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Special Edition

Preliminary study on the characterization of *in natura* malt residue from a brewery for potential use as an adsorbent in removing Reactive red 120 from aqueous solution

Estudo preliminar da caracterização do resíduo de malte *in natura* de uma cervejaria para o uso potencial como adsorvente na remoção de vermelho reativo 120 de solução aquosa

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ABSTRACT

Malt residue is the main by-product of the brewing process and representing around 85% of the by-products generated in this segment. Due to its abundance and considering the high development of the beer market in recent years in Brazil and worldwide, there is also great concern regarding environmental issues to its final disposal, making it necessary to develop alternatives that generate products of greater added value and that can reduce environmental impacts. Given the growing demand for alternative adsorbents, especially for agro-industrial residues, this study aimed to carry out a preliminary characterization of malt residue to assess its potential as *in natura* adsorbent, to add value to the residue as well and to contribute to the mitigation of impacts on the environment. The malt residue was dried, ground, and classified, and this material was given the name of fresh malt residue (RMIN). For the characterization of RMIN, pH stability test analysis, zero charge point (pH_{PCZ}), thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM) were performed. After characterization, preliminary adsorption tests were carried out to remove a textile dye, in this case, Reactive red 120. As a result of the characterization analyses, the malt has a relatively stable pH when in aqueous suspension and the value pH_{PCZ} found, was close to neutral, thus demonstrating the potential for removal of acidic substances. The result of the thermogravimetric analysis shows mass losses in temperature ranges characteristic of the presence of lignocellulosic compounds that make up the malt, which is corroborated by the results of the FTIR analysis, since the spectra revealed the presence of functional groups, such as group hydroxyl, carbonyl group, alkanes, and alkenes, related to the presence of cellulose, hemicellulose, and lignin. These functional groups can interact with the groups of the Reactive red dye 120 molecule, helping to remove them from an aqueous solution. Through SEM analysis it was possible to observe morphological changes when comparing the adsorbent particles before and after the adsorption process. The potential as an *in natura* adsorbent was evaluated through preliminary tests of adsorption, followed by filtration, whose system showed 30% removal. However, studies to determine the optimal adsorption conditions, kinetic and isotherm studies, and thermodynamic studies are still necessary to better understand the phenomenon. Studies to determine the useful life of the RMIN, as well as studies in pilot units or continuous systems, are also still needed to enable its use on a larger scale.

Keywords: Malt Residue; Adsorption; *In natura* adsorbent

RESUMO

O resíduo de malte é o principal subproduto do processo cervejeiro, representando cerca de 85% dos subprodutos gerados deste segmento. Devido a sua abundância e considerando o alto desenvolvimento do mercado cervejeiro nos últimos anos no Brasil e no mundo, há também uma grande preocupação no que tange as questões ambientais em relação a sua disposição final, tornando-se necessário o desenvolvimento de alternativas que gerem produtos de maior valor agregado e que possam diminuir os impactos ambientais. Tendo em vista o crescimento pela procura de adsorventes alternativos, em especial aos resíduos agroindustriais, este estudo teve por objetivo realizar de forma preliminar a caracterização do resíduo de malte a fim de avaliar seu potencial como adsorvente *in natura*, de forma agregar valor ao resíduo bem como para contribuir para a mitigação dos impactos ao ambiente. O resíduo de malte foi seco, moído e classificado e a este material foi atribuído o nome de resíduo de malte *in natura* (RMIN). Para a caracterização do RMIN, análises de teste de estabilidade de pH, ponto de carga zero (pH_{PCZ}), análise termogravimétrica (TGA), espectroscopia de infravermelho com transformada de Fourier (FTIR), microscopia eletrônica de varredura (MEV) foram realizados. Após a caracterização, testes de adsorção preliminares foram realizados visando a remoção de um corante têxtil, neste caso, o vermelho reativo 120. Como resultado das análises de caracterização, tem-se que o malte possui pH relativamente estável quando em suspensão aquosa e o valor de pH_{PCZ} encontrado, foi próximo da neutralidade, demonstrando assim potencial para remoção de substâncias ácidas. O resultado da análise termogravimétrica mostra perdas de massa em faixas de temperaturas características da presença de compostos lignocelulósicos que compõe o malte, o que é corroborado pelos resultados da análise de FTIR, uma vez que os espectros revelaram a presença de grupos funcionais, como: grupo hidroxila, grupo carbonila, alcanos e alcenos, relacionados a presença de celulose, hemicelulose e lignina. Esses grupos funcionais são capazes de interagir com os grupos da molécula do corante vermelho reativo 120, auxiliando na sua remoção de solução aquosa. Por meio da análise de MEV foi possível constatar alterações morfológicas ao comparar-se as partículas adsorventes antes e após o processo de adsorção. O potencial como adsorvente foi avaliado por meio dos testes preliminares de adsorção, seguido de filtração, cujo sistema apresentou 30% de remoção. Entretanto, estudos para determinação das condições ótimas de adsorção, estudos cinéticos e de isotermas e estudos termodinâmicos ainda se fazem necessários para compreender melhor o fenômeno. Estudos para determinação da vida útil do RMIN, bem como estudos em unidades piloto ou sistemas contínuos também ainda se fazem necessários para viabilizar um uso em maior escala.

Palavras-chave: Resíduo do malte; Adsorção; Adsorvente *in natura*

1 INTRODUCTION

The global brewing industry has shown exponential growth in the last 10 years, producing around 191.10 million kiloliters of beer in 2018 (KIRIN HOLDINGS, 2019). With the increase in beer production, proportionally, there is also an increase in the production of residues, among which malt stands out, which constitutes 85% of the total by-products generated in the process. Considering that Brazil is the third (3rd) largest producer in the world, it has a high availability of malt residue for technological exploration.

The beer production process consists of the stages of grinding, mashing, boiling, cooling, fermentation, maturation, and filtration. After the filtration stage, the beer is bottled and pasteurized, ready for consumption. The malt residue originates from the wort filtration stage, in which the wort, the liquid part, goes to the subsequent stages of the process, with the solid part (used malt grains) being retained with the aid of sieves that use the husks themselves of the malt present in the wort as filtering elements (LOPES *et al*., 2015; MELLO; VERGÍLIO; MALI, 2013; MILDEMBERG, 2019).

The chemical composition of the malt residue may vary depending on the type of barley used, malting, and mashing conditions to which this residue is subjected in the brewing process, and can also be changed by the time of harvest (MELLO; VERGÍLIO; MALI, 2013). Such waste is usually not reinserted in the process, making it a potentially viable source for the exploration of new resources, such as for the production of animal feed, due to its high nutritional value and its low acquisition cost, in the production of handcrafted bread, among other destinations (LOPES *et al*., 2015). Additionally, several studies have proposed alternatives to convert this residue to add value, such as in biogas production (PANJIČKO *et al*., 2017), detoxification of liquid waste (MAITI *et al*., 2017), in obtaining biofuels in biorefineries (OUTEIRIÑO *et al*., 2019), in biodegradable foam trays (MELLO; MALI, 2014), as well as studies involving its use as an adsorbent in dyes (FONTANA;

CECHINEL, 2016; FRANCISKI *et al*., 2018; MILDEMBERG, 2019; SAFARIK; HORSKA; SAFARIKOVA, 2011).

The industry, in general, produce effluents that return to water bodies, but they still have contaminants, which often are found in low concentrations, however, these are capable of causing harm to the environment, ecosystem, health, and quality of life of living beings. Faced with this problem, it creates the need to find alternatives for the removal of such contaminants, enabling the minimization of the impacts (LIMA *et al*., 2017; MILDEMBERG, 2019). In this sense, adsorption appears as an interesting alternative, as it is an easy-to-operate treatment technique, providing, in addition to lower waste generation, low cost for implementation.

Thus, considering that adsorption consists of a separation technique that allows the use of adsorbents of natural origin, from biomass (biosorbent), the abundance of malt residue, which is biodegradable, renewable residue with a low acquisition cost (MILDEMBERG, 2019; PIETROBELLI, 2007), becomes a promising alternative for the removal of dyes regarding the cost/efficiency (DÁVILA, 2016; MILDEMBERG, 2019). Based on the above, the present study aims to present the characterization of malt residue, as well as preliminary tests to assess their potential use as an adsorbent in nature to the removal of a textile dye, Reactive red 120 aqueous solution by the technique of adsorption.

2 MATERIAL AND METHODS

The following are materials and methods used to implement this study.

2.1 Obtaining and preparing the adsorbent

The malt residue was supplied by Cervejaria Takaha Cervejas Especiais, located in the city of Feliz, Rio Grande do Sul state in Brazil. Soon after collection, the residue was dried in a vacuum oven with nitrogen circulation (Marconi ma-030), at 105 °C, for 48 hours. After the drying process, the malt residue was triturated in a domestic blender, Walita HL 3253 model with a power of 60 Hz. The granulometric standardization was carried out using Tyler series sieves (TPL–Tudo para Laboratórios). Particles with dimensions in the range of 150 μm to 600 μm (equivalent to mesh openings of 20 and 100 mesh, respectively) were selected, according to the study by Mildemberg (2019). This material was given the name of *in natura* malt residue, known by the acronym RMIN (according to Brazilian Portuguese language).

2.2 Characterization of malt residue

The pH stability test consisted of monitoring the pH of the malt residue in an aqueous suspension over time. For this, 5.00 g of *in natura* malt residue were added to a beaker with 500 mL of distilled water under constant agitation in an Even model 78HW^{-1} magnetic stirrer, for 8 h and 30 min, interrupted when the pH value reached stability. The pH was checked at pH meter 210- Lab 1000 mPa at 30 min intervals.

For determining the zero point of charge (pH_{PCZ}), weighed 0.10 g of RMIN and then was added a weighed 100 ml of distilled water (H_2O) pH adjusted properly. For pH adjustment solutions of 0.1 mol L^{-1} HCl or NaOH were used so that the following pH values were obtained: 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, and 12. Then, the samples remained for 24 h in a Shaker model LUCA-222 incubator, under 100 rpm agitation, at room temperature of approximately 27 ºC (ROBLES E REGALBUTO, 2004). At the end of the experiment, the pH of each sample was measured again, and the zero charge point (pH_{PCZ}) was obtained by the mean of the values of the inflection point of the curve obtained by plotting the initial pH by the end (ROBLES E REGALBUTO, 2004).

For the thermogravimetric analysis (TGA) of *in natura* malt residue, TGA Q500 equipment - TA instruments was used, with an analysis performed under an atmosphere of nitrogen (N_2) and a heating ramp of 10 °C min^{-1} to 800 °C according to a methodology adapted from Bachmann *et al*. (2020).

The organic functional groups present in the *in natura* residue and after the adsorption test were identified through Fourier transform infrared spectroscopy (FTIR). For this purpose, the FTIR analysis was performed in a Nicolet 360 Avatar-Thermo Fisher Scientific equipment, conducted in transmission mode, between 400 and 4000 cm^{-1}.

Finally, Scanning Electron Microscopy (SEM) was used to determine the morphological structure of the malt residue before and after the adsorption process. The analysis was carried out in a TM3030Plus - Hitachi equipment, with a secondary electron detector, accelerating voltage at 15 kV, with a magnification of 800 and 2000 times.

2.3 Adsorption test

The adsorption tests were carried out using the Reactive red 120 textile dye (Sigma-Aldrich) as adsorbate, and the adsorbate solutions were prepared from a stock solution with a concentration of 1000 mg L^{-1}. For the reading of the samples, an ultraviolet-visible spectrophotometer (UV-Vis) - CRG series-Hitachi was used, in which, first, the wavelength (range 400 to 900 nm) in which the dye absorbed the greatest amount of light in the presence of solution at a concentration of 20 mg L^{-1}. For the calibration curve dye solutions were prepared with concentrations of 12.5; 25; 50; 75; 100 mg L^{-1}.

The adsorption tests were performed with an adsorbate solution at 20 mg L^{-1}, a dosage of 1.00 g of RMIN according to studies promoted by Portinho (2016), and named after the adsorption test as RMAD. The samples were subjected to mechanical agitation in an Ethik Technology bench shaker, at 100 rpm, with a fixed time of one (1) hour. Afterward, simple filtration was performed, with the aid of quantitative filter paper - CAT No. 99-291-125, of lignocellulosic composition, to read the aliquot in UV-Vis, with a maximum wavelength of 535 nm as previously performed by the scan. Thus, the adsorption system consisted of the adsorption test followed by filtration.

Additionally, it is noteworthy that the pH of the solution and its corresponding electrical conductivity was verified in a DM 31-Digimed device before and after adsorption.

The determination of removal efficiency was performed using equation (1):

$$R,\% = \left(\frac{C_i - C_f}{C_i}\right) * 100 \tag{1}$$

Where: R is the removal percentage, Ci and Cf are the initial and final concentrations of the aqueous solution of Reactive red 120, in mg L^{-1}.

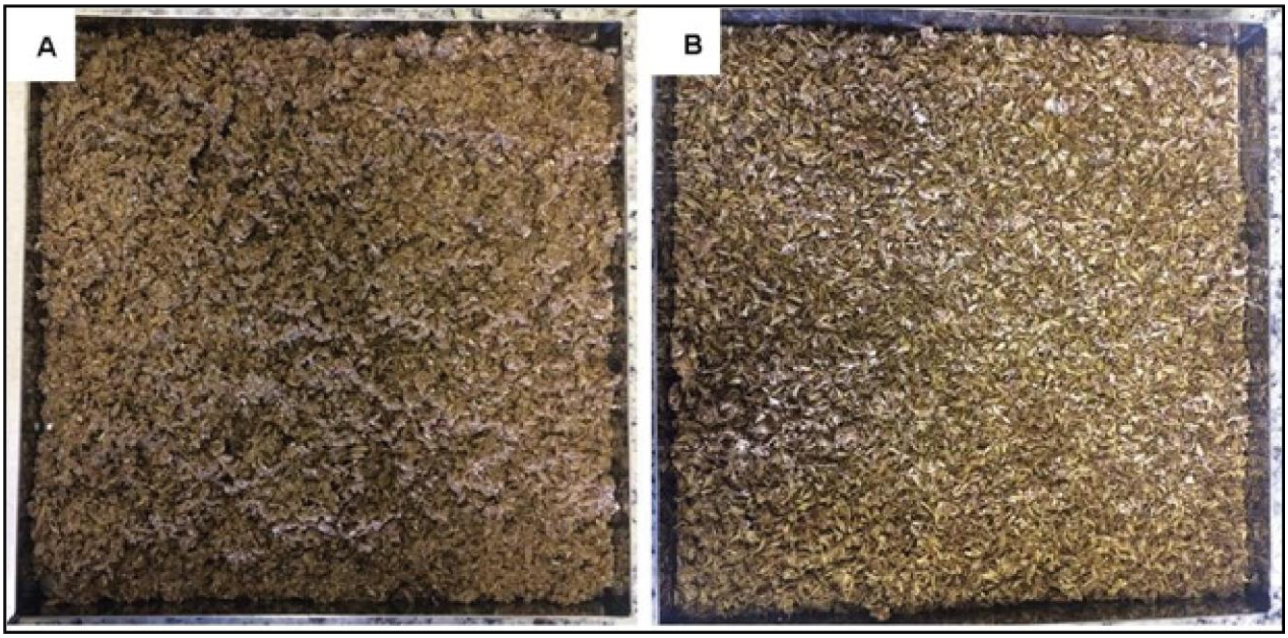
3 RESULTS AND DISCUSSION

Through Figure 1, it is possible to show that the malt residue before drying has a pasty appearance (Figure 1A), while after being subjected to drying as shown in Figure 1B, its particles became looser between them, causing a change in size and shape of its grain. This change is attributed to the reduction in the moisture content inside the grain, which when presented in a pasty form has a high moisture content, which varies from 77-81%, due to the processing step that gives rise to it (MUSSATTO, DRAGONE E ROBERTO; 2006).

After drying, the pH stability test was carried out to verify whether the malt residue would cause any change in the pH of the water as shown in Figure 2A, while the potential of the malt residue for the adsorption process on cationic and anionic species, was determined through its pH_{PCZ} and calculated through the inflection points of the curve, which was obtained from the initial and final pH values of the solution, generating the initial pH *versus* final pH graph as shown in Figure 2B.

From the stability test (Figure 2), it was possible to evidence that the pH did not show a sharp fluctuation during the analysis period. Whereas the aqueous solution in contact with the *in natura* malt residue remained stable and pH near neutrality, with an average of 6.41 ± 0.10.

Figure 1 – Is shown malt residue before and after drying

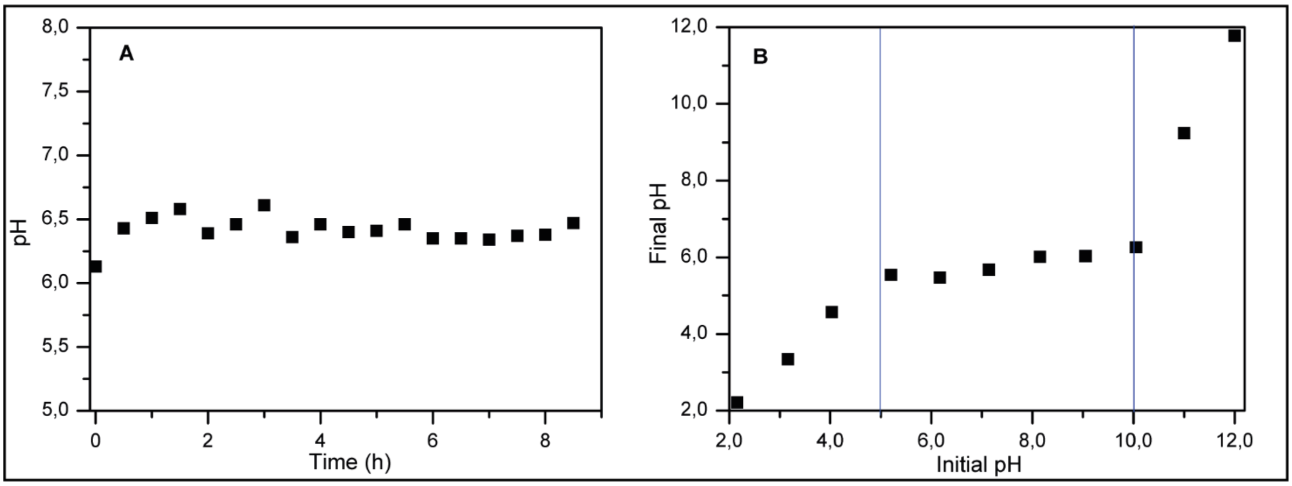


Source: Authors, 2021

Concerning pH_{PZC}, observing the behavior of the final pH as a function of the initial pH of the aqueous phase, between the values of pH 5.00 to 10.00 (Figure 2B), the net surface charge is close to neutrality, being pH_{PZC} the average value obtained for the malt residue was 6.00 when considering the initial and final pH. This value is consistent with that found by Mazetto *et al* (2017), which was obtained in the result value of 6.65. The small difference between the result obtained experimentally and the value found in the literature may be related to the equipment used for the measurement and also to the characteristics of the malt residue, which can vary depending on the type of malt, harvest time batch, and malting conditions (MUSSATTO; DRAGONE; ROBERTO, 2006). It is important to highlight that at values below the pH_{PCZ} obtained, the surface of the adsorbent is positively charged, providing a tendency for greater adsorption of anions, to balance the positive charges. Thus, it is easier to adsorb anionic species, such as

Reactive red 120. Therefore, when the pH of the solution is above the pH_{PZC} value, the tendency will be for cations to be more easily adsorbed, facilitating the removal of cationic species (DEOLIN *et al*., 2013; MAZETTO *et al*., 2017; OLIVEIRA, 2016).

Figure 2 – A) Graph of pH measurements over the eight (8) hours. B) Graph of the behavior of the final pH as a function of the initial pH of the aqueous phase in pH_{PCZ} analysis



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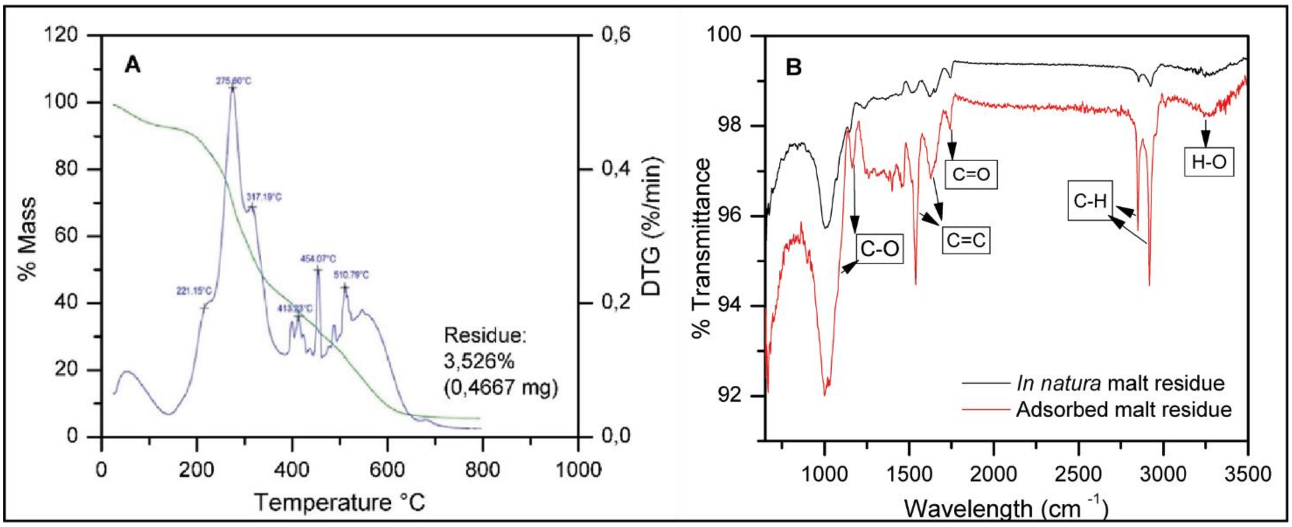
In Figure 3, the Thermogram of the RMIN (Figure 3A) and the FTIR spectrum of the RMIN and RMAD (Figure 3B) are shown.

As can be seen in Figure 3A, the malt residue showed three regions of mass loss, which are related to the substances that constitute the malt residue. The first region is related to the removal of fixed moisture present in the sample, represented at up to approximately 200 °C, with a mass loss of approximately 15%. From the heating temperature of 220 °C to 400 °C, the second region is presented, demonstrating the degradation of cellulose and hemicellulose, with peaks at 275.6 °C and 317.19 °C, represented by a mass loss of 43.19%, where the similar result was found by Mildemberg, (2019), having in his study 55% loss for the malt residue. Finally, the third region comprises temperatures of 400 °C to 650 °C, wherein the lignin degradation occurs, with a weight loss of 28.83%. Subsequently, with further increase in temperature to 800 °C, it appears that weight loss is stabilized, making complete volatilization of the lignocellulosic material present in the malt residue, thus providing a residual ash content of 3.526%.

Figure 3 – A) RMIN thermogram. B) *In natura* malt residue spectrum (RMIN) and after adsorption (RMAD)



Source: Authors, 2021

To identify the functional groups on the surface of the malt residue, the FTIR analysis was performed as shown in Figure 3B, and it is possible to observe the main active sites present in the adsorbent, in which they are responsible for the surface charge due to its dissociation, in addition to being responsible for the capture of species found in aqueous media to be adsorbed (OLIVEIRA, 2016).

Thus, according to the spectra, there is a slight interference with the absorption band in the region between 3000 and 3500 cm^{-1}, with a peak at 3246.44 cm^{-1} to RMIN and 3247.69 cm^{-1} for the residue of adsorbed malt (RMAD). This wavelength represents the vibrations of the stretching of the -OH bond, hydroxyl group and can be attributed to cellulose, lignin or hemicellulose groups present in the malt residue (PAVIA; LAMPMAN; KRIZ, 2009; FERRAZ *et al*., 2015; FONTANA *et al*., 2016). According to studies by Stjepanović *et al*. (2019), these peaks can be attributed to -OH elongation vibrations due to the inter and intramolecular hydrogen bonding of polymer fibers such as cellulose and lignin. The hydroxyl group may be responsible for the interactions between the constituent molecule of the adsorbate, through the formation of hydrogen bonds (SOTELO *et al*., 2012).

The bands between 2750 and 3000 cm^{-1} peak present in the sample RMIN 2925.59 cm^{-1} and 2854.95 cm^{-1} to RMAD. This region corresponds to alkanes, stretching vibrations of C-H aliphatic chains (PAVIA; LAMPMAN; KRIZ, 2009). According to the studies of Ferraz *et al*. (2015), Fontana *et al*. (2016) e Stjepanović *et al*., (2019), peaks between 2960 cm^{-1} and 2850 cm^{-1} demonstrate the presence of (CH_2 and CH_3), primary carbon and secondary carbon, peaks that may belong to cellulose, lignin or hemicellulose.

It was also possible to observe three peaks with a similar functional group, C=O, between the 1500 and 2000 cm^{-1} bands. The peak at 1739.33 cm^{-1} to RMIN and 1739.56 cm^{-1} for the RMAD characteristic region of an aldehyde, identifies the stretch vibration of the carbonyl group, which is identified peaks between 1740 and 1720 cm^{-1} (PAVIA; LAMPMAN; KRIZ, 2009). Santos *et al*. (2015) identified a similar peak and attributed it to the acetyl and uronic ester groups (sugar-acid produced during the brewing process), as belonging to hemicellulose or the ester linkage of the carboxylic group present in lignin and/or in hemicellulose.

The peak of 1621.02 cm^{-1} for RMIN and 1627.63 cm^{-1} for RMAD refer to alkene C=C, identified between the bands of 1600 to 1680 cm^{-1} (PAVIA; LAMPMAN; KRIZ, 2009), peak similar to the one found in the study by Stjepanović *et al*., (2019), which addresses that these bands are associated with cyclic aromatic groups. The band of 1537 cm^{-1} for RMIN and 1539.02 cm^{-1} for RMAD is characteristic of an alkene identified as aromatic between 1475 cm^{-1} and 1600 cm^{-1} (PAVIA; LAMPMAN; KRIZ, 2009), attributed to aromatic rings found in lignin (FERRAZ *et al*., 2015; FONTANA *et al*., 2016).

The peaks observed at 1150.61 cm^{-1} for RMIN and 1166.01 cm^{-1} RMAD can be attributed to the stretching of the C–O bond of carboxylic, alcohol, ether, ester, and anhydrous groups (PAVIA; LAMPMAN; KRIZ, 2009). Fontana *et al*. (2016) found similar peaks in their study, referring to this band as belonging to the carboxylic, aliphatic ether, or tertiary alcohol groups, which are evidenced between the regions of 1070 cm^{-1} and 1150 cm^{-1}.

Thus, with the FTIR analysis, we identified the major functional groups present on the surface of the *in natura* adsorbent, which are mainly related to the presence of cellulose, hemicellulose, and lignin, as seen in the works of Ferraz *et al*. (2015) e Fontana *et al*. (2016). It is noted that the bands of RMAD, have a higher peak intensity compared to RMIN, which may be related to the amount of material used for analysis. The shifts highlighted when compared to the bands and RMIN RMAD peaks can be associated with a probable binding process adsorbate with the surface of the adsorbent, indicating the occurrence of adsorption.

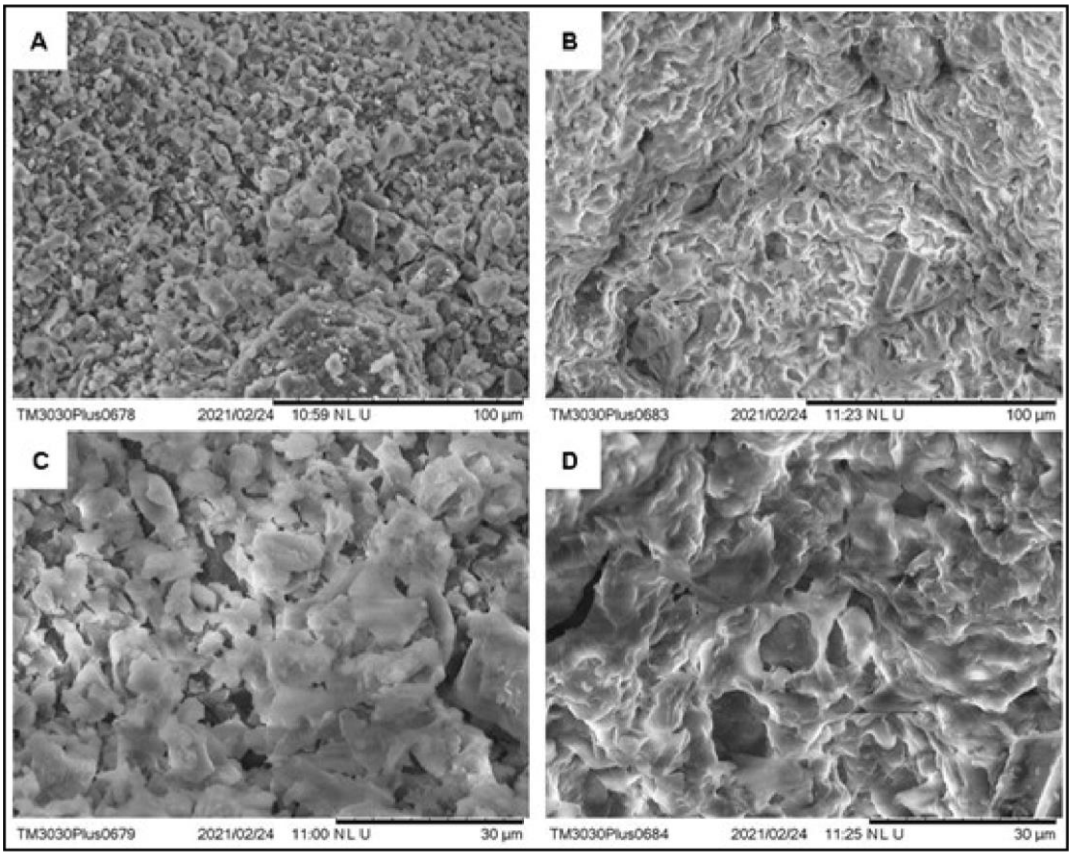
To evaluate the morphology of malt residue before and after the adsorption test, the SEM analysis was performed (Figure 4) as shown below.

Through Figure 4, it is verified that the adsorption process of Reactive red dye 120 on the surface of the adsorbent caused a difference in the morphological structure of the material when comparing the materials before the adsorption process (RMIN) and after the adsorption process (RMAD). Thus, it appears that RMIN can be a viable alternative for dye removal.

Figure 5 shows the scan graph obtained for the dye (Figure 5A), as well as the calibration curve used to read the samples (Figure 5B).

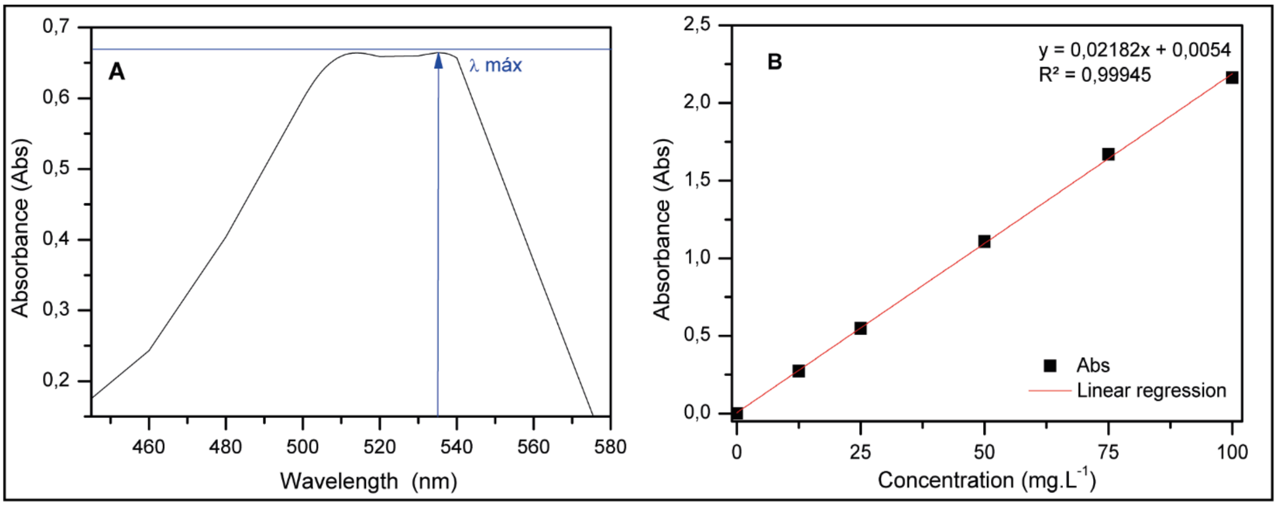
Acordina to Figure 5A, it can be seen that the wavelength at which the maximum absorption of the UV/Vis radiation to the Reactive red dye 120 occurs at 535 nm (indicated by arrow), which is equivalent to that found in literature according to studies promoted by Dávila (2016) and also according to the one provided by the Sigma-Aldrich reagent manufacturer (2019).

Figure 4 – A) RMIN and B) RMAD are images with the magnification of 800x with a secondary electron beam and C) RMIN and D) RMAD are images with the magnification of 2000x with a secondary electron beam



Source: Authors, 2021

Figure 5 – A) Scanning graph of the Reactive red dye solution 120. B) Calibration curve graph of the Reactive red dye solution 120



Source: Authors, 2021

Afterward, the calibration curve was constructed with the λ_{max} obtained for the dye (535 nm). With the analysis data, a graph of adsorbate concentration versus absorbance was constructed, forming the dye calibration curve (Figure 5B). The graphical representation of the equation of the line and the correlation coefficient were used for determining the initial and final concentrations of the solutions used in the adsorption process, and from these values, one could calculate the percentage stain removal. The results obtained after adsorption and simple filtration are shown in Table 1.

Table 1 – Reactive red solution removal experiments

Experiment	**Initial concentration (mg L^{-1})**	**pH**		**Conductivity (µS cm^{-1})**		**Removal %**
		Initial	**Final**	**Initial**	**Final**	
1	22,64	6,85	6,08	25,7	123,9	29,90
2	21,92	6,51	5,89	24,7	147,2	30,34

(Experimental condition: 120, 20 mg L^{-1}, in 1.00 g of RMIN, for one (1) h stirring at 100 rpm)
Source: Authors, 2021

In the initial and final pH values, there was little variation for this parameter as previously evidenced by the stability test, in which the malt pH was stable for eight hours. Malt is a lignocellulosic material in which the pH of the solution can influence the balance and dissociation of its functional groups. The 6.00 value obtained for pH_{PCZ} may be related to the low removal efficiency of the adsorption/filtration system (~30%), since the average pH of the aqueous solution is 6.57, slightly above pH_{PCZ}, considered neutral pH. The adsorbent has predominantly negative charges on its surface when the pH of the solution is above its pH_{PCZ}, exhibiting the behavior of attracting cations and repelling dyes of anionic origin due to the negative charges that come into contact with water and repel ions (VASQUES *et al*., 2011). The pH_{PCZ} value obtained in this study indicates that the adsorbent may be able to remove ions in an acidic pH solution or cationic dyes because with a pH solution below pH_{PCZ}, the functional groups will not be dissociated and probably protonated, in other words, will be in acidic conditions and the material will present an anion attracting behavior (OLIVEIRA, 2016).

Based on the pH_{PCZ} data, the pH of the medium would not favor the adsorption of Reactive red 120 in malt residue and simple filtration, but the removal of Reactive red 120 dye of 30.12% with a standard deviation of 0.31 was obtained, which can be associated with physical and/or chemical interactions between the surface of the adsorbent and the molecule of the adsorbate. To confirm this fact, the FTIR analysis of the adsorbent can confirm this, since there are hydroxyl groups on its surface that can interact through hydrogen bonds with the dye molecule, in which due to intermolecular forces, they may keep the dye on the surface of the adsorbent (SOTELO *et al*., 2012).

The electrical conductivity of the solution was a factor that increased after the adsorption test. Initially, the solution showed an average electrical conductivity of 25.2 $\mu S\ cm^{-1}$, and after the adsorption process, 135.5 $\mu S\ cm^{-1}$. This reveals that there is an increase in the concentration of ions in the solution and this suggests that it may be related to the presence of Chlorine ions (Cl^-), Sodium (Na^+), and oxygenated sulfur ions (SO_3^{2-} or SO_4^{2-}) from sulfonic groups ($-SO_3H$) present in the Reactive red dye molecule 120 (ATKINS; DE PAULA, 2014).

Finally, to evaluate the use of malt residue as an adsorbent for dye removal, Table 2 presents a compilation of the removal efficiency of different studies that used this residue as an adsorbent.

Table 2 – Studies with malt residue as adsorbent for textile dyes

Adsorbate	**Adsorbent**	**Operating conditions**	**Removal %**	**Reference**
Reactive red 120	*In natura* malt residue	Agitation =100 rpm; Adsorbent=10 g L $^{-1}$; C_i = 20 mg L $^{-1}$; t = 1 h.	30,12 ± 0,31	Present study
Aniline blue Acridine orange Methyl green Congo red Crystal violet	Iron-modified malt residue	Adsorbent= 0,3 g L $^{-1}$; C_i = 70 mg L^{-1}; t = 4 h.	71 26 1 2 75	Safarik; Horska; Safarikova (2011)

Continued...

Table 2 – Conclusion

Adsorbate	**Adsorbent**	**Operating conditions**	**Removal %**	**Reference**
Solimax orange	*In natura* malt residue	Agitation=150 rpm; pH = 1,5; C_i = 50 mg L^{-1}; t = 2 h.	97,7	Fontana *et al*. (2016)
Methylene blue	Malt Residue Activated Charcoal	Adsorbent= 2 g L^{-1}; C_i = 100 mg L^{-1}; t = 1 h.	99	Mildenberg, (2019)
Methylene blue	*In natura* malt residue	Agitation=150 rpm; Adsorbent=1,0 g L^{-1}; pH = 6,5; C_i = 50 mg L^{-1}; t = 2 h.	10	Franciski *et al*. (2018)
	Pyrolyzed Malt Residue		40	
	Malt residue after activation by pyrolysis and CO_2		70	

Source: Authors, 2021

Based on the results presented in Table 2, the removal efficiencies are quite variable and can be changed depending on the adsorbate, established operating conditions, such as the amount of adsorbent, adsorbate, and pH of the medium. The removal found in the present study, of 30.12%, was satisfactory because in the operational conditions used, there was no use of additional physical or chemical treatments on the adsorbent. It is important to note that the malt residue was dried after receiving it from the brewery and there was no pH adjustment of the fluid phase, as can be seen in the operating conditions in table 4 carried out by (FONTANA *et al*., 2016), without prior washing and, even so, it was possible to observe a removal efficiency superior to the studies by Franciski *et al*. (2018) and Safarik, Horska and Safarikova (2011).

4 FINAL COMMENTS

The malt residue as the main by-product of the brewing industry process makes it abundant for the development of alternative value-added applications, such as helping to treat textile effluents using the adsorption technique. These effluents contain contaminating substances in their composition capable of causing damage to the environment and malt residue can be an alternative to minimize possible impacts, due to its surface properties.

Characterization of *in natura* malt residue showed pH stability, being close to neutrality, additionally, the pH_{PCZ} value obtained (6.0) may imply the capacity of the malt residue to adsorb both cationic and anionic species. Through the FTIR analysis, it was observed that after adsorption, there were displacements of the bands, increasing the intensity, changes can be attributed to the functional groups of the malt residue. In addition, with this analysis, the functional groups present on the residue surface were identified, namely: the hydroxyl group, carbonyl group, alkanes demonstrating the presence of primary carbon and secondary carbon, which are attributed to cellulose, lignin and hemicellulose, present in the malt residue, and finally, alkene associated with aromatic cyclic groups found in lignin. TGA analysis also confirms the presence of compounds such as cellulose, hemicellulose, and lignin according to the mass losses corresponding to these compounds as a function of temperature. The images of the adsorbent surface obtained by SEM enabled the surface characterization of the adsorbent material, indicating a modified structure after the dye adsorption process when compared to the adsorbent before the biosorbent process.

Finally, the adsorption tests carried out for the RMIN through the present study, showed potential use for the removal of Reactive red dye 120 in aqueous solution, presenting a removal efficiency of 30.12% ± 0.31. Thus, *in natura* malt residue has the potential to contribute to the reduction of Reactive red 120 concentration. Which, due to the pH_{PCZ} found for malt, could favor removal at acidic pH. Finally, from the results obtained in this study and the challenges encountered, it can be stated that the RMIN and filtration system has potential in the treatment of effluents containing Reactive red 120, when not subjected to changes in its conditions.

It is suggested for future work, carrying out tests to determine pH, residence time, a concentration of solid adsorbent and adsorbate, to carry out kinetic tests for the determination of adsorption equilibrium isotherms, as well as thermodynamic studies, enabling a greater understanding of the phenomenon of adsorption. In addition, evaluation of the useful life of the adsorbent, as well as studies aiming at the application of the RMIN in continuous processes and pilot units is also necessary, to enable the use of malt residue on an industrial scale and also assign the disposal RMAD's environmentally appropriate end.

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