ADSORPTION OF METHYL ORANGE ONTO YELLOW PASSION FRUIT PEEL (PASSIFLORA EDULIS SIMS) MODIFIED WITH NITRIC ACID AND SODIUM HYDROXIDE

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ABSTRACT: Brazil is the world's largest producer of passion fruit, and its peel is a residue of the juice production industries. This material is rich in pectin, which, when removed by acid or basic treatments, leaves behind a lignocellulosic residue that can be utilized as an adsorbent. In this study, we examined the utilization of passion-fruit peel treated with nitric acid and sodium hydroxide as an adsorbent for acidic dyes. The adsorption of methyl orange was studied in batch, varying the initial concentration of dye from 100 to 1000 mg L^{-1} and the temperature from 298 to 348 K. The passion fruit peel proved to be a promising adsorbent for the methyl orange dye, with adsorption capacities ranging from 263.16 to 322.58 mg of dye per gram of adsorbent Treating the sample with either acid or base enhanced the adsorption capacity, with the basic treatment proving more effective. The adsorption process follows the Langmuir model, and its kinetics can be mathematically described by the pseudo-second order equation. Diffusion studies revealed that the diffusion within the solution influences the results, serving as the rate-limiting step of the process. The adsorption of methyl orange onto passion fruit peel is an exothermic process. It occurs with decreasing entropy, and the Gibbs free energies obtained indicate that the process is spontaneous at temperatures near room

temperature. The enthalpy values indicate that the adsorption of methyl orange over passion fruit peel is a physical process.

1 | INTRODUCTION

Synthetic dyes have played a significant role in various industries, including textiles, cosmetics, food, and pharmaceuticals, due to their ability to impart vibrant colors and enhance product appeal. Efforts to mitigate the environmental impact of synthetic dyes included advancements in wastewater treatment technologies. Adsorption, photocatalysis, and advanced oxidation processes were studied for their effectiveness in removing synthetic dyes from industrial effluents [1,2].

Adsorption is a widely studied phenomenon in the field of environmental science and engineering, as it offers a promising method for removing pollutants from water and other liquids using various adsorbents, including agricultural waste materials like fruit peels [3,4].

Brazil is the world's largest producer of passion fruit, and its peel is a residue of the juice production industries. This material is rich in pectin, which, when removed by acid or basic treatments, leaves behind a lignocellulosic residue that can be utilized as an adsorbent [5]. Passion fruit peel (PFP) is a type of agricultural waste that has gained attention as a potential adsorbent due to its abundant availability, low cost, and high surface area. The porous structure of PFP contains various functional groups such as hydroxyl, carboxyl, and phenolic groups, which can facilitate adsorption processes

In the literature, there are studies on adsorption systems using passion fruit peel as the adsorbent and different dyes as adsorbates. Pavan and colleagues [6, 7, 8] tested yellow passion fruit peel for the adsorption of methylene blue and found an adsorption capacity of 44.70 mg.g^{-1}. Lin and colleagues [9] studied the adsorption of methylene blue and methyl violet on passion fruit peel, finding adsorption capacities of 324.7 and 485.4 mg·g^{-1}, respectively, for these cationic dyes. Brito and colleagues studied the adsorption of eriochrome black on modified passion fruit peel, obtaining adsorption capacities ranging from 196 to 303 mg.g^{-1}, depending on the type of modification performed [3].

Passion fruit peel has also been used as an adsorbent for toxic metals in aqueous solutions. Jacques and colleagues [10] studied the adsorption of Cr(III) and Pb(II), finding maximum adsorption capacities of 85.1 mg.g^{-1} and 151.6 mg g^{-1} for Cr(III) and Pb(II), respectively. Chao and colleagues [11] studied the adsorption of heavy metals on various adsorbents in fixed-bed columns and found that the optimal adsorption condition occurred when the pH of the solutions was equal to 6. For passion fruit peel, adsorption capacities of 80 mg.g^{-1} for Pb(II) and 60 mg·g^{-1} for Cd(II) were found. Campos-Flores and colleagues [12] investigated the adsorption of Cr(III) onto untreated passion fruit peel and obtained a maximum adsorption capacity of 29.933 mg·g^{-1}, considering passion fruit peel as an effective adsorbent for this metal. They noted that it can remove over 50% of the Cr(III)

present in solution.

In addition to the use in its natural state, some studies make modifications to passion fruit peel with the aim of improving its adsorption capacity. Gerola and colleagues [13] studied the adsorption of Pb(II) on passion fruit peel modified with sodium hydroxide and citric acid, observing an increase in the adsorption capacity for the peel modified with citric acid. Modification of passion fruit peel through amination reaction produced a material capable of adsorbing 675.65 mg·g^{-1} of Cr(VI) in a batch process, reaching equilibrium in 90 minutes. This adsorption capacity was sufficient to reduce the metal levels in effluents to permissible levels in the experimental solution [14].

In the adsorption of cationic dyes, the modification of passion fruit peel with sodium hydroxide [15] resulted in a more efficient adsorbent for methylene blue adsorption compared to untreated material. Passion fruit peel was modified through carboxylation reaction and tested for methylene blue adsorption in aqueous solution. The material exhibited a significant increase in adsorption capacity, with a maximum adsorption of 1775.76 mg·g^{-1} for methylene blue [16]. The material showed high selectivity for the dye and excellent reusability, even after six cycles of adsorption-desorption.

This study presents an investigation into the adsorption of the acid dye Methyl Orange onto modified yellow passion fruit peel using nitric acid or sodium hydroxide. Methyl Orange, whose IUPAC name is sodium 4-[[4-(dimethylamino)phenyl]azo]benzenesulfonate, is an anionic azo-type dye, water-soluble, utilized as a textile dye for various fibers, and employed as a colorant in the cosmetic and food industries [17, 18]. Dyes containing aromatic and azo groups, –N=N–, are extremely toxic, carcinogenic, and teratogenic, posing risks to the environment and organisms [19].

2 | MATERIALS AND METHODS

2.1 Preparation of Adsorbent

The passion fruit peel samples were ground, washed with deionized water, and dried in a circulating air oven at 150°C for 24 hours to remove more volatile essential oils. A portion of this material was treated with 0.1 mol.L^{-1} nitric acid for 90 minutes at 100°C, and another portion was treated with 0.1 mol.L^{-1} sodium hydroxide under the same time and temperature conditions to remove pectin (adapted from KULKARNI et al. [20]). The resulting material was filtered, washed with deionized water, and dried at 105°C for 24 hours in a circulating air oven. The samples were labeled as MF02 (untreated), MF03 (acid-treated), and MF04 (base-treated).

Each sample underwent particle size separation for further evaluation. The samples were sieved on a vibrating table using 40, 60, 100, and 200 mesh screens, corresponding to particle sizes of 0.420; 0.250; 0.149; and 0.074 mm, respectively.

2.2 Physical Characterization of the Adsorbent

The X-ray diffraction patterns of the samples were obtained using a Shimadzu XRD-6000 instrument, operating with CuKα radiation at a voltage of 40 kV, a current of 30 mA, and a graphite monochromator in the 5 – 80° 2θ region at a scanning rate of 2°.min^{-1}.

Morphological analysis was performed using a Hitachi S-3400N scanning electron microscope under low vacuum conditions to eliminate the need for metallization.

Thermogravimetric (TG) and differential thermal analysis (DTA) were conducted using a Shimadzu TGA-60H instrument, from 25 to 1000°C at a heating rate of 10°C.min^{-1} under a synthetic air flow of 50 mL.min^{-1}.

2.3 Determination of Extractives, Hemicellulose, Cellulose, and Lignin

The method for extractives determination was developed adapting the existing methodology in the literature [21, 22, 23]. To determine the amount of extractives, 1g of biomass was placed in contact with 60 mL of analytical grade acetone under reflux at a temperature of 60°C for 6 hours. After this time, the sample was filtered and dried in an oven at 105°C until a constant mass was achieved. The difference in mass before and after extraction was considered as the amount of extractives.

For hemicellulose content determination, 1g of biomass, after the removal of extractives, was placed in contact with 150 mL of 0.5 mol.L^{-1} sodium hydroxide under reflux at 80°C for 3.5 hours. After this time, the sample was washed with deionized water until the solution's pH reached 7. The sample was dried in an oven at 105°C until a constant mass was achieved. The difference between the sample's mass before and after treatment corresponds to the hemicellulose content.

The lignin content was determined by using 1g of dried biomass, after the removal of extractives, in contact with 30 mL of 98% sulfuric acid. After 24 hours of contact at room temperature, the mixture was heated to 100°C for 1 hour, cooled, and filtered. The filtrate was dried in an oven at 105°C until a constant mass was achieved. The mass of the residue is recorded as the lignin content.

The cellulose content is calculated by difference, considering that extractives, hemicellulose, lignin, and cellulose are the only components of all the studied materials.

2.4 pH of Adsorbent Suspensions

The procedure followed the method adopted by Al-Degs et al. [24]. The samples were agitated in distilled water at a proportion of 10% (w/v) for 3 hours at room temperature, and the pH was measured using a MARTE MB-10 potentiometer with a glass electrode.

2.5 Surface Acidity and Basicity

Surface acidity and basicity studies were conducted according to Al-Degs et al. [24]. For the determination of surface acidity, the samples were agitated in 10 mL of a 0.01 mol.L^{-1} sodium hydroxide solution for 24 hours at room temperature. After this period, the samples were filtered, and the remaining NaOH in the solution was titrated with 0.01 mol.L^{-1} hydrochloric acid using a MARTE MB-10 potentiometer and a glass electrode. Surface basicity was determined similarly, using a 0.01 mol.L^{-1} HCl solution for agitation. The remaining acid was titrated with 0.01 mol.L^{-1} NaOH. The results were expressed in mmol of H^{+} or OH^{-} per gram of adsorbent.

2.6 Point of Zero Charge (PZC)

The pH of the point of zero charge of the samples was determined using the solid addition method, as described in Brito et al. [3,4]. Twelve vials containing pH solutions ranging from 2 to 13 (pH$_0$) and 0.1 g of adsorbent were agitated for 24 hours at room temperature, and the final pH was measured using a MARTE MB-10 potentiometer and a glass electrode. The difference between the final pH and the initial pH (ΔpH) was plotted against the initial pH, and the point where ΔpH = 0 was taken as the point of zero charge pH (pHPZC).

2.7 Effect of Mass and Granulometry of Adsorbent

To determine the appropriate mass for kinetic and thermodynamic studies, a preliminary test was conducted using methyl orange solutions with a concentration of 100 mg.L^{-1} at room temperature, with the four granulometries obtained for this study. The adsorbent mass ranged from 50 to 1500 mg. The samples were agitated in 100 mL Erlenmeyer flasks containing 25 mL of the dye solution for 24 hours. The sample used for this test was the ground, washed, and dried peel at 150°C (MF02), and the pH used was 6.76, which was the pH of the solution prepared with deionized water. Final concentrations were measured using a UV/VIS FEMTO 700 Plus spectrophotometer.

2.8 Effect of Solution pH on Adsorption

To study the effect of pH on adsorption, the pH of the methyl orange solutions was adjusted within the range of 2 to 12 by adding 0.1 mol.L^{-1} NaOH or 0.1 mol.L^{-1} HCl. The solutions, with an initial concentration of 100 mg.L^{-1}, were then agitated with 0.1 g of adsorbent at room temperature for 24 hours. Final concentrations were measured using a UV/VIS FEMTO 700 Plus spectrophotometer, and pH was measured using a MARTE MB-10 potentiometer with a glass electrode. The sample used in this test was MF02. As methyl orange changes color within the pH range of 3.1 to 4.4, new calibration curves were created

for solutions at different pH levels.

2.9 Kinetic, Thermodynamic, and Adsorption Isotherm Experiments

To evaluate kinetic models and adsorption isotherms, batch studies were conducted using 100 mL Erlenmeyer flasks containing 25 mL of the dye test solution with initial concentrations ranging from 100 to 1000 mg.L^{-1}. The adsorbent mass was approximately 0.1 g based on other experiments, and the pH of the experiments was always the same as the initial solution, varying between 6.7 and 6.8. The mixture was agitated at room temperature for different contact times. After agitation, the solutions were filtered using filter paper, and the final dye concentration was determined using a UV/VIS FEMTO 700 Plus spectrophotometer. Contact times varied from 15 to 240 minutes, and experiments with 24 hours of agitation were taken as equilibrium time. Adsorption isotherms were constructed with a 24 hours contact time. The effect of temperature on adsorption was investigated within the range of 298 – 348 K (25 to 75°C) using the same batch experiment approach.

3 | RESULTS AND DISCUSSION

3.1 X-ray diffractograms

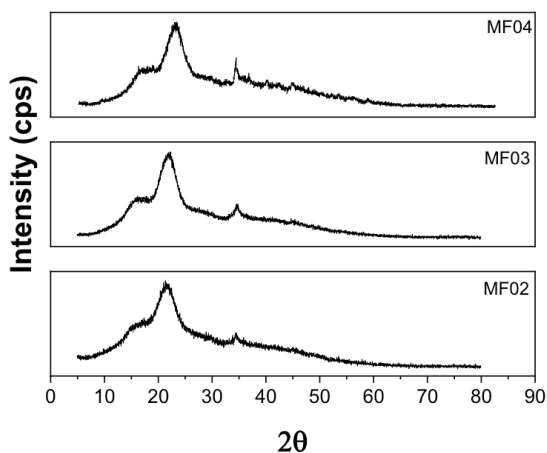The X-ray diffractograms of the passion fruit peel samples are shown in Figure 1.

Fig.1 X-ray diffractograms of the passion fruit peel samples

The X-ray diffractograms of the passion fruit peel samples are shown in Figure 1. The three samples exhibited similar diffraction profiles, indicating that the chemical treatment did not significantly alter their structure. The observed peaks correspond to the cellulose diffraction planes in the presence of amorphous material [25] and are characteristic of low

crystallinity lignocellulosic materials.

The shoulder at around 16°2θ can be attributed to the overlap of peaks corresponding to the (1,-1,0) and (1,1,0) planes of cellulose in samples with high content of non-crystalline materials such as lignin and hemicellulose, as previously reported by Tserki et al (2005) and Ghali et al (2009). The peaks at 22°2θ and 34.9°2θ correspond to the (0,0,2) and (0,4,0) planes of cellulose, respectively [26,27]. The crystallinity of the samples was calculated according to equation 1 [27]:

$$CI = \frac{I_{002} - I_{AM}}{I_{002}} \times 100 \qquad (1)$$

Where $I_{(002)}$ is the intensity of the peak corresponding to the crystalline material (2θ = 22°) and $I_{(AM)}$ is the intensity of the peak corresponding to the amorphous material (2θ = 18°). The obtained values are presented in Table 1.

Sample	Cristallinity index (%)
MF02	38.2
MF03	46.3
MF04	45.2

Table 1 – Crystallinity of the passion fruit peel samples

The chemical treatments increased the crystallinity index of the sample. Ghali et al. [28] reported that alkaline treatments of lignocellulosic materials remove amorphous material such as lignin, increasing the cellulose concentration and consequently the crystallinity of the sample. Acidic treatments remove pectin and hemicellulose from the material [20] as well as other amorphous materials. Thus, the concentration of crystalline material increases in relation to amorphous material, leading to an increase in the crystallinity index.
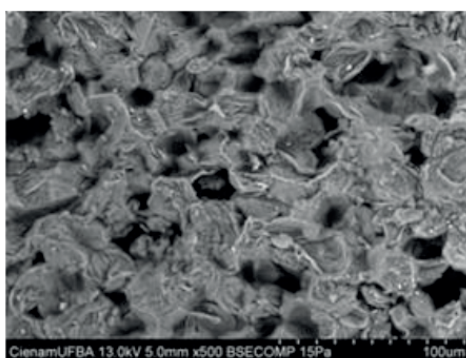
3.2 Morphological analysis by scanning electron microscopy

The surface morphology of yellow passion fruit peel was studied by SEM and is shown in Figure 2.
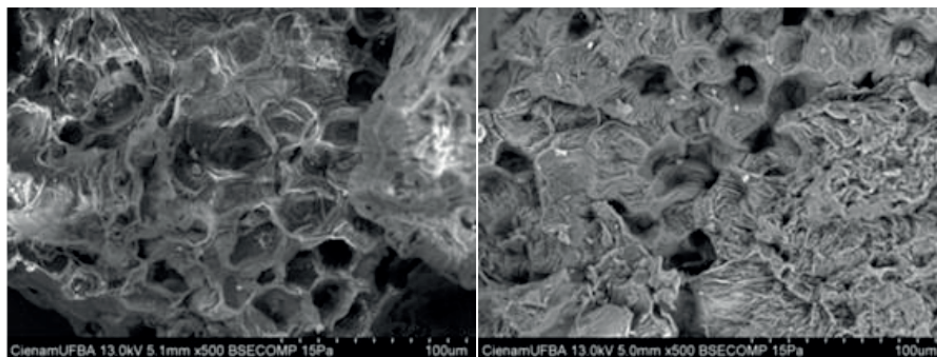
(a)   (b)

(c)

Fig. 2 - Micrographs of samples (a) MF02, (b) MF03, and (c) MF04.

The material exhibits a cellular structure with cavities measuring approximately 20 μm, suggesting its potential effectiveness as an adsorbent. Under 500x magnification, the material's surface does not show significant alterations due to the various treatments. However, samples MF03 and MF04, treated with acid and base respectively, display the presence of clustered material, likely resulting from the removal of pectin and lignin.

3.3 Analysis of extractives, hemicellulose, cellulose, and lignin

Lignocellulosic biomasses consist mainly of lignin, cellulose, and hemicellulose. Understanding the original composition of these materials and how it can be modified through chemical treatments is crucial for their effective use as adsorbents. The results detailing the composition of passion fruit peel samples are summarized in Table 2.

Contents	Results (%)		
	MF02	MF03	MF04
Extractives	21.41	14.64	14.63
Hemicellulose	14.42	10.70	12.00
Lignin	25.05	18.19	10.24
Cellulose	39.12	56.47	63.13

Table 2 – Analysis of passion fruit peel samples.

These findings highlight the cellulose-rich nature of passion fruit peel biomass, likely exhibiting a certain degree of crystallinity, as evidenced by the XRD results. The data in Table 2 reveal that both acidic and alkaline treatments significantly reduced the extractives content. These extractives encompass pectin, essential oils, and other components inherent in passion fruit peel, removable by both acidic and alkaline methods [20, 29]. Acidic treatment primarily removed hemicellulose, whereas alkaline treatment led to a higher removal of lignin. Consequently, the sample treated with sodium hydroxide exhibited a higher cellulose concentration.

BECKERMANN and PICKERING [30] assert that alkaline treatment removes the materials acting as binders in biomass, namely lignin, pectin, and hemicellulose. Consequently, the remaining material from these treatments had its cellulose content increased, a fact confirmed by the rise in crystallinity index. Therefore, passion fruit peel, after pectin extraction (a high-value-added product), yields a residue suitable for low-cost adsorbent use.

3.4 Thermogravimetric Analysis

Throughout the adsorbent preparation process, the passion fruit peels were not exposed to thermal treatments exceeding 150°C. Nevertheless, chemical treatments might have induced alterations in the material's properties. Several of these changes can be discerned through thermal analysis. The thermogravimetric analysis of the passion fruit peel samples is depicted in Figure 3.
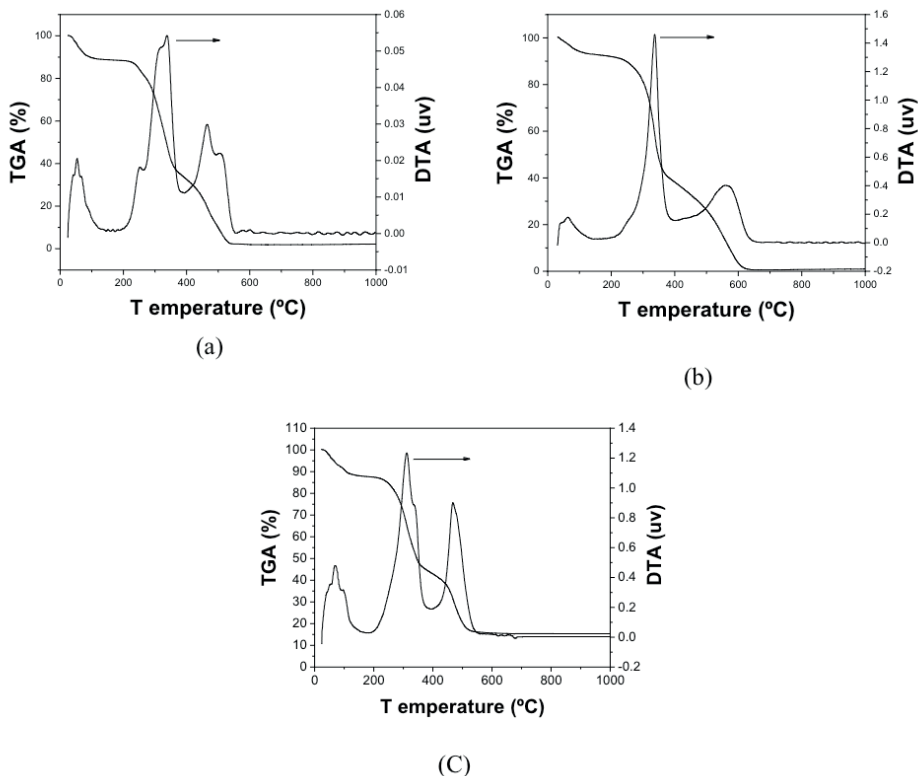
Fig. 3 – Thermogravimetric Analysis of passion fruti peel samples:(a) MF02; (b) MF03; (c) MF04

The mass loss up to around 150°C can be attributed to the evaporation of water and more volatile essential oils from the passion fruit peel. Sample MF02 (Fig. 3-a), which did not undergo chemical treatment, exhibits a broad peak between 200 and 400°C, appearing to be the overlap of three peaks at 200, 300, and 340°C, respectively, corresponding to the decomposition of pectin, hemicellulose, and cellulose. Niu et al. [31] and Orozco et al. [32] investigated the pyrolysis of fruit peels and attributed the mass loss events between 200 and 400°C to the decomposition of pectin (up to 200°C), hemicellulose (200 – 300°C), and cellulose (350 – 400°C).

Sample MF03 (Figure 3-b), treated with nitric acid, presents only one peak in the 200 – 400°C range, at around 350°C, attributed to cellulose decomposition. The pectin decomposition peak was not expected in this sample because, as previously discussed, the acidic treatment should have removed this material from the passion fruit peel. The acid treatment also removed hemicellulose from the sample, which might have contributed to the decrease in the corresponding peak of its decomposition, possibly overlapping with the cellulose decomposition peak due to the reduced quantity of this component in the sample.

Sample MF04 (Figure 3-c), treated with sodium hydroxide, exhibits peaks between

200 and 400°C, which can be attributed to residual pectin, hemicellulose, and cellulose decomposition, indicating that the acidic treatment is more effective in removing pectin and hemicellulose than the basic treatment. These results corroborate the values found in Table 2.

3.5 Acid-base properties of the material

After 3 hours of agitation at room temperature, the pH of the aqueous suspensions of the adsorbent samples (Table 3) remained stable, showing no significant variation. This stability suggests that there was no release of acidic or basic components from the adsorbent into the solution. Additionally, the treatments performed on samples MF03 and MF04 did not leave any surface residues that might leach into the solution.

Sample	pH
Deionized water	6.74
MF02	6.40
MF03	6.10
MF04	6.82

Table 3 – pH of the aqueous suspensions of the adsorbents

Table 4 presents the surface acidity and basicity results for the adsorbents, determined using the titration method.

Sample	Acidity (mmol/g)	Basicity (mmol/g)	B/A ratio*
MF02	4.71	1.24	0.26
MF03	3.33	0.31	0.09
MF04	2.37	0.79	0.33

*The ratio of basic sites to acidic sites

Table 4 – Surface acidity and basicity of the adsorbents

All samples exhibit a higher quantity of acidic sites, suggesting their potential as good adsorbents for cationic pollutants [33]. However, since Methyl Orange is an anionic dye, this characteristic might diminish the adsorption capacity of the material used in this study.

Surface acidity and basicity are significantly altered by chemical treatments. The sample treated with nitric acid (MF03) experienced a slight reduction in acidity compared to the untreated sample, possibly due to the removal of acidic compounds present in the passion fruit peel, perhaps through their solubilization during treatment in an acidic medium

at 100°C. These species could have contributed to the surface acidity of the samples if they had not been removed. The decrease in acidity also suggests that no residual acid from the treatment remained on the sample surface.

The decline in acidity in the sample treated with NaOH (MF04) may be a result of the reaction between acidic surface groups and hydroxyl ions from the strong base, rendering these groups unsuitable for adsorption. Additionally, the previous discussion suggests the potential solubilization of surface acidic species.

Moreover, the basicity of the samples decreased after the chemical treatments, signifying neutralization or destruction of basic surface groups due to reactions with nitric acid (MF03) or sodium hydroxide (MF04), respectively.

The ratio between the quantity of basic sites and acidic sites (B/A) serves as an indicator of surface acid-base characteristics [33]. At B/A > 1 indicates more basic sites on the surface with a negative charge. B/A = 1 suggests an equal number of basic and acidic sites, reflecting a neutral surface. B/A < 1 signifies a prevalence of acidic sites and a positive charge. Considering Methyl Orange's acidic nature, a less acidic surface is preferable for this study.

All samples demonstrated B/A < 1, confirming the predominance of acidic sites. However, the MF03 sample, treated with HNO_3, exhibited the lowest B/A ratio, indicating increased surface acidity post-treatment. In contrast, the MF04 sample (treated with NaOH) displayed reduced acidity compared to the untreated sample that underwent no chemical treatment.

3.6 pH of Point of Zero Charge (PZC)

The pH of point of zero charge provides indications regarding the degree of surface ionization of the adsorbent and its potential interaction with the adsorbate [33]. Generally, the adsorbent surface becomes positive if it accepts protons from the solution or negative if it releases protons into the solution. The pH at which the adsorbent surface is neutral is referred to as pH_{PZC} (point of zero charge). Figure 4 presents the results of determining the pH of PZC for the passion fruit peel samples used in this study. Table 5 displays the values found for each sample.
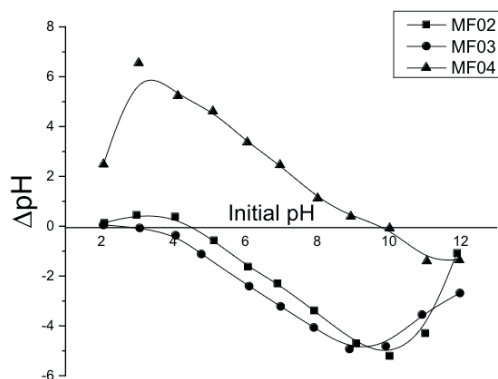
Fig. 4 – pH of PZC for passion fruit peel samples

SAMPLE	pH$_{PZC}$
MF02	4.50
MF03	2.45
MF04	9.84

Table 5 – pH of PZC for passion fruit peel samples

The pH$_{PZC}$ values of samples MF02 and MF03 are below 7, indicating predominantly acidic surfaces. Sample MF04, on the other hand, displayed a pH$_{PZC}$ higher than 7, suggesting that the NaOH treatment made the surface more basic. Furthermore, the pH$_{PZC}$ of sample MF03 indicates an increase in surface acidity after the treatment with HNO$_3$. These results align with the B/A ratio shown in Table 4 and the pH of the aqueous suspensions of the adsorbents (Table 3). They suggest that samples MF02 and MF03 would serve as effective adsorbents for basic pollutants, while sample MF04 would be suitable for adsorbing acidic pollutants.

3.7 Effect of adsorbent mass and particle size

Figure 5 illustrates how varying the adsorbent mass impacts the percentage of dye removal across different particle sizes obtained in this study.

It is observed that the removal percentage increases with decreasing particle size, as expected. Smaller particles minimize diffusion limitations and provide greater contact between the adsorbent and the dye, enhancing the adsorption rate.
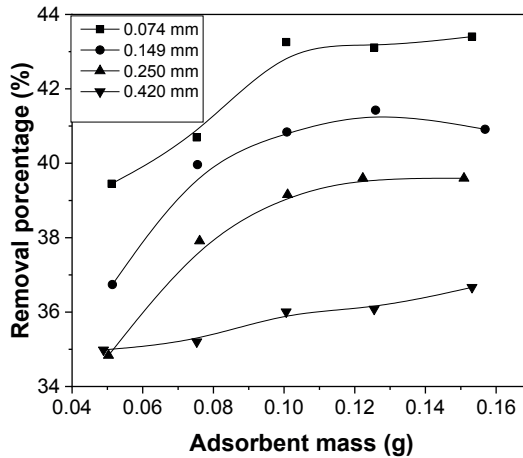
Fig. 5 - Variation in the percentage of Methyl Orange removal with the adsorbent mass for different particle sizes obtained. Initial concentration (Ci) = 100 mg.L^{-1}, pH = 6.70; Temperature (T) = 298K, sample MF02.

The removal percentage increases with the rise in adsorbent mass up to approximately 0.1 g. However, for larger masses, there is no further increase in dye removal.

Based on the results of these preliminary tests, the kinetic and thermodynamic experiments were conducted using an adsorbent mass of approximately 0.1 g with a particle size of 0.074 mm, for 25 mL of Methyl Orange solution at concentrations ranging from 100 to 1000 mg L$^{-1.}$

3.8 Effect of solution pH on adsorption

The adsorption of dye molecules strongly relies on pH due to the surface functional groups of the adsorbent, responsible for interacting with these molecules, which can become protonated or deprotonated, leading to different surface charges in solutions at distinct pH values [34, 35]. Figure 6 shows the impact of pH variation on the adsorption of Methyl Orange.
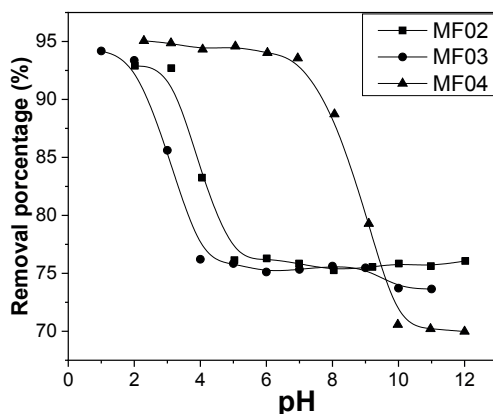
Fig. 6 - Influence of pH on the adsorption of Methyl Orange. T = 298K, C_i = 100 mg.L^{-1}.

As anticipated from the pH_{PZC} results (Table 5), the adsorption is favorable for pH values ≤ 4.0, except for sample MF04, which showed a pH_{PZC} of 9.84. Srivastava et al. [36] mentioned that cation adsorption is enhanced at pH > pH_{PZC}, as the surface becomes negatively charged, whereas anion adsorption is favored at pH < pH_{PZC} due to the positively charged surface.

The findings in this study support this assertion and indicate the influence of polarization effects on Methyl Orange anion adsorption. Similar trends were observed by Kim et al. [37] in Congo Red adsorption on orange peel and by Mokhtari et al. [38] in Methyl Orange adsorption on CuS-impregnated activated carbon.

Figure 6 demonstrates that pH does not substantially affect adsorption within the pH range from 5.0 to 8.0, with a decline in dye removal noted for samples MF02 and MF03 within the pH range of 2.0 to 4.0. Sample MF04 exhibited the highest removal rates, displaying a reduction only beyond pH = 8.06.

Considering that between pH = 5.0 and pH = 8.0, adsorption remains relatively unaffected despite the decline in the removal percentage, the kinetic and thermodynamic experiments were conducted at the original pH of the aqueous solutions, consistently close to the pH of deionized water, ranging from 6.5 to 6.8. This choice simplifies the adsorption system and reduces costs associated with adjusting the solution's pH.

3.9 Adsorption Isotherms

The adsorption isotherms of Methyl Orange on passion fruit peel samples are depicted in Figure 7, for a contact time of 24 hours, pH = 6.8, and room temperature (298K). The adsorption process was studied by fitting the obtained data to Langmuir, Freundlich, Dubinin-Radushkevich, and Temkin equations to identify the model that best describes the

adsorption process. Models with linear regression coefficient (R^2) values closest to unity were deemed suitable for describing the Methyl Orange adsorption system on passion fruit peel.

The isotherm graph illustrates that saturation has not been reached for samples MF03 and MF04, implying that more concentrated solutions than those used in this study could be employed. Sample MF02 appeared closer to saturation, suggesting a lower adsorption capacity.
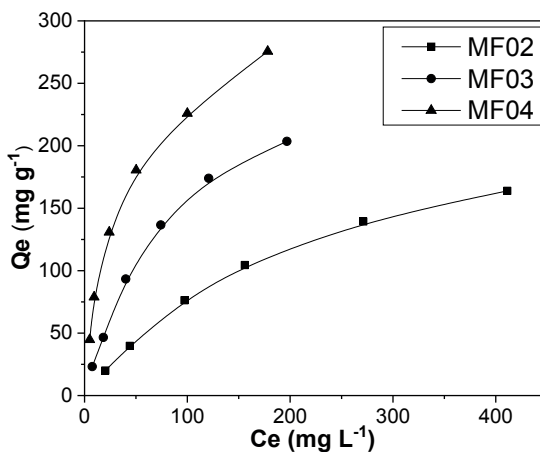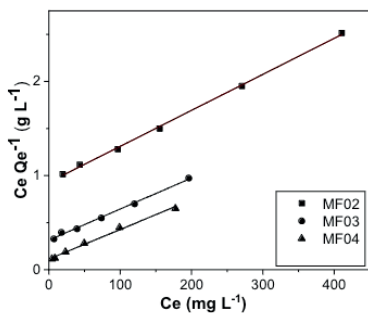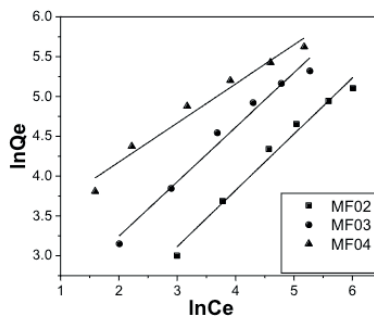

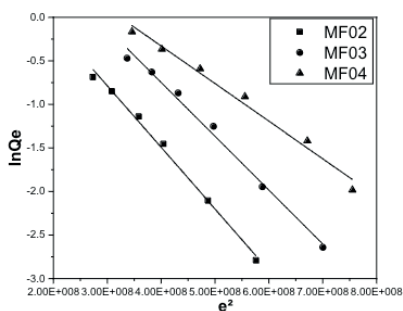**Fig.7** – Adsorption isotherms for methyl orange. T = 25°C; pH = 6,8; t = 24 hours

Figure 8 shows the linearization of the isotherms according to the studied models. The parameters obtained for each model are displayed in Table 7. The mathematical models used to study the isotherms are described in the supplementary material.
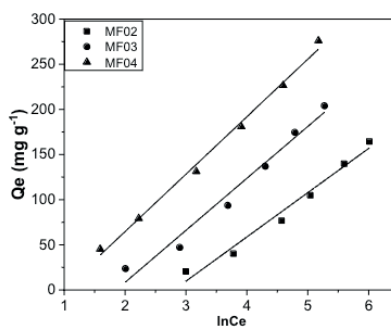
Fig. 8 - Linearization of the isotherms according to the (a) Langmuir, (b) Freundlich, (c) Dubinin-Radushkevich, and (d) Temkin models. T = 298K, pH = 6.8, t = 24 hours.

The Langmuir model displayed the most favorable linear correlation coefficients. According to the Q_{max} values derived from the Langmuir isotherm (Table 6), treating the passion fruit peel with HNO_3 or NaOH enhances its adsorption capacity for Methyl Orange. Particularly, the base treatment yields a material with a higher adsorption capacity. R_L values obtained from the Langmuir isotherm fall within the range of $0 < R_L < 1$, indicating the favorable nature of Methyl Orange adsorption on passion fruit peel across all samples.

The values of n from the Freundlich isotherm also correspond to favorable adsorption. These values also suggest that the interaction between the adsorbate and the adsorbent is not very strong, indicating a potential occurrence of dye desorption in the process. This aspect of the system was not studied in this work.

Isotherm model	Parameters	MF02	MF03	MF04
Langmuir	Q_{max} (mg.g^{-1})	263.16	303.03	322.58
	K_L (L.mg^{-1}) x 10^3	4.1	10.8	29.6
	R_L	0.71	0.48	0.25
	R^2	0.9989	0.9982	0.9986
Freundlich	n	1.01	2.23	2.04
	K_F (mg g^{-1}).(L mg^{-1})$^{1/n}$	1.01	0.53	0.31
	R^2	0.9832	0.9603	0.9617
Dubinin- Radushkevich	B_{DR} x 10^9 (mg^2 kJ^{-2})	7.06	6.18	4.31
	Q_s (mmol g^{-1})	3.78	5.6	4.02
	Q_s (mg g^{-1})	1238	1834	1318
	E (kJ mol^{-1})	8.41	8.99	10.77
	R^2	0.9939	0.9913	0.9838
Temkin	B (J mol^{-1})	36.9	45.8	58.3
	a_T (L mg-1)	0.039	0.046	0.145
	R^2	0.9808	0.9765	0.9809

Table 6 - Parameters derived from the isotherms for the adsorption of Methyl Orange. Temperature (T) = 298K, pH = 6.8; time (t) = 24 hours

Although the correlation coefficients obtained for the Dubinin-Radushkevitch model are high, the maximum adsorption capacity values obtained are much higher than the experimental values, leading us to conclude that this model is not the most suitable for describing this adsorption system. However, we can analyze the obtained values for the energy E from the Dubinin-Radushkevich equation and consider that they indicate, for all samples, a process of physical adsorption. This is confirmed by the values of the B factor from the Temkin equation, even though this model also has lower correlation coefficients for the linearization of the isotherms.

The results of the adsorbed quantity obtained for samples MF03 and MF04 are higher than for the untreated sample. Hot acidic fruit peel treatment is one of the methods for pectin extraction found in the literature [39]. Thus, the increased adsorption capacity for sample MF03 could be attributed to surface modification by pectin extraction, which might have increased the access of molecules to adsorption sites. The increased adsorption capacity for sample MF04 could be attributed to the increased basicity of the surface, favoring the adsorption of acidic dyes.

The pH used in the adsorption experiments may have influenced the Q_{max} results because samples MF02 and MF03 present negatively charged surfaces for pH above 4.50

and 2.45, respectively (Table 5). As the adsorption experiments were conducted at pH = 6.8, the surfaces of these materials would be negatively charged, reducing the efficiency of adsorption for anionic dyes. Since sample MF04 has a pHpzc = 9.84, its surface would be positively charged at the pH used in the adsorption experiments, thus increasing the amount of Methyl Orange adsorbed by this sample.

However, adjusting the solution pH would introduce additional costs to the process, requiring the use of more reagents, thus not meeting the requirements of low-cost adsorption processes. Based on material and reagent cost data, it is estimated that it is more advantageous to invest solely in treating the adsorbent to increase adsorption capacity rather than adjusting the pH of the adsorption process itself.

Furthermore, treating the adsorbent involves the use of environmentally less harmful reagents than adjusting the solution pH. pH adjustment would generate residues to remove the dye, which is not desirable from the perspective of environmentally friendly processes.

Table 7 presents a comparison of the maximum adsorption capacity from Langmuir for the adsorption of Methyl Orange on various adsorbents under conditions similar to those used in this study. The yellow passion fruit peel used in this study exhibited the best adsorption capacities.

There aren't many comparative studies available in the literature to relate to the adsorption system discussed here. The studies presented in Table 8 are the ones that most closely resemble the experimental conditions of this study, suggesting that the adsorbent derived from passion fruit peel could be considered a viable alternative for water purification. However, it is still necessary to evaluate the kinetic and thermodynamic data to gain a more comprehensive understanding of these materials' behavior as adsorbents.

Adsorbent	Q_{max} (mg.g^{-1})	Ref.
Halloysite nanotubes	13.56	[40]
Chrysotile nanotubes	31.46	[40]
Poppy leaves treated with L-arginine	90.44	[41]
NiO nanoparticles	121.95	[42]
CuO nanoparticles	188.68	[42]
Tangerine peel activated carbon	196.08	[43]
MF02	263.16	This work
MF03	303.03	This work
MF04	322.58	This work

Table 7 - Comparison among various adsorbents for Methyl Orange adsorption

3.10 Adsorption Kinetics

The adsorption of Methyl Orange was studied as a function of contact time to determine the kinetic model that best describes the process. The results of the variation in the amount adsorbed over time are shown in Figure 9.
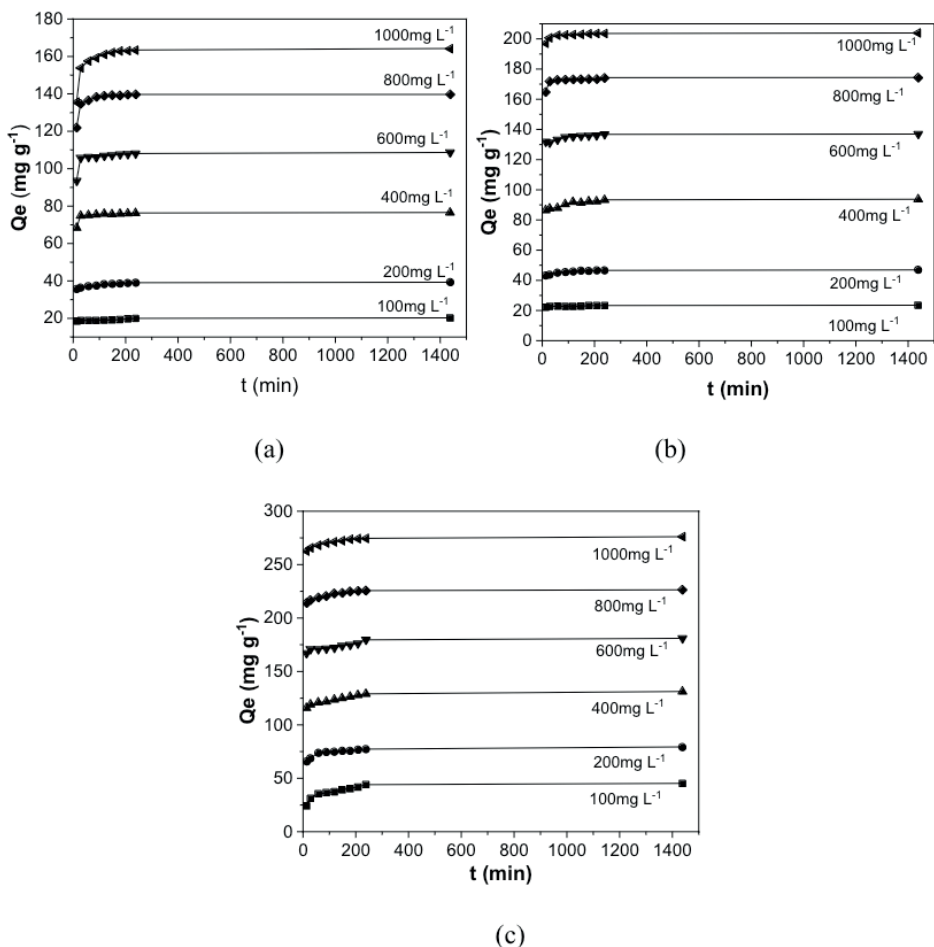

(a)   (b)

(c)

Fig. 9 - Effect of contact time on Methyl Orange adsorption for samples (a) MF02, (b) MF03, and (c) MF04. T = 25°C, pH = 6.8, and Ci = 100 to 1000 mg.L^{-1}.

The results showed that the adsorption of Methyl Orange reaches equilibrium in about 60 minutes for all passion fruit peel samples. The amount adsorbed increases with the increase in the initial concentration for all samples.

The kinetics of the adsorption process was studied using the pseudo-first order, pseudo-second order, Elovich, Boyd, and intraparticle diffusion (Weber-Morris) models. The kinetic modeling of adsorption is presented here for the initial concentration of Methyl Orange of 1000 mg L^{-1} [44 – 47]. The mathematical models used to study the kinetics of

adsorption are described in the supplementary material.

Figure 10 shows the graph obtained for the pseudo-first-order modeling at room temperature and an initial concentration of Methyl Orange of 1000 mg L-1.
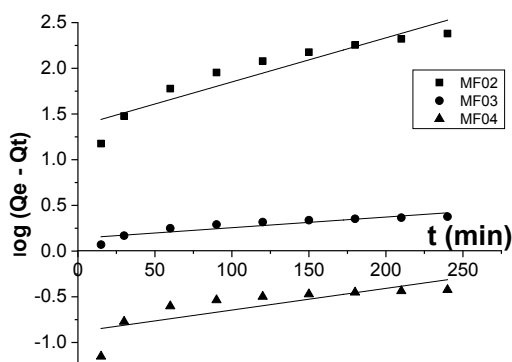

Fig.10 - Pseudo-first-order model for Methyl Orange adsorption on passion fruit peel. Ci = 1000 mg L-1, T = 298K, pH = 6.7

The graphs of $\log_{10}(Q_e - Q_t)$ versus t presented very low linear correlation coefficients, indicating that this model does not describe the kinetics of Methyl Orange adsorption on different passion fruit peel samples. Furthermore, the results presented in Table 8 have no chemical significance as the rate constants calculated (from equation 13, supplementary material) were negative. It can also be observed in Table 8 that the calculation of the adsorbed amount at equilibrium (Qe) showed results significantly distant from the experimentally obtained values, confirming that the pseudo-first-order model is not suitable to describe the obtained results.

Figure 11 shows the graphs obtained for the pseudo-second-order model, for an initial concentration of 1000 mg L-1, at room temperature, and with deionized water at pH 6.8.
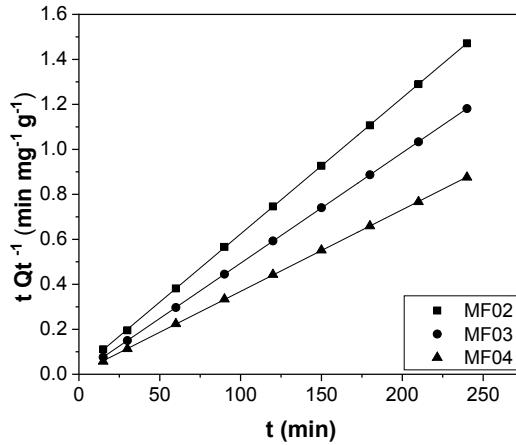
Fig. 11 - Pseudo-second-order model for the adsorption of methyl orange on passion fruit peel. Ci = 1000 mg L^{-1}, T = 298K, pH = 6,8

The obtained correlation coefficients were greater than 0.999 for all tested samples, indicating that the pseudo-second-order model describes well the adsorption of methyl orange on passion fruit peel. This model is considered more empirical than theoretical [47,48], being applicable to systems where experimental simulation closely resembles real conditions, as in our experiments (room temperature, without pH adjustment, batch experiments). The pseudo-second-order model also assumes the possibility of ion exchange between the adsorbate and adsorbent. However, the thermodynamic data, presented in the next section, do not suggest that chemical interactions are occurring in this system. Thus, the pseudo-second-order model is a good mathematical description of the process but does not provide an indication of the adsorption mechanism taking place (whether physical or chemical).

In Figure 12, we observe the graph obtained for the Elovich kinetic model under the same conditions used for the other models.
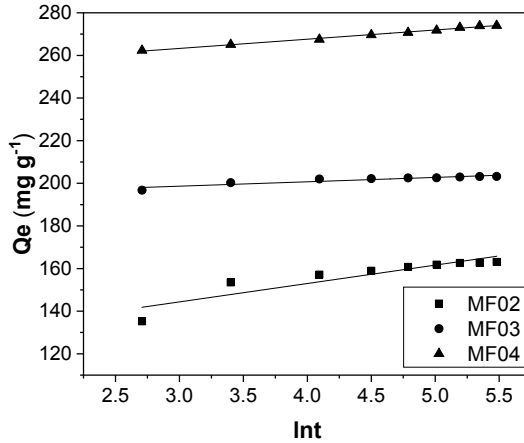
Fig. 12 – Elovich model for methyl orange adsorption onto passion fruit peel. Ci = 1000 mg L^{-1}, T = 298K, pH = 6,8

The R^2 values for the Elovich modeling were very low compared to the pseudo-second-order model, indicating that this equation is not suitable for describing the kinetics of methyl orange adsorption on passion fruit peel. The α values were extremely high, suggesting an initial rapid adsorption, which was confirmed by the low t_0 values. However, results obtained for other initial concentrations showed that the expected increase in α and β constants with increasing initial concentration, as reported in the literature [45], did not occur; instead, values varied randomly. Furthermore, the Elovich constants obtained in this study do not agree with values from similar conditions in other studies [49, 50]. Based on these considerations, we conclude that the Elovich model does not describe the kinetics of the adsorption process studied in this work.

KINETIC MODEL	PARAMETERS	MF02	MF03	MF04
PSEUDO-FIRST ORDER	kad (min^{-1}) x 10^3	-11.05	-2.76	-5.53
	Qe (mg g^{-1})	23.37	1.38	0.13
	Qe EXP (mg g^{-1})	163.88	203.59	275.58
	R^2	0.8814	0.8151	0.6408
PSEUDO-SECOND ORDER	k_2(g mg^{-1}.min^{-1}) x10^3	2.0	8.6	2.5
	Qe (mg g^{-1})	163.9	206.1	277.8
	QeEXP (mg g^{-1})	163.88	203.59	275.58
	R^2	0.9998	1	0.9997

Table 8 – Parameters obtained for the kinetic modeling of methyl orange adsorption on passion fruit peel. Ci = 1000 mg L^{-1}, T = 298K, pH = 6,8

The mechanism of the adsorption process is not always clear from the models used

in this study. Moreover, liquid-phase adsorption is always subject to rate-limiting steps, such as film diffusion and intra-particle diffusion. To study the rate-limiting step of this process, the Boyd, and Weber-Morris models were employed [47, 50 – 53].

Figure 13 displays the graph obtained for the application of the Boyd equation to the experimental data, for an initial concentration of 1000 mg.L^{-1}. Table 9 summarizes the values found for B and for the diffusion coefficient (Di), calculated from the expression:

$$B = \frac{\pi^2 D_i}{r^2} \qquad (2)$$

Where r is the molecule radius (m) [54] assuming that it has spherical shape.

The plot of Bt versus t for the adsorption of methyl orange on passion fruit peel exhibited reasonable linearity, especially for sample MF04, but does not pass through the origin. This behavior indicates that adsorption is controlled by external mass transfer and not by pore diffusion within the particle, as expected since passion fruit peel particles do not present a well-defined pore structure. This observation is reinforced by the low values of B found, resulting in very low values for the diffusion coefficient, Di, indicating that the molecule diffusion in the solution is slow and likely the process controlling the adsorption rate.
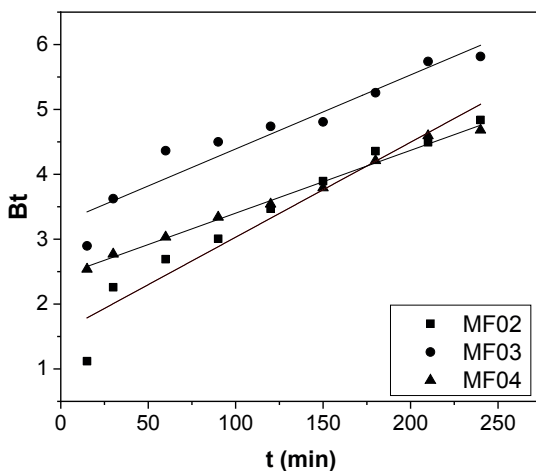

Fig.13 – Plot of Boyd for the adsorption of methyl orange onto passion fruit peel, Ci = 1000 mg L^{-1}, T = 298 K, pH = 6,6.

The diffusion processes can also be investigated using the Weber-Morris model [55], described in supplementary material.

Figure 14 displays the Weber-Morris plots for the adsorption process of methyl orange on the tested samples at an initial concentration of 1000 mg L^{-1}, pH = 6.7, and room
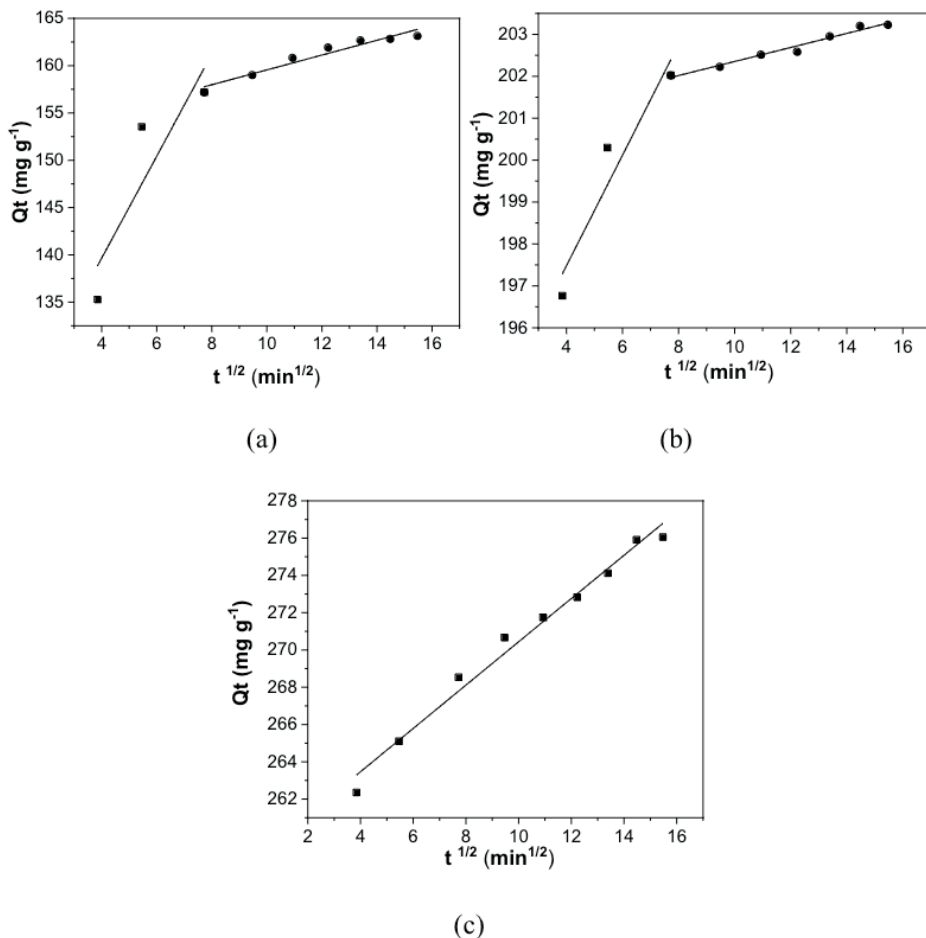
temperature (298K).

Fig. 14 – Weber-Morris plots for adsorption of methyl orange onto passion fruit peel. (a) MF02, (b) MF03, (c) MF04

The Weber-Morris model suggests that if the first linear segment (initial stages of adsorption) has a zero linear coefficient (meaning the line segment intersects the origin), then intraparticle diffusion controls the adsorption process. However, if the linear coefficient is not zero, the process governing adsorption might be the diffusion in the film surrounding the particle, where the thickness is assigned to the linear coefficient in mg.g^{-1}.

It can be observed that the plots are linear but do not pass through the origin, indicating that intraparticle diffusion is not the main determining factor for the adsorption rate. For samples MF02 and MF03, the plots show two diffusion stages, which can be attributed to diffusion in the solution and diffusion in the liquid film surrounding the particle. For sample MF04, only one stage is observed, attributed to film diffusion. The values of

'c' were consistently high, indicating the film effect's importance in the diffusion process. The results suggest that the limiting step of the process was likely diffusion in the solution, followed by diffusion in the film surrounding the particle, and no diffusion occurred in the pores, as expected for the non-porous particles of this material."

MODEL	PARAMETERS	MF02	MF03	MF04
BOYD	B	0.015	0.011	0.0097
	D_i (m^2 min^{-1})	1.01×10^{-20}	7.90×10^{-21}	6.70×10^{-21}
	R^2	0.9370	0.9180	0.9915
WEBER &MORRIS	$k_{i,1}$ (mg.g^{-1}.min$^{-1/2}$)	5.38	1.32	1.04
	C_1 (mg g^{-1})	117.91	192.17	259.10
	R^2_1	0.7980	0.9157	0.9883
	$k_{i,2}$ (mg.g^{-1}.min$^{-1/2}$)	0.78	0.17	-
	C_2 (mg g^{-1})	151.64	200;66	-
	R^2_2	0.9411	0.9734	-

Table 9 – Parameters for Boyd and Weber – Morris modelling

The results obtained with the various kinetic models indicate that the adsorption process of methyl orange on passion fruit peel can be mathematically described by the pseudo-second-order model. However, there are diffusional limitations in the solution, possibly due to the agitation speed used in the experiments, which are influencing the process.

3.11 Effect of Temperature and Thermodynamic Variables

Figure 15 shows the adsorption isotherms of methyl orange for samples MF02 to MF04, at the temperatures studied in this work.
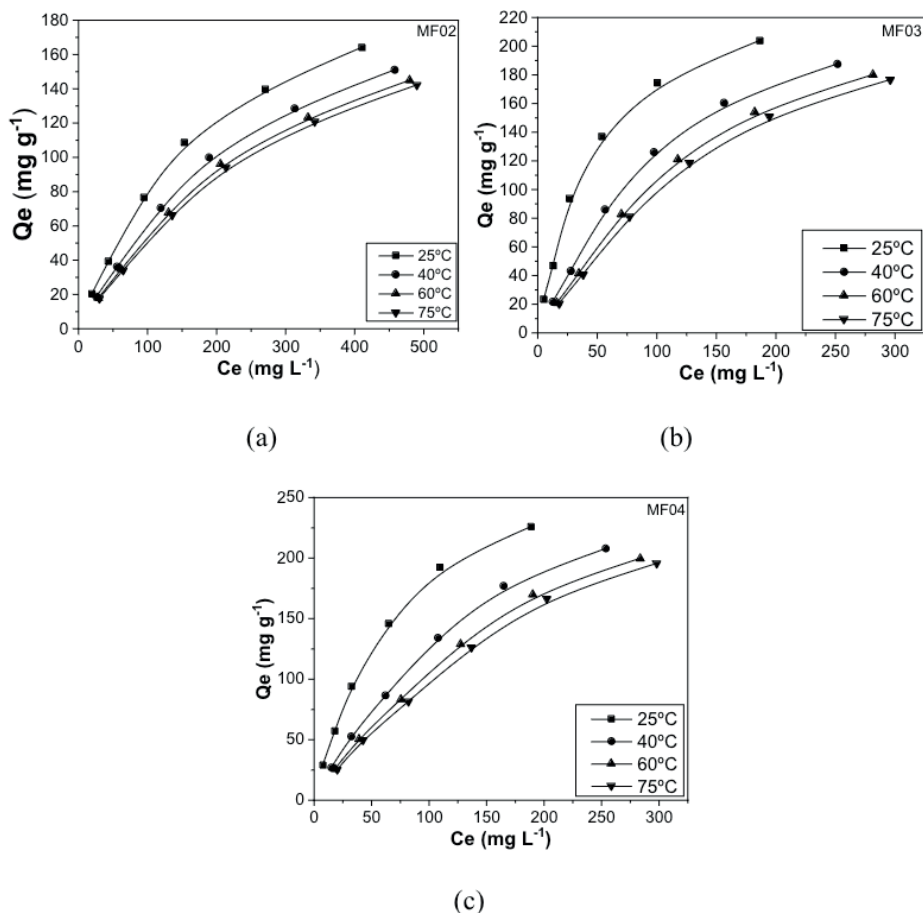
(a)

(b)

(c)

Fig. 15– Adsorption isotherms at various temperatures, pH = 6,8; t = 24 horas. (a) MF02; (b) MF03; (c) MF04

The adsorbed amount decreases with increasing temperature, as expected for an exothermic process. The values of the thermodynamic parameters - enthalpy, entropy, Gibbs free energy, as well as the equilibrium constants - were determined using equations 3 to 5 [3, 4] and are summarized in Table 10.

$$\log K_C = -\frac{\Delta H^0}{2.303RT} + \frac{\Delta S^0}{2.303R} \qquad (3)$$

$$\Delta G^0 = -RT \ln K_C \qquad (4)$$

$$K_C = \frac{C_{ads}}{C_e} \qquad (5)$$

The thermodynamic study results indicate an exothermic nature of the adsorption

process across all tested samples, aligning with the depicted decrease in adsorption capacity as the temperature rises, as seen in Figure 16. This process occurs with a reduction in entropy, as anticipated, given that molecules exhibit greater organization when adsorbed onto a surface compared to when in a solution.

The obtained Gibbs free energy values suggest that the adsorption of methyl orange on the various samples is spontaneous at near-ambient temperatures but becomes gradually less spontaneous with increasing temperature. These free energy and enthalpy values affirm the assumption that the process primarily involves physical adsorption.

SAMPLE	T (K)	K_c	ΔH^0 (kJ mol^{-1})	ΔS^0(J K^{-1}.mol^{-1})	ΔG^0(kJ.mol^{-1})
MF02	298	1.43	-5.35	-15.28	-0.89
	313	1.18			-0.44
	333	1.08			-0.23
	348	1.04			-0.12
MF03	298	4.36	-10.06	-22.17	-3.64
	313	2.97			-2.84
	333	2.55			-5.59
	348	2.37			-2.51
MF04	298	4.29	-9.97	-21.99	-3.61
	313	2.94			-2.81
	333	2.52			-2.56
	348	2.36			-2.48

Table 10. Thermodynamic parameters obtained for the adsorption of methyl orange on passion fruit peels

4 | CONCLUSION

The passion fruit peel has emerged as a promising adsorbent for the dye methyl orange, displaying adsorption capacities ranging from 263.16 to 322.58 milligrams of dye per gram of adsorbent. Treatment of the sample with acid or base has shown an overall improvement in adsorption capacity, yet the base treatment exhibited more effectiveness in enhancing the adsorption capacity.

The kinetics of the process can be accurately described mathematically by the pseudo-second-order equation. Studies on diffusion indicate that solution diffusion significantly influences the results, acting as the rate-limiting step of the process.

The adsorption of methyl orange onto passion fruit peel is an exothermic process, resulting in a decrease in entropy. The obtained Gibbs free energies suggest that the process is spontaneous at temperatures close to room temperature (298 K).

Comparative analysis with other methyl orange adsorption processes reported in the literature highlights that passion fruit peel can serve as an effective adsorbent for this

dye, with the base treatment yielding the most favorable material for adsorption at room temperature. Moreover, the results imply that passion fruit peel might also serve as a viable adsorbent for other acidic dyes besides methyl orange. Nonetheless, further studies are required to refine our understanding of the kinetics involved in the adsorption process.

DECLARATIONS

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