

Thermodynamic and kinetic study of the adsorption of dyes on modified graphene oxides

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Abstract

This study investigates the adsorption mechanisms of Methylene Blue (MB) and Methyl Orange (MO) dyes on four porous materials: activated carbon from Cashew Nut Shells (ACNS), graphene oxide (GO), and two graphene oxides with different oxidation levels (GOHOS and GOLOS). ACNS was prepared using H₃PO₄, while GO was synthesized via the modified Hummer method and subsequently modified through sonication. Adsorbents were derived from Cashew Nut Shells and mandarin peels. Characterization involved N₂ adsorption isotherms, FTIR, and Raman spectroscopy. Langmuir, Freundlich, Redlich-Peterson, and Toth isotherm models were employed, with the Freundlich model fitting best. MO exhibited maximum adsorption on GOHOS and ACNS. Kinetic studies suggested pseudo-second order kinetics. The Elovich model provided a reasonable fit, indicating non-uniform diffusion. Thermodynamic analysis indicated spontaneous and endothermic adsorption of MO and MB. The study suggests that while diffusion plays a role, boundary layer diffusion may also influence the adsorption process.

Keywords: Adsorption; Waste Solid; Activated Carbon; Graphene Oxide; Thermodynamic; Kinetic,

1. Introduction

The escalating industrial activity has led to the widespread discharge of diverse organic compounds, including hazardous dyes, into wastewater, posing significant environmental and health risks. Efforts to mitigate this pollution have intensified, focusing on developing cost-effective and efficient treatment methods. While various techniques such as reverse osmosis and advanced oxidation offer promise, their scalability and cost often hinder widespread implementation [1-34]. Adsorption emerges as a viable solution, with materials like metal-organic frameworks showing potential due to their unique properties, albeit with some synthesis limitations. Municipal solid waste, once discarded, now offers a valuable resource for producing adsorbents like activated carbon, addressing environmental challenges sustainably. Meanwhile, graphene oxide, renowned for its surface area and functional groups, has gained attention as a dye adsorbent. However, comprehensive studies on the adsorption mechanisms of dyes like methylene blue (MB) and methyl orange (MO) using different adsorbents remain scarce [22-33]. This study aimed to fill this gap by investigating the adsorption of MB and MO on activated carbon from cashew nuts, graphene oxide from sugarcane bagasse, and two graphene oxide samples with varying oxidation degrees. Characterization techniques, batch experiments, and various models were employed to understand the adsorption process comprehensively. By elucidating the adsorptive properties of these materials, this research contributes to enhancing our understanding of organic contaminant removal and advancing wastewater treatment methods.

2. Materials and Methods

2.1 Preparation of activated carbon and synthesis of Graphene Oxides

GO synthesis using the modified Hummers method.

This study introduces a novel method for obtaining graphite and subsequently graphene oxide from mandarin peels. The peels undergo drying, cleaning, and pyrolysis, followed by exfoliation to obtain graphite. Graphite is then mixed with NaNO₃ and H₂SO₄, with KMnO₄ gradually added under constant stirring. After completing the reaction and washing steps, the solution undergoes centrifugation to separate the precipitate, which is then

heated to produce graphene oxide powder. This meticulous process ensures purity and stability, essential for subsequent scientific applications [35, 36].

Graphene oxides, variation of the oxidation degree of graphene oxides: Synthesis of graphene oxide with high oxidation state (GOHOS) and graphene oxide with low oxidation state (GOLOS)

The synthesis of graphene oxide (GO) samples, GOHOS and GOLOS, involved a meticulously controlled procedure. For GOHOS, a Pyrex glass reactor was utilized, where concentrated sulfuric acid, graphite, and NaNO_3 were combined under cryostat conditions to disperse solids in the acid. KMnO_4 (3.5 M) was gradually added over 6 hours to prevent agglomeration, followed by heating and stirring to induce the oxidation reaction. The mixture was then transferred to double deionized water and stirred to promote hydration and secondary oxidation. After the addition of H_2O_2 to remove excess KMnO_4 , the reaction was completed with further stirring. The solution was left to settle and filtered by ultra-centrifugation to obtain GOHOS.

On the other hand, GOLOS synthesis followed a similar process with adjusted parameters. Graphite, sulfuric acid, and NaNO_3 were shaken in a Pyrex glass reactor under cryostat conditions for perfect dispersion. KMnO_4 (1.5 M) was added in fractions over 6 hours to avoid sudden increases in temperature. After stirring at room temperature, the mixture was transferred to double deionized water under controlled temperature and stirring conditions to induce hydration and secondary oxidation. H_2O_2 was added slowly to remove excess KMnO_4 , and the mixture was left to settle before being labeled as GOLOS.

Both GOHOS and GOLOS underwent a purification process to remove impurities. This involved acid washes and multiple water rinses to eliminate excess acid. The obtained masses were washed until neutral pH was achieved, followed by sedimentation and filtration. The resulting precipitate was further washed with double deionized water and dried either through oven or freeze-drying methods. The dried product was then ready for subsequent analysis and homogenization. This rigorous synthesis and purification process ensured the production of high-quality graphene oxide compounds suitable for various scientific applications

2.2. Preparation of activated carbon from Cashew Nut Shells

To achieve carbonization and subsequent effective activation of the Cashew Nut Shells, the oils they contain are initially extracted, which are removed by mixing the ground walnut shells with hexane (RA Sigma Aldrich), in a 1:5 ratio and leaving the mixture for 5 days in a bath with a temperature of 10 °C, to reduce the evaporation of hexane. The shells thus treated are then exposed to ambient air for 12 hours and then dried at 110 °C for 48 hours. They are then impregnated with H_3PO_4 solution (RA Sigma Aldrich) in a weight ratio of 4:1 (H_3PO_4 : shells), stirring continuously under a glass case in the laboratory, and heating this mixture on a heating plate at ~85 °C for 4 h, to take the material to an oven at 110 °C for 24 h. The carbonization of the impregnated shells was carried out in a horizontal tubular furnace (Carbolite, 12/75/700 model TZF, USA). These were heated to 400 °C at 20 mLmin^{-1} under an inert atmosphere using nitrogen gas and the final temperature was maintained for 3 h. Then the sample was washed exhaustively in batches, using double deionized water until the pH of the filtrate remained constant, and was finally dried at 110 °C for 48 h. The activated carbon was thus labeled ACNS.

2.3. Characterization of the samples synthesized in this research

X-ray diffractograms and nitrogen adsorption isotherms at 77 K were analyzed to determine the textural properties of materials. XRD analysis utilized a Bruker D2 PHASER diffractometer, while nitrogen adsorption measurements were conducted using an ASAP 2020 volumetric adsorption analyzer. Samples were degassed at 250°C for 4 hours before analysis. The surface area was determined via the Brunauer-Emmett-Teller (BET) method with data obtained at relative pressures between 0.04 and 0.35. Pore size distribution (PSD) was calculated using nonlocal density functional theories (NLDFT) and Quenched Solid Density Functional Theory (QSDFT), considering cylindrical, split, and combined pores. Raman spectroscopy and XRD were employed to analyze graphitization levels and crystalline forms, respectively [28-40].

2.4. Determination of the concentrations of the dyes (MO and MB) on each adsorbate from aqueous solution and study of adsorption equilibrium data.

Before starting the sorption experiments, the respective calibration curves were obtained at various known concentrations of MO and MB (5–800 mg/L). All samples, including a blank, were determined using a Thermo

Scientific Genesys 30 UV-VIS spectrophotometer. The respective absorbances were recorded for the MO and MB at (λ_{\max}) 663 nm and 465 nm respectively. The calibration curve was obtained by plotting the corresponding absorbances as a function of the concentrations of MO and MB; Here values of $R^2= 0.9999$ were obtained, which allowed us to be sure that they could be used as measuring curves for each dye. Batch adsorption experiments of MO and MB were carried out in Erlenmeyer flasks; All experiments were kept in a thermostat bath at different temperatures: 298 K, 303 K, 313 K and 323K[41-46]. The dye adsorbed per unit weight of adsorbent was calculated using Eq. (1) at 25 °C and maintaining constant stirring at 300 rpm for 200 min. To control the pH, it was adjusted with ~0.1 M HCl or NaOH. Initially, concentrated solutions of 500 ppm of MO and MB were prepared and diluted before each test [47-51]. The experiments were carried out at pH 9 (selected by us in previous studies as the pH at which the largest amount of dye is adsorbed) for both MB and MO, using 0.025 g of adsorbent with 50 mL of MO solution and MB, in order to determine the adsorption equilibrium period in a time range from 0 to 800 min at 298 K. For this purpose, previous studies were carried out (these results are not presented here, as it is not the scope of this research) to establish what was the optimal dose of the adsorbent and what was the appropriate pH of each dye, where the maximum adsorption capacity occurs. Concentrations (as already mentioned above) were determined using a Thermo Scientific Genesys 30 UV-VIS UV-Vis spectrophotometer. The amounts of unadsorbed MB and MO that remained in the solutions were determined at a maximum absorption length of (λ_{\max}) 663 nm and 465 nm respectively, to find the amount of MB and MO adsorbed on each adsorbent synthesized in this research (ACNS, GO, GOHOS and GOLOS). To calculate the adsorbed amount, the following equation was used:

$$q_e(\text{mg g}^{-1}) = \frac{V(C_i - C_e)}{m} \quad (1)$$

where C_i (mg/L) is the initial concentration of dye, C_e (mg/L), is the final equilibrium concentration of the respective dye, V (L) is the volume of the MB or MO and m is the mass (g) of the adsorbent. With the values obtained for q_e , the adsorption isotherms (C_e vs q_e) of each of the evaluated systems were determined. The Langmuir, Freundlich, Redlich-Peterson and Tóth models were applied. All assays were performed in triplicate. Solutions were prepared with a predetermined initial concentration of MO and MB in the range of 10–800 ppm. Then 25 mg of adsorbents were added to the solutions. The solutions at pH = 9 were placed in the incubator with shaking at 350 rpm and a temperature of 25 C for different residence times in the range of 2 to 200 min.

2.5 Adsorption kinetic models

To investigate the adsorption kinetics of MO and MB on the synthesized adsorbents, pseudo-first order (PFO) [50], pseudo-second order (PSO) [51] models were used. and intraparticle diffusion (IPD) [52], the latter also considered as a model that illustrates the movement of adsorbents and resistance within the porous network, is the only one that was derived from Fick's second law of diffusion, can write according to Equations (2), (3) and (4) respectively:

$$q_t = q_e(1 - e^{-k_1 t}) \quad (2)$$

where:

q_t = adsorption capacity at time t , q_e = equilibrium adsorption capacity, t = time, k_1 = pseudo-first-order adsorption constant

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

where:

q_t = adsorption capacity at time t , q_e = equilibrium adsorption capacity, t = time, k_2 = pseudo-second-order adsorption constant.

$$q_t = k_{id} t^{0.5} + C \quad (4)$$

where:

t , k_{id} is the intraparticle diffusion rate, where q_t is the amount adsorbed (mg/g) at time t and C is the deviation of the line from the coordinate origin. The adequacy of each model was determined using the coefficient of determination (R^2).

For these kinetic experiments, 200 mg of each adsorbent were taken and added to 50 mL of solution containing the MB and MO dyes and left there with magnetic stirring at 250 rpm; For these kinetic studies, solutions with initial concentrations of 200 to 500 ppm were used. Following certain time intervals, portions of 1 mL of sample were extracted from the suspension. The concentrations of MB and MO solutions were determined using a UV-Vis spectrophotometer at a λ_{\max} wavelength of 663 nm and 464 nm, respectively. An absorbance-concentration

calibration curve was established based on the Beer-Lambert Law method, as. It was already explained above. The amount of MB and MO adsorbed at equilibrium, the adsorption capacity (q_e) at equilibrium time was calculated according to equation (1) [53]. The Elovich model [54] was also applied.

2.6. Thermodynamic modeling of adsorption process

One of the important aspects of thermodynamics is to investigate whether the adsorbate-adsorbent interaction is physical or chemical, which is why it is necessary to determine the thermodynamic parameters of the adsorption system to identify whether it is a physical or chemical process. Here the adsorption parameters associated with thermodynamics were calculated, including the change in Gibbs free energy (ΔG° ; KJ.mol⁻¹), the change in enthalpy (ΔH° ; KJ.mol⁻¹) and the change in entropy (ΔS° ; KJ.mol⁻¹K⁻¹). by the following equations:

$$\Delta G^\circ = -RT \ln K_c^\circ \quad (5)$$

where K_c° is the adsorption thermodynamic equilibrium constant, R represents the universal gas constant (8.314 J mol⁻¹ K⁻¹) and T is the temperature (K).

The correlation between ΔG° , ΔH° and ΔS° can be obtained as indicated in the following equation, according to the law of thermodynamics:

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \quad (6)$$

Furthermore, the thermodynamic variables ΔH° and ΔS° of the system can be determined by the linearized Van't Hoff equation using the relationship between the values of K_c° and T (see Eq. 7):

$$\ln K_c^\circ = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (7)$$

3. Results

3.1. Characterization of adsorbents: ACCS, GO, GOHOS and GOLOS

The Raman spectrum (not shown here) of the ACNS sample exhibits two prominent peaks at 1346 cm⁻¹ (D peak) and 1587 cm⁻¹ (G peak), indicative of lattice defects and C=C stretching vibrations, respectively. Additional bands at 2678 cm⁻¹ (2D) and 2840 cm⁻¹ (S3) suggest the presence of few-layered carbon material and the graphitic nature of the activated carbon. The degree of graphitization (R) calculated as ~0.815 indicates a relatively high graphitization index. On the other hand, the Raman spectra (which we do not show here due to space) of GO and its derivatives (GOHOS and GOLOS), which show broadened D and G bands compared to graphite, suggesting an increase in amorphous carbon and structural defects. ACNS XRD patterns confirm the presence of typical nanostructures associated with activated carbon, with variations in interlayer spacing indicative of molecular nanostructure diversity. GO XRD patterns reveal peaks consistent with GO and crystalline graphene oxide, with altered oxidation levels influencing peak intensities and interlayer spacing. Oxidation-induced chemical interactions cause changes in layer spacing, and higher oxidation levels result in the appearance of imperfections within the graphene sheets. GOHOS exhibits sharp peaks and high intensity, indicating large crystallites and higher order, while GOLOS shows broad bands, suggesting the presence of amorphous graphite residues. FTIR spectra (not shown here) of ACNS and GO derivatives show characteristic bands corresponding to hydroxyl and carboxylic groups, with slight variations between GO samples. Overall, these analyzes provide detailed information on the structural characteristics and modifications of the synthesized materials, contributing to a comprehensive understanding of their properties and potential applications [54-58].

N₂ adsorption-desorption isotherms at 77 K and BET area analysis for the synthesized adsorbates, derived from municipal waste solids such as mandarin peels (ACNS) and cashew shells (GO), were performed and the results are shown in Table 1, along with the pore size distribution (PSD) calculated using the QSDFT kernel. The ACNS sample exhibits a type Ia isotherm with minimal hysteresis, indicating slight development of mesoporosity [59-64]. The volume and surface values of the micropores align well with the isotherm obtained, indicating typical characteristics of activated carbon. On the contrary, GO samples show higher pore volume and BET area, and GOHOS demonstrates the highest values, attributed to various degrees of oxidation. The average pore width increases with oxidation, particularly notable in GOHOS, due to the oxidation treatment. The characteristic energy values suggest a good adsorption potential for nitrogen molecules. Interestingly, ACNS exhibits the largest BET area among the synthesized materials. GO samples show variable BET surface areas, and GOHOS and GOLOS show higher values than GO, indicating higher mesoporosity due to oxidative treatment. The PSD reveals significant heterogeneity, with variations in pore width observed between samples. N₂ adsorption-desorption isotherms confirm the presence of micropores in ACNS and mesopores in GO samples. Table 2 presents PSD data using NLDFT and QSDFT models, highlighting better

fits with the latter, particularly for GO samples. The isotherms of N₂ at 77 K presented a form of the Type IV(a) isotherms for GO samples, with larger hysteresis loops for GOHOS and GOLOS, indicating effective oxidation. The QSDFT kernel with the cylindrical slit model provides the best fit on all samples, in agreement with the experimental results and the energetically heterogeneous surfaces.

Table 1. ACNS and GO's: Analysis of S_{BET}, DA, and BJH models from Nitrogen Adsorption Isotherms at 77 K

Sample	S _{BET} * [m ² g ⁻¹]	DA Model				BJH Model	
		V _{micropore} [cm ³ g ⁻¹]	E _{or} [kJ.mol ⁻¹]	n	Pore radius [Å]	V _{mesopore} [cm ³ g ⁻¹]	Pore radius [Å]
GO	85	0.07	3.91	3.1	15.4	0.23	34.2
GOHOS	344	0.24	4.87	2.6	34.6	0.67	78.9
GOALS	205	0.18	4.03	2.8	22.1	0.44	45.6
ACNS	1125	0.45	10.34	23	26.8	0.58	49.3

*Adjusted according to the IUPAC method, 2015.

¹⁰ Brunauer, Emmett, & Teller Method.

Table 2. Adsorbent Samples: data report of PSD with kernels NL-DFT and QS-DFT, fitting error.

Samples	NL-DFT								
	Pore volume cyl [cm ³ g ⁻¹]	Average width of pore cyl [Å]	E [%]	Pore volume cyl-slit [cm ³ g ⁻¹]	Average width of pore cyl- slit [Å]	E [%]	Pore volume slit [cm ³ g ⁻¹]	Average width of pore slit [Å]	E [%]
GOALS	0.38	6.8	0.833	0.40	1.6	0.882	0.33	2.34	1,126
GOHOS	0.32	7.0	1,032	0.35	1.5	1,432	0.31	2.05	1,130
GO	0.21	7.1	2,034	0.23	1.7	2,211	2.02	2.1	1,142
ACNS	0.45	6.8	1985	0.50	2.1	2,351	0.51	2.2	0.700

QS-DFT									
GOALS	0.38	7.1	0.143	0.40	2.6	0.122	0.33	23	0.220
GOHOS	0.32	7.0	0.209	0.35	2.0	0.211	0.31	2.1	0150
GO	0.21	6.9	0.163	0.23	1.9	0.139	2.02	2.4	0.233
ACNS	0.45	6.8	0.196	0.50	2.4	0.182	0.51	2.0	0.353

3.2. Adsorption isotherms from aqueous solution of dyes on adsorbents

The adsorption of dyes like MO and MB onto synthesized materials is influenced by factors such as temperature, pH, and initial concentrations. While high initial concentrations enhance adsorption capacity due to a stronger driving force, excessive concentrations don't proportionally increase adsorption due to limited available sites on adsorbent surfaces. Various models, including Langmuir, Freundlich, Redlich-Peterson, and Toth [65-68], are employed to describe adsorption processes using variables like q_e (amount of solute adsorbed per gram of adsorbent at equilibrium) and C_e (concentration of solute in the solution at equilibrium). In this study, each model is applied to MO and MB adsorption data, and fitting parameters are determined based on original adsorption data. The Freundlich model consistently shows the best fit (R² > 0.99), indicating multilayer adsorption and heterogeneous surfaces. Both dyes exhibit weak acid and anionic characteristics, with adsorption isotherms describable by the Freundlich model, showing maximum adsorption amounts (q_{max}) at 25°C. Notably, for GOHOS, adsorption was more favorable. The order of adsorption capacity for MO and MB was GOLOS > ACCN > GOHOS > GO, with MO having greater adsorption capacity. The Freundlich constant (K_F) also followed the order of MO > MB, verifying the consistency of the results. Adsorption of ACNS by MO and MB is attributed to physical and chemical factors, including Van der Waals forces and electrostatic forces. ACNS's

porous structure with a large surface area is conducive to efficient adsorption, with chemical adsorption involving strong interactions between functional groups of each dye and activated carbon surface groups. Regarding GO samples, their developed BET surface and flat structure facilitate adsorption via physical interactions like Van der Waals forces and hydrophobic interactions. Chemical interactions are likely, considering graphene oxide's active sites for interactions with dyes, including hydrogen bonding or acid-base interactions facilitated by surface functional groups like hydroxyl and carboxyl groups. Overall, graphene oxide offers greater selectivity and adsorption capacity compared to activated carbon due to its two-dimensional structure and specific surface properties.

Adsorption on graphene oxide may be faster due to its high surface reactivity compared to activated carbon. The regeneration (desorption) capacity of graphene oxide may be different from activated carbon due to the different surface and chemical interactions involved. That is to say, the adsorption mechanism involves a combination of physical and chemical interactions between the dyes and the surface of the adsorbent material.

On the other hand, carry out the kinetic study of the adsorption process which plays an important role, because it allows us to know the characteristics such as efficiency and adsorption mechanism, and consequently the possible applications of each adsorbent prepared in this research. Therefore, this study was carried out as mentioned in the procedural part, using the pseudo-first order (PFO), pseudo-second order (PSO), intraparticle diffusion (IPD) and Elovich models. The equations that describe each model are shown in Table 3.

Table 3. Equations of the different kinetic models used to study the adsorption mechanisms.

Model	Equation	Reference
Pseudo-first order	$q = q_e(1 - \exp(-kt))$	[50]
Pseudo-second order	$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t}$	[51]
Elovich	$q_t = \frac{1}{\beta} \ln(1 + \alpha\beta t)$	[54]
Weber and Morris, Intraparticle Diffusion (IPD)	$q_t = k_{id}\sqrt{t} + C_i$	[52]

q_t (mg/g): Amount of adsorbate adsorbed at a time "t"
 t : Time (min)
 Q_e (mg/g) amount of adsorbate adsorbed at equilibrium
 K_1 : Lagergren adsorption constant (min^{-1})
 k_2 : Pseudo-second order rate constant (g/mg min)
 α (mg/g min) and β (g/mg): Constants of the Elovich model
 k_{id} and C_i : Constants of the intraparticle diffusion model

Pseudo-first order (PFO) and pseudo-second order (PSO) kinetics are employed to investigate the adsorption mechanism, involving valence forces like covalent and ion exchange interactions between the adsorbate and adsorbent. While the PFO model represents reversible interactions or physical adsorption, the PSO model describes chemical bonds formation. The intraparticle diffusion (IPD) model elucidates rate-limiting steps and diffusion resistance in dye adsorption, aiding in understanding the adsorption mechanism.

Adsorption kinetics experiments involved varying initial concentrations (200 to 500 ppm) of each dye, monitored over a range of 2 to 200 minutes. The adjustments for PFO, PSO, Elovich, and IPD models provide insights into the adsorption kinetics. Notably, adsorption equilibrium for MO on GOHOS was achieved faster (60 minutes) compared to MB (120 minutes). The nonlinear adsorption kinetics and fit values to each model are presented in Figures 6a and 6b and Tables 4 and 5. Both the pseudo-first order ($R^2 > 0.98$) and pseudo-second order ($R^2 > 0.99$) models fit well to the experimental data, suggesting a combined adsorption mechanism involving both physisorption and chemisorption.

The Elovich model, with R^2 values ranging from 0.96 to 0.97, demonstrates chemical interactions between MO and MB and the functional groups of the adsorbents. This indicates a non-uniform distribution of adsorption energy and non-uniform diffusion processes, aligning with the experimental results.

IPD modeling reveals multiple kinetic steps involved in MO adsorption on various adsorbents. Three distinct stages are observed: external diffusion, intraparticle diffusion, and equilibrium attainment. The adsorption process is driven by both physisorption and chemisorption mechanisms, with boundary layer diffusion influencing the overall process. Rapid adsorption in the initial stage is attributed to boundary layer diffusion, while slower adsorption in the second stage is due to intraparticle diffusion. Equilibrium adsorption is achieved in the third stage.

In summary, the adsorption kinetics of MO and MB on different adsorbents involve complex mechanisms encompassing physical and chemical interactions, with IPD modeling providing valuable insights into the multi-step process [51-55].

Table 4. Parameters of the adsorption kinetics of Methyl Orange (MO) on the samples synthesized at 298.15 K; $C_0=200$ ppm

Models	Parameters.	GO	GOHOS	ACNS	GOHOS
PFO	q_e , exp (mg/g)	64.476	75.765	95.859	112.765
	k_1 (min ⁻¹)	0.0309	0.0290	0.0278	0.0207
	q_e , cal(mg/g)	66.867	78.765	100.432	123.456
	R^2	0.9878	0.9854	0.9834	0.9899
PSO	k_2	0.000342	0.00000104	0.0000209	0.0000289
	q_e ,cal(mg/g)	70.345	98.987	100.665	125.432
	R^2	0.9999	0.9996	0.9998	0.9998
ID	k_{diff}	1.798	2.298	2.987	3.165
	C	0.765	0.534	0.503	0.442
	R^2	0.9398	0.9598	0.9698	0.9598
Elovich	α ((mg/g.min)	7.543	13.65	16.34	15.87
	β (g/mg)	0.01965	0.007654	0.004687	0.03254
	R^2	0.9765	0.9798	0.9796	0.965

Table 5. Parameters of the adsorption kinetics of Methylene Blue (MB) on the samples synthesized at 298.15 K; $C_0=200$ ppm

Models	Parameters.	GO	GOLOS	ACNS	GOHOS
PFO	q_e , exp (mg/g)	44.567	63.411	75.432	93.653
	k_1 (min ⁻¹)	0.0351	0.0302	0.0243	0.0212
	q_e , cal(mg/g)	46.765	66.321	77.543	102.212
	R^2	0.9843	0.9832	0.9976	0.9848
PSO	k_2	0.000432	0.00000201	0.0000303	0.0000234
	q_e ,cal(mg/g)	62.761	71.865	82.865	110.547
	R^2	0.9994	0.9994	0.9998	0.9995
ID	k_{diff}	1.576	2.097	2.243	2.534
	C	0.563	0.435	0.402	0.387
	R^2	0.9212	0.9432	0.9421	0.9421
Elovich	α ((mg/g.min)	6.398	11.34	14.65	13.87
	β (g/mg)	0.01687	0.008778	0.005676	0.02476
	R^2	0.9632	0.9673	0.9743	0.9709

Finally, a thermodynamic study of the adsorption between the dyes and the adsorbents was carried out to determine the thermodynamic parameters (ΔG° , ΔH° and ΔS°), carrying out experiments at different temperatures, and the results are summarized in Table 8. The studies were directed to investigate whether the adsorption of MO and MB on ACCN, GOHOS, GOLOS and GO correspond to exothermic or endothermic

reactions. The thermodynamic parameters are very revealing for the adsorbate-adsorbent systems studied where negative ΔG values were obtained, which confirms that the adsorption of the dyes studied here are adsorbed on the materials prepared spontaneously and is favored from the point of view thermodynamic; This is in good agreement with what was found in the adsorption capacity results and with the kinetic models. The energy values obtained for ΔG , between indicate a physisorption reaction of MO and MB and the adsorbents. While the positive values of ΔH (150.78 kJ/mol) reveal that it is an endothermic process of adsorption of MO and MB [3, 53]. A positive ΔS (0.51 kJ/mol · K) observed during the adsorption of MB and MO dyes suggests that there is randomness in the molecules of these dyes on the ACCN, GOHOS, GOLOS and GO surfaces at the different temperature [54].

Table 6. Thermodynamic parameters of MO and MB adsorption onto adsorbates. Experimental conditions: V = 50 mL; [MB] = 50 mg L⁻¹, adsorbent dosage (ma) = 0.02 g, contact time: 60 min and working temperatures from 20 to 50 °C.

T(K)	Dye	Sample	ΔG° (kJmol ⁻¹)	ΔH° (KJmol ⁻¹)	ΔS° (Jmol ⁻¹ K ⁻¹)
298	MO	GOHOS	-5.987	45.766	86.265
303	MO	GOHOS	-7.309		
313	MO	GOHOS	-9.786		
323	MO	GOHOS	-10.765		
298	MO	ACNS	-3.765	39.113	74.345
303	MO	ACNS	-5.654		
313	MO	ACNS	-7.943		
323	MO	ACNS	-9.436		
298	MO	GOLOS	- 4.765	40.987	79.776
303	MO	GOLOS	- 6.165		
313	MO	GOLOS	- 8.321		
323	MO	GOLOS	- 8.996		
298	MO	GO	-2.867	33.998	68.983
303	MO	GO	-3.964		
313	MO	GO	-5.231		
323	MO	GO	-7.076		
298	MB	GOHOS	- 4.987	40.763	80.837
303	MB	GOHOS	- 5.987		
313	MB	GOHOS	- 6.997		
323	MB	GOHOS	- 7.097		
298	MB	ACNS	- 4.102.	36.098	70.673
303	MB	ACNS	- 5.387		
313	MB	ACNS	- 6.045		
323	MB	ACNS	- 6.895		
298	MB	GOLOS	- 4.687	38.654	73.982
303	MB	GOLOS	- 5.523		
313	MB	GOLOS	- 6.000		
323	MB	GOLOS	- 6.783		
298	MB	GO	- 2.043	29.893	65.986
303	MB	GO	- 3.514		
313	MB	GO	- 4.894		
323	MB	GO	- 6.982		

4. Conclusions

Four adsorbent materials were prepared from municipal waste solids and were given an important added value. studied in detail the adsorption processes of Methyl Orange and Methylene Blue on four carbonaceous materials. The adsorption isotherms fit well using a Freundlich model and the results showed that the adsorption capacities of the prepared adsorbents were higher than those reported in the literature. This is correlated with developed surface area and the surface chemistry of each adsorbent. It was found that the adsorption capacity of MO was greater when purchased with MB; This is associated with the greater surface and chemical interactions of this dye with the surfaces of each of the adsorbents. The GOHOS adsorbent had a higher adsorption capacity for MO (anionic) (215.3 mg/g), while for GO it had a lower adsorption capacity (78.3 mg/g). The elimination mechanism of the two dyes by the adsorbents was governed mainly by electrostatic adsorption and with a mixture of physical and chemical adsorption according to the results of the kinetic studies. Regarding the results of the adsorption kinetics, for both dyes and the adsorbates, the pseudo-second order model followed, while the IPD model showed three steps that explain the diffusion of the MO and MB into the porous system of the materials. Thermodynamic studies show that the adsorption processes are spontaneous in nature and are favored by thermodynamics. The activated carbon obtained from Cashew nut shells (ACNS) also showed to be a material that obtained from a municipal solid waste is promising for retaining MO and M, with a result comparable to that of GOHOS.

Acknowledgments:

The authors thank you MinCiencias by economic funds approved by the projects titled "Biocatalysts supported on porous and graphenic materials for the degradation of contaminants emerging from the manufacture of plastics and the use of agrochemicals", Contract No. CT ICETEX 2023- 0814 CD 1101- 890-82458. The authors thank the Framework Agreement between Universidad de Los Andes and Universidad Nacional de Colombia— Bogotá and the act of agreement established between the Departments of Chemistry of both institutions. The Prof. Dr. Juan Carlos Moreno-Piraján also thank the grant project No. INV-2023-162- 2735 by the Facultad de Ciencias (Universidad de los Andes, Bogotá, Colombia).

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