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ORIGINAL RESEARCH ARTICLE

Thermodynamic study of the adsorption of an azoic dye by a lignocellulosic residue in an aqueous medium

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ABSTRACT

Roasted and ground coffee residue was investigated as an adsorbent lignocellulosic material capable of removing methyl orange dye from aqueous solutions by means of batch adsorption experiments. The effects of experimental parameters on the adsorption behavior, such as initial dye concentration, adsorbent dosage, initial pH and temperature were studied. A better adsorption of the dye was observed at acid pH, low temperature and with an adsorbent dosage of 6 g/L. A Pseudo-second order kinetics was found according to the Lagergren kinetic model. A maximum adsorption capacity of 1.3 mg methyl orange per gram of adsorbent was calculated by fitting the Langmuir model. The adsorption of methyl orange on the adsorbent analyzed was found to be exothermic in nature. The roasted and ground coffee residue was found to be viable for the primary treatment of wastewater contaminated with azoic-type compounds.

Keywords: Roasted Ground Coffee; Kinetics; Adsorption Isotherms; Dye Removal; Sorption

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1. Introduction

Colored wastewater is discharged mainly by the textile, cosmetics, food and paper industries. Color is the first evidence of the pollution generated, as these wastes also cause a reduction in dissolved oxygen and a decrease in light penetration, which affects the photosynthetic processes of aquifers. Many industrial dyes and pigments have toxic and non-biodegradable characteristics and are therefore persistent in the environment. Dyes are classified as cationic, anionic and nonionic, depending on the ionic charge in the molecule, and it is the cationic dyes that have reported the highest toxicity[1-3].

There are physical, chemical and biological processes for the removal of colorants from wastewater, which have their own economic and technical limitations. These processes applied individually are not able to completely degrade or mineralize the color contributing molecules. Although biological processes have been considered effective, the need for large areas, high residence and acclimatization times, and the recalcitrant nature of some dyes are the major limitation for their implementation[4,5].

The degradation of contaminants by chemical or biological processes can produce small amounts of toxic and carcinogenic by-products; this is why conventional methods such as coagulation, flocculation, reverse osmosis, electroflotation or membrane filtration are recommended, which capture the contaminant from the aqueous matrix and eliminate it as a solid residue. The most widely used technology is adsorption with-activated carbon, but this absorbent has a high manufacturing cost and high energy consumption in its regeneration. Due to the above, many natural sorbents have been tested to efficiently reduce the concentration of dyes in aqueous solutions, among which are clays, zeolites, silica and, to a greater extent, residues from the agricultural industry due to their high content of lignocellulosic material (also because they are available in large quantities and lead to the minimization of a subsequent thermal treatment)[4,6,7].

Several adsorbents have been reported in studies (corn husks, rice husks, coconut husk dust, egg shells and cassava husks) that can be considered as an alternative to activated carbon as an adsorbent or complement to the current methods of treatment of colored industrial effluents[4,7,11].

The adsorption capacity of these materials depends, to a large extent, on the ionic forces generated in the solution, the chemical composition of the adsorbent and the pH of the solution; it can also be affected by the concentration of the contaminant, the temperature, the contact time, the particle size of the biomaterial, its porosity and the presence of other species in the solution. The analysis of adsorption processes requires a thermodynamic study that is usually expressed with “adsorption isotherms”, which are essential for the design, calculation of efficiencies and costs of the process. Adsorption isotherms can provide information about the humidity of the monomolecular layer (monolayer) and the strength, by means of the adsorption-desorption enthalpies; they also allow determining the degree of adsorption that can be achieved, the amount of sorbent required and the effect of other variables[12-14].

An example of a hazardous water-soluble dye is methyl orange, an azo derivative that is used from pharmaceutical applications to 5% dye colorant[15]. It exhibits acute oral toxicity with an LD50 in rat of 60 mg/kg, and has been tested as a carcinogen[1].

The growing concern for environmental protection and the preservation of natural resources has led to the promotion of new technologies that reduce water consumption, control effluent discharges and generate lower environmental impacts.

The present work shows results of the adsorption capacity of the roasted and ground coffee residue (CTM), tested on methyl orange solutions as adsorbate. This would represent an exploitation of this residue for the treatment of industrial wastewater contaminated with azoic compounds. The influence of several parameters such as adsorbent dosage, pH, dye concentration and temperature on the adsorption capacity was evaluated. The thermodynamics of adsorption and changes in Gibbs free energy, enthalpy and entropy were studied as parameters required for process scaling. The equilibrium data were analyzed by means of adsorption isotherms. The hypothesis of the project was that the roasted and ground coffee residue has adsorbent activity on azoic compounds, which is affected by parameters such as pH, since these modify the surface characteristics of the adsorbent.

2. Methodology

2.1 Sorbate

Methyl orange is an azoderivative. Its commercial compound name is 4-dimethylaminoazobenzene sulfonic acid sodium salt (**Figure 1**). The methyl orange used is from the Merck trading house.

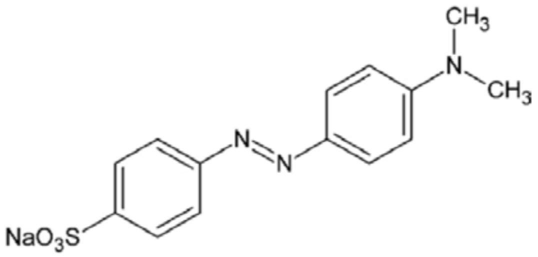

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Figure 1. Structure of methyl orange.

2.2 Sorbent

The material used was obtained from the coffee dispenser of the Institución Universitaria Colegio Mayor de Antioquia, which is a residue of roasted and ground coffee (CTM).

(1) Particle size. The material obtained was sieved with 710 µm, 500 µm, 425 µm and 355 µm meshes for 10 minutes; a higher percentage was retained on the 425 µm mesh.

(2) Heat treatment. In order to obtain the final product, the material was treated with the following procedure: drying for two hours at 110 °C to avoid microbial growth, treatment via soxhlet with distilled water for five hours for three times to free it from impurities[10], and drying for 24 hours at 110 °C. The treated material was stored in a desiccator.

(3) Characterization. The residue was classified as: unactivated, activated and post-treatment. The materials were characterized by thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and specific surface area (BET).

2.3 Adsorption kinetics

The adsorption kinetics experiments were performed by means of a batch experimental design and were carried out by establishing the influence of several parameters (initial dye concentration, adsorbent concentration, temperature and pH). All tests were performed in beakers with a volume of 100 mL of distilled water, and were magnetically stirred at 200 rpm. The concentration of methyl orange was measured initially and then every 15 min in the adsorption process by means of a spectrophotometer (Lab Scient UV-1100), at a maximum absorbance wavelength of 462 nm; the samples taken were previously filtered through a 0.45 µm pore size cellulose filter (Whatman). The dye concentration was calculated by linear regression of a previously performed calibration curve ($A = 0.0606C$, $R^2 = 0.9994$).

The amount of dye adsorbed at any time t, q_t (mg/g), was calculated by means of the mass balance relationship[11]:

$$_t = \frac{V(C_0 - C_t)}{W} \tag{1}$$

Where C_0 and C_t are the initial concentrations, and at a time t for methyl orange (ppm), respectively; V is the volume of the solution (L) and W is the mass of the adsorbent (g).

(1) Effect of adsorbent concentration. The adsorbent dose is a very important parameter in an adsorption study as it determines the capacity of the adsorbent to treat a colored solution of a given initial concentration. The study was conducted at 25 ± 0.5 °C, a concentration of 20 ppm methyl orange and at pH 6; the adsorbent concentration was varied in four levels from 4 to 10 g/L. A graph presenting the amount adsorbed with respect to time was analyzed for each of the adsorbent dosage levels.

(2) Effect of adsorbate concentration. The adsorption of the dye depends on the relationship between its concentration and the available binding sites on the surface of the adsorbent. The study was carried out at 25 ± 0.5 °C, at pH 6 and an adsorbent concentration of 6 g/L; the concentration of methyl orange was varied at four levels: 10, 15, 20 and 25 ppm. A graph showing the amount of adsorption with respect to time was made for each of the adsorbate concentration levels.

(3) Effect of pH. For the system, at a temperature of 25 ± 0.5 °C, an adsorbent concentration of 6 g/L and a methyl orange concentration of 20 ppm, the pH was varied at five levels: 2, 4, 6, 8 and 10. A plot of the degree of adsorption versus time was made for each of the pH levels.

(4) Effect of temperature. The effect of temperature was evaluated at a pH of 6, an adsorbent concentration of 6 g/L and an adsorbate concentration of 20 ppm; the temperature was varied at five levels: 25, 30, 35, 35, 40 and 45 °C. A graph of the adsorption percentage versus time was analyzed for each of the temperature levels.

(5) Adsorption kinetics. The adsorption mechanism of the adsorbent-adsorbate system was analyzed by means of an evaluation of the adsorption kinetics. For this purpose, the Lagergren models for pseudo-first and pseudo-second order are used[11].

The pseudo-first order model assumes that the adsorption rate with respect to time is proportional to the difference between the adsorption capacity at equilibrium (q_e) and the amount adsorbed in a given time (q_t)[11], as shown in equation 2.

$$\frac{q_t}{dt} = k_1(q_e - q_t) \tag{2}$$

And that integrating becomes:

$$ln(q_e - q_t) = \ln q_e - k_1 t \tag{3}$$

The pseudo-second-order model assumes that the rate-limiting step involves chemisorption,

$$\frac{q_t}{dt} = k_2(q_e - q_t)^2$$

(4)

Which integrating becomes:

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

(5)

The proposed orders were plotted with the data obtained for the evaluation of the effect of the initial adsorbate concentration.

2.4 Validation of adsorption kinetics

The Chi-square distribution (equation 6) was used as an error function to validate the kinetic model. A lower value of this error analysis will indicate a better fit of the curve[16] methylene blue (MB. The variables q_{exp} and q_{cal} are the experimentally determined and model-calculated equilibrium adsorption quantities, respectively.

$$= \sum_{i=1}^{n} \frac{(q_{exp} - q_{cal})}{q_{cal}}$$

(6)

2.5 Adsorption isotherms

Adsorption isotherms describe how contaminants interact with adsorbent materials and relate the given equilibrium between them. Freundlich, Temkin and Langmuir isotherms were used to investigate adsorption behavior.

The Freundlich isotherm model describes adsorption on heterogeneous surfaces with sites having different adsorption energies[4]. The Freundlich equation is given as:

$$e = K_F \frac{C_e}{n}$$

(7)

With its linear shape:

$$\log(q_e) = \log(K_F) + \frac{\log(C_e)}{n}$$

(8)

Where K_F is the Freundlich adsorption constant relative to the adsorption capacity of the adsorbent (L/g), q_e is the amount of adsorbate at equilibrium (mg/g), C_e is the concentration of adsorbate at equilibrium (mg/L), and n is a dimensionless constant that can account for the adsorption intensity of the system. The values of K_F and n can be calculated from the intercept and slope of the graph log (q_e) vs. log (C_e)

The Langmuir isotherm model assumes that adsorption occurs at specific homogeneous sites on the adsorbent (monolayer adsorption with finite capacity)[3]. The Langmuir equation[3] is given as:

$$e = \frac{\max K_L C_e}{1 + K_L C_e}$$

(9)

With its linear shape:

$$\frac{e}{q_e} = \frac{1}{q_{\max} K_L} + \frac{e}{q_{\max}}$$

(10)

Where K_L is the Langmuir adsorption constant (L/mg), q_e the amount of adsorption at equilibrium (mg/g), and $q_{\max}$ is the theoretical maximum adsorption capacity (mg/g). A plot of C_e/q_e versus C_e yields the values of $1/q_{\max}$ (intercept) and $1/q_{\max} K_L$ (slope). K_L is an important tool for the calculation of the dimensionless equilibrium parameter that explains the favorability of the adsorption process and is calculated according to equation 11[3].

$$L = \frac{1}{(1 + K_L C_0)}$$

(11)

The Temkin isotherm model applies to systems in which the adsorption enthalpy is inversely proportional to the adsorption capacity. The Temkin equation is given as[3]:

$$e = B_1 \ln K_T + B_1 \ln C_e$$

(12)

Where B_1 is a constant relative to the heat of adsorption and is defined by the expression $B_1 = RT/b$, with b the Temkin constant (J/mol), T in Kelvin and $R = 8.314$J/molk; and K_T is the equilibrium binding constant or Temkin thermal constant (L/g). From a plot of qe versus $\ln C_e$ one can calculate B_1 (slope) and K_T (the intercept is $B_1 \ln K_T$).

2.6 Thermodynamic study

Based on the fundamental concept of thermodynamics it is assumed that in an isolated system no energy can be gained or lost, and entropy change is the only driving force. It is possible to determine the spontaneity of a process by calculating these two factors. The enthalpy and entropy changes will be obtained respectively from the slope and intercept of the linear plot of lnK_d with respect to 1/T of the equation:

$$\ln K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{13}$$

Where $K_d = q_e/C_e$, T is the temperature in Kelvin and R is the gas constant. The change in Gibbs free energy is calculated by equation 14 or equation 15[3].

$$G = H - T\Delta S \tag{14}$$

$$G = -RT \ln K_d \tag{15}$$

3. Results and discussion

3.1 Characterization of the adsorbent

The specific surface area calculated by the BET (Brunauer-Emmett-Teller) method for the residue screened by the 32 mesh, has a value of 0.2648 ± 0.0144 m^2/g, which increases considerably for the heat-treated residue to 0.6558 ± 0.0219 m^2/g.

The TGA study reveals two endothermic stages in the region between 0 °C and 250 °C, corresponding to the loss of the moisture retained in the material[17] thermogravimetric analysis (TGA) and of volatile compounds that compose the adsorbent, which are represented at approximately 290 °C; since the first signal in the unactivated adsorbent (**Figure 2**) is higher than the activated one (**Figure 3**), it can be concluded that the signal corresponds to the release of moisture contained in the material. Given the above, it follows that the treatment temperature is not sufficient to remove all the moisture contained in the material. In the region above 300 °C, two exothermic events are observed for the unactivated and activated adsorbent (**Figure 2** and **Figure 3**); these signals correspond to the final decomposition of the material. In **Figure 4**, the exothermic desorption of the biosorbate is observed at approximately 480 °C, indicating a strong affinity of methyl orange to be adsorbed on the studied material.

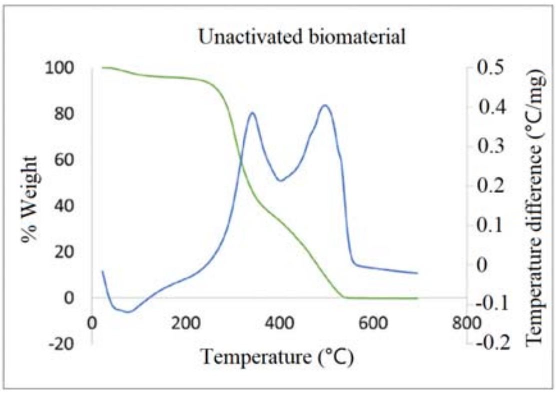

Figure 2. DSC-TGA adsorbent without activation.

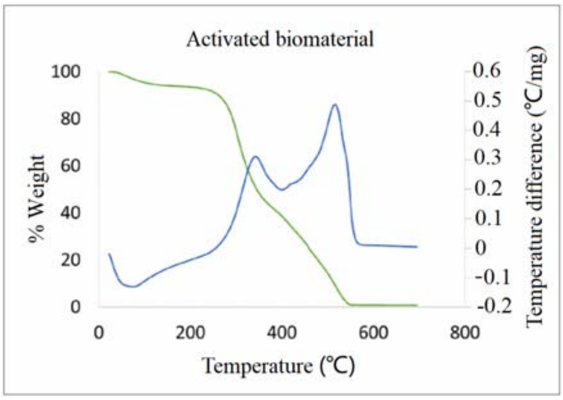

Figure 3. DSC-TGA activated adsorbent.

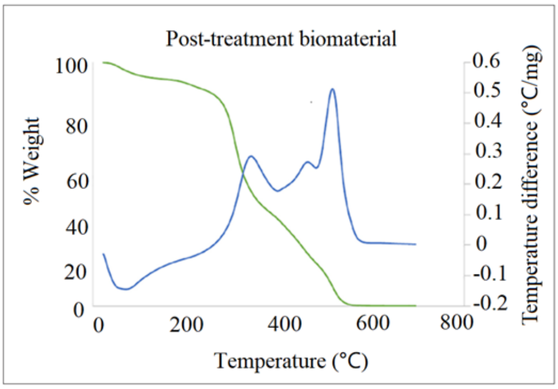

Figure 4. DSC-TGA post-treatment adsorbent.

3.2 Effect of CTM adsorbent dose

The effect of the CTM adsorbent dose on the amount of dye removed is shown in **Figure 5**. It is observed that the amount of dye removed is very low at any of the doses applied, and that, in general, adsorption at the beginning is relatively fast and then reaches equilibrium due to the decrease in the number of vacant surface sites. A maximum of removal is evidenced with 6 g/L, from which it can be deduced that a greater number of sites of interaction with the dye and less desorption effects are present. Because of the above, 6 g/L was the amount used for the other experiments.

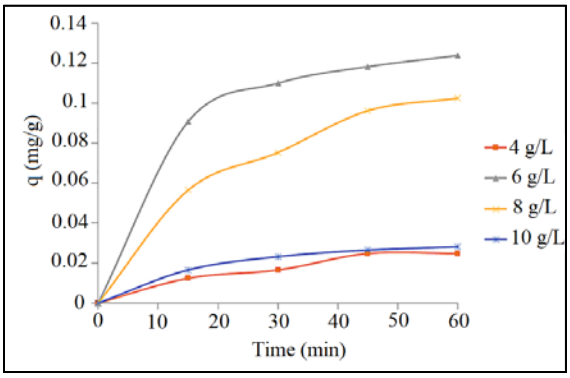

Figure 5. Effect of ctm adsorbent dose on the removal of methyl orange at 20 ppm concentration at 25 °C.

3.3 Effect of adsorbate concentration

The effect of initial dye concentration on adsorption was examined at four concentration levels (10, 15, 20 and 25 ppm). **Figure 6** shows that the 20 ppm concentration of methyl orange provides a significant driving force and increases adsorption, however, higher concentration presents problems possibly due to the existence of repulsive forces between the solute molecules and the adsorbent.

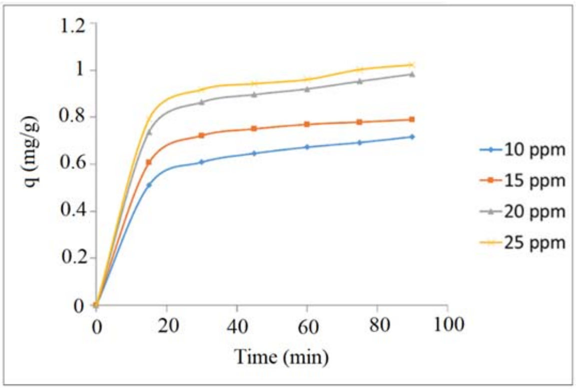

Figure 6. Effect of the initial concentration of methyl orange at 25° C with 6 g/L of CTM adsorbent.

3.4 Effect of temperature

Figure 7 shows that the adsorption of methyl orange decreases with increasing temperature; it is then proposed that this is an exothermic process, which is attributed to the adsorption arising from Van der Waals and dipole forces associated with low heats of adsorption[11].

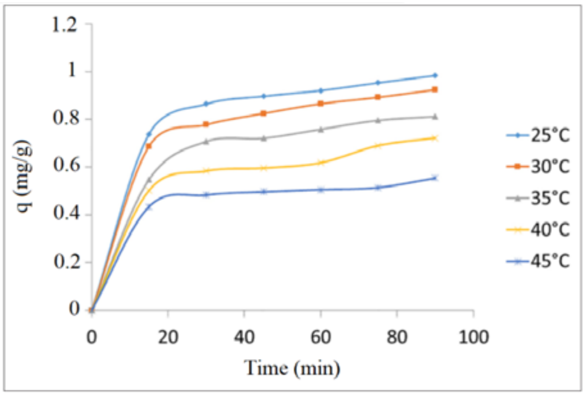

Figure 7. Effect of temperature on the percentage removal of methyl orange with initial concentration 20 ppm and 6 g/L of CTM adsorbent.

3.5 Effect of initial pH

Adsorption is determined by the surface charge of the adsorbent and the state of the adsorbate in the solution. **Figure 8** shows how at a pH of 4 the highest percentage of dye removal is obtained. High adsorption is observed at pH 2 and 4, but decreases towards pH 6. Methyl orange with a ka of 1.6 x 10^{-4} can be in its neutral form (switterion) at acidic pH (**Figure 9**), or in its dissociated form at basic pH and present in equal concentrations at a pH of 3.8.

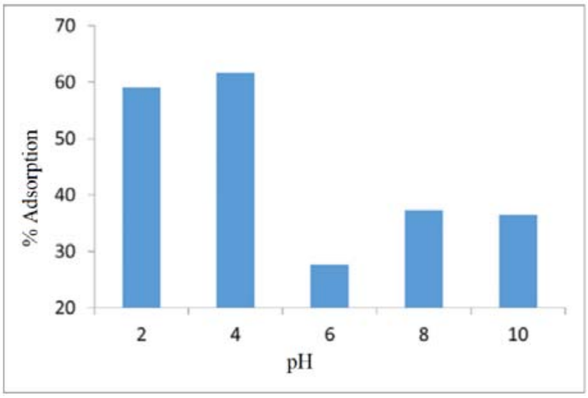

Figure 8. Effect of pH on the percentage removal of methyl orange with initial concentration 20 ppm at 25 °C and 6g/L of CTM adsorbent.

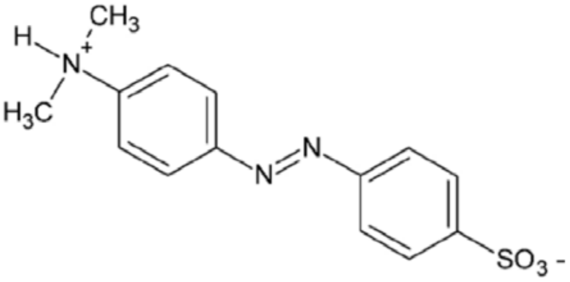

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Figure 9. Switterion of methyl orange.

Therefore, the high adsorption at pH below 4 may be due to the fact that the adsorbent has anionic characteristics and its charges are being neutralized by the positive pole of the switterion. The decrease in adsorption at pH above 4 may be due to repulsion between species with the same charge[16].

3.6 Adsorption kinetics

According to the representations in **Figure 10** and **Figure 11**, it can be inferred that the pseudo-second order model describes the adsorption kinetics of methyl orange on the ground coffee-based adsorbent. The calculated parameters of the kinetic models and the results of the validation with X^2 are reported in **Table 1**, in which it is observed that, according to the values of R^2 and X^2 for the pseudo-second order, the assumption that this model governs the adsorption kinetics is adequate[11].

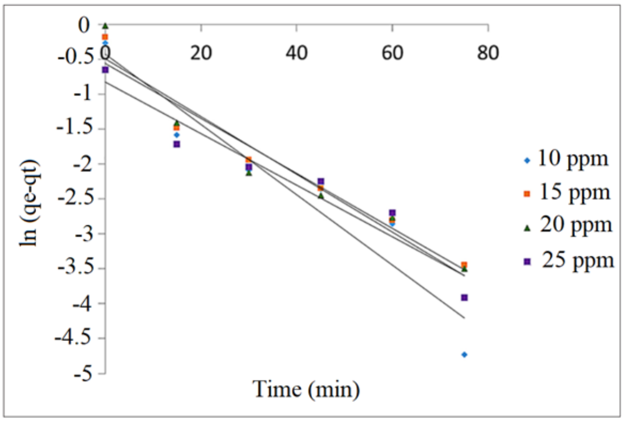

Figure 10. Pseudo first order fit of methyl orange adsorption on CTM adsorbent**.**

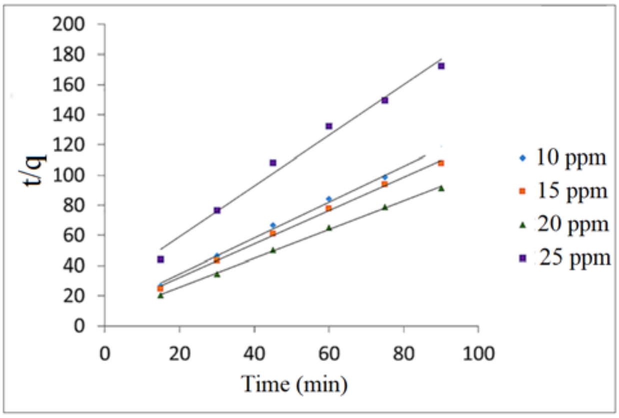

Figure 11. Pseudo-second order fit of methyl orange adsorption on CTM adsorbent**.**

Table 1. List of parameters obtained for pseudo-first order and pseudo-second order adsorption of methyl orange on CTM adsorbent

	Initial concentration of methyl orange (ppm)			
Constants	10	15	20	25
$q_{experimental}$ (mg/g)	0.7694	0.8333	0.9831	0.5215
Seudoprimer order				
$q_{calculated}$ (mg/g)	0.6530	0.5731	0.6150	0.4405
K_1 (min^{-1})	0.0503	0.0394	0.0415	0.0370
R^2	0.9130	0.9513	0.9278	0.9267
X^2	0.0207	0.1182	0.2202	0.0149
Seudoprimer order				
$q_{calculated}$ (mg/g)	0.8386	0.9001	1.0436	0.5927
K_2 (g mg^{-1} min^{-1})	0.1334	0.1266	0.1416	0.1125
R^2	0.9970	0.9981	0.9989	0.9868
X^2	0.0057	0.0050	0.0035	0.0086

Table 2. Calculated parameters for Freundlich, Langmuir and Temkin isotherms

Isotherm	**Constant**	**Value**
Freundlich	K_F	2.29562
	n	3.09310238
	R^2	0.9924
Langmuir	q_{max} (mg/g)	1.30310138
	K_L (L/g)	43.3559322
	R_L	0.00230118
	R^2	0.9997
Temkin	B_1	0.7685
	K_T (L/g)	11.1102066
	b (J/mol)	3223.90631
	R^2	0.9934

Table 3. Thermodynamic parameters for methyl orange adsorption on CTM adsorbent

ΔH (kJ/mol)	**ΔS (J/mol K)**	**ΔG (kJ/mol)**				
		298 K	303 K	308 K	313 K	318 K
-16,15	-32.35	-64.76	-64.57	-60.74	-60.64	-49.92

3.7 Adsorption isotherms

Table 2 reports the parameter values calculated for the isotherms of the Freundlich, Langmuir and Temkin models. The Langmuir isotherm best describes the adsorption of methyl orange on the ctm adsorbent (R^2 = 0.9997), suggesting that it is characterized by homogeneous adsorption (monolayer) and its capacity was calculated to be 1.3031 mg/g by the model fit, which is a non-negligible value considering the azoic nature of the compound[18].

3.8 Adsorption thermodynamics

The values of ΔH, ΔS and ΔG are shown in **Table 3**. The negative value of the enthalpy change

(ΔH) shows that this adsorption process is indeed exothermic. The negative value of the entropy change (ΔS) reflects a decrease in randomness at the adsorbent/solution interface during the process. The values of the change in Gibbs free energy (ΔG) are negative, indicating that the adsorption process occurs spontaneously. The ΔG values increase with increasing temperature, suggesting that the adsorption process is less spontaneous at higher temperatures.

4. Conclusions

The potential of roasted and ground coffee residue as adsorbent material in the removal of methyl orange from aqueous dilutions was investigated. The effects of experimental parameters such as initial dye concentration, adsorbent doses, initial pH and temperature were studied. The pH and adsorbent dosage were the parameters with the greatest effect on the adsorption of methyl orange. The highest adsorption occurred at an adsorbent dose of 6 g/L and for pH values equal to or lower than 4. The experimental data showed a decrease in adsorption with increasing temperature, suggesting an exothermic adsorption process, which was later verified by changes in enthalpy and Gibbs free energy. The resulting adsorption processes showed a best fit to the pseudo-second order kinetics according to the Lagergren model, implying that such processes occur by chemical adsorption with the functional groups existing on the adsorbent surface. The maximum adsorption capacity of methyl orange was estimated to be 1.3 mg per gram of adsorbent according to the Langmuir isotherm model. It was concluded that the ctm adsorbent can be a viable alternative for the removal of azo dyes in primary treatment of industrial effluents.

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Conflict of interest

The authors declared that they have no conflict of interest.

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