higher than the value of pH_{pzc} , the acid groups of pectin (galacturonic acid) are in the deprotonated form. Under this condition OP interacts preferentially with cationic species.

The complex structure of the agrowaste has similitude with the soil organic matter; that is, their functional groups contain electron pairs nonbinding that can interact with the protons present in the liquid phase in equilibrium; therefore in this case, the evaluation of surface acidity by measurement of pH can also show any fluctuation. This effect can be evaluated measuring the pH of suspensions in different saline solutions. The protocols of characterization of soils indicate to use KCl 1 M and CaCl_2 0.01 M [26]. The results of pH drop between both measures ($\text{pH}_{\text{water}} - \text{pH}_{\text{KCl } 1.0\text{M}} = 0.77$ and $(\text{pH}_{\text{water}} - \text{pH}_{\text{CaCl}_2 0.01\text{M}}) = 0.31$, which were obtained for OP confirming that this is a biosorbent with strongly acidic character, coincide with the low value of pH_{pzc} (Table 2). In the first measurement, the pH drop is a consequence of the replacement of the hydrogen ions of the surface functional groups by the potassium from the solution, causing a decrease in the pH. Since CaCl_2 is a weak base, it causes an impoverishment in hydroxyl ions whose, although has an effect similar to increased of protons produced in the previous case, magnitude is lower.

The concentration of surface groups present in this type of lignocellulosic adsorbents is significantly higher than that found in commercial activated carbons. For example, commercial activated carbon F-400 (Calgon Carbon) exhibits a functional group concentration between 0.4 and 0.6 meq g^{-1} , with a slightly basic feature, which provides a zero charge point between 7.3 and 7.9 [2, 27].

The quality of adsorbents, activated carbons particularly, is evaluated in terms of their adsorptive power and superficial area. The Methylene Blue Index that quantifies the amount of dye necessary to cover the total surface of the particles is widely used to evaluate the active carbon and other alternative adsorbents. The nonpolar nature of the Methylene Blue molecule and its molecular size (8.4 Å) (Table 1) suggests that the adsorption occurs at the macropores and mesopores.

The Methylene Blue Index of Brewer's spent grains and the Orange peel is shown in Table 2. The values obtained confirm the observations of morphological analysis; that is, BSG has a mesoporous structure. These results are comparable with the Index of the active carbons prepared from sugarcane bagasse and coconut shell (79.6 and 10.5 mg g^{-1} , resp.) and less than the value of cellulose materials such as cotton [28, 29]

The estimation of specific surfaces of BSG and OP using the adsorption of Methylene Blue was 206.2 $\text{m}^2 \text{g}^{-1}$ and 567.3 $\text{m}^2 \text{g}^{-1}$, respectively. Both values obtained for other low-cost biosorbents, such as peanut shells, olive stones, bamboo cane, and date stones, have the same order of magnitude (368–394 $\text{m}^2 \text{g}^{-1}$) [30].

3.2. Equilibrium Isotherm. The most widely models used to describe the adsorption equilibrium are the Langmuir [31] and Freundlich [32] isotherms, which are shown in (3) and (4), respectively:

$$q_e = \frac{q_{\text{max}} b C_e}{(1 + b C_e)}, \quad (3)$$

where q_{max} is the maximum adsorption capacity (complete monolayer) (mg g^{-1}) and b is associated with interaction energy between adsorbate and adsorbent (L g^{-1}):

$$q_e = k_F C_e^{1/n}, \quad (4)$$

where k_F is the equilibrium constant ($\text{mg g}^{-1} (\text{L mg}^{-1})^{1/n}$) and n is a parameter associated with the affinity between adsorbate and adsorbent.

Figures 3 and 4 show the dependence between equilibrium concentrations of both phases for adsorption of BB41, RB5, and AB1 dyes on Brewer's spent grains and Orange peel, respectively.

Additionally, the parameters and their standard deviations, obtained by fitting the Langmuir and Freundlich models, are shown in Tables 3 and 4. The experimental data adsorption equilibrium of dyes on BSG can be interpreted adequately by the Freundlich model ($R^2 > 0.96$), whereas with the Langmuir model a better quality of fit was obtained for the BB41 and RB5 adsorption on Orange peel ($R^2 > 0.97$). The values of maximum adsorption capacity of the dyes on OP are higher than BSG, 5, 2.5, and 2-fold for BB41, RB5, and AB1, respectively.

The magnitudes of b parameters of the Langmuir isotherm indicate that the interaction energies between the dyes and adsorption sites of the BSG, are greater than those obtained with BSG (Table 3), probably due to the acidic nature of this latter provided by the carboxylic functional groups. In the case of adsorption of RB5 on OP this

TABLE 3: Langmuir model parameters.

Dye	Brewer's spent grains				Orange peel			
	q_{\max} (mg g ⁻¹)	b (L mg ⁻¹)	R^2	$\sum e^2$	q_{\max} (mg g ⁻¹)	b (L mg ⁻¹)	R^2	$\sum e^2$
BB41	32.4 ± 2.3	0.021 ± 0.007	0.772	66.5	157.2 ± 4.2	0.021 ± 0.002	0.992	108.4
RB5	22.3 ± 1.9	0.0077 ± 0.0019	0.911	12.2	62.6 ± 14.8	0.0012 ± 0.0004	0.977	8.2
AB1	19.8 ± 0.3	0.019 ± 0.001	0.985	1.26	45.3 ± 7.5	0.0086 ± 0.0042	0.737	102.2

TABLE 4: Freundlich model parameters.

Dye	Brewer's spent grains				Orange peel			
	k_F (mg g ⁻¹)(mg L ⁻¹) ^{-1/n}	N	R^2	$\sum e^2$	k_F (mg g ⁻¹)(mg L ⁻¹) ^{-1/n}	n	R^2	$\sum e^2$
BB41	5.54 ± 0.70	3.51 ± 0.28	0.962	11.4	15.72 ± 3.06	2.50 ± 0.25	0.951	625.9
RB5	1.46 ± 0.26	2.42 ± 0.19	0.967	4.6	0.21 ± 0.06	1.31 ± 0.09	0.980	7.0
AB1	3.67 ± 0.43	3.77 ± 0.30	0.962	3.4	3.08 ± 1.39	2.42 ± 0.48	0.822	130.3

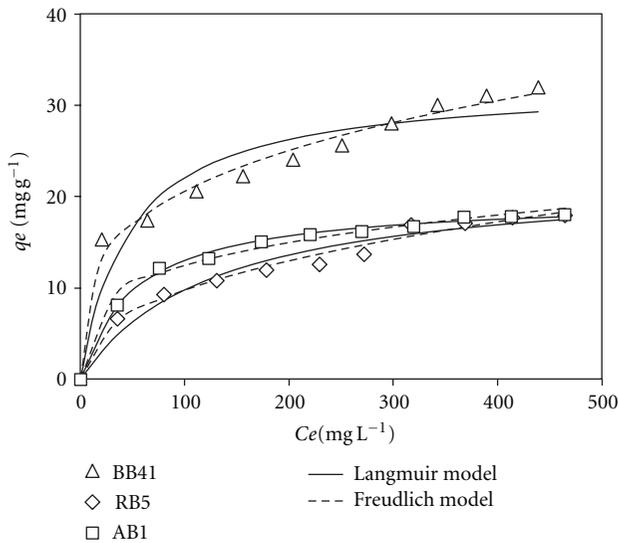


FIGURE 3: Adsorption isotherms of dyes on Brewer's spent grains. Experimental conditions: temperature: 25°C; pH (natural): 4.0 (BB41), 5.0 (RB5), 5.3 (AB1); particle size; 0.25–1.00 mm.

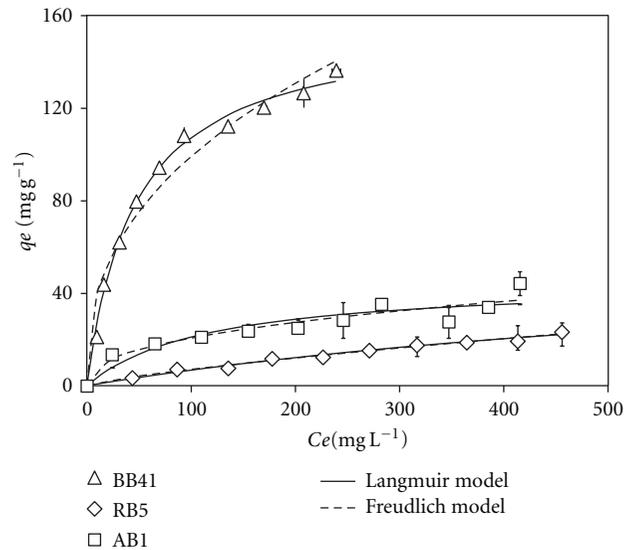


FIGURE 4: Adsorption isotherms of dyes on Orange peel. Experimental conditions: temperature 25°C; pH (natural): 4.4 (BB41), 5.5 (RB5), 4.9 (AB1); particle size: 0.25–1.00 mm.

parameter is 20 times lower with respect to the one obtained for the basic dye, whereby the isotherm is almost linear. The partition constant was estimated in 0.0528 with a correlation coefficient of 0.96. This means that the removal of dye by OP is only caused by a phenomenon of partition and the interactions occur primarily with adsorption sites existing on the outer surface of this waste. This result also is originated for the lower hydrophobicity and higher charge density that has RB5 in respect to the other dyes.

In another study performed with the orange peel, reported similar results for the adsorption of basic and acid dyes. The maximum adsorption capacity of acid dyes is between 40 and 65 mg g⁻¹, and the magnitude of the interaction parameters is equal to that obtained in this study (0.001–0.008 L mg⁻¹) [33]. On the other hand, the maximum adsorption capacity of malachite green on OP was determined in 483 mg g⁻¹ [34]. Similarly, the maximum

adsorption capacity reported for the acid dyes uptake (Acid Yellow 17 and Acid Blue 25) on Brewer's spent grains is equivalent to that obtained in this work [35].

Although both adsorbents have an adsorption capacity of dyes, of different ionic behavior, significantly lower than those reported for commercial activated carbon and that their interaction energies are also lower, they have a higher density of functional groups [1, 2, 26, 36]. In particular it has been reported that the adsorption capacity of RB5 by activated carbon is 175 mg g⁻¹ [37]. Despite this, the adsorption capacities obtained with the Orange peel indicate that its use in the removal of dyes from waste water can be an attractive option, especially for those of basic type.

3.3. Kinetic Modeling. The pseudo-second-order rate expression has been used to describe adsorption that involves valence forces through electrons shared or exchanged between

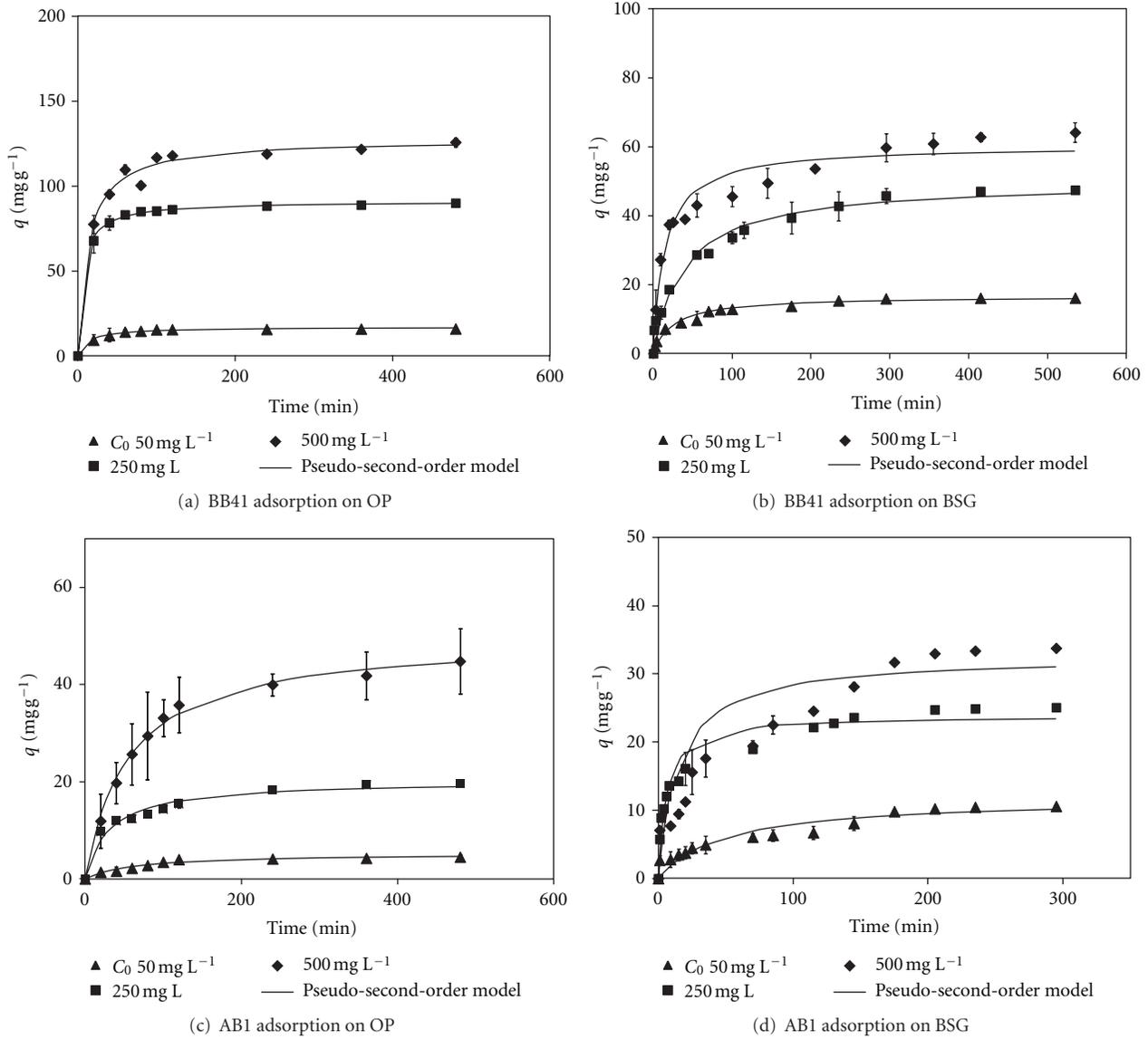


FIGURE 5: Kinetic modeling of dye adsorption on agroindustrial wastes.

the adsorbent and adsorbate, such as covalent interactions and ion exchange [38]. Recently this kinetic model (5) has been successfully applied to the adsorption of pollutants from aqueous solutions:

$$\frac{dq}{dt} = k_2 (q_e - q)^2, \quad (5)$$

where k_2 is the pseudo-second-order rate constant ($\text{g mg}^{-1} \text{min}^{-1}$), q_e is the amount of dye adsorbed at equilibrium (mg g^{-1}), and q is the amount of dye adsorbed at time t (mg g^{-1}).

Equation (6) is obtained by integrating (5) using the boundary conditions $t = 0$ to $t = t$ and $q = 0$ to $q = q$:

$$q = q_e \left[1 - \frac{1}{(1 + k_2 q_e t)} \right]. \quad (6)$$

The progress curve of the adsorption capacity (6) was properly interpreted by the pseudo-second-order model (Figure 5); the coefficients of determination are in the range 0.90–0.99. The results indicate that the adsorption capacity was increasing to the extent that the initial concentration of dye was higher because the driving force has been enhanced. However, for the adsorption of dyes onto BSG using the greater initial concentration (500 mg L^{-1}), the intraparticle diffusion restriction appears very early, which is consistent with the porous morphology of this adsorbent. The diffusive control intraparticle is more notable to the extent that the molecular weight increases. Figures 5(b) and 5(d) show the adsorption of BB41 and AB1 whose ratio of molecular weights is 1 : 1.3 (Table 1). Therefore this effect is manifested most significantly with the dye RB5.

TABLE 5: Parameters of pseudo second order model.

		Basic Blue 41			
C_0 (mg L ⁻¹)		q_e (mg g ⁻¹)	$k_2 * 10^3$ (g mg ⁻¹ min ⁻¹)	R^2	$\sum e^2$
50	BSG	16.67 ± 0.51	2.30 ± 0.39	0.979	8.23
	OP	16.87 ± 0.29	4.08 ± 0.51	0.992	1.75
250	BSG	49.88 ± 2.06	0.51 ± 0.11	0.972	97.03
	OP	91.15 ± 0.33	1.67 ± 0.68	0.999	2.89
500	BSG	60.38 ± 2.09	1.08 ± 0.23	0.952	225.96
	OP	127.46 ± 2.60	0.61 ± 0.09	0.989	143.81
		Acid Black 1			
50	BSG	11.85 ± 1.02	1.68 ± 0.59	0.904	14.52
	OP	5.21 ± 0.33	2.98 ± 0.76	0.961	0.78
250	BSG	23.87 ± 0.80	6.97 ± 1.35	0.948	44.95
	OP	20.26 ± 0.82	1.57 ± 0.32	0.971	8.66
500	BSG	32.65 ± 1.77	2.04 ± 0.62	0.920	135.85
	OP	49.85 ± 1.05	0.36 ± 0.03	0.995	9.15
		Reactive Black 5			
50	BSG	10.07 ± 0.46	7.30 ± 0.13	0.990	1.18
	OP	3.18 ± 0.10	3.40 ± 0.39	0.993	0.05
250	BSG	17.38 ± 0.61	0.62 ± 0.09	0.991	3.32
	OP	20.03 ± 0.34	1.87 ± 0.17	0.994	1.67
500	BSG	97.5 ± 35.10	0.01 ± 0.00	0.975	81.73
	OP	40.32 ± 2.37	0.46 ± 0.11	0.958	47.89

The decay curves of RB5 concentration (C/C_0 against t) obtained for adsorption on OP at different initial concentrations of dye, overlap. This result indicates the absence of diffusion intraparticle, and therefore, the process is governed only by the external mass transfer. The high molecular weight of RB5 and the structure nonporous of OP are the causes of this behavior.

The parameters of pseudo-second-order model, q_e and k_2 , and their standard deviations are shown in Table 5. The equilibrium adsorption capacity of OP was higher than BSG; specifically the values for BB41, RB5 and AB1, are respectively, 6-, 2.5- and 2-fold higher. The equilibrium capacities for both adsorbents increase as the initial dye concentration is increased. The kinetic parameter k_2 , obtained for Orange peel, decreases steadily to the extent that the initial dye concentration increased, while for BSG it does not show a clear trend as a consequence of the restrictions imposed by the diffusion intraparticle.

4. Conclusion

The present study shows that the agroindustrial wastes biomass such Orange peel and Brewer's spent grains has significant potential as biosorbents for the removal of basic dyes from its aqueous solution, because their surfaces are predominantly negatively charged. The results indicated that the Orange peel presented a higher maximum capacity of adsorption than Brewer's spent grains for the cationic dye, Basic Blue 41, as well as for the anionic dyes, Acid Black 1, and Reactive Black 5.

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