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Removal of Methylene Blue from a residue as a low-cost biosorbent: peanut hull (*Arachis hypogaea*)

Eduarda Bertoletti Duarte
Graduate Student (Master's Degree) in Cleaner Technologies, Unicesumar, Brazil.
eduardabertoletti@gmail.com

Luciana Cristina Soto Herek Rezende
Professor, Unicesumar, Ph.D. Researcher at the Cesumar Institute for Science, Technology, and Innovation, Brazil
lucianarezende17@gmail.com

Natália Ueda Yamaguchi
Professor, Unicesumar, Researcher at the Cesumar Institute for Science, Technology, and Innovation, Brazil

ABSTRACT

The textile industry is still very relevant for people's everyday life and their production of goods, however, throughout the production chains, there are impacts on the environment, such as the elimination of effluents with the presence of dyes used in the production processes. These substances can cause environmental contamination if untreated, and the proper treatment for them is adsorption. This technique, although efficient, has a high cost, which favors the use of natural adsorbents, especially the usage of abundant residues in the environment. Therefore, this paper aims at using an agro-industrial residue, peanut hulls, produced on a large scale, as an adsorbent in the treatment of wastewater using the dye methylene blue. The Bel® SPECTRO S-2000 UV-visible spectrophotometer at a wavelength of 664 nm was used to analyze the absorbance of the dye concentrations. These data were used in the construction of the calibration curve, where the values found were calculated to obtain the adsorption capacity, which allowed us to identify the efficiency of the biosorbent. The results obtained were compared with the literature, and although the experiment had different conditions, the peanut hulls presented an adsorption capacity of 4.26925 mg/g, which represents an efficiency. Nevertheless, further studies are needed to carry out other analyses to evaluate the conditions that allow an increase in the adsorption capacity.

Keywords: Adsorption; Textile dye; Agro-industrial waste.

1. INTRODUCTION

Industrialization over the decades has had a direct impact on urban and technological development, providing benefits to society; however, to satisfy the population's demand, production becomes excessive and leads to the scarcity of natural resources (BAPTISTA, 2010; SILVA, 2019). The environmental issue is a topic that has been increasingly studied, especially with the population growth that leads to increased production and, consequently, increased generation of waste and wastewater (BARROS et al., 2020).

In studies with sustainability, the reduction of waste generated and treatment is a growing practice in the world scenario, causing increasing research reintroducing waste in new production chains and new processes, increasing lifetime waste, and reducing early disposal (TOMBINI et al., 2021).

Among the different sectors, the textile industry is known as a polluting chain because it is a large consumer of freshwater and has a significant generation of potentially toxic wastes in water bodies (COSTA, 2020). Along the production chains, there is the generation of waste and effluents that are discharged into water bodies, causing environmental impacts (SILVA, 2019).

The aforementioned sector is very influential in the daily life of the population and its production is constantly growing, but like any anthropic activity, there are impacts, and in the case of the textile industry, there is the generation of complex effluents formed by several chemical substances (SILVA, 2019). Among these substances, dyes are released when they do not adhere to the fiber in the washing phase. (SILVA; ZANUTTO; PIETROBELLI, 2019; SILVA, 2019). There is a variable range of dyes used in the industry, among which methylene blue stands out for its use on a variety of fabrics such as acetate, cellulose, cotton, rayon, and polyester (SAMSAMI et al., 2020).

In this scenario, it is necessary to treat them before disposing of them in water bodies to avoid environmental contamination and the resident biota, but many treatment methods have high costs and low efficiency (FONTANA et al., 2016). In addition to environmental contamination and resident biota, some dyes can cause human diseases such as allergies, dermatitis, and skin rashes (LIMA et al., 2008).

Thus, there is an increase in studies that use waste, especially lignocellulosic materials, as a treatment because it has a continuous production, is renewable and sustainable, and the acquisition cost is low (COSTA, 2020; MUSSATO et al., 2009).

Adsorption is a commonly used technique due to its high efficiency, although it has a high cost due to the material used in the process, then the use of biosorbents shows efficiency in terms of cost-effectiveness because they are abundant natural materials that require little or no prior processing, such as the use of waste as biosorbents (MILDEMBERG, 2019; COSTA, 2020).

Among biosorbents, plant residues have gained some importance for their efficiency as wastewater treatment materials, such as rice husks, sugarcane bagasse, malt bagasse, oilseed husks, fruit and vegetable peels and seeds (MILDEMBERG, 2019).

The peanut (*Arachis hypogea*) crop develops well in different climates and temperatures, in Brazil has become a good alternative for producers to increase their income (FREITAS, 2011). The peanut seed presents a composition rich in vitamins, nutrients, and proteins (BARROS et al., 2020; FREITAS, 2011). And the oil extracted is used in the food sector as the production of margarine and cooking oil and is included in the cosmetic and pharmaceutical industries (BARROS et al., 2020; FREITAS, 2011).

However, if the peanut shell is not used in the food industry then it is considered a residue, representing 30% of grain production, and its use is currently as fuel for boilers and food for cattle and poultry (GATANI et al., 2013). However, peanut production in Brazil is significantly large in crops, with the 2019/2020 estimated production of 670.4 thousand tons, with a significant generation of the shell (FIESP, 2021). And it is important to use this waste to reduce the amount of discarded waste.

Thus, the use of an agroindustrial residue produced annually on a large scale as a biosorbent presents itself as a sustainable alternative. It allows the valorization of a by-product and follows the objectives of the 2030 Agenda for the reuse of waste (Sustainable Development).

2. OBJECTIVES

The objective of this research was to evaluate the peanut hull as a biosorbent material of methylene blue found in textile effluents, contributing to the valorization of waste and reducing the inadequate and premature disposal of these by-products. As a specific objective, the adsorption capacity of the material was evaluated and compared with previously published studies.

3. METHODOLOGY

The studies were carried out in May 2022 in the Interdisciplinary Laboratory of Biological and Chemical Analysis of the main campus of Cesumar University, Maringá/PR.

3.1. Adsorbent preparation

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The peanut hull was purchased from Sacolão Popular, located in Curitiba, state of Paraná, Brazil. The shell was separated from the kernel by hand and kept in another open container to remove the moisture.

The shell was placed in a baking pan and then in the Mueller Moderatto four-burner stove at 160°C (320 Fahrenheit) for 20 minutes, monitoring the state of the hull every 5 minutes. The hull was then chopped in the processor to reduce the size of the biosorbent particles.

The crushed peanut hull was filtered through a sieve to reduce the particle size of the biosorbent. And the resulting powder was stored in a container with a lid for transportation.

Then, 0.1 g of the biosorbent was weighed in duplicate on the Sartorius Practum® 224-10BR analytical balance. Then, a 10-ppm methylene blue solution was added to each vial. These vials were placed in the Lucadema® Floor Shaker magnetic stirrer at a controlled temperature of 25°C (77°F) at 150 rpm for 1 hour.

3.2. Spectrophotometer calibration

The 1, 2, 5, 10, and 20 ppm methylene blue solutions were used to calibrate the Bel® SPECTRO S-2000 UV-visible spectrophotometer at the wavelength of 664 nm, as well as distilled water.

Calibration information is provided in the table below:

Table 1: Information about the calibration

Concentration	Absorbance	Average
0	0	0
1 ppm	0.107	0.105
1 ppm	0.103	
2 ppm	0.285	0.279
2 ppm	0.273	
5 ppm	0.683	0.678
5 ppm	0.673	
10 ppm	1.295	1.293
10 ppm	1.291	

Source: Authors, 2022

The 20-ppm concentration was ignored for technical reasons. Using the information in Table 1, the calibration curve was plotted, and the equation of the straight line was determined using Excel®, where the adsorption capacity of the methylene blue dye was determined using Equation 1 and the percentage retention was determined using Equation 2:

$$q = \frac{(C_0 - C)V}{m}$$ Equation 1

$$\% = \left(1 - \frac{C}{C_0}\right) \times 100$$ Equation 2

Source: CITADIN; CECHINEL, 2018

In these equations, q (mg/g) is the adsorption capacity in mg (milligrams) of methylene blue per g (grams) of biosorbent. C0 (mg/L) is the initial concentration of methylene blue. C (mg/L) is the methylene blue concentration after one hour, V (L) is the volume of the solution, and m (g) is the mass of the biosorbent (CITADIN; CECHINEL, 2018).

4. RESULTS

The biosorbent obtained after the drying, grinding, and sieving stages is shown in Figure 1.

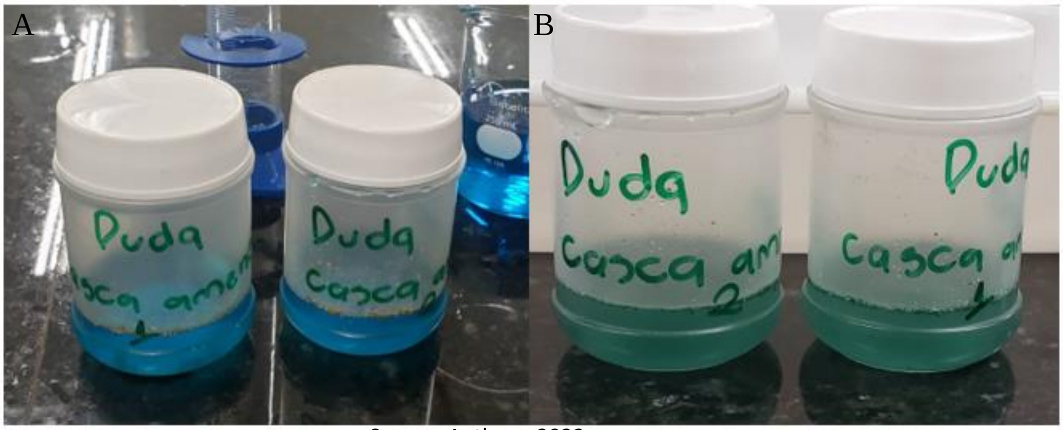
After the sieve analysis, the biosorbent showed a finer powder aspect, and this process affected the available surface area, according to Worch (2012), the smaller the material, the greater the available adsorption area.

Figure 1: Prepared waste material

Source: Authors, 2022

First, 0.1006 g of peanut shell powder was weighed into container number 1 and 0.1027 g into container number 2 on the Sartorius Practum® 224-10BR analytical balance. Then 50 ml of dye was added to each container as shown in Figure 2a. Figure 2b shows how the container with the experiment looked after one hour in the shaker.

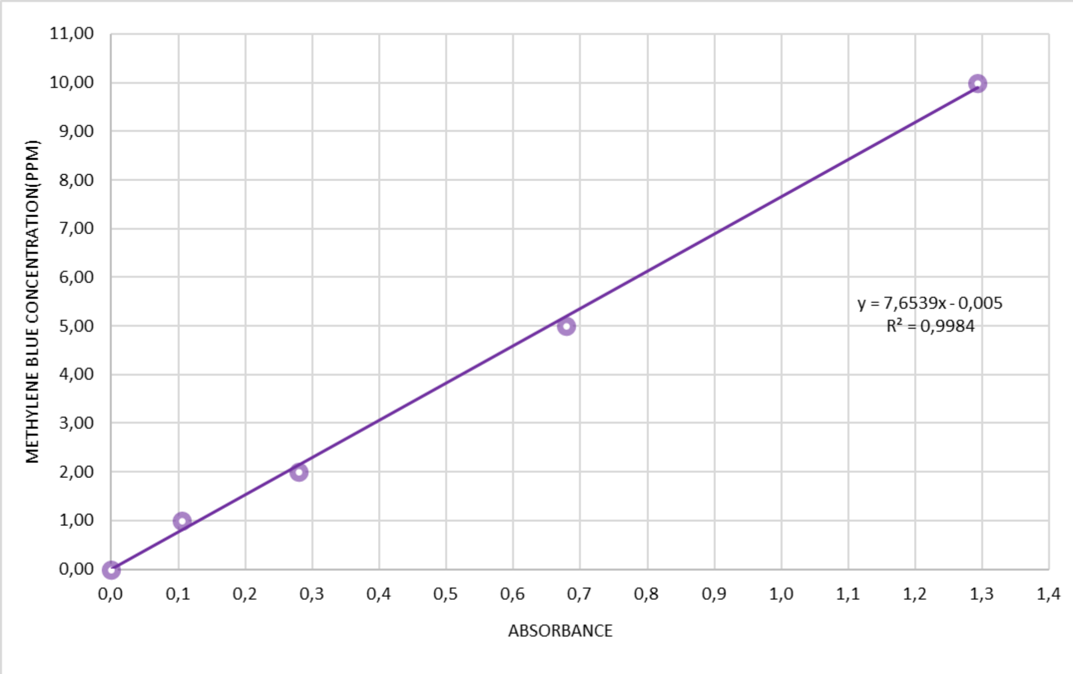
Figure 2: A- Start of experiment B- Container after treatment



Source: Authors, 2022

The calibration curve shown in Figure 3 was constructed from the values obtained by measuring different concentrations of methylene blue dye (Table 1) and is presented as follows:

Figure 3: Spectrophotometer calibration curve



Fonte: Authors, 2022

The evaluation in the spectrophotometer shows that the residue has an absorbance of 0.185 at a concentration of 0.1006 g and an absorbance of 0.170 at a concentration of 0.1027 g. The equation of the straight line was given by Y = 7.6539x - 0.005, where R2 is equal to 0.9984.

The adsorption capacity of peanut shell on methylene blue dye is expressed in Equation 1:

$$\frac{q = (9{,}891 - 1{,}353)0{,}05}{0{,}1} \qquad q = 4{,}26925\ mg/g$$

In other words, 0.1 g of the adsorbent, in this case, the peanut hull, can remove 4.27 mg/g of methylene blue. As detailed by Guimarães et al. (2012), the rapid adsorption in a short period, in this case, one hour, demonstrates the efficiency of the peanut hull as a biosorbent.

Using equation 2, it was possible to evaluate that the residue removed 86.32% of the dye, demonstrating its good removal capacity.

$$\% = \left(1 - \frac{1{,}353}{9{,}891}\right) \times 100$$

As observed by Beltran et al. (2020), the increase in the percentage of removal increases with the concentration of the biosorbent, but at the same time, the increase in the adsorption capacity leads to a decrease in the concentration of the biosorbent, which emphasizes the need for studies that evaluate different concentrations of the residue that will make the adsorption more efficient.

Reis et al. (2017) evaluated three different concentrations of malt bagasse (0.2 g, 0.4 g, and 0.6 g) as adsorbent and observed that the increase in the amount of adsorbent is inversely proportional to the adsorption capacity, which is observed in Equation 1.

The chemical composition of peanut hulls is due to the lignocellulosic fibers, composed of cellulose, hemicellulose, and lignin (SANTOS, 2019; NUNES, 2014). In terms of their structure, the fibers intertwine in structural arrangements and form cavities that promote adsorption (SANTOS, 2019; MOREIRA, 2010).

In addition, Nunes (2014) considered the material a good precursor for activated carbon due to its lignocellulosic composition and low moisture, protein, and fat content.

Table 2 shows the articles used to compare the results found, and the discussion is shown below.

Table 2: Comparison table of published articles

Author	Residues	Adsorptive capacity (mg/g)
This study	Peanut shell	4,27
Silva et al., (2018)	Peanut shell	29,01
Barros et al., (2020)	Peanut shell	3,65
Citadin e Cechinel (2018)	Grape pomace	19,00
Cavalcante, Maia Júnior e Braga (2017)	Buriti leaf stalk	58,17
Shakoor e Nasa (2016)	Lemon peel	227,30
Hameed (2009)	Jackfruit peel	285713,00
Antunes et al., (2018)	Pineapple peel	17,12
Beltran et al., (2020)	Tangerine peel	100,73

Fonte: Authors, 2022

In their work, Silva et al. (2018) prepared an adsorbent from a peanut hull as an activated carbon with 20 g of the residue for phenol removal in an aqueous solution. The results of the activated carbon were compared with those of the peanut hull. The authors observed that the adsorptive capacity increased with increasing agitation, they maintained an agitation of 300 rpm for 6 hours. They also evaluated that the activated carbon from peanut hulls made the residue a better biosorbent. The activated carbon of Nunes (2014), counted with a moisture content of 4.3%, showed satisfactory results as a good adsorbent and with the removal of crystal violet dye in an aqueous medium.

Barros et al. (2020) used peanut hulls as an adsorbent for methylene blue. The authors evaluated 10 different pH conditions to assess the adsorption. 1.0 g of residue was used with constant agitation of 250 rpm at 25ºC (77ºC), and different conditions were used in this study. Eleven tests were performed with 3 of two concentrations, 25 and 75 (mg/L), each at these pH (7, 8, 9) and at each time (4, 6, 8 hours). The best result was obtained in the experiment with 75 mg/L concentration, pH 7 for 4 hours, which resulted in an adsorption capacity of 3.65 mg/g.

Other studies in the literature have also relied on the adsorption capacity of different biosorbents, Citadin and Cechinel (2018) evaluated the adsorption capacity of waste, in this case, grape pomace. In their work, they used 4 g/L of bagasse and Remazol Blue RR dye solution with a concentration of 100 mg/L and evaluated the absorbance in a UV-visible spectrophotometer with a wavelength of 603 nm, but unlike this work, the authors kept the experiment under stirring for 48 hours. The adsorptive capacity obtained in the experiment was

19.0 mg/g, a value significantly higher than that found in our study, but the conditions of the experiment were different, making it impossible to compare both studies.

Cavalcante, Maia Júnior, and Braga (2017) evaluated the potential of the stem of the *buriti* leaf (*Mauritia flexuosa*) as an adsorbent material in the removal of methylene blue dye. The authors used two masses of adsorbent (0.05 and 0.1 g) and 50 mL of methylene blue in agitation for 2 hours at 150 rpm, and up to this point, the methodology carried out in our paper is very similar to theirs. However, the authors allowed the experiment to stand for 24 hours. It was observed that the maximum adsorption capacity of 58.17 mg/g was obtained in the experiment at 30ºC (86ºC), which represents an acceptable adsorption value.

Shakoor and Nasa (2016) studied lemon peel as a low-cost adsorbent for methylene blue dye. And the maximum adsorption capacity was 227.3 mg/g, using 0.05 g of waste and 25 mL of adsorbate on a stirrer for three hours.

In the literature, other authors have used different wastes as adsorbents for methylene blue dye, such as pineapple peels (ANTUNES et al., 2018), jackfruit peels (HAMEED, 2009), tangerine peels (BELTRAN et al., 2020), parsley stalks, cucumber peels, and watermelon seed shells (AKKAIA; GUZEL, 2013), as well as pine nut peels (ROMÃO; VIANA, 2018).

Several papers have carried out previous treatments with acids and bases and pH adjustment to improve the efficiency of biosorbents and increase their binding properties with the material, in addition to evaluating the effect of pH (BELTRAN et al., 2020; SANTOS, 2019; SHAKOOR; NASA, 2016; SILVA et al., 2018; SILVA; OLIVEIRA, 2012; BARROSO; LOPES; CUNHA, 2019).

However, although our work presents a potentially efficient result, the comparative analysis with the cited literature could not be performed on a deeper scale due to the different conditions and treatment of the residue in each experiment. The work used one hour to evaluate the adsorption capacity, but this proved to be a short time compared to other articles.

However, it is possible to conclude that the peanut hull presented a promising efficiency as a biosorbent in the removal of methylene blue dye, a substance widely used in the textile industry and its effluents, which require treatment before disposal in water bodies. Furthermore, new studies evaluating different conditions and variables are needed to develop an even more efficient biosorbent.

5. CONCLUSION

This work seeks the valorization of agroindustrial waste generated on a large scale. Using the peanut hull for the adsorption of contaminant components, in this case, an organic dye actively found in effluents from textile industries, methylene blue.

Throughout the experiment, it was possible to measure the efficiency of the peanut hull as a methylene blue adsorbent. However, studies are still needed to evaluate different concentrations of waste, treatments, and pH that make the biosorbent more effective in the treatment.

Thus, using a residual with potential within a costly wastewater treatment technique makes the process more sustainable and environmentally friendly, while still providing a high cost-benefit ratio.

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