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Study of the use of food waste as bioadsorbents to remove methylene blue dye

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ABSTRACT

The disposal of untreated effluents and the lack of efficient and effective treatment have raised concerns. In this sense, methylene blue dye is classified as a priority contaminant among the dyes released into industrial effluents. It is used in several segments, such as dyeing cotton, silk, paper, paints, among others. In this context, the use of bioadsorbents obtained from food waste to remove methylene blue dye would be a viable alternative, as it allows the use of waste generated in large quantities and at low cost, in addition to being an environmentally friendly alternative. Totally correct and sustainable. Therefore, the main objective of this work was to study the use of food waste as bioadsorbents in the removal of methylene blue dye. To achieve this, bio-adsorbents were produced from food waste, such as chicken eggshells, passion fruit peels and orange peels, in natura, thermally activated and chemically activated. The characterization of the bioadsorbents produced was carried out through analyzes of specific surface area, thermal behavior, morphology and structure, in addition to determining yield. The performance of the bioadsorbents was comparatively evaluated in the batch adsorption process to remove the methylene blue dye. The adsorption tests showed that the bioadsorbents developed were efficient in removing the dye, showing removal of more than 64%. The samples that obtained the best results were passion fruit peel, with thermal (MT) and chemical (MQ) treatment, and orange, with chemical treatment (LQ), achieving dye removals greater than 98%, due to their high specific surface areas. It was not possible to obtain adsorption isotherms for samples MQ and LQ, due to the high percentages of dye removal achieved, even for the different initial concentrations studied.

Keywords: Methylene Blue; Food Waste; Bioadsorber.

1. INTRODUCTION

Humanity has grown significantly and the changes 3suffered by the environment are worrying society, the population is growing and so is consumption. This increases industrial production and, to mitigate the effects caused, researchers have studied new technological means [1]. Water is of great importance for human life and the planet. Some water pollutants are the dye, textile and paper industries, which produce a large amount of water with contaminants, released into rivers and springs, harming life and causing various effects [2]. These wastewaters with dyes discarded without adequate treatment cause several pollution problems, which can affect aesthetic merit, prevent the penetration of sunlight and reduce photosynthesis activities [3].

The industry, especially the textile industry, uses different dyes to satisfy the demand for different colors and shades that consumers require. Most of the dyes used in industry are due to their high resistance, which interferes with the treatment processes of these effluents [1]. One of the most used dyes in the industry is methylene blue, which is cationic. Thus, the search for efficient techniques for treating effluents with dyes has been growing, highlighting the use of the adsorption process, a method that has gained considerable attention in recent studies [4].

When released without treatment into water bodies, it impairs the penetration of sunlight, which reduces photosynthesis and the oxygen available in this environment [5]. Thus, the search for efficient techniques for treating effluents with dyes has been growing, highlighting the use of the adsorption process.

Adsorption has a well-known use with regard to the process of separating substances, being used in several industrial branches for various purposes. This process is a mass transfer operation, in which solids,

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called adsorbates, concentrate on the surface of a substance dissolved in a fluid, called an adsorbent, making separation possible. Thus, the external surface of the adsorbents is of great importance, that is, the larger this surface, the better the efficiency of the adsorption process [6].

However, the use of expensive adsorbents has been highlighted as a potential limiting factor. The use of cheaper and more effective bioadsorbents, derived from a variety of basic materials, such as agro-industrial waste, has been investigated by researchers [7]. Efficient and lower-cost alternatives have been studied to produce bioadsorbents, which promote the removal of contaminants through adsorption, using food waste, such as peels and seeds [8]. Since food production is one of the main industrial sectors in Brazil and the generation of waste in agro-industrial activities is quite significant, leading to the search for its use as an alternative to minimize the damage caused [9].

In this context, the present work aims to study the use of food waste as bi-adsorbents in the removal of methylene blue dye.

2. EXPERIMENTAL PROCEDURES

2.1. Materials

The Neon brand methylene blue dye was used in the analyzes as an adsorbate and was prepared in different concentrations through dilutions with distilled water. Passion fruit, orange and chicken egg peels were collected from food waste, between the months of July and August 2022, and used as bioadsorbents, undergoing washing, grinding, drying, thermal and chemical activation. For chemical activation, 85% phosphoric acid and sodium bicarbonate were used, both from the Química Moderna brand.

2.2. Preparation of bioadsorbents

The preparation of the bioadsorbents began with washing in running water and drying in an oven at 80 °C for 24 hours. Afterwards, the samples were fragmented and sieved. At that moment, the fresh samples were separated.

Then, the samples were separated into porcelain crucibles and taken to a muffle furnace at 550 °C for 2 hours to produce bioadsorbents with thermal activation. Chemical activation was carried out in an acidic medium with 85% H_3PO_4, in a 1:1 ratio, mixing with a glass rod, followed by heat treatment in a muffle furnace at 550 °C for 2 hours. In chemical activation, after cooling in the desiccator, washing was carried out with 1% $NaHCO_3$ in a funnel with filter paper three times. Then, they were washed three times with distilled water and dried in an oven at 110 °C for 24 hours.

The muffle used was from the Cienlab brand. Table 1 describes the 9 bioadsorbents developed.

2.3. Characterization of bioadsorbents

To determine the surface area of bioadsorbents and know the size and distribution of their pores, gas adsorption analysis was used using the BET method. The BET analysis presents values of specific surface areas for the residue bioadsorbents, considering that the specific surface area is of paramount importance for the adsorptive process and where the dye is fixed for its removal. The equipment used was Quantachrome and Nova 220e model. Previously known quantities of samples spent 3 hours heating in a vacuum tube until reaching a temperature of 150 °C, after which they were cooled to cryogenic temperatures and exposed to nitrogen gas at controlled and different pressures.

Table 1: Bioadsorbents developed in the work.

BIOADSORBENT DEVELOPED	USED FOOD WASTE	RESIDUE OF FOOD USED
MIn	Passion fruit	In nature
LIn	Orange	
OIn	Egg	
MT	Passion fruit	Thermally activated
LT	Orange	
OT	Egg	
MQ	Passion fruit	Chemically activated
LQ	Orange	
OQ	Egg	

To understand the morphology and structure of the bioadsorbents developed, scanning electron microscopy analysis was carried out, making it possible to verify in an expanded manner whether or not pores were formed and relate it to the adsorptive power of each sample. Therefore, the formation of pores and microstructures present on the surface of the samples was verified by morphological analysis of the bioadsorbents, known as Scanning Electron Microscopy (SEM). This analysis was carried out using Jeol brand equipment and model JSM-6510LV. The samples initially had to pass through Denton Vacuum equipment, which performed the metallization with a thin layer of gold, and then micrographs of each one were obtained at voltages of 5 and 10 kV and different magnifications.

To verify the properties of the materials and their respective degradation temperatures of the components, thermal stability analysis, known as Thermogravimetric (TGA), was used. The technique was used to evaluate the dominant stages of thermal degradation of the main constituents of bioadsorbents. To verify the properties of the materials and their respective degradation temperatures of the components, thermal stability analysis, known as Thermogravimetric (TGA), was used. The equipment used was Shimadzu and model TGA-51. The analysis conditions were in a nitrogen atmosphere with a flow rate of 50 mL/min, a heating ramp of 10 °C/min and a temperature range of 25 to 1000 °C.

2.4. Determination of yield

Determining the yield is of great importance in this study to evaluate the viability of bioadsorbent production and understand the loss of material according to the treatments carried out. Before and after each process, the samples were weighed and Equation 1 was used to calculate the yield, in percentage, of the samples.

$$\text{Performance (\%)} = M_F/M_I \times 100 \quad (1)$$

Where Mf is the final mass of the bioadsorbent produced, in grams, and MI is the initial mass of the material, in grams.

2.5. Preparation of methylene blue solutions

To prepare methylene blue solutions, dilutions were made with the dye in distilled water using a standard solution of 200 mg/L concentration. Such dilutions were made in a volumetric flask.

By using the same dye and equipment, to quantify the concentrations of methylene blue in the solutions and at the end of the adsorption process, the calibration curve of Equation 2, obtained by GOETZ *et al*. [10], on the PerkinElmer UV-VIS spectrophotometer.

$$\text{Abs} = 0{,}06\ \text{Conc} \quad (2)$$

Before the rounds of analysis of the bioadsorbent samples in the UV-VIS spectrophotometer, the proof in white with distilled water, as well as checking the concentration of the standard dye solution before dilutions.

2.6. Adsorption tests

To obtain an adsorbent concentration of 12 g/L, the adsorption tests were carried out by adding approximately 0.24 g, weighed on an Ohaus brand analytical balance, of the bioadsorbents produced, each separately, in 20 mL of the dye solution with an initial concentration of 75 mg/L and natural pH (6.0), keeping under stirring for 30 minutes at room temperature. After this period, the bioadsorbents were separated by centrifugation, in a Novatecnica model NT 830 centrifuge, for 15 minutes at a speed of 3000 rpm and the final concentration of the dye in solution was determined using the UV spectrophotometer. VIS, at a wavelength of 665 nm, in order to verify the efficiency of the bioadsorbents developed in the adsorption process. 9 batch adsorption experiments were carried out, one with each bioadsorbent, in addition to 6 tests to obtain adsorption isotherms, in order to verify the adjustment to the Langmuir and Freundlich models. These tests to obtain the isotherms were carried out at initial dye concentrations of 50, 100 and 125 mg/L, for the samples with the best performance, which were MQ and LQ.

For each experiment, the percentage of dye removal (%RC) was calculated, according to Equation 3.

$$\%RC = [(C_i - C_f)/C_i] \times 100 \quad (3)$$

Where Ci is the initial concentration of the dye (mg/L) and Cf is the final concentration of the dye (mg/L).

3. RESULTS AND DISCUSSIONS

3.1. Assessment of the characterization of bioadsorbents

3.1.1. Assessment of the specific surface area

According to MELO *et al*. [11] the adsorption intensity is proportional to the specific surface area, since the adsorption process is a surface phenomenon. The adsorption capacity and rate are directly related to BET, making it possible to evaluate the distribution of the pores and better choose the bioadsorbent. Table 2 presents the results of the specific surface area analysis of the developed bioadsorbents.

In Table 2 it can be seen that the samples obtained from eggshells did not improve with thermal and chemical treatments. PIRES [12] used eggshell as an adsorbent in the adsorption process to remove phosphorus. The author evaluated different heat treatment temperatures, verifying that there was an improvement in the adsorption capacity of samples treated at temperatures up to 600 °C. The temperature used for heat treatment was 550 °C for all samples, which may justify the lower specific surface area obtained for bioadsorbents obtained from eggshells and consequently a lower adsorption capacity.

For samples of orange peels, a significant improvement can be seen when exposed to chemical treatment. PIRES [12] evaluated this residue with heat treatment at different temperatures, the highest being 450 °C and observed that the BET of this sample presented the best result, of 0.420 m^2/g, still much lower than that obtained in this work.

The passion fruit peel showed a significant improvement with heat treatment and an even more significant improvement with chemical treatment. A similar result was observed by CASTRO [13], who evaluated magnetic activated carbon from passion fruit seeds in the adsorption of methylene blue and treated it chemically with NaOH, obtaining results of specific surface area for the sample with chemical and thermal treatment at 500 °C of 690 m^2/g.

According to CALCIOLARI *et al*. [14], thermal activation causes the degradation of functional groups, which are found in fresh samples, related to the increase in the specific surface area, generating an increase in the porosity of the materials. While, according to CATELAN and MENDES [15], in chemical activation, chemical agents have the ability to dehydrate, with phosphoric acid being one of the most used for the production of activated carbon, largely due to its ability to produce structures with mesopods. These chemical agents penetrate the interior of the material and increase the pore structure by promoting the pyrolytic decomposition of the precursor materials.

3.1.2. Morphological and structural assessment

To understand the morphology and structure of the bioadsorbents developed, scanning electron microscopy analysis was carried out, making it possible to verify in an expanded manner whether or not pores were formed and relate it to the adsorptive power of each sample.

Figure 1 presents the micrographs of the bioadsorbents developed from raw passion fruit peel, thermally and chemically activated, respectively. The images can be evaluated according to the pore characteristics of each sample.

Table 2: Specific Surface Areas of the developed bioadsorbents.

BIOADSORBENT	SPECIFIC SURFACE AREA (m^2/g)
Min	0,962
MT	242,609
MQ	649,118
Lin	0,258
LT	1,392
LQ	364,740
OIn	0,394
OT	0,111
OQ	1,336

In Figure 1, it can be seen that the bioadsorbents obtained from fresh passion fruit peel have little presence of pores, with a flatter surface and few or almost no cavities. The samples that underwent heat treatment show a more porous surface with more rounded edges, possibly due to the deterioration of the chemical components that filled it. According to ALVES *et al*. [16], carbonization causes the volatilization of volatile compounds and light gases, thus causing the formation of porous cavities.

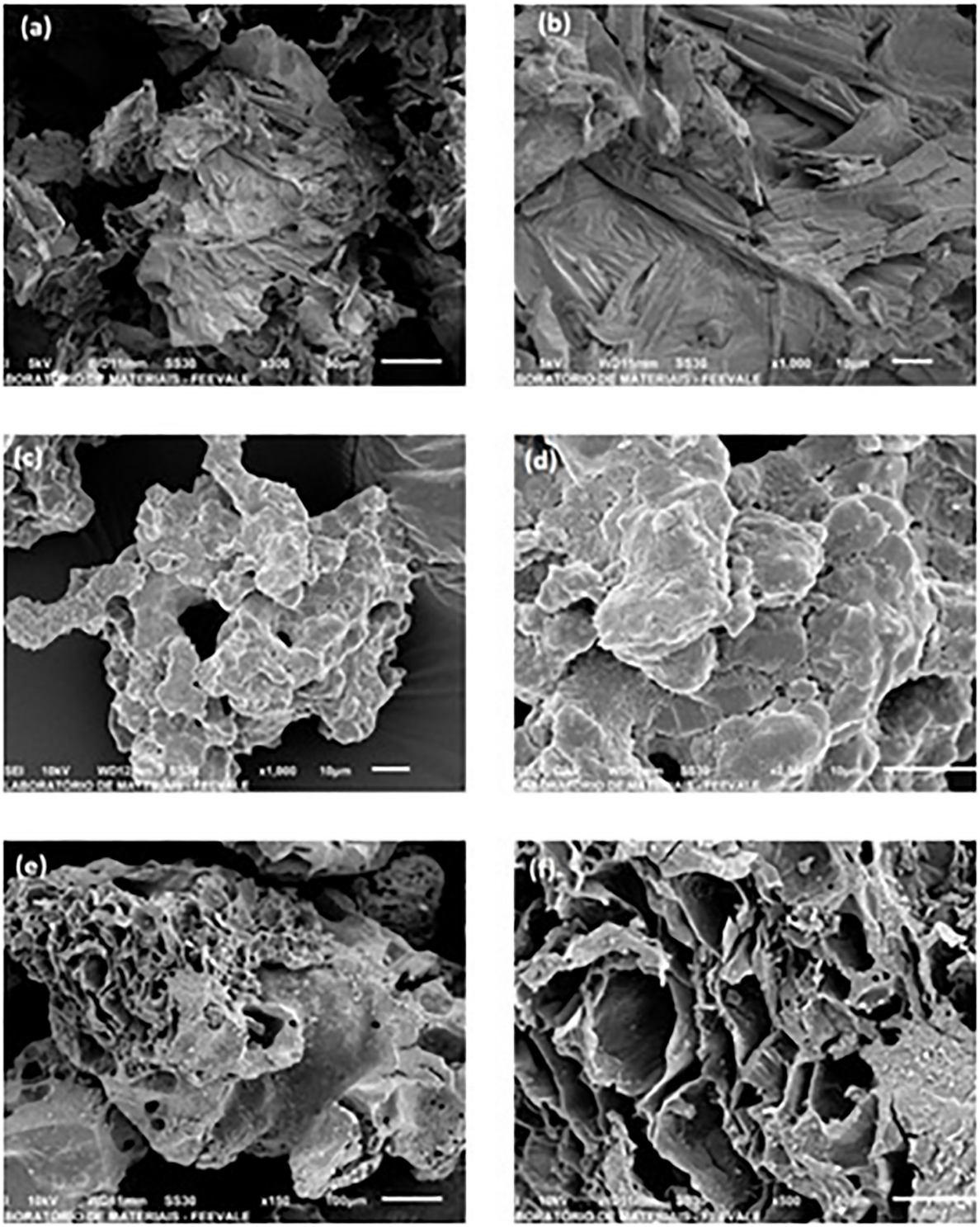

Figure 1: Micrographs of bioadsorbents developed from fresh passion fruit peel, with magnifications (a) 300× and (b) 1000×, thermally activated, with magnifications (c) 1000× and (d) 2500×, and chemically activated, with magnifications of (and) 150× and (f) 500×.

The samples that underwent treatment with chemical agents presented an irregular surface, with a large presence of elongated tubular structures, which corroborates the significant increase in the specific surface area of this sample. Due to these characteristics, a high adsorption capacity of this bioadsorbent is expected. Similar results were obtained by GOETZ *et al*. [10], who studied the use of fresh and heat-treated bamboo to remove methylene blue dye.

Figure 2 presents the micrographs of samples of bioadsorbents produced with fresh orange peels, thermally and chemically activated, respectively.

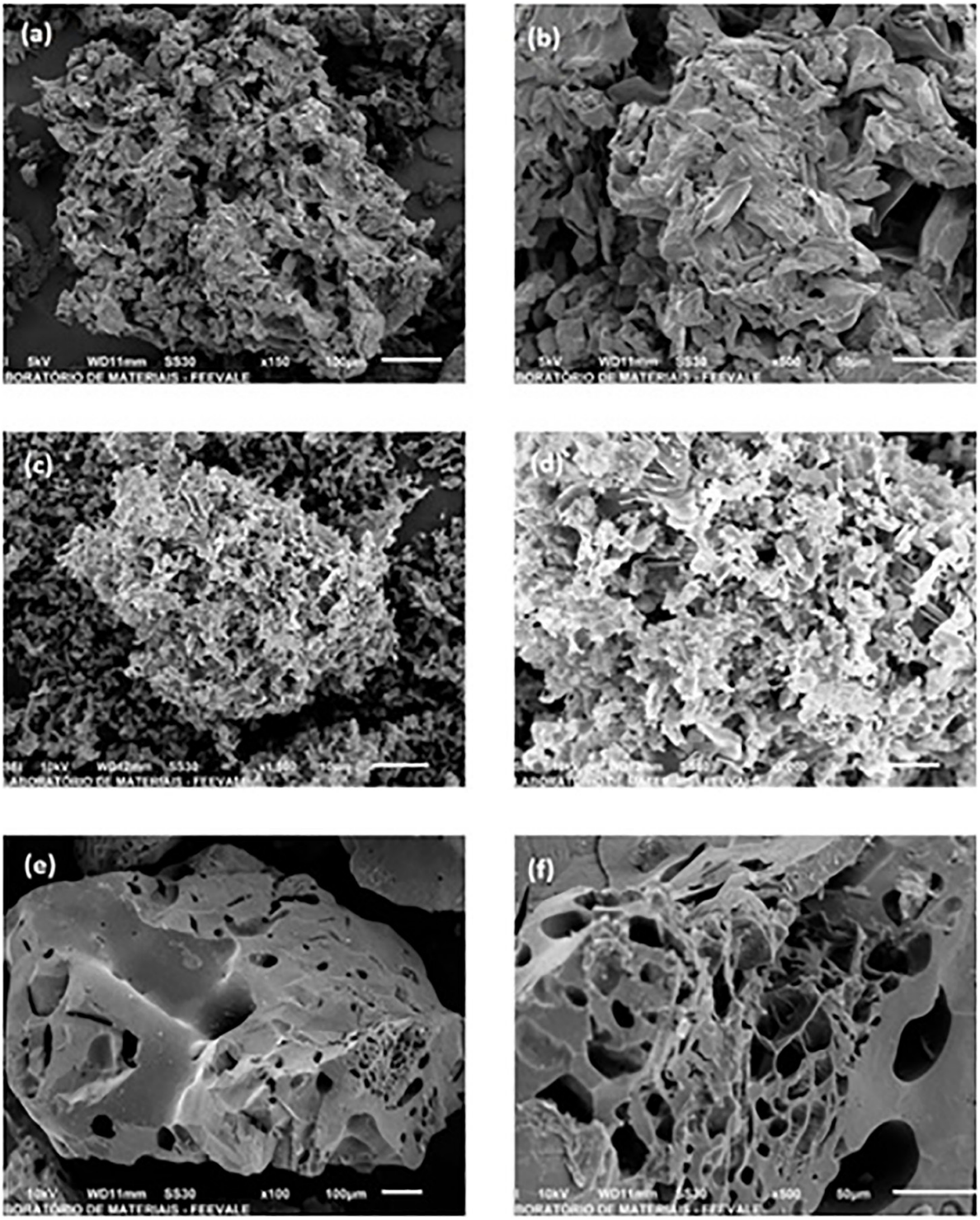

Figure 2: Micrographs of bioadsorbents developed from fresh orange peel, with magnifications (a) 150× and (b) 500×, thermally activated, with magnifications (c) 1500× and (d) 3000×, and chemically activated, with magnifications of (e) 100× and (f) 500×.

The presence of an irregular surface is observed in the fresh sample with shallow cavities. In samples with heat treatment, it was verified that there was a degradation of the material, thus forming a more irregular surface and more exposed pores, although small, which was also evidenced by CARVALHO *et al*. [17] when exposing the orange peel in a similar temperature. In the micrographs of samples with chemical treatment, it is possible to perceive a more ordered and smooth surface, with distributed and deep pores, in line with the results of specific surface area for this bioadsorbent.

Figure 3 presents the micrographs of the bioadsorbents developed from fresh eggshells, thermally and chemically activated, respectively. The bark of this residue did not show great variation when exposed to treatments. A regular and heterogeneous surface can be observed in all samples. In nature and with chemical

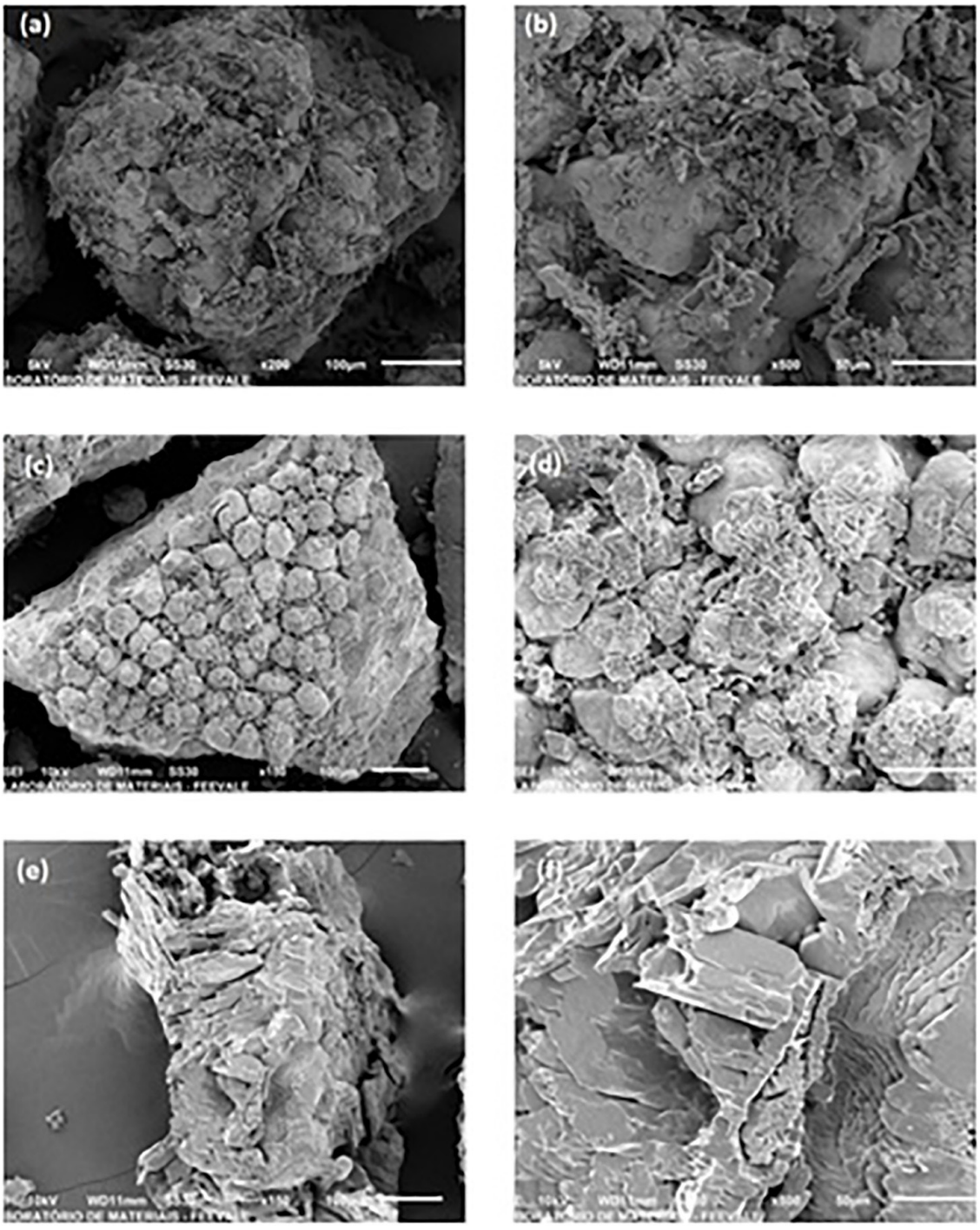

Figure 3: Micrographs of bioadsorbents developed from fresh eggshell, with magnifications (a) 200× and (b) 500×, thermally activated, with magnifications (c) 150× and (d) 500×, and chemically activated, with magnifications of (e) 150× and (f) 500×.

treatment there is no presence of pores, and with heat treatment there is the presence of small regular cavities. CARVALHO *et al*. [17] presented microscopy of eggshells with a structure similar to that found in this work.

3.1.3. Assessment of thermal behavior

The thermal behavior of the sample is obtained through thermogravimetric analysis, which observes the variation in mass in the material in relation to temperature. Figures 4, 5 and 6 shows the TGA/DTG curves of bioadsorbents developed from passion fruit, orange and egg peels.

In thermal analyses, mass loss is observed, which in turn occurs in three stages, with different temperature ranges. In the first stage, between 100 °C and 150 °C, moisture vaporization occurs and extractives are released. In the second, between 200 °C and 390 °C, which is called the active zone of pyrolysis, the most significant loss of mass occurs, in which there is the degradation of cellulose, hemicellulose and part of the lignin. While in the third stage, which occurs from 400 °C onwards, it is called the passive pyrolysis zone and is where the mass loss is lower due to the degradation of lignin, which occurs slowly [7].

These steps can be observed in the thermogravimetric analyzes of the bioadsorbents developed, in natural form, with thermal activation and chemical activation.

Table 3 Describes the three stages, as well as the temperatures and percentage of degradation for each sample of bioadsorbent developed.

According to Figures 4, 5 and 6 as well as Table 3, it can be seen that both the passion fruit peel and orange peel samples had two stages of degradation. The first in the temperature range between 89.74 °C and 191.03 °C with low degradation percentages of up to 14.543%, as the samples were previously dried in an oven and burned in a muffle furnace to avoid moisture interference in the tests carried out. The LIn sample was the only one that presented three distinct stages of mass loss, also observed by CARVALHO *et al*. [17], who used orange peel dried in an oven at 110 °C in his work and obtained a very thermal analysis curve similar. Therefore, it can be seen that the first event was due to the loss of organic components, predominantly the decomposition of hemicellulose. In the second event, the decomposition of hemicellulose and cellulose prevailed and, in the last event, hemicellulose is completely decomposed [17].

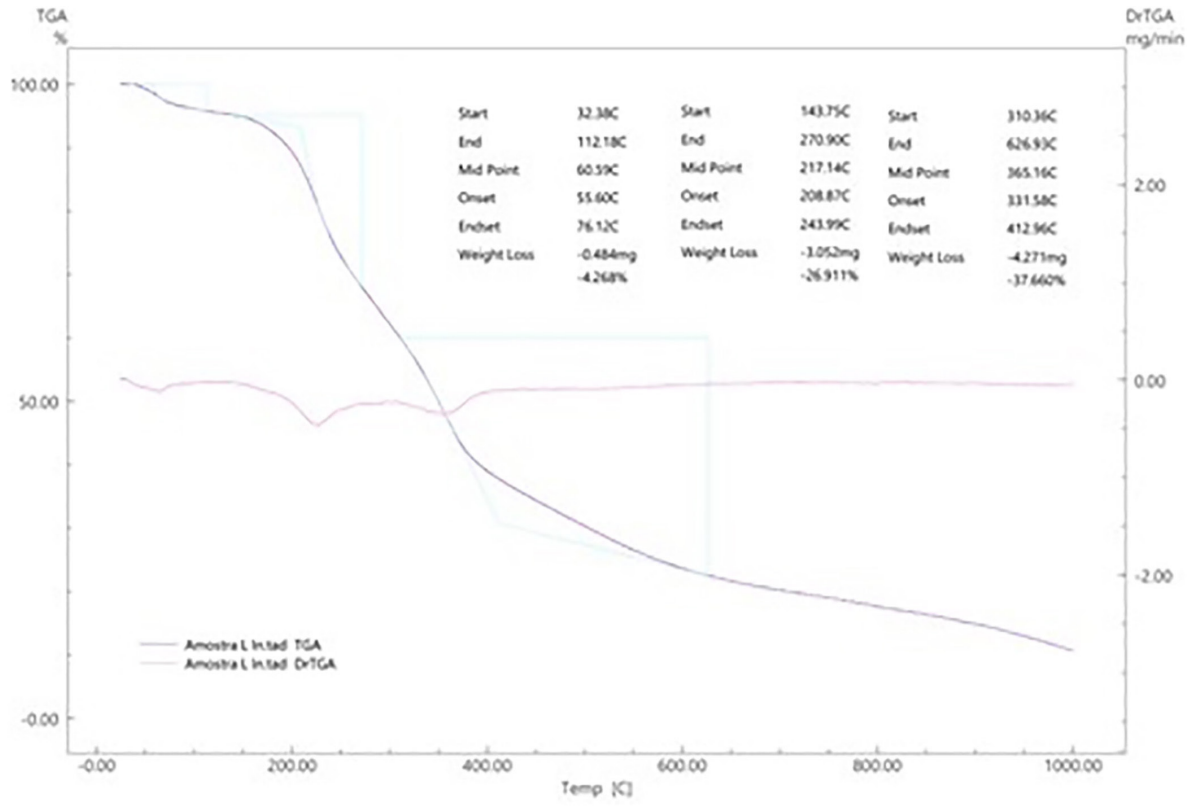

Figure 4: TGA/DTG curves of bioadsorbents developed from passion fruit peel (a) in natura, (b) thermally activated and (c) chemically.

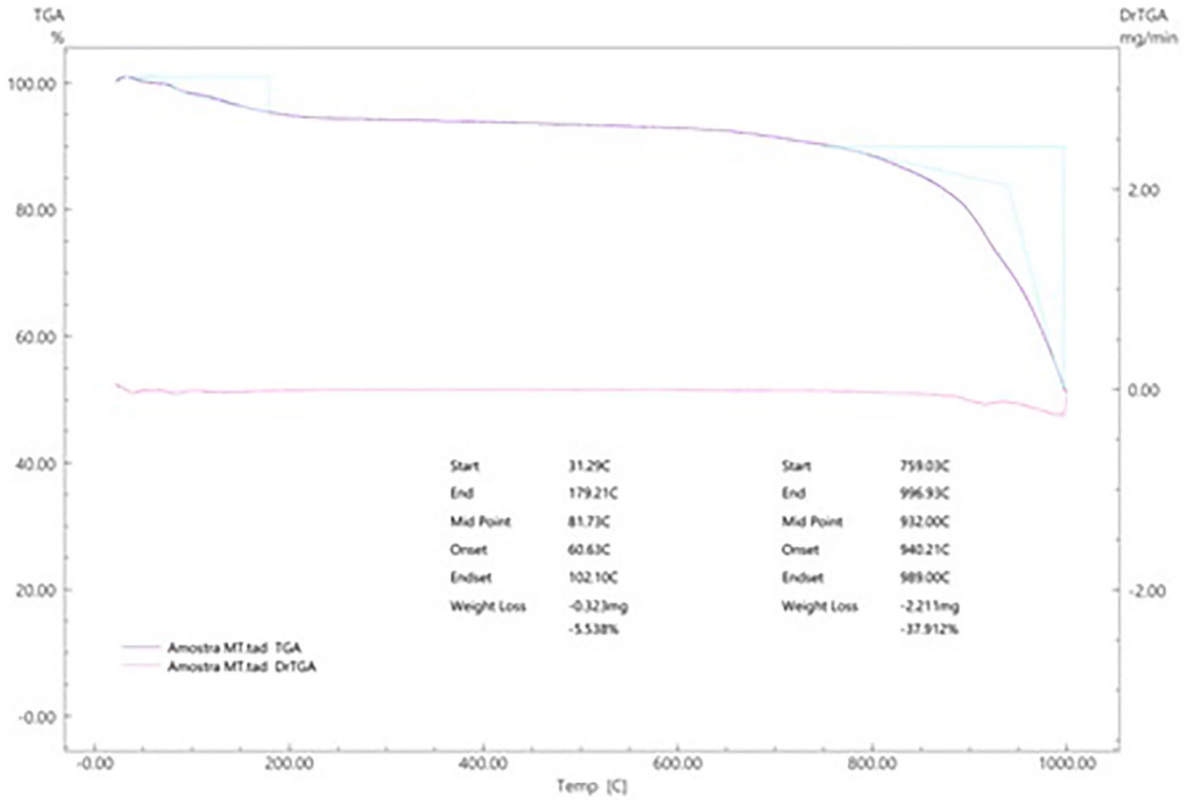

Figure 5: TGA/DTG curves of bioadsorbents developed from orange peel (a) in natura, (b) thermally activated and (c) chemically.

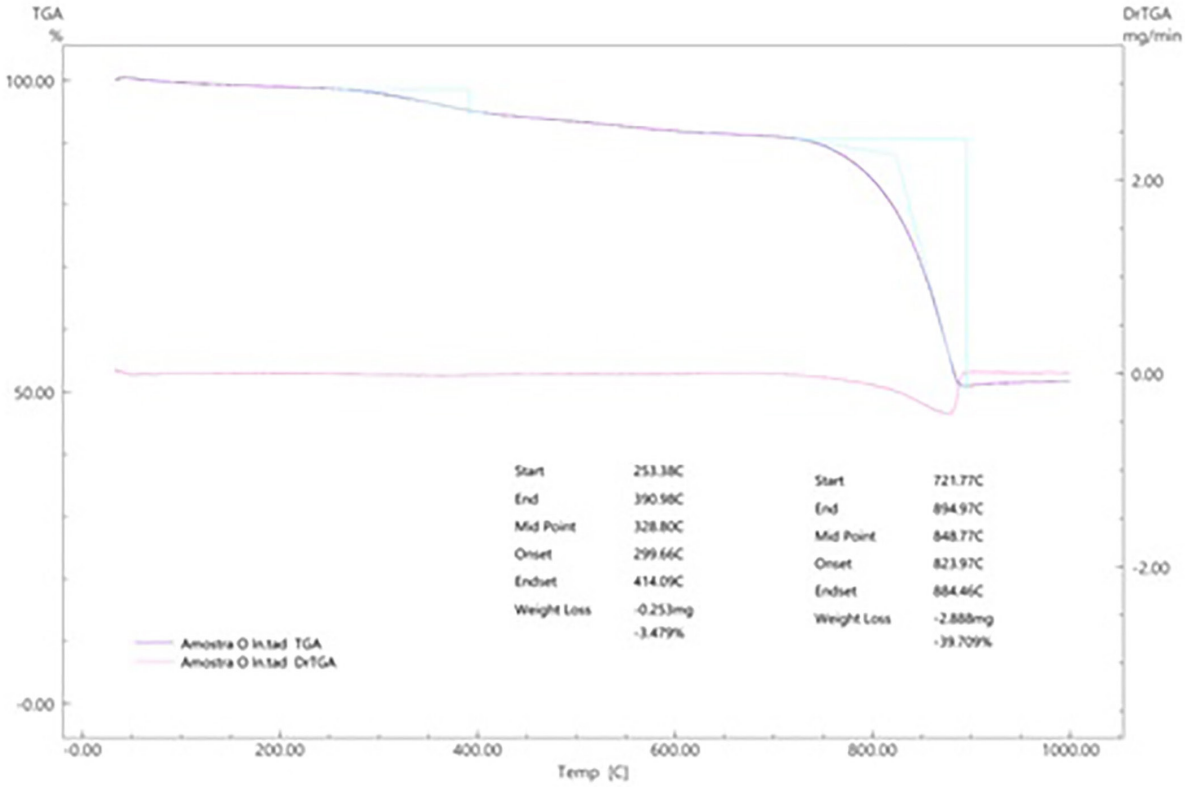

Figure 6: TGA/DTG curves of bioadsorbents developed from eggshell (a) in natura, (b) thermally activated and (c) chemically.

Table 3: Degradation at each stage of the developed bioadsorbents.

BIOADSORBENT	% DEGRADATION STEP 1	TEMPERATURE DEGRADATION STAGE 1 (°C)	% DEGRADATION STEP 2	TEMPERATURE DEGRADATION STAGE 2 (°C)	% DEGRADATION STEP 3	TEMPERATURE DEGRADATION STEP 3 (°C)
Min	2,715	89,74	67,867	520,55	–	–
MT	5,538	179,21	37,912	996,93	–	–
MQ	14,543	165,51	38,129	968,04	–	–
Lin	4,268	112,18	26,911	270,90	37,660	626,93
LT	11,967	191,03	34,069	996,09	–	–
LQ	8,386	137,47	51,349	878,29	–	–
OIn	3,479	39,98	39,709	894,97	–	–
OT	43,033	901,73	–	–	–	–
OQ	15,338	884,41	–	–	–	–

The second stage of degradation occurred at higher temperatures, from 520.55 °C to 996.93 °C, with higher percentages of mass loss. CARVALHO *et al*. [17] highlights that the degradation of pure bio-composite materials of lignin, cellulose and hemicellulose occurs at these temperature profiles. Also, the pyrolysis kinetics of lignin is continuous throughout the thermogravimetric analysis. Therefore, the loss of mass in this second stage is possibly due to the burning of these biocompounds and it is likely that these materials have great potential for transformation into activated carbons.

For eggshell samples, a similar behavior can be noted for the fresh sample, but for samples with both thermal and chemical treatment, the curve was very different. These presented only a single mass loss event. SANTOS *et al*. [6] presented TGA of the eggshell similar to that found in this work, in which he highlighted that up to 700 °C the mass loss varied smoothly and that from 784 °C the thermal decomposition of $CaCO_3$ occurs, forming -from CO_2 and CaO.

3.2. Assessment of bioadsorbent performance

Table 4 presents the results of yield calculations for bioadsorbents developed with heat treatment and chemical treatment. It can be observed that the samples with heat treatment, MT and LT, obtained an excellent yield, above 90% after heat treatment.

The chemically treated samples, MQ and LQ, showed a yield of less than 50%. A similar result was observed by CARVALHO *et al*. [17], who obtained a yield of around 22% for samples of passion fruit seeds with chemical activation of NaOH at a temperature of 500 °C observed that the mass loss at a temperature of 450 °C was 77.09% for orange peel, obtaining a yield of 22.91% SANTOS *et al*. [6].

The lower yield observed in the MQ and LQ samples can be justified by the increase in specific surface area and the presence of pores observed in the micrographs, which is probably due to the reaction with the activator and subsequent carbonization, causing a decrease in mass and ex- position of the pores [12].

According to CARVALHO *et al*. [17], activated carbon is basically composed of carbon and the presence of heteroatoms such as oxygen, hydrogen, nitrogen, among others, which can vary depending on the material. Thus, with the aim of eliminating as much as possible elements other than carbon that may exist in the material, the pyrolysis reaction is carried out. In this way, molecular carbon is maintained, which has a high specific surface area and, consequently, greater adsorption capacity.

The OQ sample resulted in a yield of 103.39%, possibly due to a chemical reaction with phosphoric acid, being observed during the process.

3.3. Assessment of adsorption tests

The adsorption tests were carried out to determine the ability to remove methylene blue dye from different bioadsorbents developed from food waste. Figure 7 shows the dye removal results, in percentage, for an initial concentration of 75.82 mg/L of methylene blue.

The bioadsorbent developed with fresh eggshells showed a dye removal percentage of 68.43%, and showed no improvement with treatments, removing 66.75% with heat treatment and 67.70% with chemical treatment. SANTOS *et al*. [6] obtained the result of removing 23.5% of $P\text{-}PO_4$ using eggshells calcined at 600 °C and at temperatures above 700 °C the removal was at least 77.7%. While, HEYLMANN *et al*. [18]

Table 4: Yield of the developed bioadsorbents.

BIOADSORBENT	PERFORMANCE (%)
MT	92.42%
MQ	23.41%
LT	96.03%
LQ	49.04%
OQ	103.39%

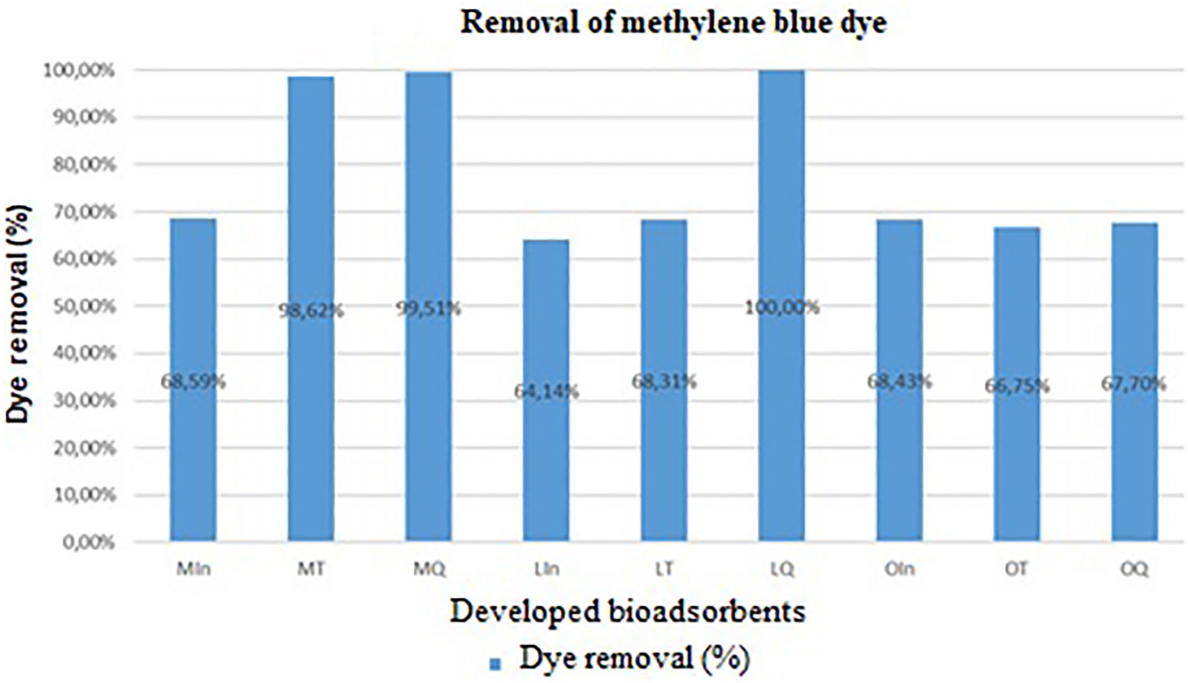

Figure 7: Results of methylene blue dye removal for the different bioadsorbents developed.

resulted in the adsorption process, with a bioadsorbent using eggshell, removing more than 90.51% of the methylene blue dye at initial concentrations of 1.0 to 9.0 mg/ L, concentrations that are lower than those used in this study.

GRALIK and BIAVA [19] observed that the composition of eggshell is basically made up of calcium oxide (CaO), which possibly explains why the treatments did not make a difference, as it would need a higher temperature for this compound to decompose. Furthermore, this behavior was expected for the eggshell, due to the result of the BET analysis, which showed small values of specific surface areas for the bioadsorbents of this residue, considering that the specific surface area is of paramount importance for the process. adsorptive and where the dye is fixed so that it can be removed. Furthermore, the micrographs of this material obtained by SEM showed a surface with few pores, which again justifies the difficulty in dye adsorption.

In fresh samples, a lower percentage of dye removal was observed, 68.59% for passion fruit peel and 64.14% for orange peel, as well as for eggshell samples. This can be justified by the characterization analyzes of these materials, since the in natura bioadsorbents presented smaller specific surface areas and the presence of few porous cavities, verified in the micrographs. A similar result was obtained by DE MARIA and MOREIRA [20] for fresh orange peel, reaching a maximum removal percentage of 55.83% of the methylene blue dye. CASTRO *et al*. [13] observed 84.2% maximum removal using fresh passion fruit peel powder to adsorb methylene blue.

The heat treatment proved to be efficient for passion fruit peel, as it removed 98.62% of the dye. While, for orange peel samples it was not as efficient, reaching a removal of 68.31%. The efficiency of the MT sample

was expected due to the BET results, which showed a high specific surface area, and SEM, showing the presence of more porous cavities, which increases the adsorption power of the material. The LT sample resulted in a low specific surface area and the presence of pores, but these were small and shallow, making the adsorption of the dye molecule difficult. SANTOS *et al*. [6] presented efficient removal results using orange peel treated at 450 °C, reaching 80% dye removal at the initial concentration of 2.5 mg/L, justifying this result, due to the fact that the sample becomes more reactive when pyrolyzed at higher temperatures and decompose the more volatile elements.

The chemical treatment was the one that showed the greatest improvement in the efficiency of passion fruit and orange peel bioadsorbents, which achieved dye removal of 99.51% for passion fruit and 100.00% for orange. For these samples, MQ and LQ, an excellent adsorption result was expected, as they obtained high specific surface areas, and the micrographs showed the large presence of deep pores, which facilitates the adsorption process, increasing the adsorbent capacity of the material. Other studies with these wastes chemically treated with 85% H_3PO_4 showed high removal efficiencies, such as BARROS *et al*. [21], who obtained activated charcoal from chemically treated yellow passion fruit peel, achieving approximately 81.6% phenol removal. MÜLLER [8] observed the removal of 90.8% of the methylene blue dye, at an initial concentration of 100 mg/L, when using charcoal from orange peel impregnated with the same acid. Therefore, the MQ and LQ samples, which presented the best results in the adsorption process for removing the methylene blue dye, were chosen for the evaluation of the adsorption isotherms.

3.4. Assessment of adsorption isotherms

To obtain the adsorption isotherms of the MQ and LQ bioadsorbents, adsorption tests were carried out with different initial concentrations of methylene blue dye, 50, 75, 100 and 125 mg/L, with the results presented in Table 5.

In Table 5 it is possible to observe that with the increase in the initial concentration of the dye (C0), the adsorption capacity (qe) also increases. GOETZ *et al*. [10] explains that increasing concentration increases adsorption efficiency, possibly due to the fact that low concentrations still present a large number of sites available for adsorption to occur. The author also finds that, when increasing the initial concentration of methylene blue, the species were distributed on the surface of the adsorbate, thus forming more chemical bonds on the surface. Figure 8 shows the percentage of methylene blue dye removal for samples MQ and LQ, respectively, varying the initial concentration of the dye.

No significant change in dye removal was observed for the different initial concentrations studied, since practically all samples achieved 100% removal, the lowest being 97.14%. HEYLMANN *et al*. [18] observed similar behavior at concentrations of 50, 75 and 100 mg/L of methylene blue dye in the adsorption process, obtaining a removal percentage of around 98%, using commercial activated carbon. GOETZ *et al*. [10] found similar behavior when evaluating fresh bamboo in the removal of methylene blue dye, which resulted in a percentage of dye removal of around 97% for concentrations of 50, 75 and 100 mg/L.

As the adsorption tests for different initial concentrations of the dye, for both the MQ and LQ bioadsorbents, achieved high removals of methylene blue, mostly 100%, it was not possible to obtain and evaluate the adsorption isotherms.

Table 5: Adsorption tests at different initial dye concentrations on MQ and LQ bioadsorbents.

BIOADSORBENT	INITIAL CONCENTRATION C_0 (mg/L)	CONCENTRATION ON BALANCE C_e (mg/L)	DYE REMOVAL (%)	ADSORPTION CAPACITY q_e (mg/g)
MQ 50	51.30	0.00	100.00%	4.28
MQ 75	75.82	0.37	99.51%	6.30
MQ 100	110.70	0.00	100.00%	9.17
MQ 125	129.10	0.00	100.00%	10.73
LQ 50	51.30	0.00	100.00%	4.24
LQ 75	75.82	0.00	100.00%	6.31
LQ 100	110.70	0.86	99.22%	9.10
LQ 125	129.10	3.69	97.14%	10.44

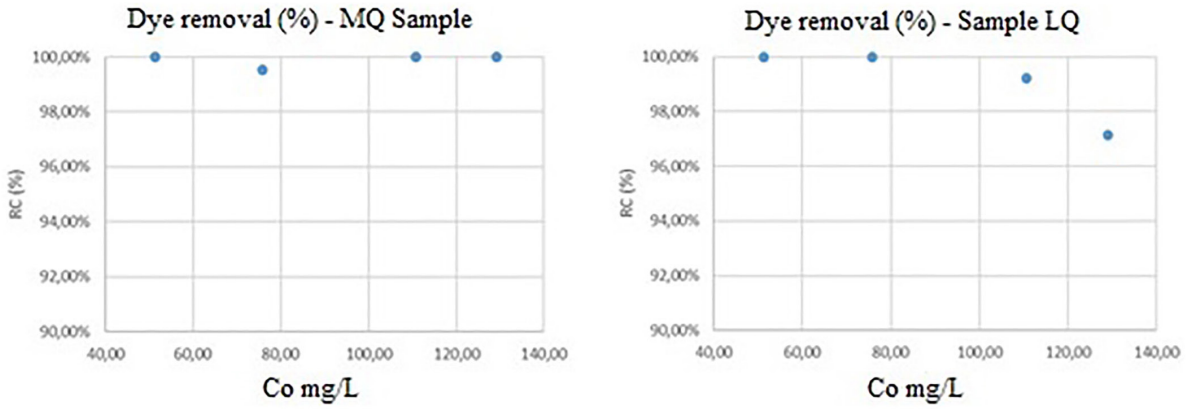

Figure 8: Dye removal versus initial concentration for samples MQ and LQ.

4. CONCLUSIONS

In the present work, several bioadsorbents were developed from food waste, these being passion fruit peel, orange peel and chicken eggshell, in natural, thermally and chemically activated forms. These bioadsorbents were characterized and evaluated in the batch adsorption process of methylene blue dye. The adsorption tests showed that the developed bioadsorbents were efficient in removing the dye, achieving removals greater than 64%. The samples that obtained the best results for dye removal were passion fruit peel, with thermal (MT) and chemical (MQ) treatment, and orange, with chemical treatment (LQ), showing removal efficiencies above 98%, which is mainly due to the high values of specific surface area presented by these bioadsorbents, since the adsorption process is a surface phenomenon. On the other hand, the fresh samples of these residues, MIn and LIn, as well as the heat-treated orange peel sample, LT, presented smaller specific surface areas and consequently lower dye removal efficiencies, reaching around 68%. The bioadsorbents developed from eggshells also showed inferior dye removal results, and showed no improvement in efficiency when thermally and chemically treated, achieving removals of an average of 67.6% of the dye. It was not possible to evaluate the adsorption isotherms for the MQ and LQ bioadsorbents, since they obtained high percentages of dye removal, practically 100% for the different initial concentrations of methylene blue. However, as a suggestion for future work, higher initial dye concentrations can be evaluated, in order to verify a difference in the percentage of removal, obtaining and discussing the adsorption isotherms. Furthermore, higher temperatures can be evaluated for the heat treatment of bioadsorbents obtained from eggshells, with the aim of improving their adsorption capacity. Furthermore, the reuse and stability of food waste as bioadsorbents can be verified. Finally, the application of bioadsorbents developed in real effluents from the textile industry can be evaluated.

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