Assessment of adsorption capacity on pallet coal

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ABSTRACT

Pallets are widely used for moving cargo, however, they are often disposed of inappropriately, due to the cost associated with their correct disposal. This study focused on transforming expired pallets into pallet coal (PC) and investigating its properties, carrying out the determination of the Langmuir isotherm, employing primary standard solutions. The results obtained with the gravimetric yield were 66.05%, which indicates an excellent cost/benefit. The isotherm obtained is characteristic of a favorable adsorption, with saturation of the sites occurring at 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 coal was estimated at 715.94m2.g-1. This study was dedicated to evaluating the adsorption capabilities of discarded material, aiming for its reuse in a more sustainable way, thus contributing to the preservation of the environment. Transforming discarded material into an adsorbent not only adds value to the product, but also significantly reduces industry costs associated with conventional disposal.

Keywords: Wooden pallet, Activated charcoal, Adsorption, Langmuir isotherms.

INTRODUCTION

We note that industrial growth is always desirable, and well-liked for human development. However, different emissions of waste and environmental pollutants are observed 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 movement of cargo made 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 around eight types of pallets, each designed for a specific function, both economic and sustainable. Among these, those planned by ABRAS (Brazilian Supermarket Association) made of wood PBR (Brazilian Standard Pallet) and plastic ones (MENDES, 2023).

Figure 1 - PBR wooden pallet.

Source: Own authorship, 2024.

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

Wood does not actually have a specific expiration date, however the wooden pallets sold have an average useful life of a maximum of 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 have not yet found a way to maximize the costs/benefits of these after their useful life, it is common to observe their abandonment in the environment (GÜLLICH, UHMANN, 2019).

Recycling, reduction and reuse are fundamental to reducing waste or inappropriate 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 waste, preserving natural resources (FONSECA, 2013)

According to Lima and Silva (2005), the savings from other energy sources can also be linked to the use of various wastes as raw materials in obtaining them, as long as they are preferably free of contaminants or substances that could harm the functioning and/or or the 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, employing pyrolysis in the production of activated carbon, has added value due to the fact that they absorb pollutants, as 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 in a low-oxidant environment, concentrating carbon and eliminating oxygen in the pyrolysis process (SILVA, ANDRADE, JÚNIOR, 2020; SILVA et al., 2022).

There are several types of coal, the main differences arising from the way of obtaining, porosity and surface area. The most common are mineral, vegetable and activated charcoal (MIMURA, SALES, PINHEIRO, 2010; GAMA et al., 2022).

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

The adsorption capacity of a material can be correlated with the surface area available there. Sometimes, the removal of carbonaceous organic compounds can be carried out simply with the controlled application of high temperatures to the material (AMÉRICO-PINHEIRO, BENINI, AMADOR, 2016).

Langmuir worked by substantiating 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 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) K_L represents the Langmuir constant which is the theoretical adsorption capacity in the monolayer, C_e the adsorbate concentration at equilibrium, Q_m the constant related to the adsorption energy and Q_e is the ratio of the amount of adsorbate and adsorbent at equilibrium (ATKINS, 2017).

According to Fernandes (2008), in the model proposed by Langmuir, the equilibrium parameter (RL) indicates favorable adsorption when 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, the adsorption isotherms are curves, which at constant temperature, can be described by mathematical equations, given that 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, and how much of the substance was adsorbed, and furthermore, whether the process is viable (DABROWSKI, 2001).

This work used wooden pallets or pallets discarded by the industry, and transformed it into activated carbon through low-temperature pyrolysis, with the aim of adding value to waste that is often incorrectly discarded and using it as an adsorbent for impurities.

METHODOLOGY

The raw material for this work were wooden pallets, after the end of their useful life, donated by companies in the city of Apucarana, State of Paraná, Brazil. These were dismantled and cut before being subjected to 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 subjected to moisture and ash content analyzes according to the Association of Official Analytical Chemists (AOAC, 1998) methodology.

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

The charcoal obtained was crushed in a Blend blender until powder was obtained and placed in airtight bottles to determine the Langmuir isotherms, according to the works of Perry (1988) and Valencia (2007) adapted by Melani et al., 2021.

The 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).

Pallet coal (PC) samples were weighed at an average mass value (m) of 0.5g. And, the erlenmeyer flasks were filled with oxalic acid ($C_2H_2O_4$) and water, as shown in Table 1, for the PC adsorption quantification verification analyzes using oxalic acid, with a concentration of 0.003 $mol.L^{-1}$.

Table 1 - Volumes of oxalic acid, water and final volume in adsorption experiments.

Experiment	$V_{Oxalic\ acid}$ (mL)	V_{Water} (mL)	V_{final} (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: Own authorship, 2024.

The samples were prepared in the laboratory, without changes in temperature (T) and pressure (P). The erlenmeyer flasks were placed in an orbital shaking incubator, *Cienlab*, *CE 725*, for 3h, at 50 rpm, using room temperature, for the effect of greater interaction between adsorbent and adsorbate.

The experiments were left to rest for 19 h, still sealed to prevent interference with the environment. Immediately after this period, the aliquots were filtered, discarding a small initial quantity when cleaning the filter paper. The pipettes were conditioned, except to remove contaminants or undesirable substances, and were then titrated with sodium hydroxide (NaOH) of 0.2 $mol.L^{-1}$, applying the phenolphthalein indicator for quantification of adsorption of oxalic acid, 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 Langmuir isotherms was carried out 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 fired, with the chemical composition of the wood and the temperature range used influencing the charcoal yield (OLIVEIRA *et al*., 2010; PETROFF & DOAT,1978).

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

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

The high performance obtained with pallets is probably justified by being obtained at a low average temperature (350ºC) and coming from pressed wood (with high density) capable of supporting 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°C to 500°C), resulting in 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 the density of the wood directly influences the charcoal yield. Additionally, companies producing charcoal try to homogenize the average diameter of the logs fired in order to reduce fines (ash) and improve the standardization of the quality of the final product (OLIVEIRA, 2009).

Data from Mello & Anunciação (2015) report that in 2013 the cost of disposing of a pallet was approximately $6.30 (six dollars and 30 cents). The companies that process and collect the pallets price according to location and quantity, and prefer to keep the values confidential. Meanwhile, on pallet sales sites, new PBR model pallets can vary from approximately $9.60 (nine dollars and sixty cents) and export standard with certificate approximately $ 24 (twenty-four dollars), subject to change according to the buyer's demand.

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

The results of the 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 in pallets.

Moisture and volatiles	Ash
12,12% ± 0,38	1,87% ± 0,37

Results expressed as Mean ± Standard deviation of triplicate analyzes

Source: Own authorship, 2024.

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

It is worth highlighting 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 work were probably subjected to dehumidification and preservation processes that corroborated the determination of humidity and volatiles.

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

The removal of moisture from wood can be done through heat treatment, creating 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).

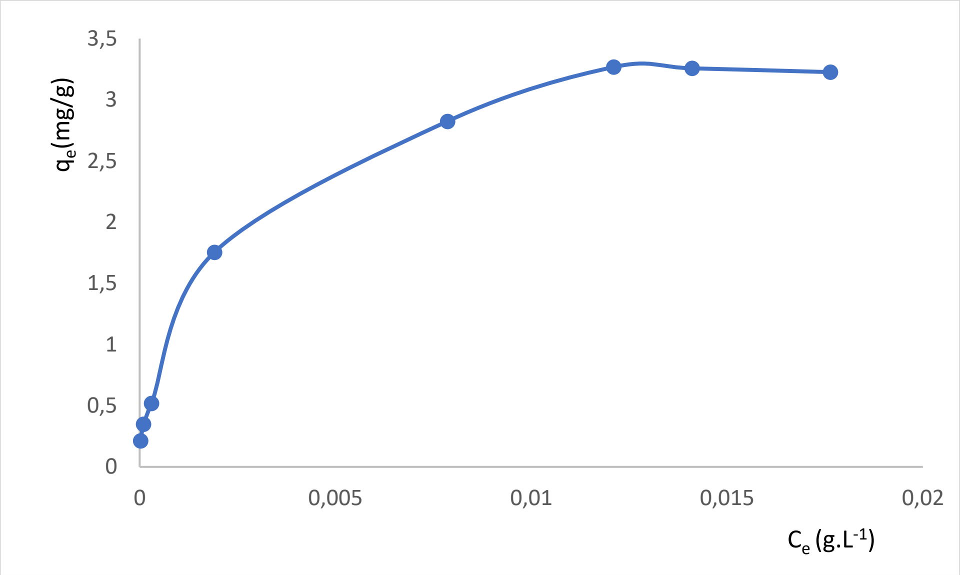
Low ash values are always preferred, in this study carried out with pallets the value obtained was equal to 1.87%, according to the parameters that are established to obtain charcoal (LOPES *et al*., 2013).

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

The results of the mass ratio of raw material used per mass of charcoal produced from pallets was on average equal to 3.92 ± 0.59 $g.g^{-1}$. Results below those obtained by Santos & 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 PC.



Source: Own authorship, 2024.

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

The type I isotherm obtained shows that the adsorbate and the adsorbent have affinity. Additionally, it is observed that the first region of the curve appears highly vertical (evidence the formation of the monolayer) probably due to the adsorption of micro pores followed by the plateau (limit saturation corresponding to the filling of the micro pores) characteristic of the isotherms described by Langmuir (BRUNAER *et al*., 1938; HAMADAOUI & NAFFRECHOW, 2007).

In Figure 2, you can see a saturation of active sites (plateau) in pallet coal close to 0.014 $g.L^{-1}$, which may indicate a high adsorption capacity, in relation to its production cost, remembering that this work was carried out with material discarded. Additionally, a layer with a concentration of 3.3 $mol.L^{-1}$ was formed.

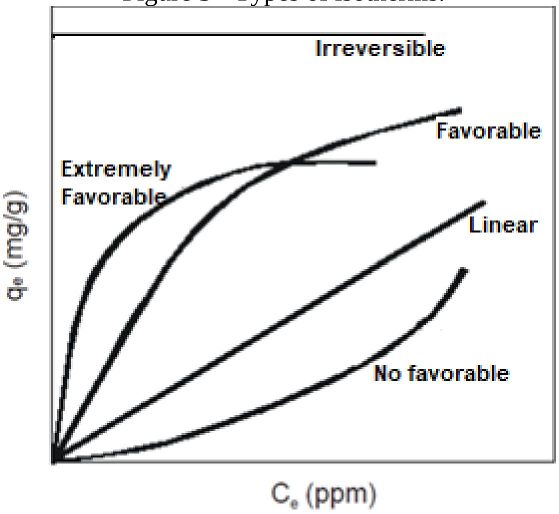
According to Nascimento *et al*. (2014), as the contact between the adsorbate and the adsorbent occurs, molecules and ions circulate from the solution to the surface of the adsorbent, until reaching a constant equilibrium concentration of the solute in the liquid phase (C_e).

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 by Schons (2010) presented Figure 3, with different types of isotherms to facilitate their characterization, where qe is the maximum amount of solute retained in the adsorbent at equilibrium and Ce is the concentration at this equilibrium.

Figure 3 - Types of isotherms.



Source: SCHONS, 2010.

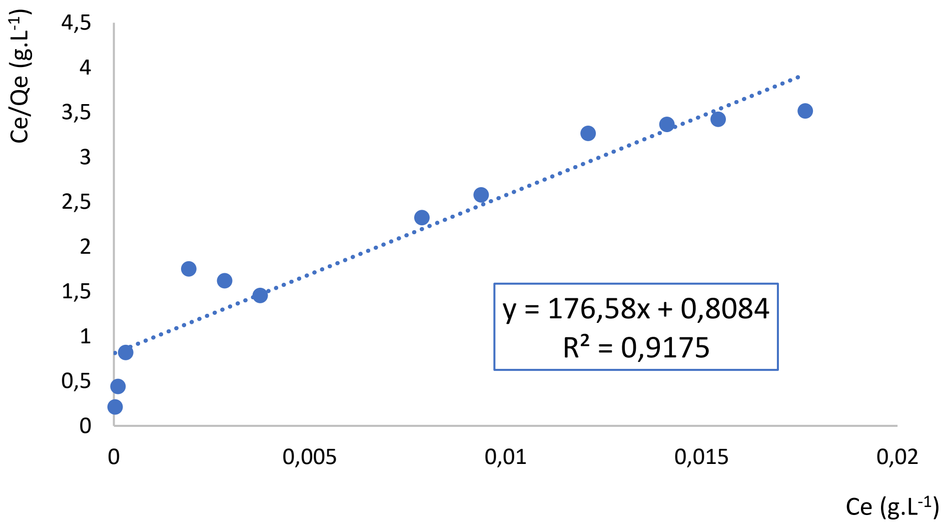
The visual comparison between Figure 2 and Figure 3 indicates that the adsorption of oxalic acid on CP was extremely favorable (SCHONS, 2010).

H-type isotherms (high affinity), is an act where the L-type curve, this being a special case, where 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 high affinity for the adsorbent, working as follows, the amount adsorbed at the beginning is high, but soon after reaching equilibrium (SCHONS, 2010).

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

Figure 4 – Langmuir isotherm for PC.



Source: Own authorship, 2024.

The equation obtained from 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 Langmuir isotherms.

Parameter	Q_m (mol.g^{-1})	K_L (L.mol^{-1})	R_L	Active coal area (m^2.g^{-1})
CP	5,66x10^{-3}	218,43	6,96x10^{-3}	715,94

Source: Own authorship, 2024.

According to estimates by 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 commercially available pine activated charcoal. It is interesting to highlight that the PC was made with pallets treated to support loads.

Costa *et al.* (2015) worked with charcoal from walnut shells, not activated (408 m^2.g^{-1}) and activated with $ZnCl_2$ (427 m^2.g^{-1}). In relation to this work, the PC was 40% to 43% higher in the 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 matter adsorbed per gram of adsorbent (mol.g^{-1}).

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

The maximum amount of oxalic acid adsorbed by pallet charcoal was equal to 5.66x10^{-3} mol.g^{-1}. This value was approximately 50% higher than the study carried out by FOYA *et al.* (2014), with activated charcoal from tamarind seeds with oxalic acid, which 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 (K_L), the theoretical adsorption capacity in the monolayer obtained in PC 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 the study by Melani *et al*. (2021), with green coconut shell charcoal (167.59 L.mol^{-1}) and commercial pine activated carbon (227.16 L.mol^{-1}).

The R_L value in 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 (coal) adds value to this waste, preserving the environment and helping to minimize the practice of abandoning this material irregularly.

It is important to highlight that the use of discarded pallets to produce a new product (coal) can promote greater awareness in the logistics, storage and productivity sector, expanding the next possibilities for reusing discarded material.

Brazil imports activated carbon from China at a cost ranging from 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 your own charcoal from (discarded) pallets can be a differentiator in the cost/benefit ratio for 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 larger sources of activated carbon should be encouraged in order to optimize environmental supplies.

However, charcoal made from pallets has shown to have great potential in establishing itself as a good adsorbent, in addition, being economically and environmentally viable.

CONCLUSION

This work transformed solid waste, the expired pallet, into charcoal. The gravimetric yield result 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 amounts from the companies to carry out proper disposal.

With the construction of the Langmuir isotherm, applying the adsorption of oxalic acid, it was evident that the adsorption was favorable with PC, with the saturation of the sites being close to 0.014 g.L^{-1} with a layer close to a concentration of 3.3 mol. L^{-1}.

The Langmuir isotherms obtained through the experiment showed significant results, with an r^2 value equal to (0.9175).

The PC obtained an active area of 715.94 $m^2.g^{-1}$, these results were obtained with expired pallets. These values are 40% to 43% higher than those found by Costa *et al*. (2015) with walnut shell charcoal, not activated (408 $m^2.g^{-1}$) and activated with $ZnCl_2$ (427 $m^2.g^{-1}$).

The maximum amount of oxalic acid adsorbed by 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 wooden pallets, which went through an entire cycle of use in industry, and that in many cases, after saturation, they are discarded irregularly in nature.

This work focused on studying the adsorption capabilities of the discarded material, planning and predicting whether there would be feasibility for a new way of using the product, with the main bias of contributing to the environment.

Transforming discarded material into adsorbent adds value to the product and, in addition, substantially reduces the industry's cost of regular disposal.

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