

## Materials for methylene blue adsorption

Materiais para adsorção de azul de metileno

Materiales para adsorción azul de metileno

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### Abstract

Adsorption is a surface phenomenon, in which the adsorbate is adhered to an adsorbent material and have been study for the removal of textile dyes, which have high toxicity to the aquatic environment. One of the dyes that stands out is methylene blue, which is organic, basic, aromatic, heterocyclic and molecular formula ( $C_{16}H_{18}ClN_3S$ ). In this study, we aim was to carry out a bibliography review in national and international scientific journals with articles published in the period from 2005 to 2019, of the adsorbent materials for the adsorption of the methylene blue dye. The materials reported are: mango seed powder, wheat husks, activated carbon obtained from rattan sawdust, activated carbon prepared from coconut shell, garlic shell, NaOH modified pummell shell, activated carbon (coconut shell and modified with NaOH), activated carbon (pea peel), HCl modified watermelon peel, potato peel,  $ZnCl_2$  activated cashew nut peel, mesoporous carbon obtained from fish scales, pineapple peel and bamboo. Our review indicate that the adsorbent materials found in the literature for methylene blue adsorption have high adsorption capacities. The adsorption capacities are high and depend on several parameters, which influence the adsorption (pH of the medium, mass and particle size of the adsorbent material, concentration of adsorbate (methylene blue), temperature and time of contact of the adsorbate with the adsorbent.

**Keywords:** Adsorption; Material adsorbent; Methylene blue; Adsorbate.

### Resumo

A adsorção é um fenômeno de superfície, em que o adsorbato fica aderido num material adsorvente, e vem sendo estudado para remoção de corantes têxteis, os quais possuem elevada toxicidade para o meio aquático. Um dos corantes que merece destaque é o azul de metileno, que é orgânico, básico, aromático, heterocíclico e fórmula molecular ( $C_{16}H_{18}ClN_3S$ ). O objetivo do trabalho foi realizar uma revisão bibliográfica em revistas científicas nacionais e internacionais com artigos publicados no período de 2005 a 2019, dos materiais adsorventes para adsorção do corante azul de metileno. Os materiais relatados são: pó da semente de manga, cascas de trigo, carvão ativado obtido a partir de serragem de rattan, carvão ativado preparado a partir da casca de coco, casca de alho, casca de pummelo modificada com NaOH, carvão ativado a partir da casca de ervilha, casca de melancia modificada com HCl, casca da batata, casca da castanha de caju ativada com  $ZnCl_2$ , carbono mesoporoso obtido a partir de escamas de peixe, casca de abacaxi e bambu. Assim, os materiais adsorventes encontrados na literatura para adsorção de azul de metileno possuem elevadas

capacidades de adsorção, e que dependem de diversos parâmetros como: pH do meio, massa e tamanho da partícula do material adsorvente, concentração do adsorbato (azul de metileno), temperatura e tempo de contato do adsorbato com o adsorvente.

**Palavras-chave:** Adsorção; Material adsorvente; Azul de metileno; Adsorbato.

### Resumen

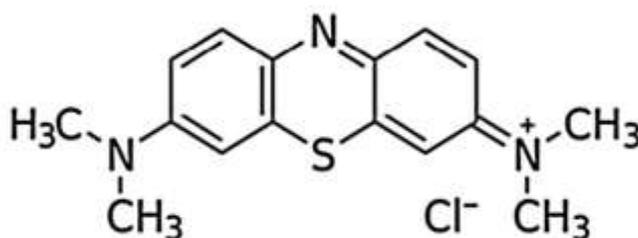
La adsorción es un fenómeno superficial, en el que el adsorbato se adhiere a un material adsorbente, y se ha estudiado para la eliminación de tintes textiles, que tienen una alta toxicidad para el medio ambiente acuático. Uno de los colorantes que destaca es el azul de metileno, que es una fórmula orgánica, básica, aromática, heterocíclica y molecular ( $C_{16}H_{18}ClN_3S$ ). El objetivo del trabajo fue llevar a cabo una revisión bibliográfica en revistas científicas nacionales e internacionales con artículos publicados en el período comprendido entre 2005 y 2019, de los materiales adsorbentes para la adsorción del colorante azul de metileno. Los materiales informados son: polvo de semillas de mango, cáscaras de trigo, carbón activado obtenido de aserrín de ratán, carbón activado preparado a partir de cáscara de coco, cáscara de ajo, cáscara de pomelo modificado con NaOH, carbón activado (cáscara de coco y modificado con NaOH), carbón activado (piel de guisante), piel de sandía modificada con HCl, piel de patata, piel de anacardo activada con  $ZnCl_2$ , carbono mesoporoso obtenido de escamas de pescado, piel de piña y bambú. Por lo tanto, los materiales adsorbentes encontrados en la literatura para la adsorción de azul de metileno tienen altas capacidades de adsorción, y las capacidades de adsorción son altas y dependen de varios parámetros, que influyen en la adsorción (pH del medio, masa y tamaño de partícula del material adsorbente, concentración de adsorbato (azul de metileno), temperatura y tiempo de contacto del adsorbato con el adsorbente).

**Palabras clave:** Adsorción; Material adsorbente; Azul de metileno; Adsorbato.

## 1. Introduction

Methylene blue (Figure 1) is a basic organic, aromatic heterocyclic dye, whose molecular formula  $C_{16}H_{18}ClN_3S$  (Pouretedal *et al.*, 2009). It has several applications, including wool or cotton dyeing, paper coloring, temporary hair coloring and paper coating. Because to its high adsorption capacity in solids, methylene blue is often used as a model compound to assess the ability of adsorbents to remove contaminants from aqueous solutions (Wu *et al.*, 2009). Despite having a low toxicity, methylene blue can harm the health of humans and animals by causing eye burns; nausea, vomiting and diarrhea if ingested; dyspnea, tachycardia, cyanosis, and seizure if inhaled (Senthilkumaar *et al.*, 2005).

**Figure 1.** Molecular structure of methylene blue.



Source: Dhananasekaran *et al.* (2016).

Many physical and chemical methods are employed for the treatment of effluents containing dyes, such as electrochemistry, precipitation, filtration, ozonolysis, and adsorption as the most used treatment process in the removal of methylene blue from effluents (Oliveira *et al.*, 2013).

### 1.1 Adsorption

Adsorption is one of the techniques widely applied for the treatment of effluents due to its effectiveness in removing pollutants, much superior to other techniques of reusing water in terms of initial cost, due to flexibility and ease of operation. Common adsorbents include activated carbon, molecular sieves, polymeric adsorbents and some other low-cost materials. It also does not result in the generation of harmful substances (Rafatullah *et al.*, 2010).

The adsorption process appears because of the unsaturated and unbalanced molecular forces that are present on all solid surfaces. Thus, when a solid surface is brought into contact with a fluid, there is an interaction between the force fields at the solid-fluid interface. The solid phase tends to balance these residual forces, attracting and retaining molecules, atoms or ions of the fluid on its surface. This results in a higher concentration of fluid components at the solid-fluid interface than in the fluid phase (Bansal & Goyal, 2005). The substance that accumulates in the solid phase is called adsorbate and the solid in which adsorption occurs is called adsorbent.

The type of adsorption that occurs in a given adsorbate-adsorbent system depends on the nature of the adsorbate, the nature of the adsorbent, the reactivity of the surface, the surface area of the adsorbent and the temperature and pressure of adsorption. Depending on these variables, adsorption has two distinct types: physical adsorption and chemical adsorption.

Physical adsorption or physisorption occurs when weak interparticle bonds exist between the adsorbate and the adsorbent. The forces involved in physisorption are the van der Waals forces (repulsion and dispersion) and always include London's long-range dispersion forces and short-range intermolecular repulsion. These combined forces give rise to nonspecific molecular interactions. Specific interactions come into play when polar molecules are adsorbed onto ionic or polar surfaces, but as long as there is no form of chemical bonding, the process is still consider a physisorption (Thommes, 2010). Because it has relatively low adsorption energy (physisorption), it is considered in most cases to be reversible (Coelho *et al.*, 2014). On the other hand, chemical adsorption (chemisorption) involves the chemical interaction between the adsorbed fluid and the adsorbent solid, leading to the formation of a chemical surface compound or adsorption complex. This is due to a strong interparticle bond that is present between adsorbate and adsorbent, due to the transfer and sharing of electrons. Examples of such a bond are ionic and covalent bonds. Unlike physisorption, chemisorption is an exothermic process and is consider irreversible in most cases (Dąbrowski, 2001). Furthermore, in physical adsorption, overlapping molecular layers can be form, while in chemical adsorption; a single adsorbed molecular layer (monolayer) is formed.

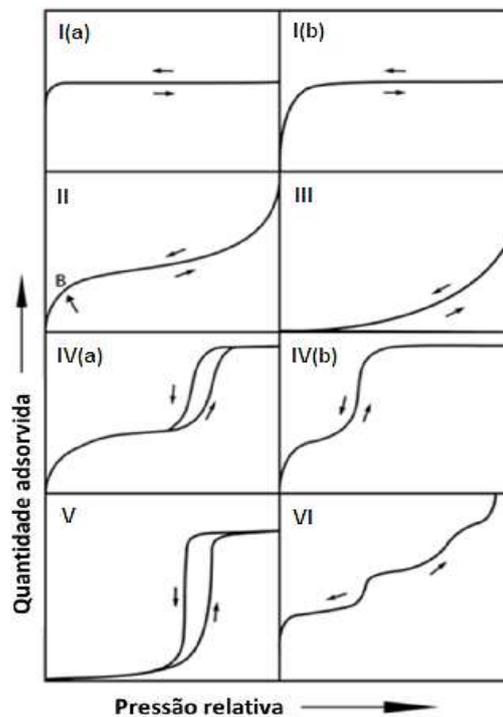
Several models of equilibrium isotherms have been introduce over the years. Some of these models have gain more importance than others due to their simplicity and, in some cases, due to their wide applicability. The precision of an isothermal model is generally a function of the number of independent parameters in the model, while its popularity in relation to the application of the process is generally a function of its mathematical simplicity (Malek & Farooq, 1996).

Isotherms provide important information about the behavior of a given adsorbent, such as its maximum adsorption capacity for a given adsorbate and estimate the minimum dosage necessary to obtain the treatment objective. It also allows the comparison between different adsorbents, evaluating the influence of variables, such as pH, temperature and contact time. Therefore, it is an excellent resource to define ideal conditions for a full-scale operation to be used later (Golin, 2007).

The adsorption capacity of any adsorbent is a function of pressure (when gases) or concentration (when liquids) and temperature. When in a process, the adsorption capacity varies with pressure at a constant temperature it is possible to obtain curves called isotherms.

Brunauer *et al.* (1938) proposed the first five types of isotherms. Each type of isotherm is relate to the type of pore involved. In addition, there is still the type VI that was propose later. The proposal for an updated classification of isotherms is show in Figure 2.

**Figure 2.** Classification of physical adsorption isotherms to according to IUPAC.



Source: Thommes *et al.*, 2015.

## 1.2 Isotherm Models

### 1.2.1 Henry Model

Henry's isotherm, governed by Henry's law, is the simplest type of isotherm. This isotherm is only valid for adsorption on uniform surfaces with low concentrations of adsorbent, due to the assumption that there is no interaction between the adsorbed particles.

The Equation 1 can describe the relationship between the concentration in the fluid phase and in the solid phase in a linear way. Where:  $Q_e$  is the adsorption capacity at equilibrium in the solid phase ( $\text{mg}\cdot\text{g}^{-1}$ ),  $C_e$  is the equilibrium concentration in the liquid phase ( $\text{mg}\cdot\text{L}^{-1}$ ) and  $K_h$  is the Henry constant.

$$Q_e = K_h \cdot C_e \quad (1)$$

### 1.2.2 Langmuir Model

The Langmuir isotherm equation is the first theoretically developed adsorption isotherm. Many of the equations proposed later and that fit the experimental results over a wide range are based on this equation or these equations were developed using the Langmuir concept. Thus, the Langmuir equation still holds an important position in theories of physisorption and chemisorption. The equation was also derive using thermodynamic and statistical approaches. The American scientist Irving Langmuir derived this Equation based on certain assumptions (Bansal & Goyal, 2005). The most important assumptions are: (i) The adsorbed particles (atoms, molecules or ions) are fixe to the surface in defined localized places, the so-called adsorption sites; (ii) Each site accommodates only one adsorbed particle, and (iii) The energy state of each adsorbed particle is the same at all locations on the surface, regardless of the presence or absence of other particles adsorbed at neighboring locations. Thus, the Langmuir model (also called the localized model) assumes that the surface is perfectly smooth and homogeneous and that the side interactions between the adsorbed particles are insignificant.

The Langmuir Equation was based on the hypothesis of a structurally homogeneous adsorbent where all the adsorption sites are identical and energetically equivalent. Theoretically, the adsorbent has a finite capacity for the adsorbate. Therefore, a

saturation value is reached beyond which no further adsorption can occur. Equation 2 represented the Langmuir Equation. The Equation 3 shows its linearized form:

$$q^* = \frac{q_{\max} \cdot b \cdot C_e}{1 + b \cdot C_e} \quad (2)$$

$$\frac{C_e}{q^*} = \frac{1}{q_{\max} \cdot b} + \frac{1}{q_{\max}} \cdot C_e \quad (3)$$

Where:  $q^*$ : Mass of the adsorbed per unit of mass of the adsorbent ( $\text{mg}\cdot\text{g}^{-1}$ );  $C_e$ : equilibrium concentration of the adsorbate in solution after adsorption ( $\text{mg}\cdot\text{L}^{-1}$ );  $q_{\max}$ : constant that indicates the adsorption capacity in the monolayer ( $\text{mg}\cdot\text{g}^{-1}$ ), and  $b$ : constant related to adsorption-free energy (adsorption equilibrium constant).

### 1.2.3 Freundlich Model

In addition to being one of the first equations used to represent equilibrium data, the Freundlich Equation was used to describe adsorption of organics from streams in aqueous solutions using activated carbon (Do, 1998). The Freundlich isotherm is one of the most widely used mathematical descriptions, generally fitting experimental data over a wide concentration range. This isotherm gives an expression covering the heterogeneity of the surface and the exponential distribution of the active sites and their energies (Hasany *et al.*, 2002).

Freundlich Equation 4 reports the amount of adsorbate in the solution in relation to that in the adsorbed phase.

$$q^* = K_f \cdot C_e^{1/n} \quad (4)$$

The constant  $K_f$  ( $\text{mg}\cdot\text{g}^{-1}$ ) relates to the adsorption capacity while  $1/n$  is a constant that relates to the intensity or energy of the adsorption, with a higher value for  $1/n$  indicating a greater change in effectiveness in relation to the different equilibrium concentrations. When  $n$  values are in the range  $1 < n < 10$ , the change in the adsorbed concentration is greater than the change in the solute concentration, indicating favorable adsorption (Ng *et al.*, 2002). This isotherm provides no saturation of the adsorbate; thereby endless surface coverage is predicted mathematically, indicating the multilayer adsorption on the surface (Erdem *et al.*, 2004).

### 1.2.4 Langmuir-Freundlich model

Langmuir-Freundlich Equation was initially presented by Sips (1948), can be given as follows according to Equation 5:

$$q^* = \frac{K_{LF} C_e^{1/n}}{1 + a_{LF} C_e^{1/n}} \quad (5)$$

Where:  $K_{LF}$ : Langmuir-Freundlich constant ( $= K_L q_m$ ), ( $\text{L}\cdot\text{m}^{-1}$ ) ( $\text{mg}\cdot\text{g}^{-1}$ ) and  $a_{LF}$ : Langmuir-Freundlich constant ( $= K_L q_m$ ), ( $\text{L}\cdot\text{m}^{-1}$ ).

The Langmuir-Freundlich isotherm model in high concentrations of adsorbate, it behaves in monolayer adsorption and shows the characteristics of the Langmuir isotherm. At low concentrations of adsorbate it is reduced therefore, it does not follow Henry's law (Subramanyam & Ashutosh, 2012).

Perform a literature search of natural and modified materials used for adsorption of methylene blue.

## 2. Methodology

The methodology used consisted of conducting a literature review in the literature using national and international scientific journals indexed from 2005 to 2019. Some works on adsorbents prepared from natural residues found in the

environment such as rice husks, wheat, guava leaf, papaya husks and others, serve for the adsorption of methylene blue in aqueous solutions, which have been researched by several national and international groups in the areas (materials and adsorption).

### 3. Results and Discussion

The adsorbent materials that relevance to be highlighted are: mango seed powder (Kumar & Kumaran, 2005); wheat husks (Bulut & Ayd, 2006); activated carbon obtained from rattan sawdust (Hameed *et al.*, 2007); activated carbon prepared from coconut shell (Tan *et al.*, 2008); garlic peel (Hameed & Ahmad, 2009); pummel bark modified with sodium hydroxide (Hu *et al.*, 2009); activated carbon obtained from coconut shell (Cazetta *et al.*, 2011); activated carbon obtained from coconut shell modified with sodium hydroxide (Cazetta *et al.*, 2011); activated charcoal obtained from pea husks (Geçgel *et al.*, 2012); watermelon peel modified with hydrochloric acid (Lakshmipathy & Sarada, 2013); potato skin (Alfredo *et al.*, 2015); cashew nut shell activated with zinc chloride (Spagnoli *et al.*, 2017); mesoporous carbon obtained from fish scales (Marrakchi *et al.*, 2017); bamboo (Santana *et al.*, 2018); pineapple peel (Antunes *et al.*, 2018) and bamboo (Santana *et al.*, 2019).

Table 1 shows the adsorbent materials found in the literature (2005-2019) for methylene blue adsorption.

Batch adsorption experiments were carried out by to test the adsorption capacity of methylene blue using mango seed powder. The equilibrium data were well adjusted to the Langmuir isotherm. The monolayer sorption capacity of mango seed powder for methylene blue sorption was  $142.857 \text{ mg.g}^{-1}$  (Table 1) at  $30 \text{ }^{\circ}\text{C}$  (Kumar & Kumaran, 2005).

Bulut e Ayd (2006) studied the use of wheat husks to remove methylene blue. It was found that the results obtained are better represented by the Langmuir equation. The maximum adsorption capacity was calculated at different temperatures:  $30 \text{ }^{\circ}\text{C}$  ( $6.56 \text{ mg.g}^{-1}$ ),  $40 \text{ }^{\circ}\text{C}$  ( $20.83 \text{ mg.g}^{-1}$ ) and  $50 \text{ }^{\circ}\text{C}$  ( $21.50 \text{ mg.g}^{-1}$ ) as shown in Table 1

Activated charcoal prepared from rattan sawdust was used Hameed *et al.* (2007) as an adsorbent for the removal of methylene blue dye from aqueous solutions. The balance data adjusted well to the Langmuir model, with a maximum monolayer adsorption capacity of  $294.14 \text{ mg.g}^{-1}$  (Table 1).

Tan *et al.* (2008) used Batch adsorption tests to determine the adsorption isotherm and kinetics of methylene blue on activated carbon prepared from coconut shell. The data obtained from adsorption of methylene blue were investigated from the time of contact (1-30h), initial concentration of methylene blue ( $50\text{-}500 \text{ mg.L}^{-1}$ ) and solution temperature ( $30\text{-}50 \text{ }^{\circ}\text{C}$ ). The maximum adsorption capacity was  $434.78 \text{ mg.g}^{-1}$  as shown in Table 1 for the monolayer model (Langmuir model).

Hameed e Ahmad (2009) evaluated the potential of garlic peel for removing methylene blue in aqueous solutions. The adsorption tests were performed according to the contact time, initial concentration ( $25\text{-}200 \text{ mg.L}^{-1}$ ), pH (4-12) and temperature ( $30 \text{ }^{\circ}\text{C}$ ,  $40 \text{ }^{\circ}\text{C}$  and  $50 \text{ }^{\circ}\text{C}$ ). The adsorption isotherms were obtained by adjusting the Langmuir, Freundlich and Temkin models. The experimental adsorption data for methylene blue adjusted well to the Freundlich isotherm. Maximum monolayer adsorption capacities were found to be  $82.64 \text{ mg.g}^{-1}$  ( $30 \text{ }^{\circ}\text{C}$ ),  $123.45 \text{ mg.g}^{-1}$  ( $40 \text{ }^{\circ}\text{C}$ ) and  $142.86 \text{ mg.g}^{-1}$  ( $50 \text{ }^{\circ}\text{C}$ ) (Table 1).

Hu *et al.* (2009) used the pummelo bark pretreated with sodium hydroxide for methylene blue adsorption. In order to investigate the effects of pre-treatment on the adsorption of cationic dyes, the kinetics and capacities of crude pummel hull (RPP) and sodium hydroxide-treated pummel hull (TPP) were compared to remove methylene blue in solutions aqueous. According to the maximum adsorption capacity obtained, the adsorption capacity of the pummelo bark increases significantly, going from  $170.60 \text{ mg.g}^{-1}$  to  $390.60 \text{ mg.g}^{-1}$  (Table 1), after treatment with sodium hydroxide.

From coconut fiber studied the adsorption of methylene blue on activated carbon and coal prepared. Using the Langmuir and Freundlich model the adsorption isotherms have been described. It was found that the Langmuir model fits well with the experimental data. The thermodynamic results also indicated that the adsorption of methylene blue occurs by chemical interaction. The maximum adsorption capacity was  $434.78 \text{ mg.g}^{-1}$  (Table 1) (Cazetta *et al.*, 2011).

Activated coals were obtained from coconut shell by activation with NaOH. The experimental data were adjusted to the four isotherm models (Langmuir, Freundlich, Toth and Redlich-Peterson), and it was found that the Langmuir model presented the best fit for the experimental data obtained in the adsorption of methylene blue, showing maximum capacity adsorption rate of  $916 \text{ mg.g}^{-1}$  (Table 1) reported by Cazetta *et al.* (2011).

**Table 1** - Materials for methylene blue adsorption.

Adsorbent material	$q_{max}$ (mg.g <sup>-1</sup> )	pH	Temperature (°C)	$C_0$ (mg.L <sup>-1</sup> )	Time (min)	Mass (g)	Reference
Mango seed poder	142.86	8	30	100	10-240	0.02	Kumar & Kumaran, 2005
Wheat husk	21.50	6.5	50	100	60	1	Bulut & Ayd, 2006
Rattan bark	294.14	-	30	100-200	300	0.1	Hameed <i>et al.</i> , 2007
Activated carbon from bamboo coconut shell	434.78	-	30-50	50-500	60-900	0.1	Tan <i>et al.</i> , 2008
Pomelo Rind	390.60	8	30	300	30	2	Hu <i>et al.</i> , 2009
Garlic peel	142.86	4	50	25-200	210	0.3	Hameed & Ahmad, 2009
Activated carbon prepared from bamboo bark	916	-	25	100-1000	150	0.025	Cazetta <i>et al.</i> , 2011
Pea pods (Pisum sativum)	246.91	2 - 11.5	25	100-350	180	1	Geçgel <i>et al.</i> , 2012
Watermelon	489.80	-	30	50	30	0.5	Lakshmipathy & Sarada, 2013
Coconut fiber	500	7.8	30	100-200	30	0.03	Al-Aoh <i>et al.</i> , 2014
Potato peel	48.7	-	25	100	60	0.2	Alfredo <i>et al.</i> , 2015
Activated coals from cashew nuts	476	9.9	-	20-200	1440	0.025	Spagnoli <i>et al.</i> , 2017
Mesoporous carbon prepared from fish scales	184.40	6	30	25-400	1440	0.2	Marrakchi <i>et al.</i> , 2017
Activated carbon prepared from bamboo	374.75	-	18	50	720	0.1	Santana <i>et al.</i> , 2018
Pineapple peel	17.12	-	30	100	240	0.1	Antunes <i>et al.</i> , 2018
Activated carbon from bamboo waste	298.82	6.8	25	50	12	0.01	Santana <i>et al.</i> , 2019

Source: Authors (2020).

Activated carbon was prepared from pea husk and used to remove methylene blue from aqueous solutions. The influence of several factors was studied, such as adsorbent concentration, initial dye concentration, temperature, contact time, pH. Kinetic studies showed that the adsorption followed the kinetic model of the pseudo-second order. The adsorption capacity in activated carbon monolayer was  $246.91 \text{ mg.g}^{-1}$  (Table 1) at  $25 \text{ }^\circ\text{C}$  reported by Geçgel *et al.* (2012).

Lakshmi e Sarada (2013) presented a study on the potential of watermelon peel, modified with hydrochloric acid, to remove methylene blue from aqueous solutions. The batch experiments were performed varying the contact time, pH, adsorbent dose, initial concentration and temperature. The adsorption equilibrium was reached in less than 30 min. The maximum adsorption capacity was  $489.80 \text{ mg.g}^{-1}$  (Table 1).

The efficiency of the adsorbent from the residue of the potato peel was evaluated by Alfredo *et al.* (2015), using the methylene blue cationic dye as adsorbate. The adsorption studies were conducted in a batch system and a fixed bed column. The Langmuir isotherm model was the one that best fitted the experimental data, with a maximum adsorbed amount of  $48.7 \text{ mg.g}^{-1}$ . The maximum adsorption capacity in the fixed bed (column) was  $35.83 \text{ mg.g}^{-1}$  (Table 1).

Spagnoli *et al.* (2017) prepared activated coals from cashew nut shells by chemical activation with zinc chloride. The structural characteristics of the carbons were characterized by adsorption of  $\text{N}_2$  at  $-196 \text{ }^\circ\text{C}$  and scanning electron microscopy. The surface chemistry was studied by Fourier transform infrared spectroscopy and potentiometric titration. The equilibrium adsorption data fitted better to the Langmuir equation for all the activated carbon studied. The relationship between the carbonization temperature and the adsorption capacity was also studied, and the carbonization temperature of  $500 \text{ }^\circ\text{C}$  resulted in the best value of adsorption capacity for methylene blue  $476 \text{ mg.g}^{-1}$  (Table 1).

Marrakchi *et al.* (2017) prepared a mesoporous carbon material from fish scales through chemical activation using sodium hydroxide (NaOH). The material obtained had an elevated surface area of  $1867 \text{ m}^2.\text{g}^{-1}$ , average pore size of  $2.5 \text{ nm}$  and average mesoporous volume of  $0.38 \text{ cm}^3.\text{g}^{-1}$ . The adsorption capacity of the material was studied for methylene blue in aqueous solutions. The Langmuir isotherm model was the one that best described the experimental data, and the maximum adsorption capacity observed for the material studied was  $184.40 \text{ mg.g}^{-1}$  (Table 1) at a temperature of  $30 \text{ }^\circ\text{C}$ .

Santana *et al.* (2018) studied bamboo as a raw material for the production of activated carbon through direct simultaneous physical-chemical activation, using phosphoric acid ( $\text{H}_3\text{PO}_4$ ) and water vapor ( $\text{H}_2\text{O}$ ) as activating agents. The adsorption studies were conducted in a batch system. The activated carbon produced had a relatively high surface area ( $1193.65 \text{ m}^2.\text{g}^{-1}$ ). The equilibrium time required for adsorption of methylene blue was 12 h and adsorption capacity obtained by adjusting the experimental data to the Langmuir model was equal to  $374.75 \text{ mg.g}^{-1}$  (Table 1).

Antunes *et al.* (2018) evaluated the use of pineapple peel as an adsorbent for removing methylene blue present in aqueous solutions. The adsorbent was obtained by drying and crushing the peel of the fruit. The granulometry of the material was equal to  $0.2 \text{ mm}$ . The adsorption tests were carried out in batches at  $150 \text{ rpm}$  and temperature equal to  $30 \text{ }^\circ\text{C}$  and  $40 \text{ }^\circ\text{C}$ . The pineapple peel showed a removal equal to  $81 \text{ wt.}\%$  of the methylene blue dye. The adjustment by the Langmuir model with the experimental data obtained, showed a maximum adsorption capacity for pineapple peel equal to  $17.12 \text{ mg.g}^{-1}$  ( $30 \text{ }^\circ\text{C}$ ) and  $10.06 \text{ mg.g}^{-1}$  ( $40 \text{ }^\circ\text{C}$ ) in Table 1.

Santana *et al.* (2019) used activated carbon produced from bamboo waste for the adsorption of methylene blue. To understand the adsorption, process the Langmuir and Freundlich isotherm models were selected. The adsorbent material produced showed rapid removal and high adsorption capacity for methylene blue ( $298.82 \text{ mg.g}^{-1}$ , Table 1).

#### 4. Final Considerations

An adsorption is a surface phenomenon, in occurs which is an adhesion of molecules of a fluid that stays on the surface of a solid adsorbed material, also according to the adsorption classification can be of two types: physisorption and chemisorption, in relation to how forces that attracts or adsorbs. The textile industries are polluting sources for the environment, mainly using one of the raw materials, which are the textile dyes, which are discarded in an inappropriate way to the environment, causing the impediment of the penetration of light in the water bodies. In this context, the research was carried out in aim to verify the solid adsorbent materials used for dye adsorption (methylene blue) from 2005 to 2019.

Thus, the adsorbent materials researched in the literature for adsorption of methylene blue were: mango seed powder, wheat husks, activated carbon obtained from rattan sawdust, activated carbon prepared from coconut shell, garlic shell, NaOH modified pummell shell, activated carbon (coconut shell and modified with NaOH), activated carbon (pea peel), HCl modified watermelon peel, potato peel, ZnCl<sub>2</sub> activated cashew nut peel, mesoporous carbon obtained from fish scales, pineapple peel and bamboo.

Subsequently, for future publication in the journal, the authors propose the use of natural adsorbent materials for the removal of methylene blue, as agro-industry waste, as they are disposed of in the environment at their final destination, without any proper treatment, thus contributing for environmental pollution. The adsorbent materials for methylene blue will be characterized by X-ray Diffraction (XRD), Fourier transform infrared (FTIR), Scanning Electron Microscopy (SEM), thermogravimetric analysis (TGA), and textural parameters (surface area, average pore volume and average pore diameter). The adsorptive tests will be conducted in batches using synthetic methylene blue solutions and tested for some natural adsorbents, such as white eggshell, marine waste and natural shell residue. Thus, studying the feasibility of natural adsorbent materials for methylene blue adsorption.

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