

## ANALYSIS OF EFFICIENCY OF ACTIVATED CARBON FROM MESQUITE POD (*Prosopis juliflora*) AS AN ADSORBENT IN REMOVAL OF GASOLINE PRESENT IN WATER BODIES

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**ABSTRACT:** Problems related to environmental contamination are an important theme and focus on research, especially when it involves fundamental resources such as water, which is vital to life. Contamination arising from industrial leaks represent a major problem when contaminant is gasoline, as its composition can be harmful to health. Thus, adsorption emerges as an extremely effective and viable method, since possibilities of biomasses found easily in nature are applied are real and cause low cost of process. In present case, algaroba (*Prosopis juliflora*) was used, which was efficient in research of Lima and Farias (2020). From these results and reviewing the literature, it was deduced that application of activated coal could increase adsorption efficiency of algaroba pod in gasoline removal in water. Thus, objective of this work was to evaluate ability to adsorption of algaroba pod coal as an adsorbent agent for removal of hydrocarbon and make a comparison between *in natura* biomass, physically activated coal (PAC) and physically and chemically activated coal (CPAC), regarding amount of contaminant removed from water. For preparation of physically activated charcoal (PAC), algarob was dried in a greenhouse,

then ground in knife mill, moving to carbonization in muffle for 30 minutes to 500 °C. For chemical activation, PAC was subjected to agitation with a potassium hydroxide solution (KOH) for 30 minutes under agitation of 140 rpm. Methodology used to kinetics and equilibrium studies was proposed by Lima *et al.* (2014). Experiments were performed to adsorption kinetics study, in which times of 05 to 60 minutes were evaluated (with 5 minutes intervals) and equilibrium adsorption, whose contaminant concentrations ranged from 5 to 50% (with rate of variation of 5%). In results of kinetics, maximum adsorption of PAC occurred at 30 minutes (5,000 g.g<sup>-1</sup>), and CPAC at 25, 50 and 60 minutes (5,000 g.g<sup>-1</sup>). In equilibrium, maximum amount adsorbed with presence of PAC was 7.13 g.g<sup>-1</sup>, with a concentration of 31.06% contaminant, while for CPAC, it was 7.13 g.g<sup>-1</sup>, with a concentration of 32, 44%. Isotherms confirmed that adsorption of PAC occurred in single and CPAC in multi -ways. However, it can be said that KOH activation was inefficient for algaroba pod coal, as the result with *in natura* material reached a maximum of 14.812 g.g<sup>-1</sup>, with concentration of 15.78%.

**KEYWORDS:** Adsorption. Gasoline. Algaroba pod. PAC. CPAC

## INTRODUCTION

Environmental problems have become increasingly critical and frequent, mainly due to excessive population growth and increased industrial activity in recent decades. In this sense, special attention must be paid to contamination of natural waters, as oil industry deals daily with problems arising from leaks, spills, and accidents during exploration, refining, transportation and storage of oil and its derivatives (CORSEUIL; MARINS, 1997).

Regarding the development of new techniques to solve problem of water contamination, adsorption is a separation and purification method widely used in wastewater treatment. Adsorption is highly effective and viable because it can be applied with adsorbent biomass found in natural vegetation, making process low-cost and highly efficient. Process aims to separate a substance of interest in one phase, isolating it from the other (FARIAS, 2022).

Adsorption is a phenomenon in which results can be obtained from a combination of physical or chemical factors. Some examples of factors that most influence adsorption process are surface area, adsorbent and adsorbate properties, system temperature, solvent nature, and medium pH. It is a process that can also be controlled by factors such as nature of adsorbent, adsorbate, and operating conditions (VIDAL *et al.*, 2014). Therefore, application of different methodologies to the adsorbent becomes a key point for improvements in the development of new adsorption techniques, such as activated carbon.

Activated carbon is a material with high adsorption capacity, making it efficient and widely used for water and wastewater treatment. However, its application is problematic due to high cost of raw material sourcing and losses during adsorbent recovery process, often making its use expensive (WERLANG *et al.*, 2013). Carbon can be sourced from various raw materials and undergoes different activation processes, including physical activation, such as carbonization, or chemical activation, using activating agents such as phosphoric acid ( $H_3PO_4$ ), sodium acetate ( $CH_3COONa$ ) and potassium hydroxide (KOH).

Based on the work of Lima and Farias (2020), which demonstrated effectiveness of fresh mesquite pods, dried at room temperature, in adsorbing gasoline from water bodies, this study aims to develop a line of research exploring different ways of applying mesquite pods to adsorb organic contaminants from water. In this case, aim is to evaluate the most effective method of activating activated carbon—physical or physical and chemical—to obtain a more efficient material. To this end, adsorption kinetics and adsorption equilibrium of each adsorbent material were observed, also analyzing their theoretical adsorption pattern through equilibrium isotherms. It is essential to compare results obtained with those of fresh mesquite pod biomass to assess their effectiveness and whether activation is compensatory.

## LITERATURE REVIEW

### Hydrocarbon Contamination

Human activities have developed throughout history, driven by new technologies. Increasing advancement of industrial technology has resulted in generation of hazardous wastewater that, if released into public sewage system without adequate pretreatment, compromises its structural integrity due to its corrosive, flammable, and explosive pollutants (SOUZA; LIMA; SILVA, 2011).

The exploitation of natural resources became even more intense after Industrial Revolution, when industrial production progressed and diversified. Although this technology often positively influences global economy and promotes job creation and income generation, it also represents a source of pollution, affecting people's quality of life and environmental preservation (CORREIA; BEZERRA, 2015). Treating these contaminants is crucial due to fundamental role water plays in life on the planet.

Gasoline is one of most important petroleum products, obtained from refining processes, being second most consumed fuel in Brazil, losing only to diesel oil. A liquid fuel is volatile and flammable, consisting of more than 400 different compounds, whose final composition depends on the origin of oil and production processes (CARVALHO; DANTAS FILHO, 2013). Physicochemical properties of gasoline

compounds, such as solubility, vapor pressure, density, viscosity, molecular weight, polarity and partition coefficient interfere with its mobility in water (FARIAS, 2022).

For the purpose of removing organic contaminants from water, studies have been performed using the adsorption technique.

## ADSORPTION

One of techniques that have high efficiency and feasibility is physical adsorption, process of which occurs by applying an adsorbent for contaminant removal. What makes this process even more viable is the possibility of applying biomass. Adsorption is an important process of purification and separation in oil, food, fine chemistry and biotechnology areas. It is a valid option for removal of diluted pollutants in liquid effluents, as well as for recovery of components of high value added diluted in industrial currents (SOUZA; LIMA; SILVA, 2011).

Analyzing possibilities in Cariri Paraibano has cactus pear forage (*Opuntia ficus*), which presented itself as an effective biomass alternative for use as adsorbent, as shown by Lima *et al.* (2016), adsorbing hydrogenocarbon contaminants present in water. In adsorption it is important to understand how equilibrium occurs, which occurs at a point where there are no changes in adsorbate concentrations in solid phase or solute in solution (LIMA *et al.*, 2019), ie, as shown to Le Châtelier principle, after applying a force, system adjusts to compensate disturbance suffered and thus achieving its balance.

### Adsorption kinetics

Adsorption kinetics is expressed as adsorption removal rate in liquid phase over time, which involves mass transfer from one or more components contained in an external liquid mass to interior of adsorbent particle, which should migrate through macropro to the inner regions of this particle (VIDAL *et al.*, 2014).

Kinetics tests are performed to evaluate effectiveness of an adsorbent and can be affected by temperature, pH, ionic force, initial adsorbate concentration, agitation, particle size and pore size distribution (NASCIMENTO *et al.*, 2014).

### Adsorption Equilibrium

Adsorption balance is essential for obtaining analytical information about an adsorption separation process. When a certain amount of solid contacts a certain volume of a liquid containing a solute that can be adsorbed, adsorption occurs until balance is reached. Equilibrium is established at the point where there is no changes in adsorbate concentrations in solid phase or solute in solution (LIMA *et al.*, 2019).

When adsorbate is placed in contact with adsorbent, molecules or ions tend to flow from aqueous medium to adsorbent surface until liquid phase concentration remains constant. At this stage it is said that system has reached the equilibrium state and adsorbent adsorption capacity ( $q$ ) is determined.

For a theoretical analysis of results, application of isotherms is fundamental because, through these, it can be theoretically explained how process occurs, relating adsorbed quantity of a particular compound and its remaining concentration (NASCIMENTO *et al.*, 2014).

Obtaining an adsorption isotherm is a simple process in which an adsorbent mass is added to a certain volume ( $V$ ) of a series of solutions, with different and known initial concentrations ( $C_0$ ). When adsorption equilibrium is reached, there is final concentration of solute in the equilibrium solution ( $C_e$ , grams or moles per liter of solution) and adsorbent adsorption capacity (NASCIMENTO *et al.*, 2014).

### *Langmuir Isotherm*

Langmuir isotherm analyzes adsorption by admitting that on homogeneous surfaces all active sites have equal affinity for adsorbate; therefore, adsorption of a site would not affect the adsorption of adjacent site to it, ie, a monolayer adsorption. With this isotherm it is possible to obtain parameters such as maximum adsorption ( $Q_m$ ) of system (monolayer saturation) and there is also equilibrium constant ( $k$ ), theoretical adsorption in monolayer (FONTANA, 2016).

### *Freundlich Isotherm*

Freundlich's isotherm is empirical and widely used, as it describes adsorption test data with very accurately, mostly in aqueous systems, as well as describing equilibrium on heterogeneous surfaces, and not assuming monolayer adsorption (MOHAN; SINGH; SINGH, 2006 *apud* FONTANA, 2016).

## Bioadsorbents

Use of biomass is an advantageous source for conversion into alternative adsorbents because it is clean and renewable, in addition to helping mitigate environmental impacts caused by improper disposal of this waste and preventing subsequent accumulation (PIQUET; MARTELLI, 2022). Adsorption process using biomass as an adsorbent has been a potentially attractive and economical alternative for treatment of various types of effluents, as its high hydrophobicity and porosity are properties that combine capillary force, generating good adsorption results for biomass (SILVA *et al.*, 2012). One factor that has encouraged investigation of new

adsorbent biomasses as alternatives for effluent treatment is the fact that it is a low-cost technology (BATISTA *et al.*, 2012).

Physicochemical nature of adsorbent material implies its ability to adsorb substances, and rate at which this occurs depends on properties such as material's specific surface area, porosity, size distribution, and specific pore volumes, in addition to the nature of precursor material (PIQUET; MARTELLI, 2022). In literature, we can find the most diverse types of bioadsorbents applied to various types of systems.

### *Mesquite (Prosopis Juliflora)*

The mesquite, introduced in the 1940s in Northeast Brazil as an alternative to solving major problems in this macroregion, such as accelerated deprecation of native Caatinga species and scarcity of animal feed during dry months, is now widespread in virtually all geo-environmental regions of Northeast Semiarid Region. Rapid expansion of mesquite has led to this exotic plant being classified as an invasive species in many areas, causing ecosystem imbalances (FÉLIX, 2019).

Study of mesquite pod as an adsorbent for removal of gasoline present in water has been carried out by LIMA and PAIVA (2022) and FARIAS (2022), which provided results that proved adsorptive efficiency of this biomass in relation to decontamination of water impregnated with gasoline.

### *Mesquite activated charcoal*

Due to its adsorptive properties, activated carbon is increasingly used in removal of organic compounds from water and gas purification, as well as catalysts and catalyst supports. Its applications extend to various sectors, such as pharmaceuticals, chemicals, food, petroleum, and water filtration (ALBUQUERQUE 2002 *apud* BRITO *et al.*, 2015). Activated carbons are highly porous materials with a high surface area and the most widely used adsorbents today, a fact related to their high adsorption capacity, which reflects their structural properties. Carbon is produced from the dehydration of raw materials and activation, followed by carbonization (BRITO *et al.*, 2015).

Knowing efficiency of natural mesquite pods as an adsorbent and good results of activated carbon from some biomasses such as umbu (BRITO *et al.*, 2015) or mesocarp from coconut (MORAIS, 2014), it is important to study efficiency of activated carbon from mesquite pods. Work developed by Paiva *et al.* (2013), which characterized activated carbon from mesquite compared to activated carbon from cashew trees, showed that activated carbon from mesquite has a higher ash content, making it a good option for energy production, for example. In addition, it has an

average percentage of fixed carbon, making it a good raw material for activated carbon production.

## MATERIALS AND METHODOLOGY

Based on the work of Lima *et al.* (2014), who used mandacaru (*Cereus jamacaru*) in particulate form to remove gasoline/diesel oil mixture, same methodology was used, applying mesquite pod (*Prosopis juliflora*) to remove gasoline present in water. All experiments were performed in triplicate.

After collection, pods were broken and placed in an oven at 60°C for 3 days to dry and, then, particled using a knife mill to achieve a particle size between 1 and 2 mm. Process of transformation into activated carbon was then carried out.

### Physically activated carbon (PAC)

To obtain activated carbon, Morais' methodology (2014) was applied, which used 660 g of mesquite pod biomass, placed in a muffle furnace for 30 minutes at 500°C for carbonization.

Figures 1(a) and 1(b) consist of biomass before and after carbonization process, respectively.

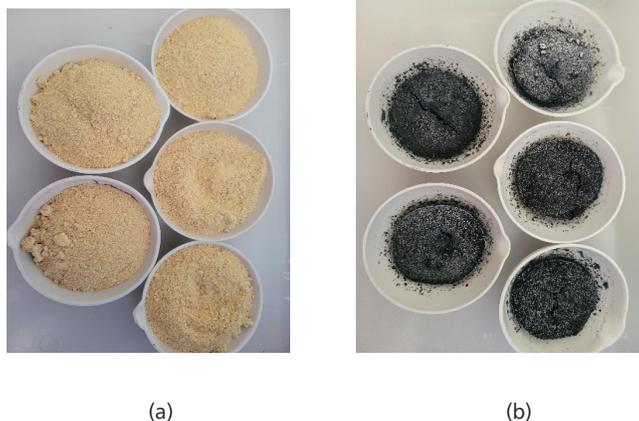


Figure 1 – Biomass powder: (a) before carbonization and (b) after carbonization.

Source: Author's collection, 2023.

Each crucible placed in the muffle furnace contained 60g of biomass. After this process, crucibles were placed in a desiccator for 24 hours. To obtain better

adsorption results, coal was washed to remove ashes from PAC pores. To do this, 30 g of PAC were placed in an Erlenmeyer flask with 300 mL of distilled water, which was placed on a shaking table at 140 rpm for 1 h. After washing process, PAC was vacuum filtered and placed in an oven for 24 hours at 35°C.

After time in the oven, physically activated carbon was ready for use in adsorption process (Figure 2).

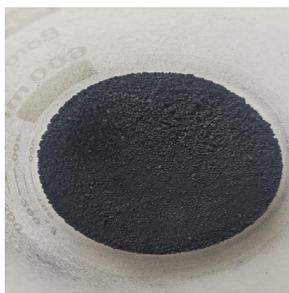


Figure 2 – Physically activated carbon.

Source: Authors' collection, 2023.

### Physically and chemically activated carbon (PCAC)

For physically and chemically activated carbon (PCAC), Morais' methodology (2014) was used. In this process, carbon was activated physically and then activated with potassium hydroxide (KOH) in a solution of distilled water and 10% potassium hydroxide. Solution was placed in an erlenmeyer flask containing 300 mL and 30 g of PAC. After 30 minutes of agitation on a shaking table at 140 rpm, carbon was vacuum filtered and placed in an oven for 24 hours. When carbon was dry, it was washed again to remove the KOH from pores.

After washing and filtering, charcoal was placed in oven again for 72 hours at 38°C. After time in oven, PCAC was ready for use (Figure 3).



Figure 3 – Physically and chemically activated carbon (PCAC).

Source: Authors' collection, 2023.

## Adsorption kinetic

For kinetics, 12 Erlenmeyer flasks were used, each containing a 52 mL solution, of which 40 mL was water, 12 mL was contaminant (gasoline), and 1.2 g was activated carbon. All flasks were shaken at 130 rpm on a shaker table for a time ranging from 5 to 60 minutes to analyze adsorption using PAC and PCAC. When time was up, solution was filtered and analyzed in a graduated cylinder to measure the final gasoline volume.

As a result, amount adsorbed in solid phase at time  $t$  was obtained, according to Equation 1:

$$q = \frac{(C_o - C)V}{m} \quad (1)$$

Where:

$q$ : amount adsorbed in solid phase at time  $t$  (g. g<sup>-1</sup>)

$C_o$ : initial adsorbate concentration (g. L<sup>-1</sup>)

$C$ : adsorbate concentration at time  $t$  (g. L<sup>-1</sup>)

$m$ : mass of adsorbent material (g)

$V$ : volume of solution (L)

## Adsorption equilibrium

Equilibrium determination experiments were performed using 10 erlenmeyer flasks containing a water/gasoline solution that varied between 5 and 50% contaminant, placed under agitation for 1 hour at 130 rpm. When time was up, solution was filtered and analyzed using a graduated cylinder, observing how much gasoline remained on final volume.

To obtain equilibrium data, Equation 2 was used.

$$q = \frac{(C_o - C_e)V}{m} \quad (2)$$

Where:

$q$  : adsorption capacity ( $\text{g} \cdot \text{g}^{-1}$ )

$C_o$  initial adsorbate concentration ( $\text{g} \cdot \text{L}^{-1}$ )

$C_e$  adsorbate concentration on equilibrium ( $\text{g} \cdot \text{L}^{-1}$ )

$V$  volume of solution (L)

$m$ : mass of adsorbent material (g)

## Equilibrium isotherms

Two isotherm models were used to try to fit the curves: Langmuir and Freundlich.

### *Langmuir Isotherm*

Langmuir isotherm relates amount of solute adsorbed on a surface to solute concentration in the solution. Assuming that adsorption occurs in a monolayer, on Langmuir isotherm, according to Nascimento *et al.* (2014), we have Equation 3:

$$q = \frac{Q_m K_L C_e}{1 + K_L C_e} \quad (3)$$

Where:

$q$  amount of solute adsorbed per unit mass of adsorbent ( $\text{g} \cdot \text{g}^{-1}$ )

$C_e$  adsorbate concentration at equilibrium ( $\text{g} \cdot \text{L}^{-1}$ )

$Q_m$  maximum adsorption capacity ( $\text{g} \cdot \text{g}^{-1}$ )

$K_L$  Langmuir isotherm constant ( $\text{L} \cdot \text{g}^{-1}$ )

Equilibrium parameter, which indicates whether adsorption isotherm will be favorable, was obtained from equation 4, according to Pinheiro *et al.* (2013):

$$R_L = \frac{1}{1 + K_L \cdot Q_m} \quad (4)$$

### Freundlich Isotherm

Freundlich isotherm is characterized by an empirical equation applicable to heterogeneous systems and assuming that adsorption occurs in multiple layers. The equation considers solid to be heterogeneous and applies an exponential distribution to define various types of adsorption sites, which have different adsorption energies (SOUSA, 2019). Equation 5 was used to apply this isotherm:

$$q = K_F \cdot C_e^{1/n} \quad (5)$$

Where:

q: amount of adsorbed solute (mg.g<sup>-1</sup>)

C<sub>e</sub>: equilibrium concentration on solution (mg.L<sup>-1</sup>)

1/n: constant related to surface heterogeneity

K<sub>F</sub>: Freundlich adsorption capacity constant (mg.g<sup>-1</sup>).

## RESULTS AND DISCUSSION

### ADSORPTION KINETICS

#### Physically activated carbon (PAC)

From data obtained by experiments with only physically activated carbon, Figure 4 was plotted.

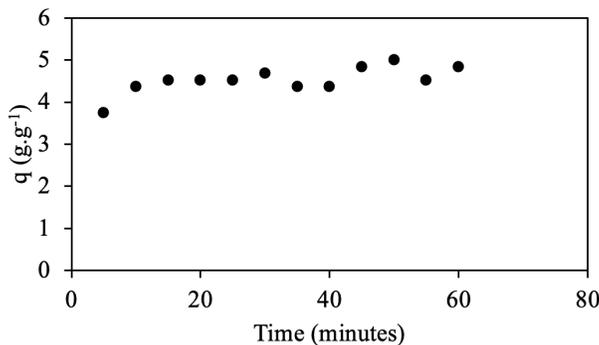


Figure 4 – Kinetic curve for water/gasoline/PAC adsorption system.

Source: Authors' collection, 2023.

Analyzing Figure 4, it can be observed that a large amount of gasoline is adsorbed within first 5 minutes, with a peak adsorption at 30 minutes, when system reaches a  $q$  value of  $4.687 \text{ g.g}^{-1}$ . Maximum adsorption occurs at 50 minutes when system reaches a  $q$  of  $5.000 \text{ g.g}^{-1}$ . However, after this maximum, the amount of gasoline adsorbed decreases, probably due to saturation of adsorbent biomass.

In the water/gasoline/forage palm system developed in Sousa's research (2019), maximum adsorption obtained was  $4.58 \text{ g.g}^{-1}$ , and it can be stated that system with PAC had a better result. Farias' work (2022), which used fresh algaroba pods in adsorption of gasoline present in water, obtained a maximum value for amount of contaminant adsorbed,  $q$  ( $5.625 \text{ g.g}^{-1}$ ), which occurred from 35 minutes onwards, with small variations up to 60 minutes, suggesting that longer contact time allowed for a better result.

Compared to system with physically activated carbon, it can be assured that PAC did not positively influence the adsorption efficiency of carob pod.

### Physically and chemically activated carbon (PCAC)

In adsorption using PCAC, similar results were obtained to adsorption with PAC, as can be seen in Figure 5.

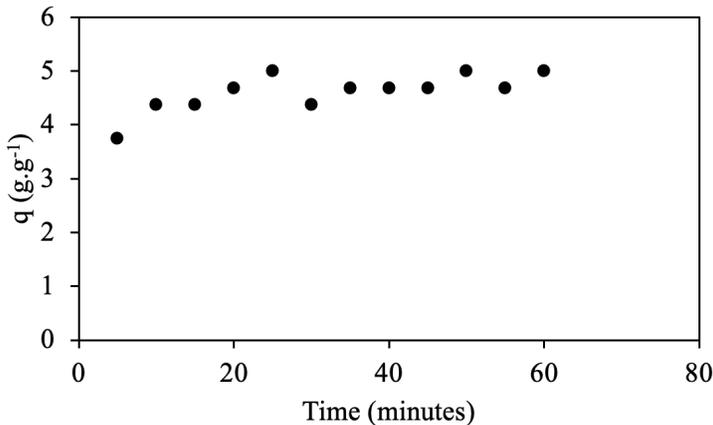


Figure 5 – Kinetic curve for a water/gasoline/PCAC adsorption system.

Source: Authors' collection, 2023.

Figure 5 shows that for system using PCAC, adsorption peaks occurred at 25, 50, and 60 minutes, all with a maximum adsorption capacity of  $5.000 \text{ g.g}^{-1}$ , a result equal to system with PAC. However, since PCAC reached maximum efficiency more

quickly (25 minutes), it can be assumed that PCAC confers greater efficiency to carob pod than PAC.

Feitosa (2018) obtained a peak amount of gasoline adsorbed of  $6.05 \text{ g.g}^{-1}$  in 55 minutes using forage palm (*Opuntia ficus*). However, Farias' work (2022), whose system was carried out with seedless mesquite, a maximum adsorbed amount of  $7.083 \text{ g.g}^{-1}$  was achieved at 35 minutes. Therefore, it can be stated that CAFQ (activated carbon from mesquite pods) did not increase the adsorptive efficiency of the biomass.

## ADSORPTION EQUILIBRIUM

### Physically activated carbon (PAC)

Figure 6 shows equilibrium curve of system with presence of PAC, relating amount adsorbed to final concentration of system.

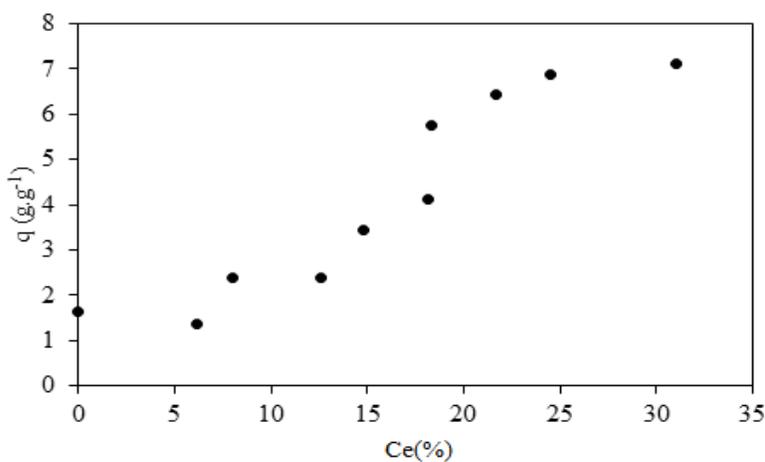


Figure 6 – Equilibrium curve for water/gasoline/PAC adsorption system.

Source: Author's collection, 2023.

Analyzing Figure 6, it can be seen that maximum adsorbed amount of  $7.13 \text{ g.g}^{-1}$  occurred at 31.06%, an interesting result when compared to Farias' work (2022), who using biomass in its natural state, obtained adsorption of 50% of contaminant of  $7.5 \text{ g.g}^{-1}$  at a concentration of 30.21%. Despite the proximity of compared values, it can be stated that activated carbon did not physically contribute to increasing the adsorptive capacity of mesquite pod.

## Physically and chemically activated carbon (PCAC)

To analyze the equilibrium of system with PCAC, isotherm shown in Figure 7 can be observed.

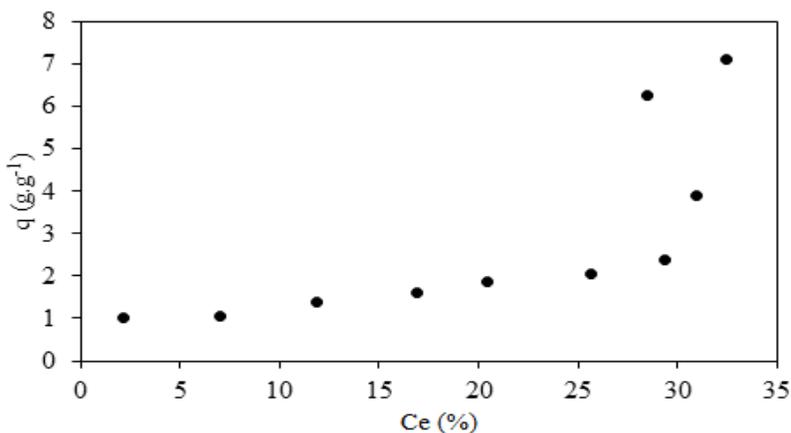


Figure 7 – Equilibrium curve for water/gasoline/PCAC adsorption system.

Source: Author's collection, 2023.

Figure 7 shows that maximum amount adsorbed with PCAC was 7.13 g.g<sup>-1</sup>, same value found in water/gasoline/CAF system, but with a higher final concentration of gasoline (32.44%), while with PAC concentration was 31.06%. Therefore, physically activated carbon achieved greater efficiency in the equilibrium..

Comparing with equilibrium data for water/gasoline/mesquite pod biomass system, studied by Farias (2022), which obtained, in 50% gasoline, an adsorbed quantity of 12.5 g.g<sup>-1</sup> of maximum adsorptive capacity with a concentration of 12.99%, it can be assured that, for studied system, mesquite pod in its natural state presented a more efficient result than systems with activated carbons.

## EQUILBRIUM ISOTHERMS (LANGMUIR E FREUNDLICH)

### PAC systems isotherms

Figure 8 refers to equilibrium curves for water/gasoline/PAC system from mesquite pods.

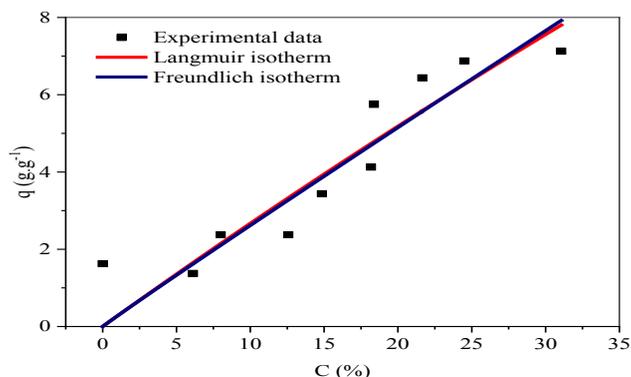


Figure 8 – Equilibrium isotherms for water/gasoline/PAC adsorption system.

Source: Author's collection, 2023.

Due to proximity of curves in Figure 18, only by analyzing numerical values can one determine which isotherm best fits. Table 2 lists results obtained from applying Langmuir isotherm using equations 3 and 4.

Parameter	Value
$K_L$ ( $L.g^{-1}$ )	0.00304
$Q_m$ ( $g.g^{-1}$ )	90.37
$R^2$	0.8496
$R_L$	0.78

Table 1 – Parameters obtained by applying Langmuir Isotherm model with PAC.

Source: Author's collection, 2023.

Observing parameters found, it is possible to see that the adjustment coefficient ( $R^2$ ) presented a considerable value, although it is possible to observe that adjustment of points was not adequate to mathematical model. The value of Langmuir constant indicates that theoretical adsorption capacity in the monolayer ( $K_L$ ) is small, but still positive when compared with research of Lima and Paiva (2022) who, using Langmuir isotherm in adsorption with fresh mesquite pods, obtained  $K_L=7.71 L.g^{-1}$  and an adjustment coefficient ( $R^2$ ) of 0.848.

For the equilibrium parameter, result is considered positive, indicating that isotherm is favorable with a considerable degree of development and spontaneity of reaction, admitting a monolayer, since, according to Schons (2022), equilibrium parameter values between 0 and 1 indicate a favorable type of isotherm. Maximum adsorption constant ( $Q_m$ ) presented a different value from experimental value, which may indicate a potential for this adsorbent at high concentrations.

Regarding the Freundlich isotherm, parameters listed in Table 2 were obtained.

Parameter	Value
$K_F$ (mg.L <sup>-1</sup> )	0.2717
n	1.023
$R^2$	0.8479

Table 2 – Parameters obtained by applying Freundlich Isotherm model with PAC.

Source: Author's collection, 2023.

Initially, it can be observed that Freundlich coefficient ( $K_F$ ), related to adsorption capacity of solid, presents a lower value when compared to Lima and Paiva's work (2022), who obtained  $K_F = 2.92$  mg.L<sup>-1</sup>. Freundlich constant (n) indicates whether process is favorable or not, with values in the range of 1 to 10 being indicative of favorable conditions for adsorption process (CARDOSO, 2018). Thus, there is a favorable constant in this case.

The adjustment coefficient yielded a result close to that of Langmuir isotherm, but since its parameters did not show such positive results, it can be stated that PAC theoretically exhibits monolayer adsorption.

## PCAC system isotherms

Figure 9 illustrates the fit of Langmuir and Freundlich models to experimental data for system with physically and chemically activated carbon.

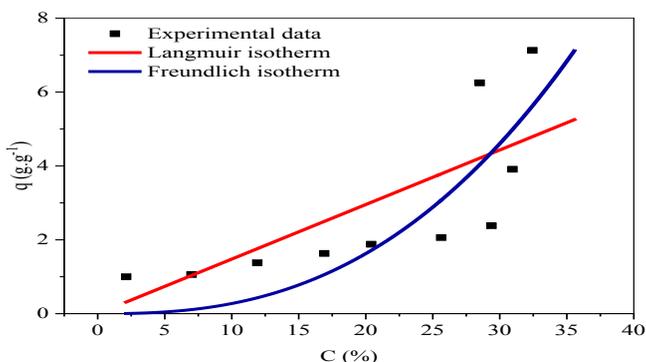


Figure 9 – Equilibrium isotherms for water/gasoline/PCAC adsorption system.

Source: Author's collection, 2023.

From Figure 19, it can be observed that Freundlich isotherm provides a better visual fit to experimental data. Regarding the parameters, Table 3 lists those related by Langmuir model.

Parameter	Value
$K_L$ (L.g <sup>-1</sup> )	6.686
$Q_m$ (g.g <sup>-1</sup> )	22,097.95
$R^2$	0.716
$R_L$	0.00000677

Table 3 – Parameters obtained by applying Langmuir Isotherm model with PCAC.

Source: Author's collection, 2023.

Analyzing the adjustment coefficient, a lower value is observed than that obtained in water/gasoline/PAC system, as seen in Table 2. Maximum adsorption capacity ( $Q_m$ ) presented a value very different from experimental value, resulting in a lack of fit, despite the good result of theoretical adsorption capacity in the monolayer.

The equilibrium parameter ( $R_L$ ) was found to be 0.00000677 which, although between 0 and 1, indicates a favorable isotherm. This extremely low value confirms that adsorption does not occur in a monolayer with PCAC.

To conclude isotherm analysis, Table 4 illustrates parameters obtained with Freundlich isotherm.

Parameter	Value
$K_f$ (mg.L <sup>-1</sup> )	7.462
n	0.3897
R <sup>2</sup>	0.8804

Table 4 – Parameters obtained by applying Freundlich Isotherm model with PCAC.

Source: Author's collection, 2023.

It can be observed that adjustment coefficient presented best result in this study. Freundlich coefficient (KF) shows a positively significant result, since in Lima and Paiva's work (2022) a KF of 2.92 mg.L<sup>-1</sup> was obtained with fresh mesquite pods. Freundlich constant (n) presented a value between 1 and 10; therefore, a favorable process is observed. Thus, it can be predicted that adsorption of water/gasoline/PCAC system occurred in multilayers.

## CONCLUSION

Analyzing results obtained in kinetics, it can be stated that both PAC and PCAC function as effective adsorbent agents, since there is a decrease in amount of gasoline in the solution from first 5 minutes. Comparing kinetic results, it can be concluded that PCAC was more efficient, since there were adsorption peaks and a maximum adsorption capacity result in the initial 25 minutes.

Regarding the adsorption equilibrium, another situation arises: PAC showed better results; however, both obtained same adsorption capacity, differing only in the final concentration. Therefore, both results are considered positive, and a better evaluation of which is the best adsorbent carbon could be made using isotherms.

Different results were obtained from isotherm analysis. In the PAC application, best fit of Langmuir isotherm confirms that adsorption occurred in a monolayer. However, in water/gasoline/PCAC system, a better fit coefficient was obtained for Freundlich isotherm, showing a better fit and, therefore, a multilayer system.

Based on analysis of results, it can be stated that physically and chemically activated carbon (PAC) is a more efficient adsorbent agent, with potassium hydroxide (KOH) being the reagent that most likely increased carbon porosity.

However, when compared to results obtained with adsorption using only particulate mesquite pods *in natura*, i.e., without transformation into activated carbon, results were lower than those obtained in that system. Therefore, activation with KOH proved inefficient for activated carbon of mesquite pod.

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