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Evaluation of untreated coffee husks as potential biosorbents for treatment of dye contaminated waters

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Abstract

The objective of this work was to propose an alternative use for coffee husks (CH), a coffee processing residue, as untreated sorbents for the removal of methylene blue (MB) from aqueous solutions. The effects of solution temperature, pH, biosorbent dosage and contact time on MB removal were investigated. The experimental adsorption equilibrium data were fitted to both Langmuir and Freundlich adsorption models. The biosorption kinetics was determined by fitting first and second-order kinetic models to the experimental data, with the second-order model providing the best description of MB adsorption onto coffee husks. pH variations did not present a significant effect on MB removal. Evaluation of thermodynamics parameters indicated that the adsorption is spontaneous and endothermic. The experimental data obtained in the present study demonstrated coffee husks to be suitable candidates for use as biosorbents in the removal of cationic dyes.

Keywords: Biosorption; Agricultural waste; Toxic pollutants

1. Introduction

Quite often large amounts of colored wastewater are generated in industries which use dyes to impart a desired color to their products (food, paper, rubber, textile, plastics), and are discharged into natural streams with undesirable consequences to the environment and to human health. Aside from unpleasant aesthetic aspects, the presence of dyes in natural streams can cause serious harm to the aquatic life by increasing toxicity and chemical oxygen demand, and by hindering photosynthetic phenomena through reduction of light penetration [1]. Also, some dyes, such as methylene blue, can cause injuries to humans and animals by direct contact (eye burns), inhalation (rapid or difficult breathing) or ingestion (nausea, vomiting, mental confusion and others) [2].

Methylene blue (MB), although used in several types of industry (dyeing of silk, leather, plastics, paper and others), has found its most suitable substrate in the synthetic textile fibers industries where it is widely used. Such extensive use often causes problems in the form of colored wastewater and adequate treatments need to be employed for its removal prior to discharge into receiving water streams. Methylene blue has a complicated chemical structure, it is resilient to fading on exposure to light and water and is, therefore, difficult to be removed from wastewaters by commonly used techniques (biological treatment and chemical precipitation). However, since it dissociates in aqueous solutions into methylene blue cation and chloride ions, it is prone to be strongly adsorbed into solids, such as activated carbons.

Adsorption processes using activated carbons have been widely proposed and used for the removal of both organic and inorganic pollutants from aqueous effluents. However, commercially available activated carbons are expensive and, in recent years, a great deal of effort has been put into the proposal and usage of low-cost adsorbents prepared from naturally occurring materials and wastes for the removal of dyes from wastewaters. Agricultural wastes are the chief raw materials being studied for this purpose, for they are renewable, usually available in large amounts and potentially less expensive than other materials to manufacture a diversity of types of adsorbents. Kannan and Sundaram [3] presented a comparative study of removal of methylene blue from aqueous solutions by adsorption onto activated carbons prepared from agricultural wastes, such as bamboo dust, coconut shell, and rice husk

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and straw. The increasing order of relative capacity values for adsorption of methylene blue was found to be smallest for bamboo dust carbon, followed by groundnut shell, coconut shell, rice husk, straw and commercially available activated carbon. The adsorbents prepared from agricultural wastes were claimed to be nearly five times cheaper than the commercial activated carbon. Başar [4] studied the adsorption of the dyes methylene blue, malachite green and crystal violet onto activated carbon prepared from waste apricot. The precursor material was chemically activated with zinc chloride and the BET surface area was determined to be of the order of 1000 m^2/g. Several isotherm models were fitted to the adsorption data, and Langmuir's and Frumkim's models were found to best represent the equilibrium data for the three dyes and waste apricot activated carbon system.

The kinetics and thermodynamics of methylene blue adsorption on wheat shells was studied by Bulut and Aydin [1]. The results demonstrated the suitability of such waste for the removal of MB from aqueous solutions with the sorbent achieving high levels of color removal with low contact times between the adsorbent and the dye. Hameed et al. [2] used bamboo as precursor material for the preparation of activated carbon and used it to remove methylene blue from aqueous solutions by adsorption. The bamboo-based activated carbon presented adsorption behavior suitably described by a monolayer Langmuir-type isotherm and the kinetic data followed a pseudo second-order kinetic model. The value for the maximum adsorption capacity was comparable to those for commercial activated carbons. Crini [5] presented a comprehensive review on the use of non-conventional low-cost adsorbents for dye removal from aqueous solutions.

The processing of coffee generates significant amounts of agricultural wastes. Coffee husks (CH), comprised of dry outer skin, pulp and parchment, are probably the major residues from the handling and processing of coffee, since for every tonne of coffee beans produced, approximately 1 tonne of husks are generated during dry processing [6]. The production of coffee in Brazil in the last 5 years ranged from 17,000 to 27,000 tonnes [7], which represents an average of over 20,000 tonnes of coffee husks being produced every year. To our best knowledge, there are no profitable uses for this type of residue and its disposal constitutes a major environmental problem in Brazil. Although combustion of coffee husks is a common practice in farms, it has already been demonstrated that major problems are prone to happen, such as agglomeration, fouling and excessive emissions, due to the low melting point of the ash of burnt coffee husks and the significant amount of volatile organic matter present in the husks [6]. Furthermore, since sustainable development should be prioritized, the development of techniques for giving additional value and reusing this type of residue should be sought.

In view of the aforementioned, the objective of this study was to investigate the potential of dry coffee husks to be used as natural untreated biosorbents for the removal of dyes from synthetic aqueous media. Methylene blue was selected as a model dye because of its ability to be strongly adsorbed onto solid materials.

2. Materials and methods

2.1. Materials

Dry coffee husks were acquired from Samambaia Farm, a coffee producer at Santo Antônio do Amparo, Minas Gerais State, Brazil. The husks were obtained from a dry processed coffee after de-hulling. MB stock solutions were prepared in distilled water. Working solutions (50–500 mg/L) were prepared by diluting the stock solution with distilled water prior to each adsorption test.

2.2. Biosorbent preparation

Coffee husks were washed with distilled water (approximately 300 mL water per g coffee husks), to remove dirt and color, and dried at 105 °C for 5 h in a convection oven. This procedure was necessary in order to assure that MB would not be adsorbed by dirt and that MB determinations would not be affected by color leached from the biosorbent. Afterwards they were treated with 2% formaldehyde solution in order to reduce organic leaching and avoid mould formation during batch adsorption [8].

2.3. Biosorption studies

Batch experiments of biosorption were performed in 250 mL Erlenmeyer flasks, with the flasks being agitated on a shaker at 100 rpm for pre-determined time intervals. The flasks were covered with aluminum foil to avoid photodegradation. In all sets of experiments, a pre-determined amount of coffee husks was thoroughly mixed with 100 mL MB solution. Effect of biosorbent concentration was studied in the range of 2–15 $g\,L^{-1}$ at a fixed dye concentration (100 $mg\,L^{-1}$). Effect of contact time was evaluated at time periods ranging from 15 min to 12 h and dye concentration ranging from 50 to 500 $mg\,L^{-1}$ at a fixed biosorbent concentration (10 $g\,L^{-1}$). Experiments were also carried out at different initial pH values ranging from 3.0 to 11.0, with solution pH being adjusted by employing HCl 0.1 M or NaOH 0.1 M. All tests were performed in three replicates. The pre-established parameters ranges (initial MB concentration, biosorbent concentration and pH) were defined based on literature reports on MB adsorption for other agricultural residues in order to allow comparison in terms of adsorption performance.

2.4. Analysis of methylene blue

After the specified time periods, 5 mL aliquots were taken from the Erlenmeyer flasks and the concentration of MB was determined by a spectrophotometer (Cole Parmer 1100 RS) at 665 nm. The amount of MB 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 and the average values were reported.

2.5. Adsorption isotherms

Both Langmuir and Freundlich models were tested for equilibrium description at 30, 40 and 50 °C. Langmuir isotherm, based on a theoretical model, assumes monolayer adsorption over an energetically homogeneous adsorbent surface containing a finite number of adsorption sites. It does not take into account interactions between adsorbed molecules. It can be represented by the following equation:

$$Q_e = \frac{q_0 K_L C_e}{1 + K_L C_e} \tag{1}$$

where Q_e corresponds to the amount adsorbed per gram of adsorbent at equilibrium ($\mathrm{mg\,g^{-1}}$), C_e is the solute concentration ($\mathrm{mg\,L^{-1}}$) in the aqueous solution after equilibrium was reached, and q_o and K_L are constants related to the maximum adsorption capacity ($\mathrm{mg\,g^{-1}}$) and the adsorption energy ($\mathrm{L\,mg^{-1}}$), respectively. The product of q_0 and K_L corresponds to the constant for Henry's Law [2]. Another characteristic parameter of the Langmuir isotherm is the dimensionless factor r, called separation factor:

$$r = (1 + K_L q_0)^{-1} \tag{2}$$

Adsorption is considered favorable when $0 < r < 1$ [9].

Freundlich's equation is an empirical model based on heterogeneous adsorption over independent sites and is given by:

$$Q_e = K_F C_{eq}^{1/n} \tag{3}$$

where K_F represents the adsorption capacity ($\mathrm{mg\,g^{-1}}$) and n is related to the intensity of adsorption [2,10].

2.6. Adsorption kinetics

The controlling mechanism of biosorption process was investigated by fitting first- and second-order kinetic models to the experimental data. The linearized first-order kinetic model is given as [2]

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{4}$$

where q_e and q_t correspond to the amount of dye adsorbed per unit mass of biosorbent (mg/g) at equilibrium and at time t, respectively, and k_1 is the rate constant for first-order adsorption ($\mathrm{min^{-1}}$). The linearized second-order kinetic model is given as [2]

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{5}$$

where k_2 is the rate constant for the second-order adsorption kinetics ($\mathrm{g\,mg^{-1}\,min^{-1}}$). The straight-line plots of $\ln(q_e - q_t)$ against t and of t/q_t against t were used to determine the rate constants and correlation coefficients for the first and second-order kinetic models, respectively.

2.7. Thermodynamic parameters

The free energy change (ΔG°), enthalpy change (ΔH°), and entropy change (ΔS°) were determined in order to evaluate the effect of temperature on MB adsorption by coffee husks. The Gibbs free energy was evaluated as

$$\Delta G^\circ = -RT \ln K \tag{5}$$

where ΔG° is the standard Gibbs free energy change (J), R is the universal gas constant ($8.314\,\mathrm{J\,mol^{-1}\,K^{-1}}$), T is the absolute temperature (K) and K is the apparent equilibrium constant, defined as [11]

$$K = \frac{C_{ad,e}}{C_e} \tag{6}$$

where C_e and $C_{ad,e}$ correspond to the equilibrium concentration of MB on the solution and on the adsorbent, respectively. Enthalpy (ΔH°) and entropy (ΔS°) values can be obtained from the slope and intercept of a van't Hoff equation of ΔG° versus T:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{7}$$

3. Results and discussion

3.1. Biosorbent characterization

The proximate composition of the coffee husks employed in the present study was determined [12] as 10% water, 11% protein, 2% lipids, 70% carbohydrates and 7% ash. The functional groups at the surface of the husks, characterized by the Boehm method, were predominantly phenolic ($2.24 \pm 0.03\,\mathrm{mmol/g_{sorbent}}$), followed by lactonic ($1.05 \pm 0.03\,\mathrm{mmol/g_{sorbent}}$), carboxylic ($0.60 \pm 0.02\,\mathrm{mmol/g_{sorbent}}$) and basic ($0.49 \pm 0.01\,\mathrm{mmol/g_{sorbent}}$) groups. The PZC value, determined by mass titration, was found to be in the range of 4.3–4.5. A more detailed description of chemical and physical attributes of this biosorbent is presented in a previous study [13].

3.2. Biosorption dynamics

The effect of contact time on MB biosorption by coffee husks is shown in Fig. 1. These results correspond to averages of three measurements, with an average standard deviation of 2.8%. Results indicate that a contact time of 12 h assured attainment of equilibrium for all initial MB concentrations evaluated up to $400\,\mathrm{mg\,L^{-1}}$. The faster adsorption of methylene blue at lower concentrations is an indication that methylene blue adsorption occurs mainly on the surface of the adsorbent. As the MB concentration increases, the adsorption process will probably occur in two stages, the first one at the adsorbent surface (faster) and the second one (slower) in the adsorbent pores. A similar behavior was reported in the literature for MB adsorption onto raw date pits [14]. This behavior could also be attributed to a possible change in adsorption mechanism (in relation to that occurring at lower MB concentrations) due to the persistent presence of a high MB solution to surface concentration gradient. However,

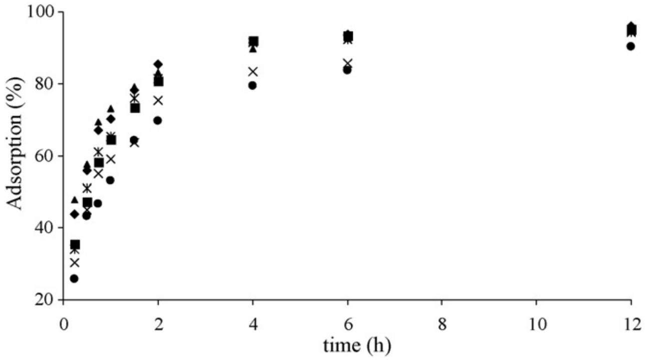

Fig. 1. Effect of contact time on MB sorption by coffee husks (30 °C, pH 8). Initial MB concentration: (♦) 50 mg/L, (■) 100 mg/L, (▲) 200 mg/L, (×) 300 mg/L, (*) 400 mg/L and (●) 500 mg/L.

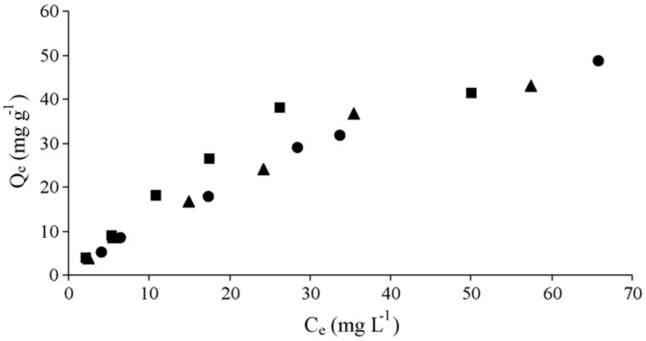

Fig. 3. Sorption isotherms of MB by coffee husks (pH 8). Temperature: (■) 30 °C, (●) 40 °C, (▲) 50 °C.

an exact explanation cannot be given since the exact mechanisms taking place cannot be ascertained from this work and further study is required if the mechanisms are to be correctly determined. It can be observed that biosorption presented a two-stage kinetic behavior, for all the initial MB concentrations, with a rapid initial adsorption during the first 2 h, followed afterwards by a much slower rate. The amount of MB adsorbed ranged from 70 to 85% after 2 h and from 90 to 96% after 12 h. Results also show that the time to reach equilibrium does not seem to be significantly affected by the adsorbate initial concentration (<400 mg L^{-1}).

3.3. Biosorption equilibrium

The results obtained for MB uptake capacity after equilibrium attainment as a function of initial MB concentration are displayed in Fig. 2 (average values with S.D. below 1%). These results show that equilibrium capacity for MB adsorption onto coffee husks increased linearly with the increase in initial MB concentration, regardless of temperature, due to the increase in the concentration gradient (driving force). Such results also indicate that the coffee husks remained unsaturated for all the evaluated conditions. It is noteworthy to mention that the pH of the MB solution was measured after all sorption tests, and pH values decreased towards the sorbent PZC value. These results indicate that the relationship between Co and q_e should remain the same for other pH values. Further discussion on the influence of pH values on MB adsorption by coffee husks is presented in Section 3.5. Sorption isotherms are presented in Fig. 3 (average values with S.D. below 1%). The shape of the curves indicate that they are favorable for adsorption. Both Langmuir and Freundlich adsorption models were evaluated for description of MB sorption isotherms (Table 1). MB adsorption from aqueous solutions by coffee husks was better described by Langmuir model in comparison to Freundlich model. An evaluation of K_r (separation factor) values presented in Table 1 corroborates the affirmative of favorable adsorption regardless of temperature, since all K_r values are within the 0–1 range. Maximum MB uptake capacity, represented by q_0 in Langmuir equation, ranged from 73 to 111 mg g^{-1}, and was higher or presented similar values to other residue-based biosorbents reported in the literature for MB adsorption at ambient temperature (Table 2). These results reinforce the feasibility of employing coffee husks as biosorbents for MB removal from aqueous solutions, since it presents good adsorption capacity in comparison to other low-cost residues. Regarding Freundlich isotherm, the slope 1/*n* ranging between 0 and 1 is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero. A value for 1/*n* below one indicates a normal Langmuir isotherm while 1/*n* above one is indicative of cooperative adsorption. An average value of 0.8 was observed for 1/*n*, corroborating the homogeneous nature of the biosorbent surface also consistent with the good Langmuir fit [2].

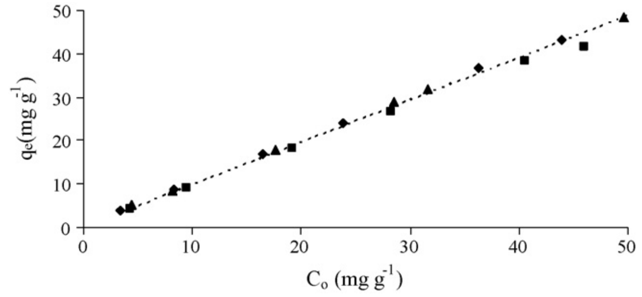

Fig. 2. MB uptake capacity by coffee husks as a function of initial MB concentration (pH 8). Temperature: (■) 30 °C, (▲) 40 °C, (♦) 50 °C. (- - -) Corresponds to a linear correlation between MB initial concentration and uptake capacity q_e (mg g^{-1}) = 0.974C_i (mg g^{-1}).

Table 1
Langmuir and Freundlich isotherm constants for MB biosorption by coffee husks

Model	30 °C	40 °C	50 °C
Langmuir			
K_L (L mg^{-1})	0.0226	0.0119	0.0229
q_0 (mg g^{-1})	90.09	111.11	72.99
r	0.33	0.43	0.37
R^2	0.9983	0.9967	0.9976
Freundlich			
K_F	2.567	1.730	2.094
n	1.29	1.22	1.30
R^2	0.9681	0.9936	0.9906

Table 2
Langmuir based maximum adsorption capacity of several biosorbents for MB adsorption at 30 °C

Adsorbent	q_0 (mg g^{-1}) (temperature °C)	Reference
Activated carbon	400 (32)	[15]
Sewage sludge[a]	114.9 (25)	[16]
Coffee husks	90.1 (30)	This study
Sewage sludge[b]	87.0 (25)	[16]
Phoenix tree leaves	80.9 (–)	[11]
Raw date pits	80.3 (25)	[14]
Rice husks	40.6 (32)	[17]
Paspalum notatum (garden grass)	31.4	[18]
Cereal chaff	20.3 (25)	[19]
Wheat shells	16.6 (30)	[1]
Posidonia oceanica (L.) fibres	5.6 (30)	[20]

[a] Anaerobically digested sludges from an urban wastewater treatment plant.

[b] Sewage sludges from an agrifood industry wastewater treatment plant.

3.4. Effect of biosorbent concentration

The effect of biosorbent concentration on the efficiency of MB removal can be viewed in Fig. 4. It is clear that the amount of dye adsorbed varied with the biosorbent concentration and that MB removal increased with an increase in biosorbent dosage. After the first 3 h of adsorption, the percent removal of MB increased from 52 to 91% with an increase in biosorbent concentration from 2 to 15 g L^{-1}. The resulting effect can be easily explained by an increase in surface area (more availability of active adsorption sites) with the increase in biosorbent mass. The amount of dye adsorbed per unit mass of adsorbent decreased with increasing adsorbent mass, due to the reduction in effective surface area. Similar behavior for the effect of adsorbent concentrations on MB sorption capacity was observed and discussed in the literature for other types of adsorbents [17,19,20].

3.5. Influence of initial pH

The effect of pH on the biosorption efficiency of MB is shown in Fig. 5. MB uptake was lower for pH 3, but did no present significant variations in the pH range from 6 to 11. The low uptake of MB under acidic conditions is probably due the presence of excess H$^+$ ions competing with the dye cation MB$^+$ for the adsorption sites and has been reported by other studies. As pH values increased above the PZC value, which was found to be in the range of 4.3–4.5 [13], the adsorbent surface became predominantly negatively charged, enhancing the electrostatic attraction between the surface and MB cations. A similar behavior has been reported by other MB biosorption studies [10,17,20]. It is noteworthy to mention that the pH of the MB solution was measured after all sorption tests, and pH values varied during sorption towards the PZC value.

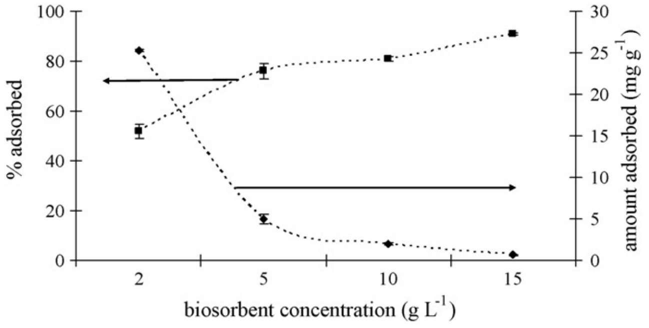

Fig. 4. Effect of biosorbent concentration on MB biosorption by coffee husks (30 °C, pH 8, c_0 = 100 mg/L, t = 3 h).

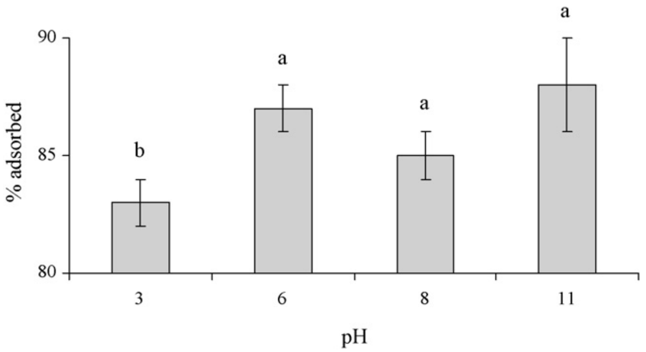

Fig. 5. Effect of initial solution pH on MB biosorption on CH (30 °C, c_0 = 100 mg/L, t = 3 h). (■) % adsorbed; (◆) amount adsorbed per unit mass. Mean values with the same letter do not differ significantly by the Tukey test at 5% probability.

3.6. Biosorption kinetics

The controlling mechanism of MB was investigated by fitting first and second-order models, given by Eqs. (4) and (5), respectively, to the experimental data for the biosorption dynamics at 30 °C. The results of the kinetic parameters are displayed in Table 3. An evaluation of the correlation coefficients indicates that MB biosorption by coffee husks was better described by the pseudo second-order model, which was developed based on the assumption that the rate limiting step may be chemisorption promoted by either valency forces, through sharing of electrons between biosorbent and sorbate, or covalent forces, through the exchange of electrons between the parties involved [21]. The values of the rate constant decreased with increasing initial MB concentration.

3.7. Thermodynamic parameters

Results for thermodynamic parameters evaluation are displayed in Table 4. The negative ΔG° values of MB at various

Table 3
Kinetic parameters for biosorption of MB onto coffee husks at 30 °C

MB initial concentration (mg L^{-1})	Pseudo first-order		Pseudo second-order	
	K_1	R^2	K_2	R^2
50	0.0092	0.0008	0.4854	0.9898
100	0.2745	0.7167	0.1673	0.9950
200	0.3484	0.7850	0.1497	0.9974
300	0.5638	0.8108	0.0608	0.9960
400	0.5675	0.9033	0.0452	0.9959
500	0.6520	0.9239	0.0305	0.9953

Table 4
Thermodynamic parameters for biosorption of MB onto coffee husks

	Temperature (°C)		
	30	40	50
K	24.52 ± 2.28	13.40 ± 2.63	16.72 ± 1.83
ΔG° (kJ mol^{-1})	−8.06 ± 0.24	−6.55 ± 0.56	−7.39 ± 0.31
ΔH° (kJ mol^{-1})		17.693	
ΔS° (kJ mol^{-1} K^{-1})		−0.0331	

temperatures indicates that the adsorption processes are spontaneous. Also, a slight decrease of the absolute value of ΔG° occurred with the increase in temperature above 30 °C. However, no significant differences were observed between 40 and 50 °C. The standard enthalpy and entropy changes of biosorption were 17.693 kJ mol^{-1} and −0.0331 kJ mol^{-1} K^{-1}, respectively. The positive value of ΔH° confirms the endothermic nature of MB biosorption by coffee husks and the negative ΔS° value confirms the decreased randomness at the solid–solute interface during biosorption. The low value of ΔS° also indicates that no remarkable change in entropy occurs.

4. Conclusions

Experiments were conducted to investigate the potential of dry coffee husks as biosorbents for the removal of methylene blue from aqueous solutions. Effects of the experimental conditions on the performance of the coffee husks as biosorbents were studied and the biosorption data were fitted by Langmuir and Freundlich models. The results were best described by Langmuir model. The maximum value of uptake capacity obtained for the coffee husks/methylene blue system was higher than the values encountered in the literature for other untreated agricultural by-products and wastes. The pH of the biosorption system did not present significant effects on the adsorption capacity for values above the determined PZC value (∼4.5). The data obtained from the sorption isotherms at different temperatures were used to calculate thermodynamic parameters, with the results indicating that the biosorption of MB onto coffee husks was spontaneous. A pseudo second-order mechanism was confirmed for the biosorption kinetics. Untreated coffee husks presented a great potential as an inexpensive and easily available alternative adsorbent for the removal of cationic dyes in wastewater treatments. Although tested only for methylene blue, one can safely assume that coffee husks will present similar biosorption performances for the removal of other cationic dyes from aqueous solutions.

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