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Peach palm and cassava wastes as biosorbents of tartrazine yellow dye and their application in industrial effluent

Resíduos do palmito pupunha e da mandioca como biossorvente do corante amarelo tartrazina e sua aplicação em efluente industrial

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In this study, the wastes from cassava (CAW) and peach palm (PPW) agro-industries were investigated as potential low-cost biosorbents for removing the tartrazine yellow dye (TAR). The by-products were prepared by washing and drying steps and characterized into physicochemical parameters and microstructure. The effects of contact time, pH, dosage and dye concentration were analyzed for the biosorbents in comparison to commercial activated carbon (AC). The biosorbents were applied to the treatment of an effluent from a juice industry containing TAR. Cellulose was the main component of the biosorbents (31.47–51.20 g 100 g^{-1}), which was correlated to the functional groups identified by ATR-FTIR spectra and the materials had a porous surface. The zero point of charge was 3.75 for PPW and 4.60 for CAW. The pH parameter had a significant effect on the adsorption process, with the maximum values of adsorption being reached at pH 2.0, with removal of 94.7% for PPW, 74.4% for CAW and 97.7% for AC, at the dosage of 7.5 g L^{-1} at 25.0 ºC. The adsorption of TAR was fast in the early stages, and at 120 min the three adsorbents reached the equilibrium. Isotherms of adsorption showed that Langmuir's and Freundlich's models fitted the best to the CAW and PPW experimental data, respectively. The wastes evaluated in this work can be an interesting alternative to TAR adsorption in the industrial effluent without being subjected to chemical treatments.
Keywords: Adsorption, tartrazine dye, wastewater.

Neste estudo, os resíduos das agroindústrias de mandioca (CAW) e pupunha (PPW) foram investigados como potenciais biossorventes de baixo custo para a remoção do corante amarelo tartrazina (TAR). Os subprodutos foram preparados pelas etapas de lavagem e secagem e caracterizados quanto aos parâmetros físico-químicos e a microestrutura. Os efeitos do tempo de contato, pH, dosagem e concentração de corante foram analisados para os biossorventes em comparação ao carvão ativado comercial (AC). Os biossorventes foram aplicados no tratamento de um efluente de uma indústria de sucos contendo TAR. A celulose foi o principal componente dos biossorventes (31,47–51,20 g 100g^{-1}), o que foi correlacionado aos grupos funcionais identificados pelo ATR-FTIR, e os materiais apresentaram superfície porosa. O ponto de carga zero foi 3,75 para PPW e 4,60 para CAW. Verificou-se que o parâmetro pH teve efeito significativo no processo de adsorção, sendo os valores máximos de adsorção atingidos em pH 2,0, com remoção de 94,7% para PPW, 74,4% para CAW e 97,7% para AC, na dosagem de 7,5 g L^{-1} a 25,0 ºC. A adsorção da TAR foi rápida nos estágios iniciais e, aos 120 min, os três adsorventes atingiram o equilíbrio. As isotermas de adsorção mostraram que os modelos de Langmuir e Freundlich se ajustaram melhor aos dados experimentais CAW e PPW, respectivamente. Os resíduos avaliados neste trabalho podem ser uma alternativa interessante para adsorção de TAR no efluente industrial sem serem submetidos a tratamentos químicos.
Palavras-chave: Adsorção, corante tartrazina, efluente.

1. INTRODUCTION

The current population growth, associated with the increased consumption of food products, results in an intensification of the agro-industrial productivity. Producers have been invested in this segment to meet this need, but the industrial yield is not total and a lot of wastes and effluents are generated [1]. In current literature agro-industrial by-products are proposed as sustainable biosorbents alternative to activated carbon, one of the most applied adsorbents in the world [2-8]. However, the high production cost of activated carbon or chemical treatments, restrict the waste application as biosorbents and, in some cases, they are even unfeasible [9].

Brazil is the world's third biggest producer of cassava (*Manihot esculenta*), with an annual production of over 17 million tons [10]. During the industrial processing of the roots, high amounts of fibrous residues, known as cassava bagasse waste (CAW), are generated. It is estimated that for each ton of cassava used in the starch production, about 928 kg of wet bagasse is generated [11]. Brazil is also considered one of the largest producers and consumers of heart-of-palm (locally known as palmito) in the world, holding for 85% of the world demand. The peach palm or pupunha palm (*Bactris gasipaes*) is one of the most cultivated palm trees for obtaining heart-of-palm in the country [12], which is an important alternative to the sustainability of the production chain, because in addition to collaborating with the reduction of predatory exploration of other species, it has a rapid growth and formation of tillers [13]. However, this sector has an estimated waste generation of 80% from raw material. This peach palm waste (PPW) is characterized as sheaths and stems, which are not used in the processing of the heart-of-palm and present great potential for reuse [14].

One important application of biosorbents is the removal of synthetic dyes characterized by chemical stability, resistance to chemical, physical and biological agents [15] and intense colors even at low concentrations [16]. The presence of these colorants in wastewater directly affects natural aquatic systems, since it decreases the entry of light in the receiving bodies, restricting photosynthesis [10]. Among the synthetic dyes commonly used in food industries, Tartrazine Yellow (TAR; Figure 1) is a colorant belonging to the functional azo-compound group [17].

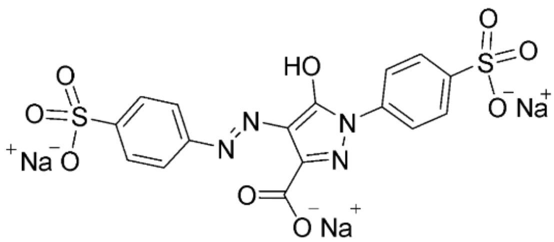

Figure 1: Chemical structure of TAR.

TAR is mainly used for having high stability to oxidation process and heat, color uniformity and relatively low cost [18]. Therefore, the removal of food dyes from liquid effluents, such as TAR, is essential to preserve the quality of water bodies. However, the use of conventional methods of treatment, such as filtration, sedimentation, among others, are not usually efficient in removing this class of pollutants [19].

This work aims to characterize cassava bagasse and peach palm waste and to study their potential in TAR adsorption in comparison with active carbon (AC). After defining the better conditions of adsorption of synthetic dye, the wastes were used to the treatment of juice processing effluent containing TAR. So, it is expected to obtain efficient and low cost biosorbents, to promote sustainable alternatives to agro-industrial wastes and to the treatment of liquid effluents.

2. MATERIAL AND METHODS

2.1 Preparation of biosorbents

Agro-industries of the state of Paraná/Brazil donated the PPW, obtained from the sheaths discarded in the canning process of heart-of-palm, and the CAW, produced after the starch extraction. Due to the high moisture of the wastes, > 90% weight/weight (w/w), they were submitted to drying in an oven with forced air circulation (Marconi MA 035) at 90 ºC for 24 h, until reach a final moisture of 10% ± 1 w/w, and they were grounded in knife mill (Solab). The dried materials were washed thoroughly with distilled water to remove impurities that could difficult the adsorption process. Then, the materials were dried again at 90 ºC for 24 h, grounded in a mini bench processor, sieved and standardized to a particle size of 0.15 mm.

2.2 Characterization of biosorbents

The protein, ash, and moisture content of the samples were determined based on the AOAC methods 920.87, 923.03, and 925.09, respectively [20]. Furthermore, the contents of neutral detergent fibers and acid detergent fibers were determined [21] to obtain the contents of cellulose, hemicellulose and lignin [22]. CAW still has starch as one of its major components, which was determined by the enzymatic method AOAC 996 [20], followed by reducing sugars determination [22]. The physicochemical analyzes were performed in triplicate.

The spectra of infrared attenuated total reflection with Fourier transform (ATR-FTIR) were obtained to identify the functional groups in the PPW and CAW biosorbents. For this purpose, the Agilent Cary 630 ATR-FTIR spectrophotometer was used, with a horizontal attenuated total reflectance accessory using a platinum diamond crystal. The spectra were obtained in the range of 650-4000 cm^{-1}, with a resolution of 8 cm^{-1} and 32 scans.

The evaluation of the biosorbents morphological characteristics was carried out with scanning electron microscopy (SEM), using a QUANTA 250 FEI microscope at a voltage of 12.50 kV. The samples were placed in a double-sided tape attached to an aluminum support and metallized with gold and subsequently analyzed at 500x, 1000x and 3000x in magnification.

The pH at the potential of zero point of charge (pH_{zpc}) of the biosorbents was determined using acid (HCl) and basic solutions (NaOH) in the region of pH 2.0 to 12.0, by diluting stock solutions of 0.1 mol L^{-1} HCl or 0.1 mol L^{-1} NaOH. Then, 0.15 g of sample and 10 mL of each solution was mixed and stirred in a shaker (Marconi, 830A) at 120 rpm for 24 h at 25 °C. From the ΔpH (pH_{final} - $pH_{initial}$) versus $pH_{initial}$ graph, the pH_{zpc} values were obtained by the $pH_{initial}$ corresponding to ΔpH equal to zero [23].

2.3 Adsorption of tartrazine dye

A stock solution of 1000 mg L^{-1} of TAR dye was prepared and the different concentrations used were prepared from this solution by dilutions. Based on a previous study [24] the adsorption capacity was evaluated using 20 mL of TAR solutions in Erlenmeyer flasks of 250 mL, at 25.0 ºC and shaker agitation at 120 rpm. After adsorption, the samples were centrifuged (Metroderm) for 60 sec at 3000 rpm and the supernatants were analyzed in a spectrophotometer (Femto, 700 Plus) with monitoring at wavelengths of 428 nm (analytical) and 800 nm (baseline). The percentage values of adsorption (% Ads) were estimated with Eq.1, where the reduction in absorbance at 428 nm reflects the dye removal.

$$Ads\ \%\ (428\ nm) = \left(\frac{Abs_{initial} - Abs_{final}}{Abs_{initial}}\right) x100\% \qquad \text{Eq. 1}$$

In which $Abs_{initial}$ refers to the absorbance at t=0 and Abs_{final}, for t =2h.

Commercial activated carbon (AC, Synth) was also studied as a model of adsorbent compound (standard) in the same conditions of the other biosorbents. The AC was used without additional treatment and presented a particle size of 8-16 mesh (1-2 mm). All the adsorption experiments were carried out in triplicate. The adsorption experimenttal process is outlined in the Figure 2.

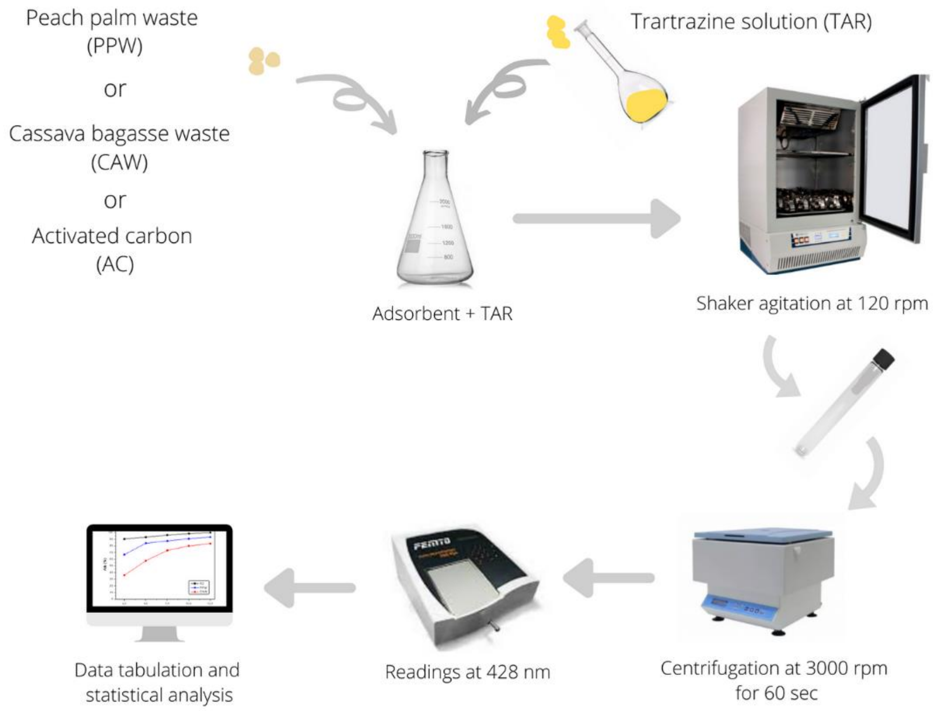

Figure 2: Scheme of the experimental sequence for analysis of adsorption.

2.3.1 Preliminary conditions of adsorption process

Kinetic studies were carried out with 20 mL of a TAR solution of 11.0 mg L^{-1} (2.1 x10^{-5} mol L^{-1}) and 150 mg of adsorbent, resulting in adsorbent dosage of 7.5 g L^{-1}. The study of the kinetic effect was aimed to analyze the equilibrium time of adsorption, which was monitored for 180 min, with a fixed pH of 2.0 at 25 °C.

The pH study was carried out to determine the medium (acid or basic) in which the adsorption is more intense, so the pH values varied from 1.0 to 9.0 were evaluated, for 120 min at 25 ºC (C_0: 11 mg L^{-1}, dosage: 7.5 g L^{-1}). The initial pH of the solutions was adjusted with hydrochloric acid (0.10 M HCl) and sodium hydroxide (0.10 M NaOH).

Then, 20 mL of dye solution (11.0 mg L^{-1}) was used to know the lowest adsorbent dosage that reaches the maximum TAR adsorption and the pH was fixed at 2.0. The adsorbent mass from 0.05 g to 0.25 g, with 0.05 g increments per experiment, was used for 120 min at 25.0 °C.

The highest dye concentration to better adsorption efficiency was determined in experiments with fixed values of pH (2.0) and adsorbent dosage (7.5 g L^{-1}), varying the TAR concentration from 2.5 to 25.0 mg L^{-1}, in increments of 2.5 mg L^{-1} per experiment, for 120 min at 25.0 °C.

2.4 Isotherms of adsorption

The experiments of isotherm adsorption were carried out in three pH values 1.0, 2.0, and 3.0, obtained by standardized solutions of HCl. It was evaluated eight dye concentrations of TAR from 2.5 to 25.0 mg L^{-1}, in increments of 2.5 mg L^{-1} per experiment), dosage of 7.5 g L^{-1} of adsorbent (AC, CAW or PPW), at 25.0 °C and 120 min, in an incubator shaker. The percentage values of adsorption (% Ads) were determinated as described in Eq. 1.

The mathematical models of Langmuir (Eq. 2-3), Freundlich (Eq. 4) and Temkin (Eq. 5), expressed in their linearized forms, were applied to data in order to define the best model for each residue [22, 24-26].

Eq. 2 shows Langmuir model, where q_{max} is the maximum adsorption capacity (mg g^{-1}), C_e is equilibrium concentration the and K_L is the Lagmuir affinity constant (L mg^{-1}). In the Langmuir isotherm the separation fator (R_L) can also be calculated (Eq. 3), as adimensionless constant, which can indicate the adsorption nature: irreversible (R_L=0), linear (R_L=1), favorabele (0<R_L<1) and unfavorable (R_L>1).

$$\frac{1}{q_e} = \frac{1}{q_{max}} + \frac{1}{K_L q_{max} C_e} \quad \text{Eq. 2}$$

$$R_L = \frac{1}{1+K_L C_0} \quad \text{Eq. 3}$$

In the Freundlich model (Eq. 4), K_F is the adsorption capacity constant the Freundlich (mg g^{-1}) and $1/n$ indicates the existence of affinity between the adsorbate and adsorvente (favorable adsorption: $1/n$ <1).

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad \text{Eq. 4}$$

According to Temkin model (Eq. 5), expressed in the linearized forms, K_T is the Temkin equilibrium constant and b is the constant related to the heat of sorption.

$$q_e = B \ln K_T + B \ln C_e \quad \text{Eq. 5}$$

2.5 Application for industrial effluent treatment

Effluent adsorption studies were carried out to evaluate the potential application of PPW and CAW as biosorbents. The effluent from a batch of orange juice, containing TAR dye in the composition, was donated by an industry of the Northwest region of the state of Paraná, Brazil, located near (~80 km) to the industries that donated PPW and CAW.

The adsorption tests on the industrial effluent were performed using 0.15 g of each biosorbent and 20 mL of effluent at pH 2.0 in Erlenmeyer flasks of 250 mL, at 120 rpm and 25.0 °C in the shaker. The experiments were performed in triplicate. Since the natural pH of the effluent was 3.5, it was necessary to acidify the samples with 0.10 mol L^{-1} HCl solution, to reach the pH 2.0, according to the previous tests carried out in this work. In this condition, a first adsorption cycle of 105 min was performed for PPW and CAW, considering the equilibrium time. Afterwards, the solid material was separated and a second adsorption cycle was carried out, with the addition of new biosorbents, for each effluent treated by the first cycle, under the same previous conditions.

The percentage of adsorption reduction (% Ads) of the treated effluent in each cycle was determined by comparing the initial and final absorbance values at 428 nm as described by Eq. 1.

After the cycles, the color parameters were determined in the effluent, based on the CIELAB color system [27, 28], using a CR-400 Chroma Meter colorimeter (Konica Minolta). The coordinate b*, with positive values, indicates the yellow color intensity. Luminosity (L*) expresses the amount of light reflected by a color, that is, the brightness of a certain object, with values ranging between 0 (black) and 100 (white).

3. RESULTS AND DISCUSSION

3.1 Characterization of biosorbents

3.1.1 Chemical Composition

The composition of by-products used in this work (Table 1) showed that biosorbents had low moisture and ashes contents, which were slightly higher in PPW when compared with CAW.

Table 1: Chemical composition (g $100g^{-1}$) of the agroindustrial biosorbents PPW and CAW.

Parameter	PPW	CAW
Moisture	9.31±0.20	8.33± 0.17
Ashes	3.50±0.08	1.80±0.05
Celullose	51.20±0.80	31.47±0.55
Hemicellulose	17.03±0.79	0.53±0.01
Lignin	7.17±0.40	0.40 ± 0.03
Starch	ND	29.40±0.85
Protein	4.37±0.29	2.37±0.01

ND - not detectable.

Cellulose was the main component of the biosorbents and its content was higher in PPW than CAW. Lower values of cellulose were reported in other studies, ranging between 32.6 and 34.2 g 100 g^{-1} for peach palm by-product [12, 14] and between 10.0 and 22.7 g $100g^{-1}$ for cassava bagasse [2, 29]. The other fibrous components – hemicellulose and lignin – were found in higher percentages in PPW when compared to CAW, and these values were lower than those presented in previous studies [12, 29]. Starch is an important component of CAW, but the value found in this work was lower than those observed in other works (40.5 to 77.0 g 100 g^{-1}) [3, 11, 29]. There was no experimental measurement of PPW starch content due to its low content. The lower contents of hemicellulose, lignin and starch than those found by the studies cited above may be related to the solubilization of these compounds, in the washing step of biosorbents preparation, leading to a concentration of cellulose. The results obtained in this study indicated that the CAW had 55.9 ± 0.9 g 100 g^{-1} of starch before washing, which shows the loss of carbohydrates during the process of material preparation. Furthermore, variation of chemical composition is common among lignocellulosic materials and it can be attributed to differences in species, plant age and cultivation conditions, such as soil, geographical location and climate [30]. In the case of cassava bagasse, such variation can also be attributed to differences in the process of starch extraction between industrial units [29].

PPW had higher protein content than CAW. The basic components present in agricultural residues such as cellulose, hemicellulose, lignin, proteins and starch can influence the adsorption process due to the presence of functional groups [31], such as hydroxyl, phenols and methoxy, which can physically adsorb dye molecules with hydrogen bonding and/or Van der Waals interactions [32].

3.1.2 Infrared Spectroscopy

The functional groups present on the surface of the PPW and CAW were identified by the ATR-FTIR (Figure 3). The spectra show that biosorbents had similar behavior regarding peaks, and the results obtained can be attributed mainly to cellulose, as the main components of the wastes [33]. The broadband centered around 3325 cm^{-1} and 3332 cm^{-1} is attributed to OH link stretches [34, 35], elongation of the hydroxyl group, alcohols, and phenols or carboxylic acid [36], belonging to the structure of cellulose, hemicellulose [37], lignin [12], and starch [34]. Moreover, the presence of moisture may have contributed to the intensity of the band in this region [33].

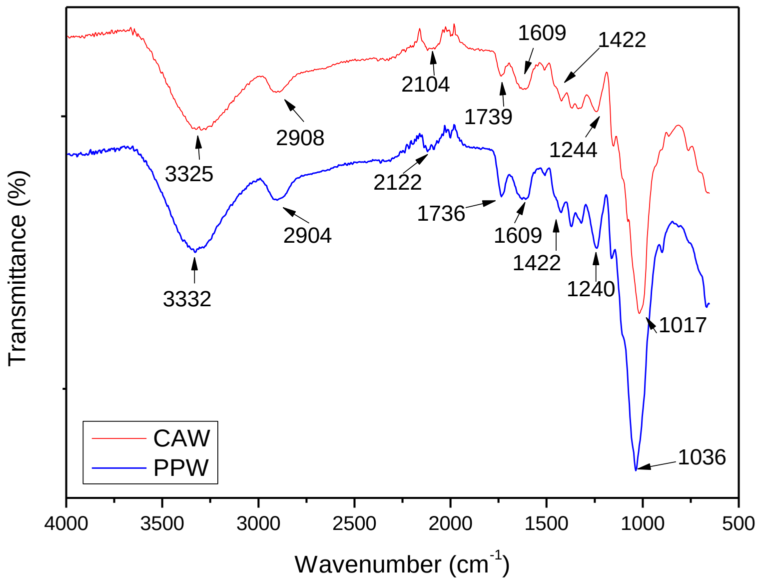

Figure 3: ATR-FTIR spectra for peach palm waste (PPW) and cassava waste (CAW).

The adsorption bands at 2904 cm^{-1} and 2908 cm^{-1} can be attributed to the C-H stretch vibration of the methyl and methylene groups [38, 39]. The vibrations seen at 1736 cm^{-1} and 1739 cm^{-1} are attributed to the C=O extension, stretching in aldehydes, ketones groups, and esters [32, 40]. Vibrations in 1609 cm^{-1} can be attributed to the carbonyl group, present in lignin and protein [33]. The bands in the region of 1422 cm^{-1} indicate torsional vibrations of O-H present in cellulose, hemicellulose and lignin structures [29]. Whereas peaks at 1244 cm^{-1} can be associated to the extended C-O vibrations of alcohol, carboxylates and phenol [41]. Finally, it was observed an elongation of C-O, C-C, and C-C-O at the 1017 cm^{-1} and 1031 cm^{-1} peaks, which can be attributed to the asymmetric C-O-C elongation of cellulose, hemicellulose and lignin [42]. The CAW spectrum at 1017 cm^{-1} can also be attributed to the amylose C-O and C-C bonds to amylopectin, constituents of starch [43].

Considering the set of bands presented in the ATR-FTIR spectra, it is possible to observe the presence of functional groups common to cellulose, hemicellulose, lignin, starch, components identified in the biosorbents (Table 1). Thus, it seems that the biosorbents investigated in this study are composed of several functional groups, which can contribute to the adsorption process.

3.1.3 Scanning Electron Microscopy

The scanning electron microscopies of the biosorbents CAW (Figure 1S) and PPW (Figure 2S) show that the materials have an irregular, heterogeneous surface with the presence of fibers, which are more characteristic in PPW.

In the micrographs of Fig. 1S it is possible to notice the presence of starch granules in the CAW, which have rounded shapes as previously reported [41]. Furthermore, it was found that the morphology of PPW (Fig. 2S) and CAW biosorbents is fragmented, rough and porous. These available spaces contribute to the adsorption process, since they provide a high internal surface area [44].

3.1.4 Zero point of charge (pH_{zpc})

Figure 4 shows the results of pH_{zpc} analyzes of the PPW and CAW biosorbents. The pH_{zpc} values correspond to the point at which the final pH curve, as a function of the initial pH, cuts the x axis [44].

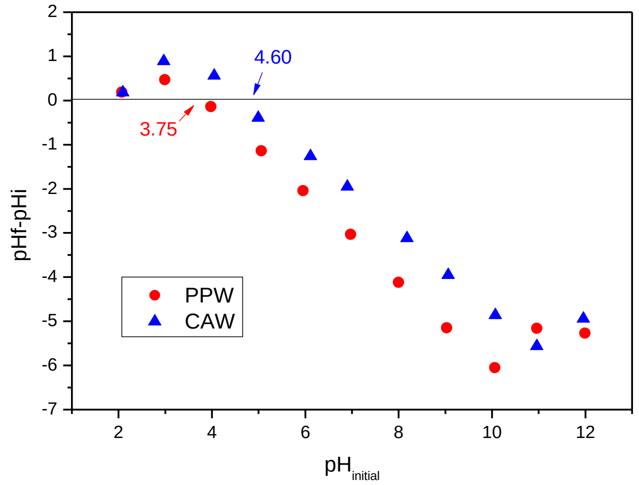

Figure 4: pH_{zpc} of PPW and CAW biosorbents.

It was observed that the pH_{zpc} of the PPW biosorbent was 3.75, whereas CAW was 4.60. These values indicate the pH necessary for the residues present zero electrically charged surfaces [44]. Therefore, the pH_{zpc} values provide significant information for the analysis of electrostatic interactions between substrates and biosorbents [22]. This is because, when the pH of the solution is higher than pH_{zpc}, the surface of the material is negatively charged. On the other hand, at pH values lower than pH_{zpc}, there is a favor in anion adsorption, since the surface is positively charged [45]. Tartrazine is an anionic dye, that is, negatively charged. Therefore, its adsorption is favored at pH values below pH_{zpc} [44].

3.2 Adsorption studies

3.2.1 Time of adsorption evaluation

The determination of the time necessary for adsorption process stabilizes is essential to ensure the dye uptake reaches a saturation point (equilibrium) [46]. Therefore, Figure 5 presents the results obtained in the analysis of the effect of contact time in the removal of TAR for the CAW, PPW, and AC adsorbents.

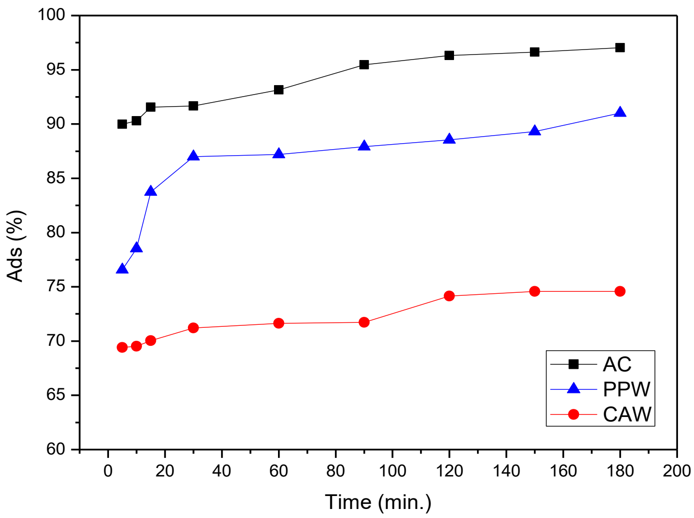

Figure 5: Effect of time removal of TAR dye for PPW, CAW and AC adsorbents. Experimental conditions: pH = 2.0, [TAR] = 11.0 mg L^{-1}, temperature = 25.0 ºC, dosage= 7.5 g L^{-1}, stirring at 120 rpm.

Figure 5 shows that TAR adsorption was fast in the initial stages, and after five minutes the percentage of removal were 90.0% ± 0.4, 76.2% ± 1.0, and 69.6% ± 0.4 for AC, PPW, and CAW, respectively. This high adsorption, which was achieved in a short period of time, indicates a high affinity between dye molecules and the surfaces of the adsorbents. Studies carried out with TAR also demonstrated rapid stabilization in the initial stages of adsorption [45, 47, 48]. For the AC (used as a model), the removal percentage has a slightly increase with time until reaching equilibrium at 90 min, with about 96.0% ± 0.1 adsorption. Notably, PPW presented a gradual increase in adsorption, reaching equilibrium in 30 min, with about 87.0% ± 0.9. On the other hand, CAW presented less variation in the percentage of adsorption, reaching equilibrium at 120 min, with approximately 74.0% ± 0.8 of adsorption. Considering the small variation in adsorption shown in Fig. 4, 120 min was standardized as the time sufficient to monitor the adsorption process under other experimental conditions (TAR concentration, pH, dosage), since saturation and adsorption process had already been identified for all analyzed biosorbents.

3.2.2 Effect of pH

The pH is a significant factor in the adsorption process, since it has a direct influence on adsorbent surface load, degree of ionization of the adsorbate functional groups, and adsorption mechanism [49]. The effect of pH on the TAR adsorption behavior is shown in Figure 6.

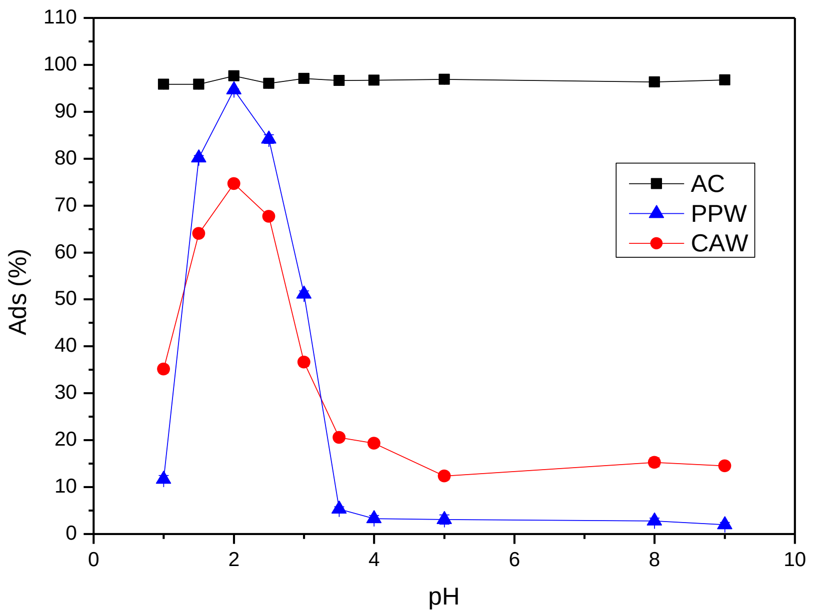

Figure 6: Effect of pH on the removal of TAR dye by PPW, CAW and AC adsorbents, in time = 120 min, [TAR] = 11.0 mg L^{-1}, temperature = 25.0 ºC, dosage = 7.5 g L^{-1}, stirring at 120 rpm.

Based on Fig. 6 it is possible to notice that the AC showed few variations in adsorption among all different pHs evaluated, with adsorption percentage remaining around 97.7% ± 0.6. Even with the effect of fillers, activated carbon has a high number of active sites easing the adsorption in different pH values [44]. Fig. 6 shows that the maximum TAR adsorption was reached at pH 2.0 for PPW and CAW, removing 94.7% ± 0.2 and 74.4% ± 0.5, respectively, which is consistent with other studies [44, 48, 50, 51]. Furthermore, it is necessary to show that the removal efficiency of TAR for PPW was similar to that of AC, with a ratio above 90%. Therefore, this residue has a great adsorptive potential, even without being subjected to carbon activation processes and chemical treatments.

When in alcali medium, a significant reduction in the efficiency of adsorption with the solution occurred. At pH 9.0 the percentage of removal was 14.5% ± 0.5 and 2.0% ± 0.5, for CAW and PPW, respectively. These values demonstrate that CAW still provides adsorption in alcali medium, but less efficiently. On the other hand, under the same conditions, the efficiency of the PPW is almost null. The materials pH_{zpc} is manly associated with this behavior. There is a significantly high electrostatic attraction force between positive surfaces of the biosorbents and anionic dye, which affects the high removal of pollutants in an acidic medium. On the other hand, with the increase in pH, the positively charged sites decrease and the adsorbent surface becomes negative, a fact that leads to lower percentages of adsorption as the pH values increase. With the results of CAW and PPW it is possible to observe that the best adsorption occurs in an acid medium and the best efficiency value is at pH 2.0 for both biosorbents.

3.2.3 Effect of dosage

The effect of the biosorbent dosage on the adsorption process (Figure 7) showed that CAW and PPW had similar behaviors, i.e., higher biosorbents concentration promote higher adsorption efficiency. In the 2.5 g L^{-1} dosage, the adsorption was 35.8% ± 0.1 for CAW and 67.0% ± 0.4 for PPW, and when the concentration increased to 12.5 g L^{-1}, the efficiency increased, reaching 83.3% ± 0.1 and 93.2% ± 0.2, respectively. In the case of AC, used as a comparison standard, the efficiency ranged from 90.4% ± 0.3 to 99.9% ± 0.1 in the same interval (2.5 g L^{-1} to 12.5 g L^{-1}).

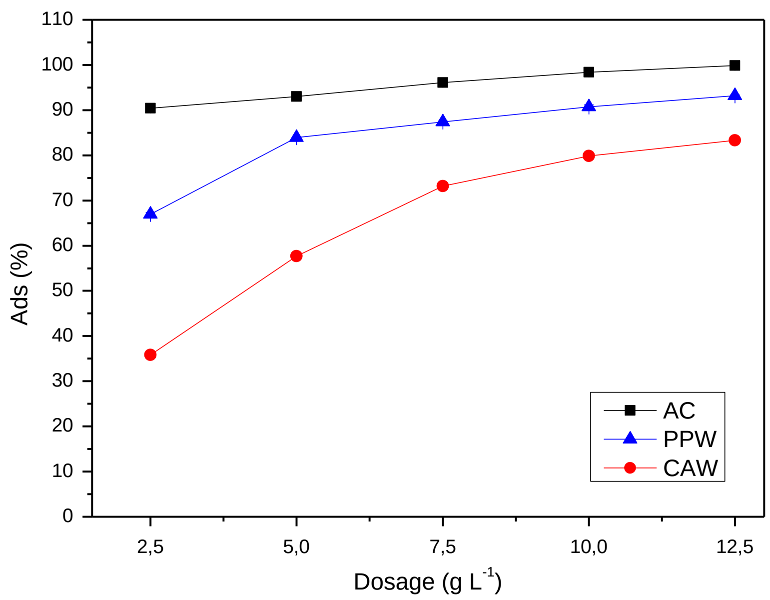

Figure 7: Effect of dosage on the removal of TAR dye for the adsorbents PPW, CAW and AC at pH = 2.0, Time = 120 min, [TAR] = 11.0 mg L^{-1}, temperature = 25.0 ºC, stirring at 120 rpm and volume = 20 mL.

This efficiency raise associated with the increase in biosorbent dosage can be explained by the high availability of adsorbent for a fixed dye concentration (11.0 mg L^{-1}). Thus, the higher the biosorbent mass the higher is the contact area, consequently a high number of active sites are available to be occupied by adsorbed TAR molecules. For subsequent experiments, the dosage of 7.5 g L^{-1} was established as the most appropriate, since this value is close enough to the limit value shown in Fig. 7 and it provides material savings.

3.2.4 Effect of dye concentration

The study of the effect of dye concentration on the occurrence of adsorption process (Figure 8) is important to assess the ability of a given mass of adsorbent to remove different concentrations of dye.

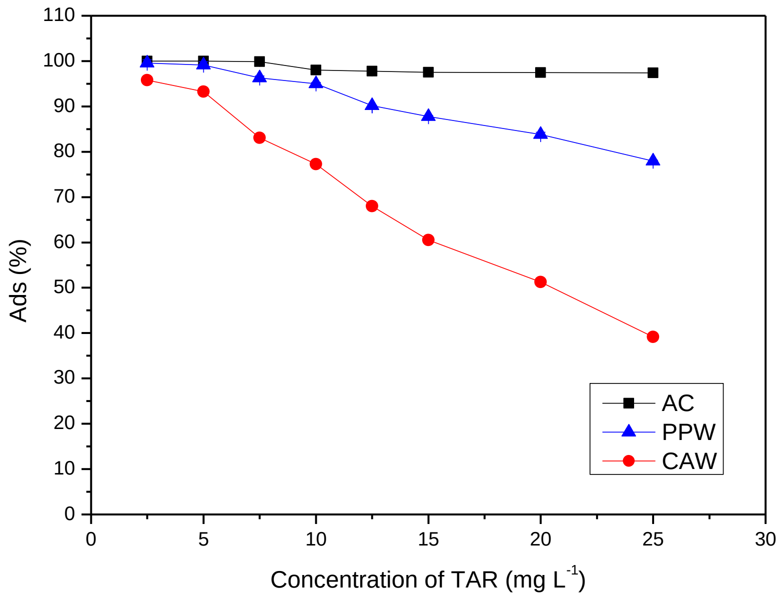

Figure 8: Effect of Concentration on the removal of TAR dye for PPW, CAW and AC adsorbents at pH = 2.0, Time = 120 min, temperature = 25.0 °C, stirring at 120 rpm.

The increase in TAR concentration from 2.5 mg L^{-1} to 25 mg L^{-1}, reduced the adsorption from 95.8% ± 0.7 to 39.1% ± 0.5 for CAW and from 99.6% ± 0.7 to 77.9% ± 0.2 for PPW. Once again, AC showed adsorption percentages close to 100%. Thus, it is possible to observe that with the increase in dye concentration, the percentage of removal of the TAR dye decreased, both for CAW and PPW. This behavior can be attributed to the fact that at low concentration values there is a reduced number of dye molecules and, therefore, there is less competition for active sites for adsorption.

The highest values of adsorption efficiency were observed in low dye concentrations, such as 2.5 mg L^{-1} and 10 mg L^{-1}, for both CAW and PPW. However, for the subsequent tests it was defined at 11.0 mg L^{-1} since this is common in industrial effluents from artificial orange juices in which the TAR dye is used. At this concentration, there was an efficiency of approximately 77.3% ± 0.1 and 95.0% ± 0.3 when using CAW and PPW as a biosorbent, respectively.

3.3 Adsorption isotherms

The adsorption isotherms are important to understand the mechanism of adsorption process, as well as to evaluate the adsorption equilibrium constants [26]. The application of the adsorption models isotherms of Langmuir, Freundlich, and Temkim for TAR by AC, CAW and PPW in pH 1.0, 2.0, and 3.0 (not shown) are expressed by statistical parameters R^2 (determination coefficient) and RSS (residual sum of squares) from linear adjustment of the models (Table 2).

Table 2: Constants of adsorption of Langmuir, Freundlich and Temkim isotherms for the removal of TAR with AC, CAW and PPW in pH 1.0, 2.0 and 3.0, at 25.0 ºC, dosage 7.5 g L^{-1}.

Adsorbents	**AC**			**CAW**			**PPW**		
pH	**1.0**	**2.0**	**3.0**	**1.0**	**2.0**	**3.0**	**1.0**	**2.0**	**3.0**
Langmuir									
$q_{máx}$ (mg g^{-1})	6.329	7.299	8.621	**1.464**	**1.414**	**1.558**	2.347	2.320	2.519
K_L (L mg^{-1})	1.295	1.070	0.817	**1.062**	**1.124**	**0.933**	2.328	2.435	2.079
R_L	0.236	0.272	0.329	**0.274**	**0.262**	**0.300**	0.147	0.141	0.161
R^2	0.953	0.980	0.983	**0.977**	**0.978**	**0.948**	0.926	0.921	0.923
RSS	0.005	0.002	0.002	**0.003**	**0.003**	**0.008**	0.017	0.018	0.019
Freundlich									
K_F	**1.866**	**1.893**	**1.900**	0.930	0.931	0.930	**1.185**	**1.186**	**1.208**
N	**1.359**	**1.319**	**1.252**	4.878	5.319	4.348	**3.086**	**3.086**	**2.793**
R^2	**0.978**	**0.991**	**0.993**	0.933	0.877	0.882	**0.978**	**0.982**	**0.969**
RSS	**0.002**	**6.6×10^{-4}**	**5.3×10^{-4}**	0.002	0.003	0.004	**0.002**	**0.002**	**0.003**
Temkim									
K_T (L mg^{-1})	10.732	10.416	9.293	37.116	59.343	22.333	18.774	18.984	15.065
B = RT/b (J/mol)	1.546	1.599	1.688	0.228	0.204	0.264	0.533	0.532	0.605
R^2	0.921	0.944	0.948	0.964	0.895	0.882	0.950	0.949	0.939
RSS	0.143	0.102	0.095	0.006	0.016	0.029	0.073	0.076	0.104

Table 2 shows that the experimental data of AC and PPW showed a better fit to the Freundlich model, since they obtained the highest coefficients of determination and the lowest error values. Freundlich's isotherm describes the adsorption on heterogeneous surfaces, with interaction between the adsorbed molecules and the formation of multilayers [17]. Therefore, the best fit to this model suggests that the adsorption of TAR by AC and PPW was not homogeneous, enabling the formation of several layers of dye on their surfaces [48]. On the other hand, CAW presented the best adjustments to Langmuir isotherm (R^2 = 0.948 to 0.978), which indicates the occurrence of monolayer adsorption [52]. In this model, the adsorbent surface has a fixed number of energetically equivalent locations and there are no interactions between the adsorbed molecules [53]. Based on these models, it was possible to determine the constant of adsorption equilibrium for each bioadsorbent.

The parameters provided by the Langmuir model (Table 2) refer to the adsorption equilibrium constant (K_L), which relates the affinity between the surface of adsorbent and the dye adsorbed and the maximum adsorption capacity ($q_{máx}$) [44]. It was found, by analyzing the $q_{máx}$ values, that AC (standard adsorbent) presents a higher adsorption capacity (6.329 to 8.621 mg g^{-1}) than PPW (2.320 to 2.519 mg g^{-1}) and CAW (1.414 to 1.558 mg g^{-1}). When comparing these values with the maximum TAR adsorption capacities, reported by different residues, similar results were observed (Table 3). Although there are similar results to the found in the present study, there is a wide variation in the literature, since the results depend on experimental conditions and, mainly, on the interval used for the equilibrium concentration.

Table 3: Comparison of the variables of Langmuir and Freundlich isotherms for the adsorption of TAR from literature.

Adsorbents	**Operation Condition**	**Langmuir**				**Freundlich**		**Ref.**
		$q_{máx}$ (mg g^{-1})	K_L (L mg^{-1})	R_L	R^2	K_F (mg g^{-1})	R^2	
Sawdust	Dosage: 5g L^{-1}, C_0: 1 to 15 mg L-^{1}, pH: 3.0, T: 25 ºC, time: 70 min	3.39	0.003	0.067	0.974	0.79	0.974	[47]
Nanoparticles (NPsFeOA) using pumpkin leaves (*Cucurbita moschata*)	10 mL of solution, C_0:25 to 120 mgL^{-1}, m:10 mg, pH: 7, T: 25 °C, time: 1200 min	75.44	0.98	-	0.97	51.87	0.93	[19]
Activated carbon of babassu coconut	Dosage: 0.2 g,L^{-1}, C_0: 15 mg L^{-1}, pH: 3.0, T: 25 ºC, time: 720 min	31.10	0.056	0.201	0.976	2.84	0.979	[44]
Moringa seeds	Dosage: 4.0 g,L^{-1}, C_0: 15 mg L^{-1}, pH: 3.0, T: 25 ºC, time: 240 min	72.08	0.051	0.218	0.943	3.05	0.936	[44]
Activated bone carbon	C_0:15mgL$^{-1,}$ m:0.2g, pH: 2, T: 25 °C, time: 600 min	17.19	0.063	0.184	0.969	1.64	0.952	[44]
Commercially-activated carbon	Dosage: 0.01 g 10 mL^{-1}, C_0: 30-200 mg L^{-1}, pH: 5.0; T: 25 ºC.	67.79	1.373	0.023	0.998	38.11	0.691	[54]

Regarding the K_L values, it was observed that PPW presented the highest values (2.079 to 2.328 L mg^{-1}), surpassing even those presented by the standard adsorbent (0.817 to 1.295) and the values reported in different studies (Table 3).

Another essential feature of Langmuir adsorption is the separation factor (R_L), estimated based on equilibrium constant (K_L) and initial dye concentration (C_0) [48]. R_L values (Table 2) showed that AC, CAW and PPW favor the adsorption of TAR in the three pH conditions ($0 < R_L < 1$) [36, 44, 50].

The results presented with the adjusted Freundlich model are expressed by the constants K_F (mg g^{-1}) and n, respectively [17, 48]. The K_F values (Table 2) ranged between 0.930 and 1.900 and they presented the following order AC> PPW> CAW. Previous studies with the TAR dye obtained similar results using sawdust and bone activated carbon (Table 3). The n values presented in Table 2 were identified for the three adsorbents studied and they represent favorable conditions for adsorption since they are higher than the unity [36, 38]. These results demonstrate that CAW and PPW biosorbents present favorable conditions for TAR adsorption, without applying high cost treatments in their production.

For AC and PPW, the best adjusted model was Freundlich's, which provides an empirical model for the process. K_F values for AC were higher than PPW, indicating that the adsorption process is more favorable in AC than PPW, as expected, since AC is an adsorbent standard. In both cases, K_F values were very similar to each other in relation to pH, indicating highly favorable processes in the studied pH values. For CAW, the best model was Langmuir's, which infers a monolayer model in which the active sites of the bioadsorbents have identical energies. In this case, the K_L values were lower than the K_F values for the AC and PPW, which is consistent with the fact that the CAW presented the lowest % Ads values in the experiments.

3.4 Potential application for industrial effluent treatment

The chemical composition of the juice effluent is quite complex and it involves a set of residues originated in the processes of manufacturing the juice, as well as substances used in the cleaning process. The previous analysis of the effluent showed an approximate pH of 3.5 and turbidity of 115 uT. According to industry data, the TAR is the main constituent of the effluent, with concentration of 11 mg L^{-1}.

In this case, the investigation of the TAR adsorption present in an industrial effluent is essential, since the results showed the efficiency of PPW and CAW in adsorbing the pure dye. According to Table 4, the luminosity (L*) of the effluent at pH 2.0 was slightly higher than the value observed in the pH 3.5, which is probably due to the protonation of the chromophoric groups of the dyes present in the effluent. Otherwise, the intensity of the yellow color (b*) was similar between the pH values evaluated.

Table 4: Percentage of adsorption reduction (% Ads) and luminosity (L) and yellow color intensity (b*) values for the initial effluent and after two adsorption cycles with the biosorbents PPW and CAW at pH 2.0 after 105 min (CAW) and 180 min (PPW), at 25.0 ºC.*

System	Treatment	% Ads	L*	b*
Effluent	pH 2.0	NA	65.4±1.2	14.3±0.4
	pH *in natura*	NA	61.7±1.0	15.5±0.3
PPW	1st cycle	55.8±3.5	87.3±1.4	1.9±0.1
(pH 2.0)	2nd cycle	81.3±4.0	91.1±0.4	1.0±0.1
CAW	1st cycle	49.5±0.2	82.6±0.2	2.2±0.1
(pH 2.0)	2nd cycle	72.1±1.7	87.8±0.6	1.1±0.1

* NA - not applicable; PPW: peach palm waste; CAW: cassava bagasse

In the first cycle the adsorption efficiency was similar for PPW and CAW (~53% of Ads reduction), and after the application of the second cycle, there was an increase in the adsorption percentage for both biosorbents, reaching 81.3% for PPW and 72.1% for CAW (Table 3). The luminosity increases after both treatment cycles, which was higher for PPW (91.1) than CAW (87.8), representing an increase of 39.2% and 34.2% in relation to the initial luminosity of the effluent, respectively, at pH 2.0. The reduction of b* values was similar for both biosorbents, and, after the second cycle, the values were 93.0% and 92.3% lower than the initial b* values, for the effluent at pH 2.0, for PPW and CAW, respectively.

The removal of these dyes by the industry generally is carried out by coagulation and flocculation processes, which require the addition of chemicals agents to alter the physical state of the dissolved / suspended solids and thus enable their removal by sedimentation [55, 56]. The main coagulants and flocculants used include metallic salts, such as polyaluminium chloride, and synthetic polymers, such as polyacrylamide [57]. However, the use of these substances can negatively affect the environment and the consumer health, due to the increase in the sludge generation and/or metals concentration in the water [57].

Considering that the wastes used in this study have been neither subjected to carbon activation processes nor chemical treatments make them cheaper, in comparison with conventional adsorbents, and less aggressive to the environment when discarded incorrectly. Furthermore, the results indicate that both PPW and CAW biosorbents can be applied for treating industrial orange juice effluents. In addition to the TAR dye, the industrial effluent contains several compounds, that can influence the adsorption capacity, since the ions present in these compounds can bind to the surface of the adsorbent and occupy active sites or cause an ionic repulsion when binding to the adsorbate. Therefore, the application of a single cycle is often not sufficient for removing all pollutant, requiring two or more cycles. Another option to increase the process efficiency, under real conditions, involves the use of fixed bed adsorption columns [58-60]. This model is already used in the treatment of industrial effluents with dyes, however, with activated carbon [61]. This theme will be addressed further in more detailed studies.

4. CONCLUSION

The biosorbents are composed of fibrous components, being cellulose the most abundant one (31.47 - 51.20 g 100 g^{-1}). Cassava bagasse also had high starch content (29.40 g 100 g^{-1}). These components were correlated with ATR-FTIR spectra. The micrographies showed that PPW and CAW biosorbents have irregular, heterogeneous and porous surface, which are considered positive characteristics for the adsorption process. Values of pH_{zpc} were 3.75 for PPW and 4.60 for CAW. The adsorption tests demonstrated that PPW had higher percentages of removal of pure dye (94.7%) than CAW (74.4%) under the following experimental conditions: T=25.0 ºC, pH 2.0, C_0=11.0 mg L^{-1}, dosage= 7.5 mg L^{-1}, time=120 min. Furthermore, PPW presented values of dye removal similar to that of commercial AC, used as a standard model. For CAW, Langmuir model provides the best fit to the experimental data, suggesting monolayer adsorption on homogeneous surface. On the other hand, the PPW results of isotherms were better described by Freundlich model, indicating the adsorption in multiple layers on a heterogeneous surface. For the treatment of industrial orange juice effluent, after two cycles, it was observed adsorption efficiency of 81.3% for PPW and 72.1% for CAW, as also, changes in the color parameters of the effluent, i.e., increase in luminosity (39.2% - 34.2%) and decrease in yellow intensity (93.0% - 92.3%). Therefore, this study presented an alternative to minimize the inadequate disposal of wastes (CAW and PPW) in the environment, with economic benefits to agro-industrial chains, considering that the use of them as biosorbent had potential to be applied in the treatment of industrial effluents.

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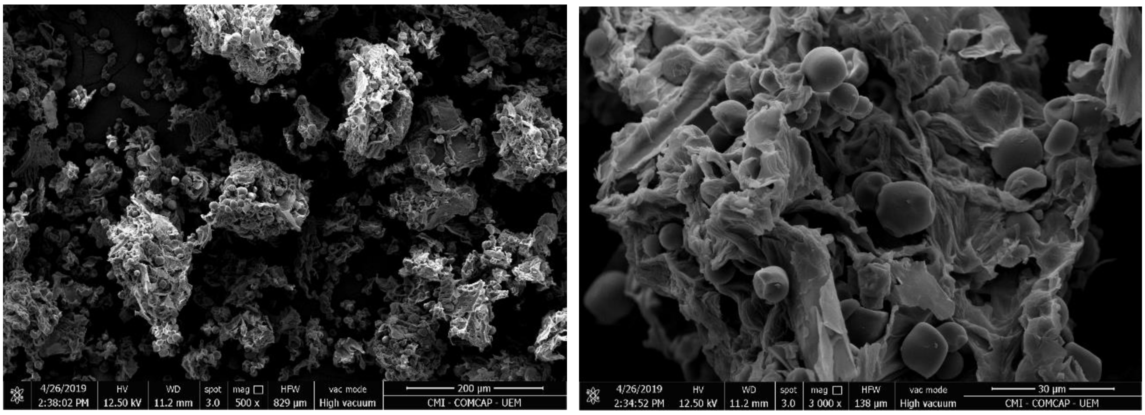
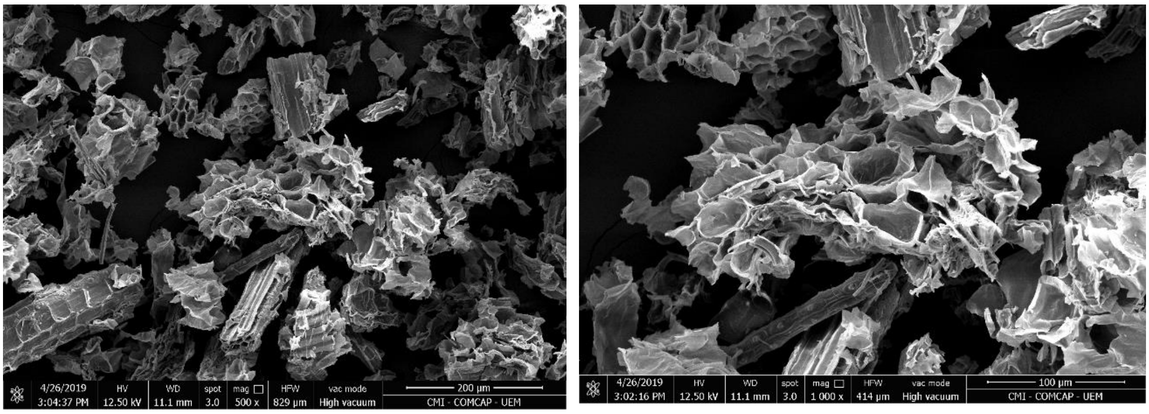
Supplementary Material



A B

Figure S1: Micrographs of the CAW with 500x magnifications (A) and 3000x magnifications (B).



C D

Figure S2: Micrographs of the PPW with 500x magnifications (C) and 1000x magnifications (D).