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Exploring the adsorption behavior on scrapped pallet

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ABSTRACT
Pallets are widely used for moving loads, but they are often disposed of improperly due to the cost associated with their correct disposal. This study focused on transforming expired pallets into pallet coal (CP) and investigating its properties, performing the determination of the Langmuir isotherm using primary standard solutions. The results obtained with the gravimetric yield were 66.05%, which indicates an excellent cost/benefit ratio. The isotherm obtained is characterized by a favorable adsorption, with saturation of the sites around 0.014 $g.L^{-1}$,, with a layer close to a concentration of 3.3 $mol.L^{-1}$. The active area of this pallet charcoal was estimated at 715.94$m^2.g^{-1}$. This study was dedicated to evaluating the adsorption capacities of the discarded material, aiming at its reuse in a more sustainable way, thus contributing to the preservation of the environment. Turning the discarded material into an adsorbent not only adds value to the product, but also significantly reduces the industry costs associated with conventional disposal.

Keywords: Wooden Pallet, Activated Carbon, Adsorption, Langmuir Isotherms.

INTRODUCTION

We note that industrial growth is always desirable, and well-liked for human development. However, there are different emissions of waste and environmental pollutants in practically the same proportions as this industrial evolution (AGUIAR, SILVA, EL-DEIR, 2019).

According to Bertaglia (2005), the pallet is a platform used in the handling of loads, built of wood or made of fiber and metal, and is widely used in the logistics and storage sector for transport activities within industry and commerce.

The wooden pallet has had a significant presence in the Brazilian market since the 1960s as a logistics facilitator in the automotive industry, and its participation remained stagnant until the mid-1980s (MENDES, 2023).

In the current Brazilian market there are about eight types of pallets, each of which is designed for a certain function, both economical and sustainable. Among these, those planned by ABRAS (Brazilian Association of Supermarkets) are made of wood PBR (Brazilian Standard Pallet) and plastic (MENDES, 2023).

Figure 1 - PBR wooden pallet.

Source: Authored by the authors, 2024.

The pallets can be produced from reforestation wood, authorized by Ibama (Brazilian Institute of the Environment), with a predominance of pine and eucalyptus trees, the latter being more prominent (HASSMADEIRAS, 2018).

The wood does not have a specific expiration date, however the wooden pallets sold have an average useful life of no more than three years, in addition to being prone to changes due to climate, fungi, and lack of appropriate maintenance (SBPALLETS, 2022).

The consumption of wooden pallets in Brazil annually is around three million, as companies still do not find a way to maximize their costs/benefits after their useful life, it is common to observe their abandonment in the environment (GÜLLICH, UHMANN, 2019).

Recycling, reducing, and reusing are key to reducing waste or improper disposal of materials. The pallet can be reused, avoiding the increase in environmental pollution and also reducing the consumption of raw materials in the purification of tailings, preserving natural resources (FONSECA, 2013)

According to Lima and Silva (2005), the economy of other energy sources can also be linked to the use of various residues as raw material in obtaining them, provided that these are preferably free of contaminants or substances that may impair the operation and/or useful life of boilers, among others. In this energy process, it is interesting to combine materials with high heat capacity in order to improve the cost-benefit of the entire action.

The use of wood waste, using pyrolysis in the production of activated carbon, has added value due to the fact that they are adsorbents of pollutants, since they have compatible porosities and enormous potential in this type of application (CZAJCZYNSKA *et al.*, 2017).

The transformation of wood waste into charcoal can be carried out by heating it in an oxidizer-poor medium, concentrating carbon and eliminating oxygen in the pyrolysis process (SILVA, ANDRADE, JÚNIOR, 2020; SILVA *et al*., 2022).

There are several types of charcoal, with the main differences being the way it is obtained, the porosity and the surface area. The most common are mineral charcoal, vegetable charcoal and activated charcoal (MIMURA, SALES, PINHEIRO, 2010; GAMA *et al*., 2022).

Activated carbon has been the most common adsorbent used in the removal of volatile compounds under gaseous conditions (AMÉRICO-PINHEIRO, BENINI, AMADOR, 2016).

The adsorption capacity of a material can be correlated with the surface area available in it. Sometimes, the removal of carbonaceous organic compounds can be accomplished simply by applying controlled high temperatures to the material (AMÉRICO-PINHEIRO, BENINI, AMADOR, 2016).

Langmuir worked on the basis of the theory of adsorption applied to homogeneous surfaces, where a monomolecular layer is formed, based on the concept that each active site accommodates only one adsorbed unit and that the energy can be distributed equally to all sites, according to equation 1 (MORAIS, 2014; MELANI *et al*., 2021).

$$\frac{C_e}{Q_e} = \frac{1}{Q_m\, K_L} + \frac{1}{K_L}\, C_e \qquad \text{Equation 1}$$

In this equation (1) KL represents the Langmuir constant which is the theoretical adsorption capacity in the monolayer, C_{is} the adsorbent concentration at equilibrium, Q_m the constant related to the adsorption energy and Q_{is} the ratio of the amount of adsorbate and adsorbent in equilibrium (ATKINS, 2017).

According to Fernandes (2008), in the model proposed by Langmuir, the equilibrium parameter (RL) indicates a favorable adsorption when the values are above zero and below one, according to equation 2 (FERNANDES, 2008).

$$R_L = \frac{1}{(1 + K_L\, Q_m)} \qquad \text{Equation 2}$$

Above all, adsorption isotherms are curves, which at constant temperature, can be described by mathematical equations, since they come from physical models, which are determined experimentally with adsorption (DABROWSKI, 2001).

The information generated from the interpretation of this equation model projects what type of adsorption occurred, how much was adsorbed of the substance, and furthermore, whether the process is feasible (DABROWSKI, 2001).

This work used the wooden pallet or pallet discarded by the industry, and transformed it into activated carbon through pyrolysis at low temperature, in order to add value to a waste that was often discarded incorrectly and use it as adsorbent of impurities.

METHODOLOGY

The raw material of this work was wooden pallets, after the end of their useful life, donated by companies in the city of Apucarana, State of Paraná, Brazil. These were disassembled and cut before being subjected to the various analyses.

Only a reasonable amount of the pallet was used to carry out the experiments, the average dimensions obtained after being cut were (2 cm x 2 cm x 4 cm) being width, height and length.

The pallets were submitted to moisture and ash content analysis according to the methodology of the *Association of Official Analytical Chemists* (AOAC, 1998).

The dough was initially weighed in triplicates of approximately 500 g which were subjected to pyrolysis with the aid of Jung muffle, *LF0212*, in different experimental temperature tests to maximize productivity. After this step, a heating isotherm was used at 350°C for 7 hours to obtain the charcoal. The initial and final masses are used in the determination of the gravimetric yield.

The charcoal obtained was crushed in a Blend blender until powder was obtained and packaged in airtight jars for the determination of the Langmuir isotherms, according to the work of Perry (1988) and Valencia (2007) adapted by Melani *et al*., 2021.

Langmuir isotherms were characterized using different concentrations of oxalic acid (primary standard) and titrated with sodium hydroxide to be quantified (PERRY, 1998; VALENCIA, 2007; MELANI *et al*., 2021).

Samples of pallet charcoal (CP) were weighed at an average mass value (*m*) of 0.5g. And, the erlenmeyers were filled with oxalic acid (C_{2H2O4}) and water (H2O), as shown in Table 1, for the analysis of quantification of CP adsorption using oxalic acid (C_{2H2O4}), with a concentration (*C*) of 0.003 mol. L-1.

Table 1 - Oxalic acid volumes, water and final volume in the adsorption experiments.

Experiment	Oxalic Vacuum (mL)	Water (mL)	Vfinal (mL)
01	100,0mL	0mL	100,0mL
02	80,0mL	20,0mL	100,0mL
03	60,0mL	40,0mL	100,0mL
04	50,0mL	50,0mL	100,0mL
05	40,0mL	60,0mL	100,0mL
06	20,0mL	80,0mL	100,0mL
07	10,0mL	90,0mL	100,0mL
08	5,0mL	95,0mL	100,0mL
09	3,0mL	97,0mL	100,0mL
10	1,0mL	99,0mL	100,0mL
11	0,5mL	99,5mL	100,0mL
12	0,2mL	99,8mL	100,0mL

Source: Authored by the authors, 2023.

The samples were prepared in the laboratory, without changes in temperature (T) and pressure (P). The erlenmeyers were taken to an orbital stirring incubator, *Cienlab*, *CE 725*, for 3 hours, at 50 rpm, using room temperature, for the effect of greater interaction between adsorbent and adsorbate.

The experiments were left at rest for 19 h, still sealed so that there would be no interference with the environment. Soon after this period, the aliquots were filtered, discarding a small initial amount, when cleaning the filter paper. The pipettes were acclimated, except to remove contaminants or undesirable substances, so they were titrated with 0.2 mol sodium hydroxide (NaOH). mol.L^{-1}, applying the phenolphthalein indicator for the quantification of oxalic acid adsorption, according to the chemical reaction:

$$H_2C_2O_4 + 2\ NaOH \rightarrow Na_2C_2O_4 + 2\ H_2O$$

With the data obtained through the experiments, the construction of the Langmuir isotherms was performed using equations 1 and 2.

RESULTS AND DISCUSSION

The result of gravimetric yield can be defined as the relationship between the amount of charcoal produced and the amount of wood baked, and the chemical composition of the wood and the temperature range used influence the charcoal yield (OLIVEIRA *et al*., 2010; Petroff & DOAT, 1978).

The gravimetric yield results obtained in this study with the transformation of pallet into charcoal was equal to 66.05%. These values are extremely satisfactory, since the methods used in traditional systems in the production of coal, in general, establish a yield in the range of 25% to 33% (BARCELLOS, 2004).

The value obtained for the gravimetric yield of the work was higher than that of Gomes (2019), who had the highest average yield in charcoal of 37.15%, from the operation with a final pyrolysis temperature of 400°C.

The high performance obtained with pallets is probably justified by the fact that it is obtained at a low average temperature (350ºC) and comes from pressed wood (with high density) capable of withstanding the transport of heavy loads (MACHADO *et al.*, 2014; BRIANE & DOAT, 1985).

During pyrolysis, volatile materials are released, which contributes to the loss of volume and mass (temperature range between 300° and 500°C), leading to a reduction in density (GOMES, 2019).

The heating rate, the nature of the raw material and the final temperature are the relevant parameters that will determine the quality and yield of the carbonized material (CLAUDINO, 2003).

The study by Brito & Barrichelo (1981) carried out with different types of wood from the Amazon region concluded that wood density directly influences charcoal yield. In addition, charcoal companies try to homogenize the average diameter of the baked logs in order to reduce fines (ashes) and improve the standardization of the quality of the final product (OLIVEIRA, 2009).

Data from Mello and Anunciação (2015) report that in 2013 the cost of disposing of the pallet is R$ 31.50 (thirty-one reais and fifty cents), or approximately $ 6.30 (six dollars and 30 cents).

The companies that process and collect the pallets, price according to the location and quantity, and prefer to keep the values confidential. Meanwhile, on pallet sales sites, new pallets of the PBR model can vary from R$ 48.00 (forty-eight reais), or approximately $ 9.60 (nine dollars and sixty cents) and export standard with certificate of R$ 120.00 (one hundred and twenty reais) or approximately $ 24 (twenty-four dollars), and may change according to the buyer's demand.

It is interesting to realize that when you compare the price of the new one in 2024 and the price of the disposal 10 years ago, the disposal costs about 66% of the new one, but nowadays the percentage can be even higher. So, in this way, the production of charcoal with the pallet becomes viable, due to its low cost.

The results of moisture and volatile content and percentage of ash obtained in the raw material are presented in Table 2.

Table 2 - Moisture and volatile content and percentage of ash on pallets.

Moisture content and volatiles	**Theory of Ashes**
12,12% ± 0,38	1.87% ± 0.37

Results expressed as Mean ± Standard Deviation of analyses in triplicate
Source: Authored by the authors, 2023.

The moisture content and volatiles obtained in this work with the pallet was equal to 12.12%, satisfactory values according to Farinhaque (1981), because for coals produced from wood, values below 25% result in a satisfactory energy use.

It is worth noting that one of the most important operations in the use of wood is drying and that this is inversely proportional to the calorific value (CAMPOS *et al.*, 1985). The pallets used in this study were probably subjected to dehumidification and preservation processes that corroborated the determination of humidity and volatiles.

Only the core of the wood is used to make the pallet, and all the wood must be debarked, before undergoing heating, to carry out the heat treatment, with an average temperature of 56 °C or 132 °F (LOGIMINAS, 2023).

The removal of moisture from the wood can be done through heat treatment, generating conditions that reduce the propensity to rot, and increase resistance to climatic variations (LOGIMINAS, 2023).

The ash content is related to the content of inorganic matter, the origin and composition of the material, which have characteristics that determine the formation of ash, generally lignocellulosic biomass has values between 0.2% and 9.5% (LOPES *et al.*, 2013).

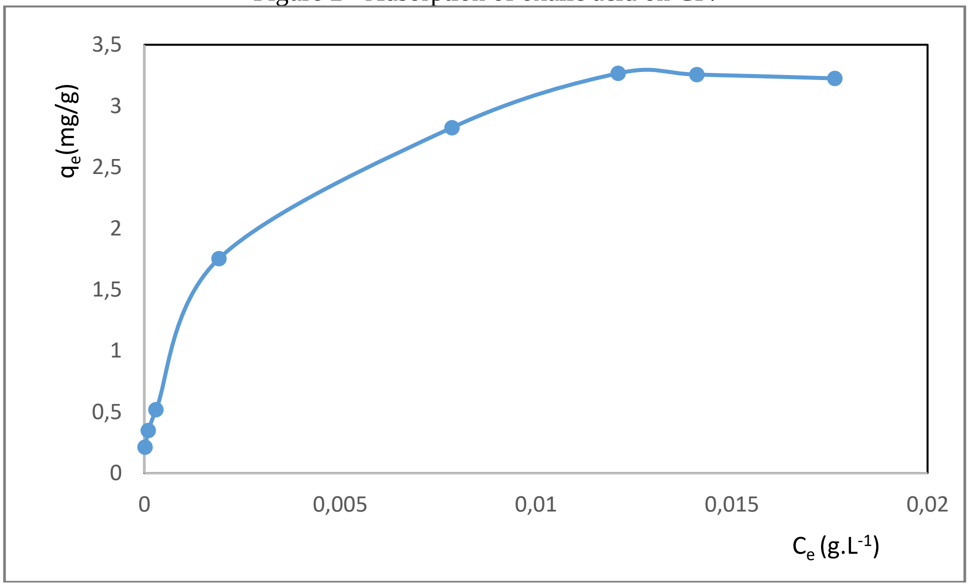
Low ash values are always preferred, in this study carried out with pallet the value obtained was equal to 1.87 %, according to the parameters that are established to obtain the coal (LOPES *et al.*, 2013).

The effect that the ash causes in the adsorption is the reduction due to the fact that it causes blockage of the carbonic matrix, and consequently promotes the preferential adsorption of water, due to its hydrophilic character (RAO *et al.*, 2000).

The results of the ratio of mass of raw material used by mass produced of coal from pallet was on average equal to 3.92 ± 0.59 $g.g^{-1}$. These results are below those obtained by Santos and Hatakeyama (2012), who obtained values of 4.5 to 5 $g.g^{-1}$using eucalyptus.

Figure 2 was constructed with values of q_e (the maximum amount of solute retained in the adsorbent at equilibrium) and C_e (concentration at this equilibrium).

Figure 2 - Adsorption of oxalic acid on CP.



Source: Authored by the authors, 2023.

The visualization of Figure 2 allows us to observe a concave isotherm characteristic of an extremely favorable adsorption (SCHONS, 2010).

The isotherm obtained, type I, shows that the adsorbate and the adsorbent have affinity. In addition, it is observed that the first region of the curve is highly vertical (evidencing the formation of the monolayer), probably due to the adsorption of micropores followed by the *plateua* (limit saturation corresponding to the filling of the micropores) characteristic of the isotherms described by Langmuir (BRUNAER *et al.*, 1938; Hamadaoui & Naffrechow, 2007).

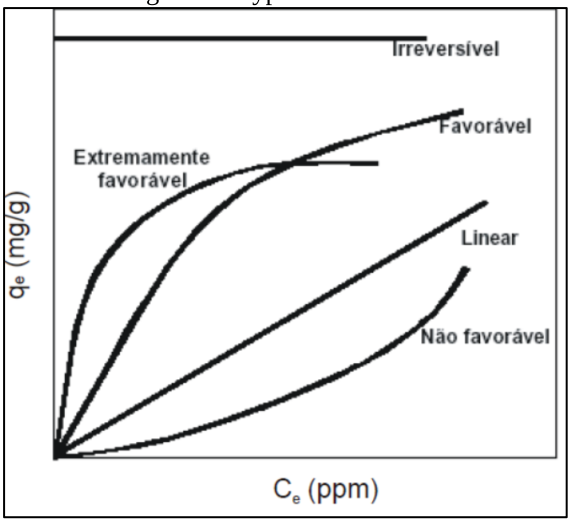
Figure 2 shows a saturation of the active sites (*plateau)* in the pallet charcoal close to 0.014 g. mol.L^{-1}, which may indicate a high adsorption capacity in relation to its production cost, bearing in mind that this work was carried out with discarded material. In addition, a layer with a concentration of 3.3 mol was formed. mol.L^{-1}.

According to Nascimento *et al*. (2014), as the contact between the adsorbate and the adsorbent occurs, molecules and ions circulate from the solution to the surface of the adsorbent until a constant equilibrium concentration of the solute in the liquid phase (C_{and}) is reached. The determination of the adsorption capacity of the adsorbent (q_e) is predicted at the moment when the equilibrium state is reached in the system, according to equation 4 (SCHONS, 2010).

$$q_e = \frac{(C_0 - Ce)\,V}{m} \qquad \text{Equation 4}$$

The work of Schons (2010) presented Figure 3, with different types of isotherms to facilitate their characterization, where q_e is the maximum amount of solute retained in the adsorbent at equilibrium and C_{is} the concentration at this equilibrium.

Figure 3 - Types of isotherms.



Cast iron: SCHONS, 2010.

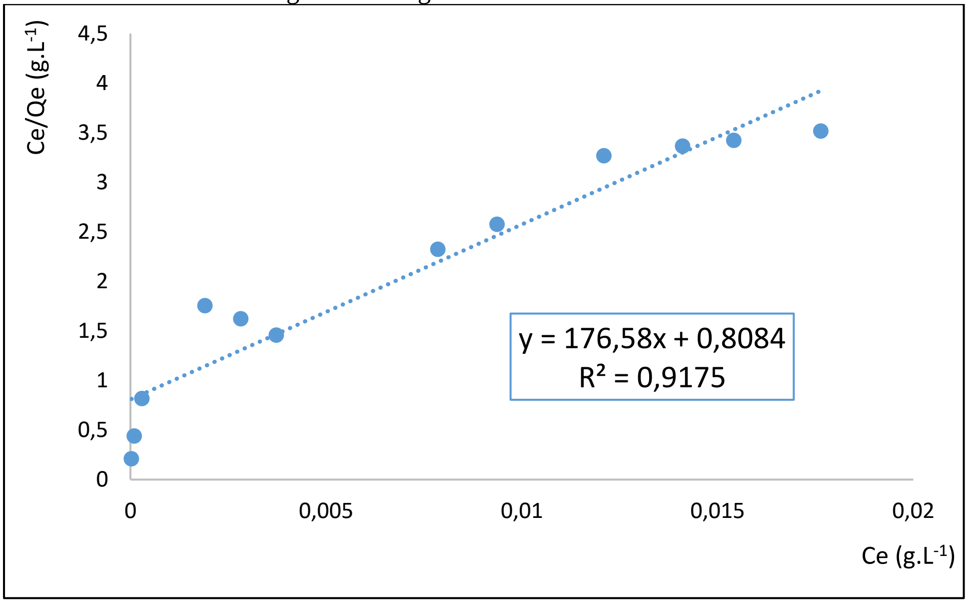
The visual comparison between Figure 2 and Figure 3 indicates that oxalic acid adsorption in CP was extremely favorable (SCHONS, 2010).

H-type isotherms (*high affinity*) is an act where the L-type curve, this being a special case, that at the time of visualization, the surface of the adsorbent has a great affinity for the adsorbed solute (FALONE, VIEIRA, 2004).

The isotherms that are expressed as type H (*high affinity*), are characteristic of when the adsorbate has a great affinity for the adsorbent, working as follows, the amount adsorbed at the beginning is high, but soon after equilibrium is reached (SCHONS, 2010).

Above all, adsorption isotherms are curves, which at constant temperature, can be described by mathematical equations, since they come from physical models, which are determined experimentally with adsorption (DABROWSKI, 2001).

Figure 4 - Langmuir isotherm for the CP.



Source: Authored by the authors, 2023.

The equation obtained in the Langmuir isotherm for pallet coal was equal to

$$\frac{C_e}{Q_e} = 176{,}58\, C_e + 0{,}8084$$

With this equation combined with equation 2, the parameters in Table 3 can be determined (FAHMI *et al*., 2021).

Table 3 - Main parameters obtained from the Langmuir isotherms.

Parameter	**Qm (mol.g^{-1})**	**KL (L.mol-1)**	**RL**	**Active coal area (m2.g-1)**
CP	5.66x10-3	218,43	6.96x10-3	715,94

Source: Authored by the authors, 2023.

According to the estimates of FAHMI *et al*. (2021), for activated carbon, the surface area of this synthetic material can vary between 100 and 500 $m^2.g^{-1}$ depending on the carbonization temperature.

Materials produced at temperatures of 350ºC obtained 523 $m^2.g^{-1}$, while those obtained at 250ºC resulted in 325 $m^2.g^{-1}$ followed by those with an area equal to 147 $m^2.g^{-1}$ at 150ºC.

The PC obtained an active area of 715.94 $m^2.g^{-1}$, values higher than those estimated by FAHMI *et al*., (2021). However, Melani *et al*., (2021) obtained values equal to 965.20 $m^2.g^{-1}$ in coconut shell charcoal and 887.35 $m^2.g^{-1}$ in commercialized pine activated carbon. It is interesting to note that the CP was made with pallets treated to support load.

Costa *et al*. (2015) worked with walnut shell charcoals, non-activated (408 $m^2.g^{-1}$) and activated with ZnCl2 (427 $m^2.g^{-1}$). In relation to this study, the PC was 40% to 43% higher in active area.

The active area was calculated by multiplying Avogadro's constant ($6,02x10^{23}$ mol) by the cross-sectional area of oxalic acid ($2,10x10^{-19}$ m^2), and by the amount of adsorbed matter per gram of adsorbent $mol.g^{-1}$).

The level of adsorption of coal to adsorb materials is dependent on certain factors, such as the distribution of active sites or pores, the surface of the activated carbon, the molecules adsorbed and the activation process (CLAUDINO, 2013).

The maximum amount of oxalic acid adsorbed by the pallet charcoal was equal to $5,66x10^{-3}$ $mol.g^{-1}$. This value was approximately 50% higher than the study by FOYA *et al*. (2014), with activated charcoal from tamarind seeds with oxalic acid that obtained values equal to $4,66x10^{-3}$ $mol.g^{-1}$.

In the comparison between the maximum amount adsorbed by PC and the study by Melani *et al*. (2021), it can be noted that the value was approximately 23% below the average values (7.35x10-3 mol.g-1).

The Langmuir constant (KL), the theoretical adsorption capacity in the monolayer obtained in the CP was equal to 218,43 $L.mol^{-1}$, a value higher than that obtained by Foya *et al*. (2014), (58,96 $L.mol^{-1}$) with tamarind seed charcoal and close to that of the study by Melani *et al*. (2021), with green coconut shell charcoals (167,59 $L.mol^{-1}$) and commercial pine activated carbon (227,16 $L.mol^{-1}$).

The LR value in the PC was above zero and below one, indicating that the adsorption process was favorable (FERNANDES, 2008).

The results obtained with PC show a product with the potential to contribute as an adsorbent. Transforming the discarded pallet into adsorbent (charcoal) adds value to this waste, preserving the environment and contributing to minimize the practice of abandoning this material in an irregular way.

It is important to point out that the use of the discarded pallet for the production of a new product (coal) can promote greater awareness in the logistics, storage and productivity sectors, expanding the next possibilities of reusing the discarded material.

Brazil imports activated carbon from China at a cost in the range of R$ 3,000.00 (three thousand reais) to R$ 7,400.00 (seven thousand and four hundred reais) per ton, that is, between $ 600 (six hundred dollars) to $ 1480.00 (one thousand four hundred and eighty dollars) (MADE IN CHINA, 2023). Producing one's own charcoal from pallets (discarded) can be a differential in the cost/benefit ratio of several companies.

The usefulness of activated carbon varies enormously as it has been applied since Roman times in primary processes of water purification, pharmaceuticals, personal hygiene, gas purging, oil recovery, sewage purification, among others (FOYA *et al*., 2014). Studies involving higher sources of activated carbon should be encouraged in order to optimize environmental supplies.

However, pallet charcoal has shown great potential to establish itself as a good adsorbent, in addition to being economically and environmentally viable.

CONCLUSION

This work transformed a solid waste, the expired pallet, into charcoal. The result of the gravimetric yield obtained was equal to 66.05%, a high value that provides an excellent cost/benefit, since the raw material was donated, or it is necessary to receive values from the companies to carry out the proper disposal.

With the construction of the Langmuir isotherm, applying oxalic acid adsorption, it was evident that the adsorption was favorable with CP, and the saturation of the sites was close to 0,014 $g.L^{-1}$ with a layer close to the concentration of 3,3 $mol.L^{-1}$.

The Langmuir isotherms obtained through the experiment showed significant results, with an r2 value equal to (0.9175).

The CP obtained an active area of 715,94 $m^2.g^{-1}$, these results were obtained with expired pallets, values 40 % to 43 % higher than those found by Costa *et al*. (2015) with walnut shell charcoals, unactivated (408 $m^2.g^{-1}$) and activated with ZnCl2 (427 $m^2.g^{-1}$).

The maximum amount of oxalic acid adsorbed by the pallet charcoal was equal to 5.66x10-3 $mol.g^{-1}$. This value was approximately 23% below the average values obtained by Melani *et al*., 2021, who worked with different coconut shell charcoals with an average value equal to 7.35x10-3 $mol.g^{-1}$.

It is important to remember that we worked with the wooden pallet, which has gone through a whole cycle of use in the industry, and which in many cases after its saturation is discarded irregularly in nature.

This work was committed to studying the adsorption capacities of the discarded material, planning and predicting whether there would be viability for a new way of using the product, with the main bias of contributing to the environment.

Transforming the discarded material into adsorbent adds value to the product and also substantially reduces the cost of the industry with regular disposal.

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