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Development of Adsorbent Materials Using Residue from Coffee Industry and Application in Food dye Adsorption Processes

Luiz Eduardo Nochi de Castro[1,2]
https://orcid.org/0000-0002-5968-8968

Débora Alessandra Jones Battocchio[1]
https://orcid.org/0000-0002-6810-8240

Leomara Floriano Ribeiro[1*]
https://orcid.org/0000-0001-6610-0061

Leda Maria Saragiotto Colpini[1,2,3]
https://orcid.org/0000-0003-3660-188X

[1]Universidade Federal do Paraná, Engenharia de Alimentos, Jandaia do Sul, Paraná, Brasil; [2]Universidade Federal do Paraná, Programa de Pós-Graduação em Biotecnologia, Palotina, Paraná, Brasil; [3]Universidade Federal do Paraná, Programa de Pós-Graduação em Engenharia e Tecnologia Ambiental, Palotina, Paraná, Brasil.

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*Correspondence: leomara.ribeiro@ufpr.br; Tel.: +55 (43) 3432-4552 (L.F.R.)

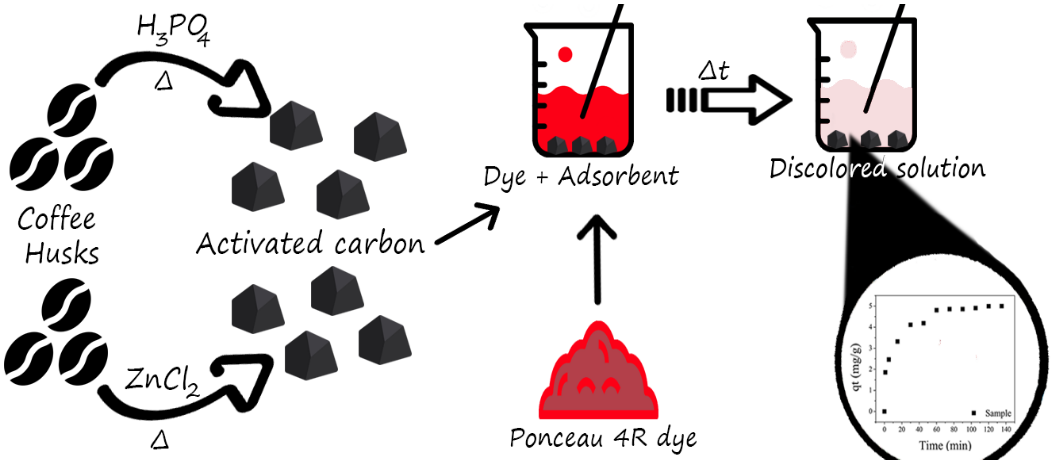
HIGHLIGHTS

- The adsorbent activated with H_2PO_4 removed around 100% of Ponceau 4R dye.
- The increase in temperature influenced the increase in maximum adsorptive capacity.
- Langmuir's isotherm was better suited to the experimental data of the Ponceau 4R dye.

Abstract: The aim of this study was to develop an adsorbent from coffee husk, residue from the coffee industry by different activation methods and to evaluate its application in the treatment of effluent containing synthetic Ponceau 4R dye. The activations were with phosphoric acid and zinc chloride, then the samples were characterized in terms of physical and chemical composition, structure and morphology, thermal behavior and kinetic and thermodynamic study. Regarding the characterization of the material, the activation with phosphoric acid showed porous morphology and a high surface area (429.7 $m^2\ g^{-1}$) and with the kinetic study it was possible to obtain an equilibrium time of 60 min and dispersion according to Elovich kinetics ($R^2 = 0.96$ and RMSE < 0.24). According to the experimental design, the adsorptive capacity can be evaluated with the significant result ($q_e = 19.87\ mg\ g^{-1}$) under the conditions of 90 min of the adsorption process and at the concentration of 2 $g\ L^{-1}$ of adsorbent. In relation to the equilibrium study the Langmuir model fit the data with coefficient of determination of $R^2 = 0.84$. Finally, the Ponceau 4R dye adsorption process using coffee husks as an activated carbon was thermodynamically favorable through the negative Gibbs free energy and positive entropy (+0.022 $kJ\ mol^{-1}\ K^{-1}$). Therefore, the use of coffee husk as activated carbon proved to be a favorable material for Ponceau 4R dye adsorption.

Keywords: Adsorption kinetics; agro-industrial waste; ponceau 4R dye; thermal analysis; thermodynamic study.

GRAPHICAL ABSTRACT



INTRODUCTION

Brazil is the world's leading producer and exporter of coffee with around 356 thousand tons in the 2019/2020 crop [1]. With the processing of coffee, the wastes generated are the spent coffee grounds, the coffee silverskin and the coffee husks, the latter being the main one, since it is estimated that for every 1,000 kg of processed coffee, 180 kg of coffee husks are generated [2,3]. Although the coffee husk is reused only as fertilizer, it has functional groups such as phenolic, lactonic, carboxylic and basic groups and is rich in organic nutrients made up of carbon molecules, therefore, it can present itself as a material with high affinity in recovering organic molecules, and can be a potential adsorbent applied in the treatment of effluents from different processes [4,5].

In the case of food effluents, significant amounts are generated daily and, due to their very varied and complex composition, they are considered an environmental problem for industries [6]. Among the main effluents are dyes with a chemical composition rich in metals, mutagenic and carcinogenic potential, in addition to being highly resistant to biodegradation [7–9]. Among the food dyes most used by the food industries is the Ponceau red dye (Ponceau 4R), as it is an anionic synthetic additive widely used to color various products, such as juices, yogurts, ice creams, carbonated drinks, among others [10,11]. In addition, this dye has high solubility, stability, wide applicability, and low cost of use. Thus, the treatment of effluents containing compounds such as Ponceau 4R has become increasingly challenging, mainly due to the presence of an azo group in its molecular structure and because it is not biodegradable like other synthetic dyes [12].

For the treatment of industrial effluents, the main methods applied are precipitation, coagulation, chemical oxidation, flocculation, among others, and these present variability in relation to their results, efficiency and cost of operation [13,14]. An alternative to traditional methods is adsorption because it has been shown to be an efficient process, simple to operate and of low cost, in addition to being able to reuse industrial waste in the form of activated carbon in this process. Activated carbon is the main adsorbent used due to its porous structure being able to adsorb compounds to its surface formed by micro, meso and macropores and can be synthesized from different sources and be efficient for adsorption of food dyes, for example [7,15].

Carbonaceous materials can be activated using several techniques and methods, including physical activation with carbon dioxide, steam and air and chemical activation with phosphoric acid, potassium hydroxide, zinc chloride, hydrogen peroxide, among other [16–21]. When choosing any of the activation methods, some factors must be taken into account, such as time spent to synthesize the material, type of reagent used and its toxicity, the characteristics of the material produced, the cost of activating the material and especially the degree of difficulty and necessary equipment [22,23].

In view of these factors, chemical activation presents itself as a viable alternative, since most reagents are non-toxic or have low toxicity, the activation occurs at low reaction time, around an hour and also at a low range of temperature around 400-600 ºC, which optimizes the processes and reduces energy and personnel costs, besides the chemicals needed being cheap most of the time, what also reduces the cost of the process and finally they produce materials with a high content of mesoporous and a high surface area, which can be used for the adsorption of high molecular weight species, such as azo-dyes [22,24–27].

In recent years, a growing trend has been the use of solid waste residuals (biomass) as biosorbents in decontamination processes, especially biomass from the food industry, such as coconut shell, orange peel, banana peel, coffee husks, among others [25,26,28–31].

Because they are waste products, these lignocellulosic materials comes at no cost of production and often has the characteristics necessary to serve as a good adsorbent, such as high concentration of minerals especially carbon, silicon and aluminum, high volatile content, which helps generate a rich pore structure and usually they are high-density materials, characteristic that positively influences the mechanical properties of the generated adsorbents [22,28]. This means that extremely efficient and low cost adsorbent materials can be obtained [31].

In this context, this study aimed to study alternatives for the reuse of coffee husks in the form of activated carbon, verifying their potential for adsorption of the industrial food Ponceau 4R dye.

MATERIAL AND METHODS

Materials

The coffee husks were obtained from the peeling process in a coffee industry, in the state of Paraná, Brazil. Samples of coffee husks were subjected to the sampling process by quartering, with subsequent separation of dirt. Then, the coffee husk samples placed in low-density polyethylene (LDPE) packages and they were vacuum sealed and stored under refrigeration at 4 ºC until all analyzes were performed.

Characterization of coffee husk

Physical and chemical characterization

In order to determine the physical and chemical composition of the coffee husk samples, the following analyses were performed: moisture content were determined gravimetrically after drying at 105 °C for 8 h; ash was determined by incineration at 550 °C for 8 h; lipid content was obtained by Goldfish extraction using ethylic ether as solvent under reflux for 3 h; protein content was measured by the micro Kjeldahl method; fiber was determined by Weende and Van Soest method [32].

Thermogravimetric Analysis (TGA)

In order to determine the best temperature range for the incineration of the samples and production of the coffee husk charcoal, the thermogravimetric analysis was performed in a thermal analyzer (STA6000 - PerkinElmer) with 6 milligrams of coffee husk that were inserted in a platinum sample holder. Nitrogen was the carrier gas at a flow rate of 20 mL min^{-1} and a temperature of 50 - 650 ºC with a ratio of 10 ºC min^{-1}.

Differential Scanning Calorimetry (DSC)

The differential exploratory calorimetry analysis was performed in a calorimeter (DSC 8500 Perkin Elmer) together with ultramicrobalance (AD-6 Perkin Elmer) with a 50 µL aluminum pan at range of 20 - 300 ºC with a constant rate of 10 ºC min^{-1} and with nitrogen gas at a flow rate of 50 mL min^{-1}.

Fourier transform infrared spectroscopy (FTIR)

The coffee husks were analyzed in spectrophotometer with Fourier Transform and integration sphere (BRUKER - TENSOR 37) by diffuse reflectance in the near infrared region (NIR) from 7,500 to 4,000 cm^{-1} with a resolution of 4 cm^{-1} and accumulating 128 scans.

Preparation of adsorbents

The coffee husks under refrigeration at 4 ºC were washed to remove foreign materials and dried in air oven at 60 °C for 5 h to remove moisture. In the sequence, the raw material was chemical activated using two methods to obtain the activated carbon: (a) activation with phosphoric acid (H_3PO_4) and (b) activation with zinc chloride ($ZnCl_2$).

For the activation using H_3PO_4, first 20 g of coffee husks are mixed with H_3PO_4 solution (85% m/v) in a proportion of 1:1 (w/v) (solid/solvent), making sure that the whole sample are wet, then the mixture was agitated for 5 min and left to rest for 8 h to complete the impregnation of the material. Then, the material was washed with approximately 100 mL of distilled water to remove the excess acid and dried at 110 ºC for 12 h. Then, the sample was carbonized at 400 ºC for 3 h with a temperature ramp of 10 ºC min^{-1}. At the end the sample was washed with sodium bicarbonate solution (2% w/v) until pH = 7 was reached, to remove excess water from the wash the sample was dried in an oven at 105 ºC for approximately 4 h or until complete drying [17].

For the activation using $ZnCl_2$, first 20 g of coffee husks are mixed with 150 mL of $ZnCl_2$ solution (15% m/v) at 80 ºC and then left to rest at room temperature for 24 h to complete the impregnation of the material, where the sample was occasionally mixed. Then, the material was washed with approximately 100 mL of distilled water to remove the excess chloride and dried at 110 ºC for 12 h. Then, the sample was carbonized at 400 ºC for 3 hours with a temperature ramp of 10 ºC min^{-1}. At the end the sample was soaked with 0.5 N hydrochloric acid solution for 24 h and then washed with distilled water until pH = 7 was reached, to remove excess water from the wash the sample was dried in an oven at 105 ºC for approximately 4 hours or until complete drying [33].

The adsorbents obtained were stored in vacuum packages at room temperature until use in the analysis of point of zero charge (PZC), Scanning Electron Microscopy (SEM) and Nitrogen (N_2) adsorption measurements.

Point of zero charge

The point of zero charge (PZC), pH_{pzc}, was determined through method "experiment of 11 points" adapted which consists of mixing 50 mg of the adsorbent in 50 mL of aqueous solution adjusting the pH from 2 to 12 using HCl (0.1 mol L^{-1}) and NaOH (0.1 mol L^{-1}). The solution containing the adsorbent was stirred for 24 h at room temperature at 190 rpm in a shaker (TE-4200 Tecnal, Brazil). At the end of this process, the equilibrium pH was determined [34]. The aqueous solution of Ponceau 4R dye at 10 mg L^{-1} has a pH of about 5.6.

Scanning Electron Microscopy

The coffee husk and adsorbents activated with H_3PO_4 and $ZnCl_2$ were analyzed using a scanning electron microscope (VEGA3 - TESCAN) using on double-sided carbon tape dried and metallized with a thin layer of gold on the surface (5 nm, 35 mA) and magnification power of 5,000x.

Nitrogen adsorption measurements

The adsorption/desorption measurements of N_2 for coffee husk and adsorbents were performed to determine the specific surface area (S_0), average pore volume (V_p) and average pore diameter (d_p) (NOVA 2000e - Quantachrome Instruments). In addition, the samples were subjected to previous activation at 150 ºC under vacuum for 3 h to determine the S_0 values by the Brunauer, Emmett and Teller (B.E.T.) method.

Adsorption studies

Preliminary assays and experimental design

Preliminary adsorption assays were performed to evaluate the adsorptive capacity of the materials (H_3PO_4 and $ZnCl_2$). The solutions containing 50 mL of Ponceau 4R dye solution (10 mg L^{-1}) and the adsorbents (2 g L^{-1}) were incubated in a shaker (TE-4200 Tecnal) for 12 h. The adsorptive capacity of the material was evaluated by removing the dye molecules by the adsorbent present in the solution according to Equation (1), using an UV spectrophotometer (model EEQ-9006, Astral Scientific) at the wavelength of 507 nm to determine concentrations.

$$\mathrm{R} = \left(\frac{C_0 - C}{C_0}\right) \mathrm{x}\ 100 \tag{1}$$

where: R (%) is the percentage of removal of the Ponceau 4R dye from the solution by the adsorbent, C_0 (mg L^{-1}) is the initial concentration, C (mg L^{-1}) is the final solution concentration.

Then, in order to optimize the quantity of dye adsorbed in the equilibrium (q_e), Equation (2), an experimental design was proposed considering the variation of the adsorbent concentration (1, 1.5 and 2 g L^{-1}) and the contact time (30, 60 and 90 min) by means of 2^2 factorial design with central point triplicate (Table 1). The adsorption assays with Ponceau 4R dye solution (10 mg L^{-1}) were performed at room temperature at 190 rpm in a shaker (TE-4200 Tecnal, Brazil).

$$q_e = \left(\frac{C_0 - C_e}{m}\right) V \tag{2}$$

where: q_e (mg g^{-1}) is the quantity of Ponceau 4R dye adsorbed at equilibrium, C_e (mg L^{-1}) is the equilibrium concentration, m (g) is the mass of adsorbent, V (L) is the volume of the solution of the dye Ponceau 4R.

Table 1. Factorial design 2^2 with central point to evaluate the adsorptive capacity of Ponceau 4R dye.

Factors	**Levels**		
	- 1	**0**	**+ 1**
Concentration (g L^{-1})	1	1.5	2
Time (min.)	30	60	90

Adsorption kinetics and isotherms

The adsorption kinetics was performed for the adsorbent with the most adequate performance in the preliminary assays, measuring 11 points (1, 5, 10, 20, 30, 40, 50, 60, 70, 80 and 90 minutes) in order to obtain the equilibrium time of the process. Consequently, the results were adjusted with the models of Equations (3) to (6) to determine the theoretical value of the quantity of Ponceau 4R dye adsorbed at equilibrium time (q_e).

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

where: q_t (mg g^{-1}) is the adsorbed quantity at time t (min), q_e (mg g^{-1}) is the adsorbed quantity in equilibrium, k_1 (min^{-1}) is the pseudo-first-order kinetic constant.

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

where: k_2 (g mg^{-1} min^{-1}) is the pseudo-second-order kinetic constant, h (mg g^{-1} min^{-1}) is the initial adsorption rate.

$$q_t = \frac{1}{\beta}\ \ln(\alpha\beta t) \tag{5}$$

where: β (g mg^{-1}) is the desorption constant, α (mg g^{-1} min^{-1}) is the initial adsorptive rate.

$$q_t = \left(k_{ip}\ t^{\frac{1}{2}}\right) + C \tag{6}$$

where: k_{ip} (mg g^{-1} $min^{-0.5}$) is intraparticle diffusion coefficient, C is constant of the intraparticle diffusion model.

Afterwards, the isotherms were carried out at three temperatures (25 C, 35 C and 45 C) with the adsorbent in the concentration at the optimum point of the factorial design and with variation in the concentration (10 to 100 mg L^{-1}) of the Ponceau 4R dye according to the models of Equations (7) and (8).

$$q_e = \frac{q_m\ k_L\ C_e}{1+(k_L\ C_e)}\ ,\ R_L = \frac{1}{1+(K_L C_0)} \tag{7}$$

where: q_m (mg g^{-1}) maximum quantity adsorbed, k_L (L mg^{-1}) constant of adsorption capacity by the Langmuir model, R_L is the Langmuir isotherm separation factor, C_0 (mg L^{-1}) maximum initial concentration.

$$q_e = k_F\left({C_e}^{\frac{1}{n}}\right) \tag{8}$$

where: k_F (L mg^{-1}) constant of adsorption capacity by the Freundlich model, n is the Freundlich exponential constant.

Thermodynamic parameters of adsorption

Based on the analysis of the adsorption isotherms, the thermodynamic behavior of the Ponceau 4R dye adsorption process was evaluated according to the enthalpy (ΔH), entropy (ΔS) and Gibbs free energy (ΔG) parameters. Thus, it was necessary to obtain the adsorption thermodynamic equilibrium constant (K_a) for the temperatures (298.15; 308.15; 318.15 K) studied, according to the Equation (9). The values of ΔH and ΔS were obtained using the angular and linear coefficients of the Van't Hoff by Equation (10). The spontaneity of the reaction was defined by the Equation (11).

$$K_a = \frac{q_e}{C_e} \quad (9)$$

where: K_a constant obtained by means of a graph of ln (q_e/C_e) as a function of q_e.

$$\ln (K_a) = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (10)$$

where: R (8.314 J mol^{-1} K^{-1}) is the universal constant of ideal gases, ΔH variation of enthalpy (kJ mol^{-1}) and ΔS (kJ mol^{-1} K^{-1}) variation of entropy.

$$\Delta G = \Delta H - T\,\Delta S \quad (11)$$

where: ΔG (kJ mol^{-1}) is the variation of Gibbs free energy and T (K) is the temperature

Statistical analyses

The results were expressed as mean ± standard deviation, the statistical analysis of the experimental data adjusted to the linear and nonlinear models was performed using Origin 8.5 software (OriginLab., Northampton, MA, U.S.A.).

RESULTS AND DISCUSSION

Characterization of coffee husk

The physical and chemical composition of the coffee husk varies according to extrinsic factors such as soil composition, the geographic location of cultivation, the process of processing and storage of the husks, as well as intrinsic factors such as the absorption capacity or water loss, coffee variety, secondary metabolites, among others. Thus, the results of the physical and chemical characterization of the raw coffee husk (Figure 1a) showed expressive values in relation to the moisture content (23.93 ± 0.23 g 100 g^{-1}), the crude fiber content (19.41 ± 3.23 g 100 g^{-1}), proteins (8.06 ± 0.66 g 100 g^{-1}) and ash (5.24 ± 0.03 g 100 g^{-1}), respectively.

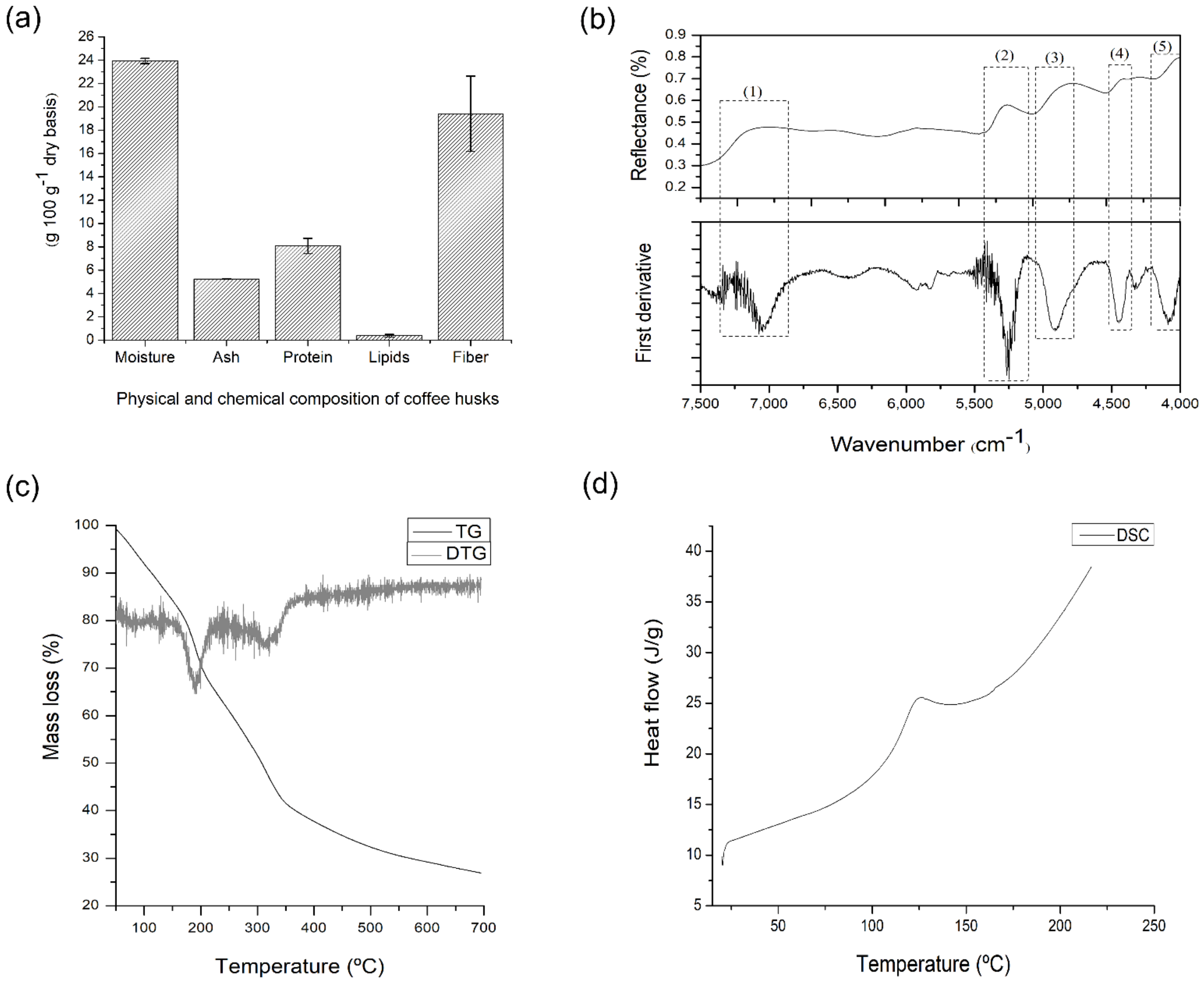


Figure 1. (a) Physical and chemical composition of coffee husks; (b) Near-infrared reflectance spectra and first derivative transformed spectra of coffee husks; (c) Thermogravimetric analysis (TG) and differential thermal analysis (DTG) of the coffee husks; (d) Differential scanning calorimetry (DSC) analysis of coffee husks.

It is noteworthy that of the constituents, the ash content can serve as an indication that the material can be used as an adsorbent, since the ash is inorganic residues that remain after the process of incineration of organic matter and has an quantity of minerals that can favor the mechanism of adsorption, such as carbon and silicon [35].

In addition, for the characterization of coffee husks, spectroscopic and thermal analyzes were performed. In the case of FTIR spectroscopy, in the near infrared region (Figure 1b), it was possible to identify characteristic peaks and associate them with the chemical structure of the components present in the coffee husks through reflectance and the first derivative. The spectrum was divided into five regions, where there were expressive bands between 6,800 and 7,250 cm^{-1} (region 1) with the first stretching overtone (O – H) linked to the water band, as well as from 5,200 to 5450 cm^{-1} (region 2) of the second overtone of carbonyl groups (C – H) associated with the presence of cellulose, between 5100 to 4,750 cm^{-1} (region 3) combination bands of O – H stretching and O – H deformation, characteristic region of tannins molecules, from 4,500 to 4,300 cm^{-1} (region 4) as the first overtone that can indicate vibrations of the C = O, C = C and C = N bonds, linked to the presence of caffeine in the coffee husk and finally between 4,250 to 4,000 cm^{-1} (region 5), region C – H stretching and C – H deformation linked to the presence of lignin [36–38].

Regarding the thermal characterization of the coffee husk, the results of the thermogram (TG) and its derivative (DTG) as well as the differential scanning calorimetry (DSC) can be seen in Figure 1c and 1d, respectively. On the one hand, by analyzing the TG/DTG curves (Figure 1c) it was possible to observe that the thermal decomposition of the coffee husk occurred in three consecutive steps. The first loss of mass occurred at approximately 150 ºC and is due to the loss of mass of water from the sample due to dehydration, which leads to a decrease of approximately 15 % of the initial mass. The following steps are due to the thermal decomposition of the sample, and the second and third mass loss events are due to the decomposition of organic compounds present in the material such as cellulose, hemicellulose and lignin, totaling a loss of approximately 70% of mass and the rest of the mass corresponds to the mineral content. On the other hand, by analyzing the DSC curve (Figure 1d) it was possible to observe the beginning of an endothermic event at approximately 110 ºC that dissolves at approximately 125 ºC, after this endothermic peak the curve only showed exothermic events of thermal decomposition. This endothermic peak is associated with sample dehydration according to TG analysis. The sample decomposition occurs in energetic terms in an exothermic way with consecutive and concomitant events, which was observed in literature [39–42].

Characterization of adsorbents

The adsorbents were characterized by PZC, SEM and N_2 adsorption/desorption measurements. In the case of the PZC results, it can be seen in Figure 2a that the pH_{PZC} values of the coffee husk ($pH_{PZC} = 6.60$) and the $ZnCl_2$ adsorbent ($pH_{PZC} = 6.12$) were higher than the $pH_{PZC} = 5.6$ value, referring to the solution of Ponceau 4R dye. Thus, the surface of the adsorbents (coffee husk and $ZnCl_2$) is negatively charged, and this causes cations to be adsorbed on the material surface to balance the negative charges. As for the H_3PO_4 adsorbent ($pH_{PZC} = 2.75$), the pH is below the pH_{PZC} of the dye, so the surface of the adsorbent is positively charged, which leads to the attraction of negatively charged charged species, it is known that dye molecules present free electrons in their structure, so there is a tendency to have a negative charge, contributing to the adsorption process [30].

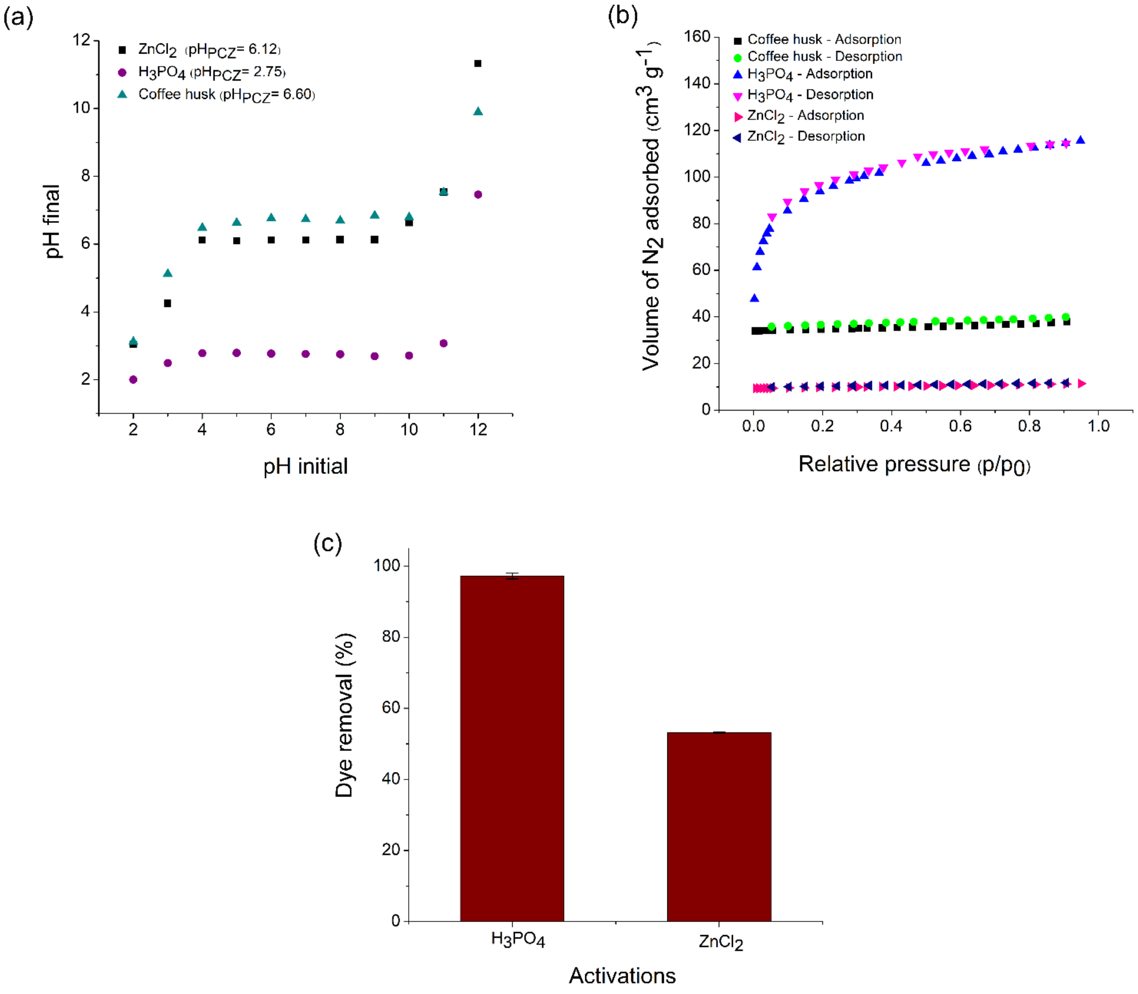
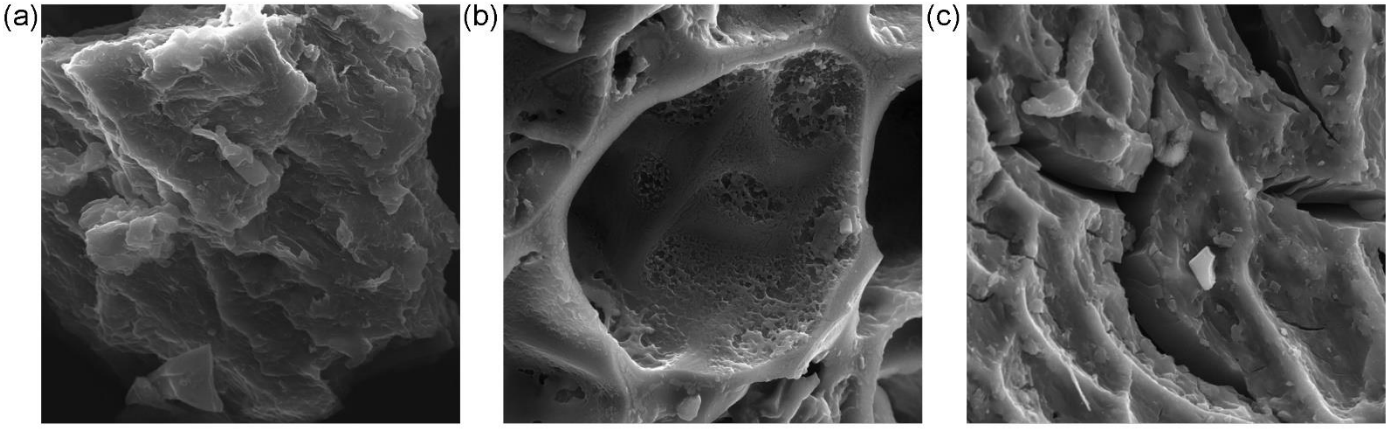


Figure 2. (a) Determination of the point charge zero (PZC) of the coffee husk and the synthesized adsorbents, with phosphoric acid (H_3PO_4) and with zinc chloride ($ZnCl_2$); (b) Isotherms of adsorption (A) and desorption (D) of nitrogen (N_2) from the coffee husk and the synthesized adsorbents H_3PO_4 and $ZnCl_2$; (c) Ponceau 4R dye removal percentage in preliminary adsorption assays with synthesized adsorbents H_3PO_4 and $ZnCl_2$.

Based on the study of N_2 physisorption for the studied materials it was possible to observe that the isotherms (Figure 2b) for the $ZnCl_2$ adsorbents and coffee husks were similar to type II isotherms, typical of non-porous or macroporous materials, while the H_3PO_4 adsorbent isotherms were similar to type I isotherms, typical of microporous materials ($d_p < 20$ Å) [43,44].

These results corroborate with the micrographs of the materials (Figure 3), where the structures of the crude material (Figure 3a) and chemically treated with $ZnCl_2$ (Figure 3c) had structure with irregular particles and with almost no presence of pores, this lack of pores in the material structure may be due to the possible process of sintering, which ends up causing a collapse of the porous structure of the material, also causing a low surface area. Both of this characteristic makes the adsorption process difficult, since the adsorbate molecules do not find a location to adsorb themselves. While the surface of the material chemically treated with H_3PO_4 (Figure 3b) showed a high pore distribution over the entire surface, an important factor in the adsorption process, since the adsorbate molecules find suitable sites to be adsorbed, a behavior similar to that found for porous materials in the literature [4,43,45].



(d)

Samples	S_0 (m^2 g^{-1})	V_p (cm^3 g^{-1})	Dp (Å)
Coffee husk	4.6	0.009	33.29
H_3PO_4 adsorbent	429.7	0.240	11.38
$ZnCl_2$ adsorbent	1.8	0.003	19.46

Figure 3. (a) Determination of the point charge zero (PZC) of the coffee husk and the synthesized adsorbents, with phosphoric acid (H_3PO_4) and with zinc chloride ($ZnCl_2$); (b) Isotherms of adsorption (A) and desorption (D) of nitrogen (N_2) from the coffee husk and the synthesized adsorbents H_3PO_4 and $ZnCl_2$; (c) Ponceau 4R dye removal percentage in preliminary adsorption assays with synthesized adsorbents H_3PO_4 and $ZnCl_2$.

In addition, the adsorbent treated with H_3PO_4 had the largest surface area around 430 m^2 g^{-1} in relation to the other materials and it had the lowest pore diameter value (11.4 Å) according to Figure 3d, which corroborates with its isotherm (Figure 2b), characterizing the material as microporous. The combination of high surface area and micropore diameter reveals the characteristics of adsorbent materials in relation to their effectiveness [43,46,47].

According to the results from micrographs and analyzes of N_2 physisorption, it was observed that the structure of the adsorbent treated with phosphoric acid would be conducive to the removal of the Ponceau 4R dye, since the structure of the material is highly porous with a high area superficial. Thus, preliminary assays were carried out to evaluate the percentage of dye removal by the materials H_3PO_4 and $ZnCl_2$, according to Figure 2c. It can be seen that the adsorbent treated with H_3PO_4 promoted removal of approximately 100 % of the dye, while the adsorbent $ZnCl_2$ managed to remove only around 50 %. Other studies in literature using coffee husks in the adsorption of dyes reported similar values to those obtained in this study, which reinforces the theory that coffee husks can be used as an adsorbent, such as removing approximately 94% of a 12 ppm solution of crystal violet dye [4], or removing approximately 99% of a 50 ppm solution of malachite green dye using acid treated coffee husks as an adsorbent [14], or removing approximately 100% of a 100 ppm solution of methylene blue dye, using hydrochar derived from coffee husks [48].

The difference in the removal of the Ponceau 4R dye by the different adsorbents observed in Figure 2c), can be explained by the characterization analysis of the materials. Through the PZC analysis, it was possible to observe that the H_3PO_4 adsorbent has its surface positively charged, which makes it suitable for the adsorption of anionic molecules, such as the Ponceau 4R dye molecules. While the $ZnCl_2$ adsorbent showed a low presence of pores in the structure and a low surface area, which hinders the process of adsorption of the adsorbate molecules in the adsorbent, in addition to having its surface negatively charged which ends up promoting repulsion among the negative charges in the reaction medium, making it a barrier to the adsorption of dye molecules and, consequently, impairing its adsorptive capacity.

Therefore, the adsorption study for the Ponceau 4R dye was performed using only the adsorbent treated with H_3PO_4, since it showed satisfactory results in preliminary assays in relation to $ZnCl_2$, and contains the expected morphological, structural and surface characteristics for a material adsorbent and it is also important to report that H_3PO_4 is more easily washed of the materials than $ZnCl_2$, which makes activation with phosphoric acid more environmentally friendly [28].

Thus, in Figure 4 the results for the H_3PO_4 adsorbent in relation to the adsorption kinetics curve are presented, as well as the models applied in the adsorption of the Ponceau 4R dye at a fixed concentration of 10 mg L^{-1} and the parameters obtained in the modeling of the data. Through Figure 4a, it can be seen that the kinetics of the dye was fast in the initial stage of the adsorptive process, where 50% of the dye present in the solution was adsorbed in less than 10 minutes. In addition, the kinetic equilibration time was approximately 60 minutes, from that point on the quantity of adsorbed dye remained constant, thus continuing the experiment using the obtained equilibrium time value.

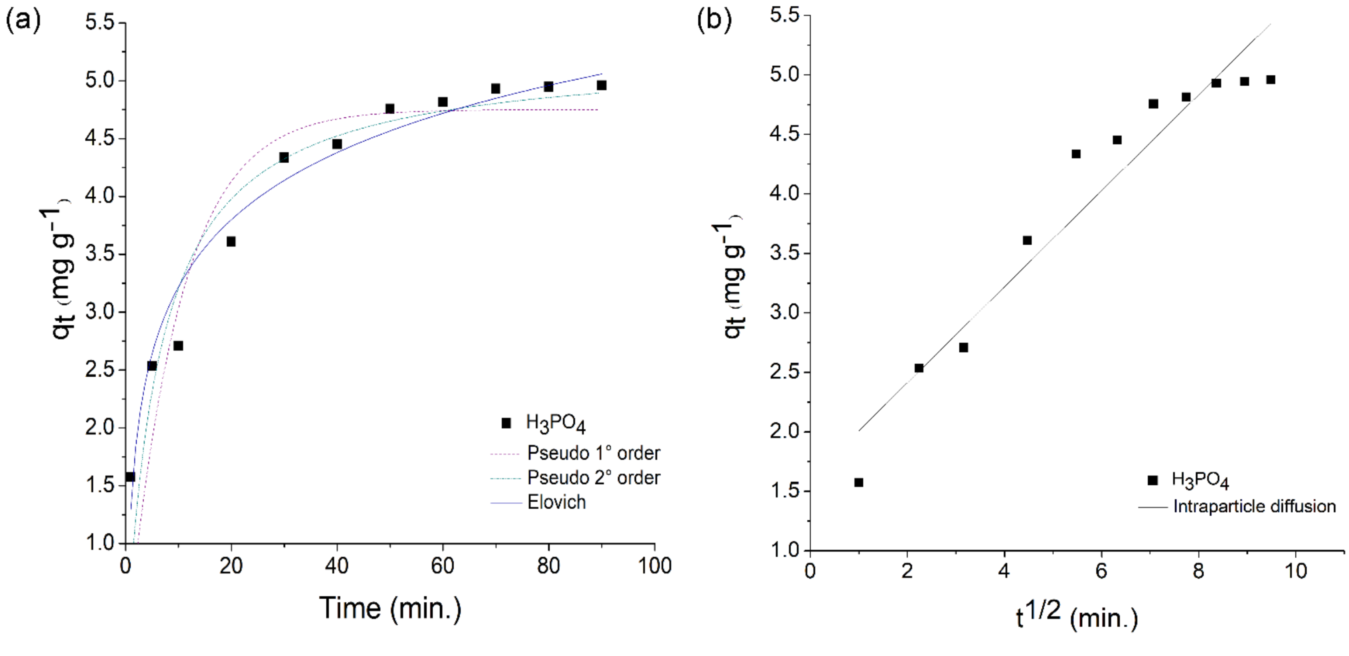


Figure 4. Models of adsorption kinetics of the Ponceau 4R dye with the adsorbent synthesized with H_3PO_4, (a) pseudo-first-order, pseudo-second-order and Elovich model; (b) intraparticle diffusion model.

The theoretical values obtained by both the pseudo-first and pseudo-second-order model, q_e (calc), agree with the values of q_e (exp). The experimental data adjusted to the pseudo-second-order model (R^2 = 0.90 and RMSE < 0.5) (Table 2). Similar results for adsorption kinetics using coffee husks were obtained [4,42], in which the pseudo-second-order model was better suited to the discoloration data of methyl violet and blue methylene dye, respectively.

Table 2. Parameters of mathematical modeling of adsorption kinetics of adsorbent chemically treated with phosphoric acid

C_0 (mg L^{-1})	q_e (exp)	**Pseudo 1° order**				**Pseudo 2° order**				
10	4.95	**k_1**	**q_e (calc)**	**R^2**	**RMSE**	**k_2**	**q_e (calc)**	**h**	**R^2**	**RMSE**
		0.10	4.75	0.82	0.50	0.03	5.24	0.82	0.90	0.37
		Elovich				**Intraparticle diffusion**				
		β	**A**	**R^2**	**RMSE**	**K_{ip}**	**C**	**R^2**	**RMSE**	
		1.19	3.91	0.96	0.23	0.40	1.61	0.92	0.33	

However, the Elovich model presented adjustment ($R^2 = 0.96$ and RMSE < 0.24) to the data experimental kinetics of adsorption of Ponceau 4R dye although it is normally used to determine the gas adsorption kinetics in heterogeneous solids, the model. For a more detailed evaluation of the kinetic behavior, it was possible to identify the stage that controls the adsorptive process, through the study with the intraparticle diffusion model. Since when intraparticle diffusion is the dominant mechanism in the adsorption process, the q_e versus $t^{1/2}$ graph should result in a straight line.

The Figure 4b showed that for times shorter than the equilibrium time (t = 60 min), the graph resulting from the data was linear, indicating that until that moment the intraparticle diffusion mechanism was dominant throughout the process, once that for the following times the value of q_t remained constant. This linearity indicated that the mass transfer process occurred through the boundary layer and the value of C = 1.61 provided an estimate of the width of the boundary layer [49]. The results of the adsorption assays were performed based on the q_e (experimental) design considering the variation of the adsorbent concentration (1, 1.5 and 2 g L^{-1}) and the contact time (30, 60 and 90 min) by means of 2^2 factorial design with central point triplicate.

The results of the statistical analysis of the response variable (q_e) were evaluated in relation to the geometric representation of the 2^2 experimental design with a central point where the central value represents the average of the result obtained from the central point of the experiment, 13.08 mg g^{-1} (Figure 5a). In addition, through the Pareto Diagram, it is possible to evaluate how the factors interfered in the response variable (Figure 5b), where Factor A (Concentration) and B (Time) had a significant statistical effect on the quantity of dye adsorbed (q_e) and the interaction between such parameters was also demonstrated by the interaction graph (Figure 5c), in which the concentration factor in the concentration *versus* time interaction, exerted a statistically significant influence under the variable response qe, since the concentration when passing the low level (1 g L^{-1}) for the high level (2 g L^{-1}), the qe value has practically tripled. While the time factor in the interaction had a low influence on the value of q_e.

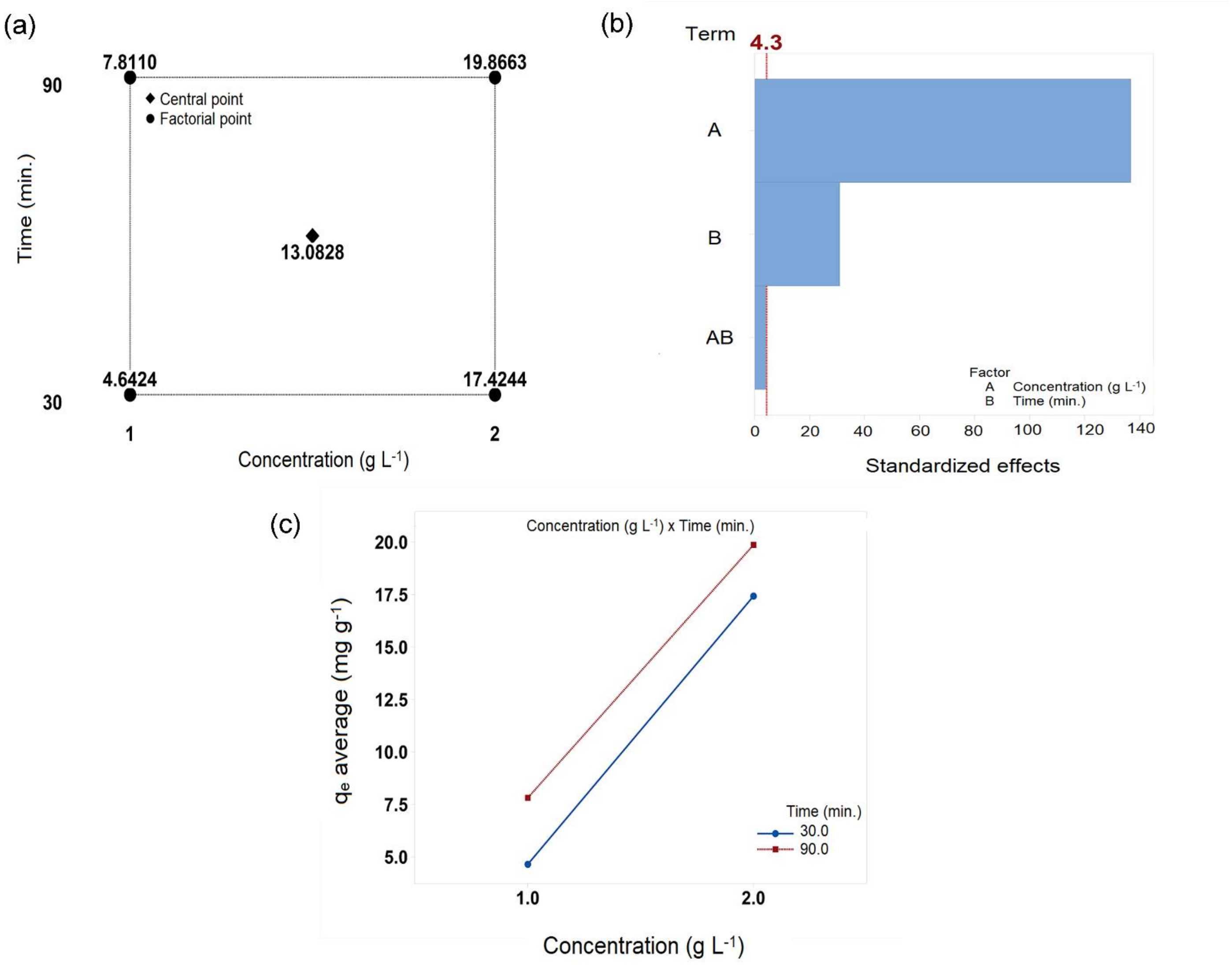


Figure 5. (a) Geometric view of the 2^2 factorial design of the adsorption assays for the H_3PO_4 adsorbent; (b) Pareto diagram of the standardized effect for $\alpha = 0.05$ of the H_3PO_4 adsorbent; (c) Effect of the interaction of the parameters analyzed in the adsorption experiments.

Thus, with the intention of maximizing the value of q_e, the ideal would be to set the concentration value at the highest level, this behavior became clearer when observing the first order response surface model (Figure 6) and the application of the first order regression model ($R_{adj}^2 = 0.999$) by Equation (12), where it can be seen that the adjustment that maximizes the quantity of adsorbed Ponceau 4R dye was obtained by fixing the adsorbent concentration at the highest level (2 g L^{-1}) in the longest time (90 min.), where a q_e of approximately 19.87 mg g^{-1} was obtained.

$$y = -0.012\, x_1 x_2 + 0.065\, x_1 + 13.140\, x_2 - 9.555 \tag{12}$$

where: y (mg g^{-1}) is the quantity of Ponceau 4R dye adsorbed, x_1 (min) is the reaction time and x_2 (g L^{-1}) is the adsorbent concentration.

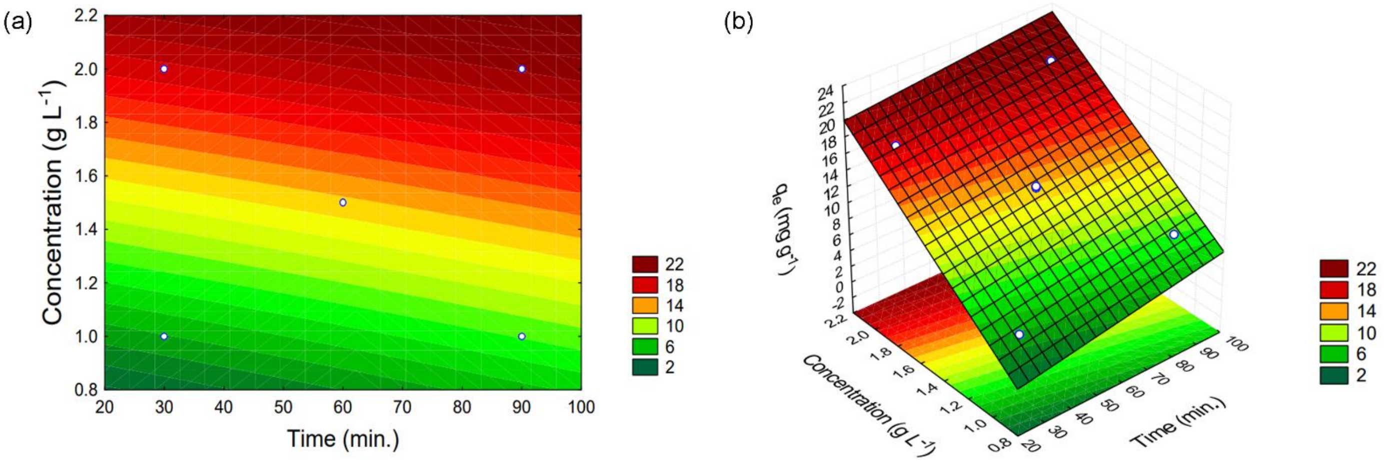


Figure 6. Graphs of contour lines and response surface methodology of the pseudo-first-order model of the H_3PO_4 adsorbent assays.

Adsorption studies

The adsorption isotherms as well as the adjusted models and the parameters obtained in the data modeling are shown in Figure 7, respectively at the proposed temperatures. Analyzing the adsorption isotherms, it was found that up to the concentration of 40 mg L^{-1}, a linear isotherm was obtained, and for the above concentrations, the shape of the isotherms indicated favorable adsorption, and the increase in temperature caused an increase in adsorbent adsorption capacity.

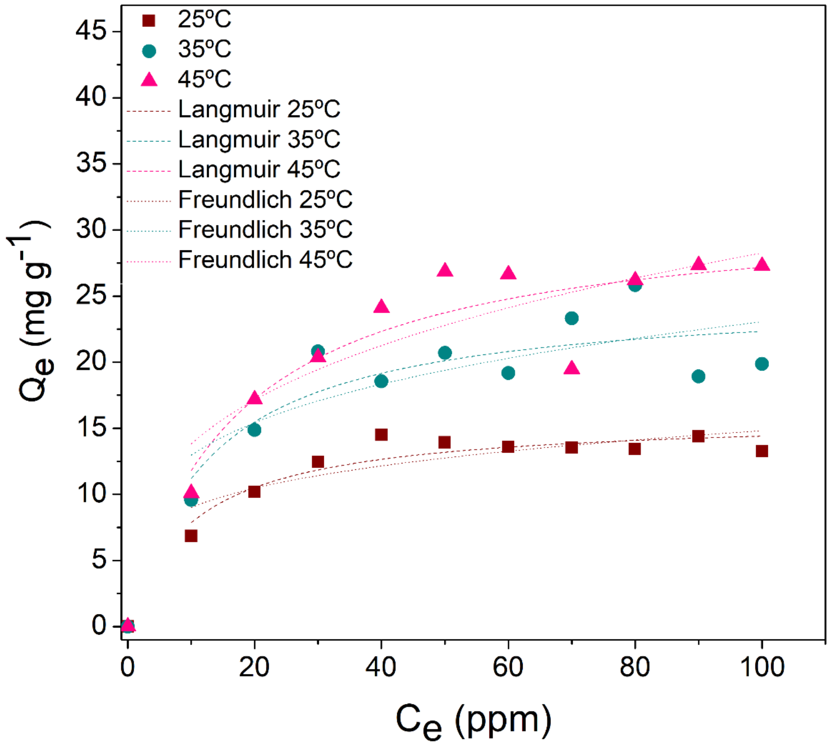


Figure 7. Adsorption isotherms of the Ponceau 4R dye for the Langmuir and Freundlich models at temperatures of 25, 35 e 45 °C

In Table 3 are the thermodynamic parameters obtained in this study in relation to the Langmuir and Freundlich isotherms and comparing the coefficient of determination and the square root of the mean error of these models, it was observed that the Langmuir isotherm showed better adjustment to the experimental data of the Ponceau 4R dye ($R^2 > 0.69$ and RMSE < 2.67) in the concentration range evaluated in this study. The parameter "n" of the Freundlich model, for all temperatures, indicated a favorable adsorption (n >1), a result that confirms the format presented by the isotherms. When analyzing the parameter "q_m" it was possible to observe that the maximum amount of Ponceau 4R dye adsorbed by the adsorbent was at a temperature of 45 ºC (q_m = 31.70 mg g^{-1}), which indicates that the process temperature influenced the process adsorption. The separation factor (R_L) of the Langmuir isotherm varied from 0.10 to 0.17, showing that the adsorption of the Ponceau 4R dye by the adsorbent was a thermodynamically favorable process.

Table 3. Parameters of the Langmuir and Freundlich isotherm models at different temperatures of adsorbent chemically treated with phosphoric acid

T (ºC)	Langmuir isotherm					Freundlich isotherm			
	q_m	k_L	R_L	R^2	RMSE	k_F	n	R^2	RMSE
25	15.80	0.09	0.10	0.84	0.96	5.48	4.63	0.65	1.40
35	25.12	0.08	0.11	0.69	2.56	7.30	4.00	0.54	3.01
45	31.70	0.05	0.17	0.78	2.67	6.77	3.22	0.69	3.17

In addition, the thermodynamic study of the adsorption process allowed to obtain at the studied temperatures T = 25 ° C (298.15 K) the values of ΔG = - 6.70 kJ mol^{-1}, T = 35 °C (308.15 K) the values of ΔG = - 6.92 kJ mol^{-1} and T = 45 ° C (318.15 K) the values of ΔG = - 7.15 kJ mol^{-1}, where the negative values of ΔG indicated that the adsorption of the Ponceau 4R dye on the adsorbent was a spontaneous and thermodynamically favorable process. The lower values of ΔG imply a greater driving force for the adsorption process, where the value of ΔG for the temperature, T = 318.15 K, was the lowest among the three temperatures evaluated. The negative value of ΔH (-0.005 kJ mol^{-1}) confirmed the exothermic nature of the adsorption process. The exothermicity of the adsorptive process was observed by other authors when using coffee husk to remove dyes from solutions [4,50]. The positive values of ΔS (+0.022 kJ mol^{-1} K^{-1}) suggest an increase in entropy at the solid-liquid interface [51,52]. In the present study, although the adsorption has an exothermic character, there was an increase in the adsorptive capacity with increasing temperature.

CONCLUSION

It is concluded with this study, that the reuse of industrial waste, coffee husk, as activated carbon can be carried out, since when it is chemically activated with phosphoric acid, the adsorbent showed high efficiency, around 100%, in the process of adsorption of the Ponceau 4R dye, due to the material's structure being highly porous, with a high surface area and positively charged, moreover, in the thermodynamic studies, negative values of ΔG and ΔH and positive value of ΔS were obtained, demonstrating that the adsorption process was spontaneous and exothermic.

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REFERENCES

1. Berk C, Barros S. Coffee Annual - Global Agricultural Information Network, USDA Foreign Agric. Serv. 2019; 20.
2. Bondesson E. A nutritional analysis on the by- product coffee husk and its potential utilization in food production. [bachelor thesis]. Swedish University of Agricultural Sciences; 2015.
3. Dal-Bó V, Lira T, Arrieche L, Bacelos M. Process synthesis for coffee husks to energy using hierarchical approaches. Renew. Energy. 2019; 142: 195–206.
4. Cheruiyot GK, Wanyonyi XC, Kiplimo JJ, Maina EN. Adsorption of toxic crystal violet dye using coffee husks: Equilibrium, kinetics and thermodynamics study. Sci. African. 2019; 5:1–11.
5. Anastopoulos I, Karamesouti M, Mitropoulos AC, Kyzas GZ. A review for coffee adsorbents. J. Mol. Liq. 2017; 229:555–565.
6. Hanafie R, Alfiana S. Variety and Characteristic of Processed Food Industry Based on Cassava. Agric. Sci. Procedia. 2016; 9:258–63.
7. Zhou Y, Lu J, Zhou Y, Liu Y. Recent advances for dyes removal using novel adsorbents: A review. Environ. Pollut. 2019; 252:352–65.
8. Wong JKH, Tan HK, Lau SY, Yap PS, Danquah MK. Potential and challenges of enzyme incorporated nanotechnology in dye wastewater treatment: A review. J. Environ. Chem. Eng. 2019; 7(103261):1-17.
9. Vacchi FI, Vendemiatti JAS, Silva BF, Zanoni MVB, Umbuzeiro GA. Quantifying the contribution of dyes to the mutagenicity of waters under the influence of textile activities. Sci. Total Environ. 2017; 601–602: 230–6.
10. Zhang J, Na L, Jiang Y, Han D, Lou D, Jin L. A fluorescence-quenching method for quantitative analysis of Ponceau 4R in beverage. Food Chem. 2017; 221:803–8.

11. Salahuddin N, EL-Daly H, El Sharkawy RG, Nasr BT. Synthesis and efficacy of PPy/CS/GO nanocomposites for adsorption of ponceau 4R dye. Polymer. 2018;146:291–303.
12. Mossmann A, Dotto GL, Hotza D, Jahn SL, Foletto EL. Preparation of polyethylene-supported zero-valent iron buoyant catalyst and its performance for Ponceau 4R decolorization by photo-Fenton process. J. Environ. Chem. Eng. 2019; 7(102963):1-7.
13. Hernández Rodríguez M, Yperman J, Carleer R, Maggen J, Daddi D, Gryglewicz G, et al. Adsorption of Ni(II) on spent coffee and coffee husk based activated carbon. J. Environ. Chem. Eng. 2018; 6:1161–70.
14. Krishna Murthy TP, Gowrishankar BS, Chandra Prabha MN, Kruthi M, Hari Krishna R. Studies on batch adsorptive removal of malachite green from synthetic wastewater using acid treated coffee husk: Equilibrium, kinetics and thermodynamic studies. Microchem. J. 2019; 146:192–201.
15. Dias JM, Alvim-Ferraz MCM, Almeida MF, Rivera-Utrilla J, Sánchez-Polo M. Waste materials for activated carbon preparation and its use in aqueous-phase treatment: A review. J. Environ. Manage. 2007; 85:833–46.
16. Moreno-Castilla J, Ferro-Garcia C, Joly MA, Bautista-Toledo JP, Carrasco-Marin I, Rivera-Utrilla F. Activated Carbon Surface Modifications by Nitric Acid. Treatments A-firing. 1995; 4386–92.
17. Patnukao P, Pavasant P. Activated carbon from Eucalyptus camaldulensis Dehn bark using phosphoric acid activation. Bioresour. Technol. 2008; 99:8540–3.
18. Pongkua W, Dolphen R, Thiravetyan P. Removal of gaseous methyl tert-butyl ether using bagasse activated carbon pretreated with chemical agents. J. Chem. Technol. Biotechnol. 2019; 94:1551–8.
19. Duan XL, Yuan CG, Jing TT, Yuan XD. Removal of elemental mercury using large surface area micro-porous corn cob activated carbon by zinc chloride activation. Fuel. 2019; 239:830–40.
20. Taer E, Apriwandi A, Taslim R, Malik U, Usman Z. Single step carbonization-activation of durian shells for producing activated carbon monolith electrodes. Int. J. Electrochem. Sci. 2019; 14:1318–30.
21. Son YR, Park SJ. Preparation and characterization of mesoporous activated carbons from nonporous hard carbon via enhanced steam activation strategy. Mater. Chem. Phys. 2020; 242 (122454):1-10.
22. Ahmed MB, Hasan Johir MA, Zhou JL, Ngo HH, Nghiem LD, Richardson C, et al. Activated carbon preparation from biomass feedstock: Clean production and carbon dioxide adsorption. J. Clean. Prod. 2019; 225:405–13.
23. Li M, Xiao R. Preparation of a dual Pore Structure Activated Carbon from Rice Husk Char as an Adsorbent for CO2 Capture. Fuel Process. Technol. 2019; 186:35–39.
24. Maciá-Agulló JA, Moore BC, Cazorla-Amorós D, Linares-Solano A. Activation of coal tar pitch carbon fibres: Physical activation vs. chemical activation. Carbon. 2004; 42:1367–70.
25. Tran HN, You SJ, Chao HP. Fast and efficient adsorption of methylene green 5 on activated carbon prepared from new chemical activation method. J. Environ. Manage. 2017; 188:322–36.
26. Üner O, Geçgel Ü, Bayrak Y. Preparation and characterization of mesoporous activated carbons from waste watermelon rind by using the chemical activation method with zinc chloride. Arab. J. Chem. 2019; 12:3621–7.
27. Castro LEN, Meurer EC, Alves HJ, Santos MAR, Vasques EC, Colpini LMS. Photocatalytic degradation of textile dye orange-122 via electrospray mass spectrometry. Braz. Arch. Biol. Technol. 2020; 63: 1–15.
28. Prauchner MJ, Rodríguez-Reinoso F. Chemical versus physical activation of coconut shell: A comparative study. Microporous Mesoporous Mater. 2012; 152: 163–71.
29. Wei Q, Chen Z, Cheng Y, Wang X, Yang X, Wang Z. Preparation and electrochemical performance of orange peel based-activated carbons activated by different activators. Colloids Surfaces A Physicochem. Eng. Asp. 2019; 574:221–7.
30. Lee SY, Shim HE, Yang JE, Choi YJ, Jeon J. Continuous flow removal of anionic dyes in water by chitosan-functionalized iron oxide nanoparticles incorporated in a dextran gel column. Nanomaterials. 2019; 9 (1164): 1-11.
31. Guimarães T, Oliveira AF, Lopes RP, Teixeira APC. Biochars obtained from arabica coffee husks by a pyrolysis process: Characterization and application in Fe(ii) removal in aqueous systems. New J. Chem. 2020; 44:3310–22.
32. AOAC. Official Methods of Analysis. Association of Association Official Analytical Chemists. Washington, DC; 2010.
33. Kumar A, Jena HM. High surface area microporous activated carbons prepared from Fox nut (Euryale ferox) shell by zinc chloride activation. Appl. Surf. Sci. 2015; 356:753–61.
34. Alves ACF, Antero RVP, Oliveira SB, Ojala SA, Scalize PS. Activated carbon produced from waste coffee grounds for an effective removal of bisphenol-A in aqueous medium. Environ. Sci. Pollut. Res. 2019; 26:24850–62.
35. Saenger M, Hartge EU, Werther J, Ogada T, Siagi Z. Combustion of coffee husks. Renew. Energy. 2001; 23:103–21.
36. Barbin DF, Felicio ALSM, Sun DW, Nixdorf SL, Hirooka EY. Application of infrared spectral techniques on quality and compositional attributes of coffee: An overview. Food Res. Int. 2014; 61:23–32.
37. Dykes L, Hoffmann L, Portillo-Rodriguez O, Rooney WL, Rooney LW. Prediction of total phenols, condensed tannins, and 3-deoxyanthocyanidins in sorghum grain using near-infrared (NIR) spectroscopy. J. Cereal Sci. 2014; 60:138–42.
38. Xiaobo Z, Jiewen Z, Povey MJW, Holmes M, Hanpin M. Variables selection methods in near-infrared spectroscopy. Anal. Chim. Acta. 2010; 667:14–32.
39. Ballesteros LF, Teixeira JA, Mussatto SI. Chemical, Functional, and Structural Properties of Spent Coffee Grounds and Coffee Silverskin. Food Bioprocess Technol. 2014; 7:3493–503.
40. Mhilu CF. Analysis of Energy Characteristics of Rice and Coffee Husks Blends. ISRN Chem. Eng. 2014; 6:1–6.

41. Orsini RR, Moscardini Filho E, Mercuri LP, Matos JR, Carvalho FMS. Thermoanalytical study of inner and outer residue of coffee harvest: Applications on biomass. J. Therm. Anal. Calorim. 2011; 106:741–5.
42. Oliveira LCA, Pereira E, Guimaraes IR, Vallone A, Pereira M, Mesquita JP, Sapag K. Preparation of activated carbons from coffee husks utilizing $FeCl_3$ and $ZnCl_2$ as activating agents. J. Hazard. Mater. 2009; 165:87–94.
43. Castro LEN, Santos JVF, Fagnani KC, Alves HJ, Colpini LMS. Evaluation of the effect of different treatment methods on sugarcane vinasse remediation. J. Environ. Sci. Heal. - Part B Pestic. Food Contam. Agric. Wastes. 2019; 54:791–800.
44. Richards R. Surface and Nanomolecular Catalysis. CRC Press, New York; 2006.
45. Othman NH, Alias NH, Shahruddin MZ, Abu Bakar NF, Nik Him NR, Lau WJ. Adsorption kinetics of methylene blue dyes onto magnetic graphene oxide. J. Environ. Chem. Eng. 2018; 6:2803–11.
46. Reffas A, Bernardet V, David B, Reinert L, Lehocine MB, Dubois M, Batisse N, Duclaux L. Carbons prepared from coffee grounds by H3PO4 activation: Characterization and adsorption of methylene blue and Nylosan Red N-2RBL. J. Hazard. Mater. 2010; 175:779–88.
47. Hirata M, Kawasaki N, Nakamura T, Matsumoto K, Kabayama M, Tamura T, Tanada S. Adsorption of dyes onto carbonaceous materials produced from coffee grounds by microwave treatment. J. Colloid Interface Sci. 2002; 254:17–22.
48. Tran TH, Le AH, Pham TH, Nguyen DT, Chang SW, Chung WJ, Nguyen DD. Adsorption isotherms and kinetic modeling of methylene blue dye onto a carbonaceous hydrochar adsorbent derived from coffee husk waste. Sci. Total Environ. 2020; 725(138325):1-10.
49. Khambhaty Y, Mody K, Basha S, Jha B. Kinetics, equilibrium and thermodynamic studies on biosorption of hexavalent chromium by dead fungal biomass of marine *Aspergillus niger*. Chem. Eng. J. 2009; 145:489–95.
50. Fasfous II, Farha NA. Removal of Cibacron Brilliant Yellow 3G-P Dye from Aqueous Solutions using Coffee Husks as Non-Conventional Low-Cost Sorbent. Int. J. Chem. Mol. Eng. 2012; 6:908–14.
51. Rajoriya RK, Prasad B, Mishra IM, Wasewar KL. Adsorption of benzaldehyde on granular activated carbon: Kinetics, equilibrium, and thermodynamic. Chem. Biochem. Eng. Q. 2007; 21:219–26.
52. Srivastava VC, Swamy MM, Mall ID, Prasad B, Mishra IM. Adsorptive removal of phenol by bagasse fly ash and activated carbon: Equilibrium, kinetics and thermodynamics. Colloids Surfaces A Physicochem. Eng. Asp. 2006; 272:89–104.