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Articles

**Kinetics and isotherms of adsorption of arsenic (III) in aqueous solution using activated carbon with nanoporous structure obtained from organic sewage sludge**

**Cinética e isotermas de adsorción del arsénico (III) en solución acuosa mediante carbón activado con estructura nanoporosa obtenido de lodos orgánicos de aguas residuales**

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## Abstract

The objective of this investigation was to study the process of absorption of As (III) ions through activated carbon nanopores derived from organic sewage sludge. The adsorption tests were carried out by placing 16 g/l of activated carbon in contact with solutions of 0.247, 0.406, 0.564, 0.683 and 0.801 mg/l of As (III) in 1L beakers at a time of 24 hours. All the tests were submitted to an agitation speed of 720 RPM, a temperature of  $28\text{ }^{\circ}\text{C} \pm 0.5\text{ }^{\circ}\text{C}$  and the natural pH of the samples. The results of carbon characterization show that this absorbent presented a nanoporous structure with the presence of functional groups (hydroxyl and carboxyl). As for the As (III) adsorption tests, it was determined that activated carbon managed to reduce the metal concentration to 0.004 mg/l, a value that is below those established by the World Health Organization (WHO) for water consumption. Finally, it was concluded that activated carbon showed a 98.4 % efficiency in the absorption of As (III) ions and the experimental data presented a bigger adjustment to the pseudo-second-order model and to Freundlich isotherm, which indicates that the process of absorption of As (III) ions is done in strongly heterogeneous centers through a physical-chemical interaction between the metal and the absorbent.

**Keywords:** Adsorption, arsenic, activated carbon, isotherms, nanopores.



## Resumen

El objetivo de la investigación fue estudiar el proceso de adsorción de iones de As (III) con carbón activado de estructura nanoporosa obtenido de lodos orgánicos de aguas residuales. La obtención del carbón activado se realizó mediante una activación química usando  $\text{ZnCl}_2$  y una activación térmica a  $650\text{ }^{\circ}\text{C}$ . Los ensayos de adsorción se realizaron colocando en contacto 16 g/l de carbón activado con soluciones de 0.247, 0.406, 0.564, 0.683 y 0.801 mg/l de As (III) en vasos precipitados de 1 l a un tiempo de 24 horas. Todos los ensayos fueron sometidos a una velocidad de agitación de 720 RPM, a temperatura de  $28\text{ }^{\circ}\text{C} \pm 0.5$  y al pH natural de las muestras en laboratorio, el cual fue 3. Los resultados de la caracterización de carbón indicaron que este adsorbente presentó una estructura nanoporosa con presencia de grupos funcionales (hidroxilo y carboxilo). En cuanto a los ensayos de adsorción de As (III), se determinó que el carbón activado logró reducir la concentración del metal hasta 0.004 mg/l, valor que está por debajo de los establecidos por la Organización Mundial de la Salud (OMS) para el consumo de agua. Finalmente se concluye que el carbón activado presentó una eficiencia de 98.4 % de adsorción de iones de As (III) y los datos experimentales mostraron un mayor ajuste al modelo de pseudo-segundo orden y a la isoterma de Freundlich, lo cual indica que el proceso de adsorción de As (III) se realiza en centros energicamente heterogéneos mediante una interacción físico-química entre el metal y el adsorbente.

**Palabras clave:** adsorción, arsénico, carbón activado, isothermas, nanoporos.



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## Introduction

In the world, it is estimated that more than 100 million inhabitants are exposed to arsenic contamination of water and food, Bangladesh, China, Taiwan, the United States and Pakistan, the countries that present an alarming content of arsenic (Chakraborti, 2016). In Latin America, approximately 4 million people are exposed to this contaminant, present in drinking water, the most affected countries are: El Salvador, Nicaragua, Mexico, Argentina, Chile, Peru and Bolivia (CRC Press *et al.*, 2008). Similarly, in Peru there are approximately more than 250,000 people exposed to arsenic due to the presence of this pollutant in natural surface water and groundwater located in the south of the country (Castro-de-Esparza, 2009). Likewise, the study of the degree of contamination by arsenic in groundwater and surface water in various districts of Peru, shows that 86 % of samples analyzed exceed the maximum concentration of 0.01 mg/l of arsenic established by the WHO (George *et al.*, 2014).

The main source of human exposure to arsenic is contaminated groundwater and the intake of this comes to produce chronic health effects such as some dermal problems that can develop into skin cancer,



bladder cancer and lung cancer (Mandal, 2017). In addition to cardiovascular, neurological and diabetic diseases, it can aggravate people's health (Kadirvel *et al.*, 2007).

In this context, to reduce the concentration of this metal and avoid its harmful effects on the environment and people's health, different treatment technologies have been used, which are: chemical precipitation, coagulation flocculation, reverse osmosis, ion exchange and adsorption. However, of all these methods mentioned, adsorption is the simplest and most cost-effective method (Bazrafshan, Faridi, Mostafapour, & Mahvi, 2013; Gallegos-Garcia, Ramírez-Muñiz, & Song, 2012; Shukla, Pai, & Shendarkar, 2006; Yao, Liu, & Shi, 2014). Among the various adsorbents that exist, adsorption on activated carbon has proven to be one of the most effective and reliable physicochemical treatment methodologies (Tefera *et al.*, 2013; Urbain, Aimé, Jacques, & Albert, 2013). Due to its large surface area and porous structure, it can adsorb dispersed gases and/or compounds present in liquids.

In recent years, much attention has been paid to the synthesis of activated carbons from sewage sludge for the adsorption of gaseous pollutants such as toluene, hydrogen sulfide, nitrogen dioxide, sulfur dioxide, and liquid pollutants such as phenol, dye, etc. (Chiang & You, 1987; Lu & Lau, 1996). Studies carried out by Rozada, Otero, Morán and García (2008) have demonstrated the efficiency of wastewater sludge as active carbon for the removal of mercury (Hg), lead (Pb), copper (Cu) and chromium (Cr) in aqueous media. Similarly, Wongrod, Simon, van Hullebusch, Lens and Guibaud (2018), and Yao *et al.* (2014) mention

when using activated carbons made from residual sludge as adsorbents, achieved the adsorption of 72 and 89.7 % of As, respectively.

Therefore, the purpose of this research was to study the kinetics and adsorption isotherms of Arsenic (III) ions in aqueous solutions with activated carbon of nanoporous structure obtained from organic sewage sludge.

## Materials and methods

### Research setting

The arsenic (III) adsorption tests using activated sludge-based activated carbon were carried out at the Chemistry laboratory facilities of the Faculty of Engineering and Architecture of the Universidad Peruana Unión (UPeU) in the city of Lima. On the other hand, the analyzes of the characteristics of the wastewater sludge and arsenic concentration of the tests were carried out in the DELTA LAB S.A.C. The characterization of activated carbon by scanning electron microscopy (SEM), in the laboratories of the Faculty of Chemical Sciences of the National University of Engineering and the analysis of Fourier transform infrared spectroscopy (FTIR), in the Laboratory of Research and Certifications (LABICER) belonging to the National University of Engineering.

## Sludge acquisition and characterization

The sludge used in this investigation was obtained from the Manchay Wastewater Treatment Plant, Pachacamac. For the characterization of active sludge, samples were taken from the sludge container, establishing 4 sampling points. Likewise, for the chemical characterization of the sludge, a 2.0 kg sample was taken, while for the microbiological characterization a 0.5 kg sample was taken. Both samples were taken to the laboratory where they were analyzed by inductively coupled plasma (ICP) analysis with atomic emission spectroscopy (AES) for the determination of metals and trace elements in water and waste; fecal coliforms with the Most Likely Numbers technique; pathogenic protozoans and helminths using the Baillenger Method.

## Synthesis of nanoporous activated carbon

The sludge obtained from the WWTP (Waste Water Treatment Plants) was dried at 105°C for 24 hours in an oven, cooled to room temperature and then crushed to a uniform size. Then, the dry sludge was put in contact with a 3M  $\text{ZnCl}_2$  solution in a ratio of 1:2; that is, each 1 g of sludge was contacted with 2 mL of  $\text{ZnCl}_2$  for 24 hours. Subsequently, the supernatant liquid was removed and the samples were dried in an oven at 105°C for 24 hours. Samples impregnated with  $\text{ZnCl}_2$  they were then pyrolyzed in a muffle at 650°C for 60 minutes. After cooling, the carbonized sample was

washed with 250 ml of HCl 1M and dried again in the oven at 105 °C for 24 hours.

The activated carbon obtained was crushed and sieved through a N° 16 mesh size sieve to obtain particles with a size of 1.18 mm. Once the activated carbon samples were obtained, they were placed in ziploc bags and stored in a desiccator with silica gel to prevent moisture uptake.

## Preparation of arsenic solutions

For experimental As water solutions on a laboratory scale, the stock solution of 1 mg/l of As (III) was prepared using 1.3337 g of  $\text{As}_2\text{O}_3$  in 1L of distilled water. The solution was stirred using a magnetic stirrer at 2000 RPM for 4 hours at a temperature of 60°C to ensure complete dilution of the compound. From this solution, decreasing concentrations of 0.80, 0.68, 0.56, 0.41 and 0.25 mg/l of As (III) were obtained, which were analyzed by the SMEWW – APHA/WWA-WEF Part method. 3114 B and C, 23rd Ed. 2017-Arsenic and Selenium by Hydride Generation/ Atomic Absorption Spectrometry (Rice, Eaton, & Baird, 2017).

## Adsorption tests

For the development of the research, previous tests were carried out to determine the optimal dose of activated carbon and the optimal agitation





time with which the other tests would work to analyze the influence of activated carbon against the various concentrations of arsenic.

The optimal dose of activated carbon was determined by duplicate tests using doses of 4, 8, 12, 16 and 20 g/l, which were put in contact with a solution of 0.25 mg/l of As (III) at room temperature. and at 720 RPM for 24 hours. With these tests it was determined that the optimal dose was 16 g/l.

The optimal test time was determined by duplicate tests using 16 g/l of activated carbon in a solution of 0.564 mg/l of As (III) at contact times of 4, 8, 12, 16, 20 and 24 hours. With these tests it was determined that the optimal contact time to carry out the subsequent tests was 24 h. Likewise, the results obtained in these tests were used to model the adsorption kinetics.

After having carried out the previous tests to determine the optimal dose of activated carbon and the optimal agitation time, the tests were carried out to determine the influence of activated carbon on the removal of arsenic and to study the kinetics and isotherms of adsorption. This test consisted of putting 16 g/l of activated carbon in contact with solutions of 0.247, 0.406, 0.564, 0.683 and 0.801 mg/l of As (III) in 1L beakers and subjecting them to stirring using a magnetic stirrer at 720 RPM for 24 hours. It should be noted that all the tests were carried out at a temperature of  $28\text{ }^{\circ}\text{C} \pm 0.5$  and an acidic pH of 3. After running the tests, the samples were filtered, preserved with  $\text{HNO}_4$  and immediately taken to a laboratory to determine the final concentration of As (III) by the SMEWW method – APHA-AWWA-WEF Part. 3114 B and C, 23rd Ed. 2017-

Arsenic and Selenium by Hydride Generation/ Atomic Absorption Spectrometry (Rice *et al.*, 2017).

## Equations and models used

### Adsorption capacity

The adsorption capacity ( $q_e$ , mg/g) of activated carbon was calculated using Equation (1):

$$q_e = (C_o - C_e) \times \frac{V}{m} \quad (1)$$

Where  $C_o$  is the initial concentration of metal in the solution (mg/l),  $C_e$  is the final concentration of metal in the solution (mg/l),  $V$  is the volume of the solution (L) and  $m$  is the mass of the adsorbent (g).

### Kinetic mathematical models

The experimental data obtained from the tests where the variation of the agitation time was carried out were analyzed using the pseudo first order and pseudo second order models.

To perform the data modeling to pseudo first order kinetics, equation 2 was used:



$$\log(q_e - q_t) = \log(q_e) - \frac{K_1}{2.303} t \quad (2)$$

Where  $K_1$  is the pseudo-first order constant ( $\text{min}^{-1}$ ),  $q_e$  and  $q_t$  are the equilibrium adsorption capacities  $y$  for a time  $t$ . The numerical values of  $k_1$  and  $q_e$  are obtained from the slope and intercept, respectively, of the linear form of the pseudo-first order equation.

To perform the data modeling to pseudo second order kinetics, Equation (3) was used:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \quad (3)$$

Where  $K_2$  is the pseudo-second order constant ( $\text{g/mg.h}$ ). The numerical values of  $K_2$  and  $q_e$  are obtained from the slope and intercept, respectively, of the linear form of the pseudo-second order equation.

On the other hand, to analyze and determine the adjustment of the experimental data to the mathematical models of adsorption kinetics, the regression design was used.

## Adsorption isotherms

The results obtained in the adsorption tests were modeled to the Langmuir and Freundlich Isotherm. The test data were modeled to the Langmuir isotherm according to Equation (4):

$$q_e = \frac{q_{max} \cdot b \cdot C_e}{1 + b \cdot C_e} \quad (4)$$

Where  $q_{max}$  is the maximum amount of metal adsorption/adsorbent weight (mg/g) and  $b$  is the adsorption equilibrium constant (L/mg). These values are obtained from the slope of the linear graph of the Langmuir isotherm.

On the other hand, to model the data to the Freundlich isotherm, Equation (5) was used:

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

Where  $K_F$  is the Freundlich constant ( $\text{mg}^{1-n} \cdot \text{L}^n/\text{g}$ ),  $n$  is the Freundlich exponent and  $1/n$  is the slope of the Freundlich isotherm graph, which indicates the adsorption intensity.

Likewise, to analyze and determine the adjustment of the experimental data to the mathematical models of the isotherms, the regression design was used.

## Results and discussions

### Wastewater Organic Sludge Analysis

Rulkens (2008) mentions that organic sewage sludge has organic material such as proteins, carbohydrates, fats and oils; inorganic material such as metals and at the same time a wide selection of living and dead organisms. Therefore, in Table 1 and Table 2 shows the inorganic and biological composition of the sludge used in this investigation.

**Table 1.** Analysis of metals by ICP of organic sludge from waters.

Metal	(mg/kg MS)	Metal	(mg/kg MS)	Metal	(mg/kg MS)	Metal	(mg/kg MS)
Aluminum	4 410	Cerium	< 0.25	Lithium	< 1.21	Silicon	100.8
Antimony	< 0.54	Cobalt	<0.10	Magnesium	6 328	Sodium	1 068
Arsenic	< 2.21	Copper	109.2	Manganese	133.3	Thallium	< 0.74
Barium	88.76	Chrome	<0.03	Molybdenum	< 0.06	Titanium	37.60
Beryllium	< 0.03	Tin	<0.73	Nickel	< 0.05	Vanadium	29.03
Boron	< 1.99	Strontium	>100.0	Silver	< 0.16	Zinc	550.7
Cadmium	< 0.04	Match	>20000	Potassium	4 298		
Calcium	31 210	Iron	4 840	Selenium	< 0.82		

**Table 2.** Biological composition of organic sewage sludge.

Organisms		Unit	Result
Coliforms	Fecal coliforms	NMP/g	$4.6 \times 10^9$
Protozoa	<i>Entamoeba coli</i>	N°Org/g	0
	<i>Endolimax nana</i>		0
	<i>Blastocystis hominis</i>		0
	<i>Entamoeba hytloptica</i>		0
	<i>Giardia duodenalis</i>		0
	<i>Balantidium coli</i>		0
	<i>Cryptosporidium sp.</i>		0
	<i>Trichomonas hominis</i>		0
Helminths	<i>Ascaris lumbricoides</i>	N° Org/g or Eggs /g	0
	<i>Strongyloides stercoralis</i>		50
	<i>Trichuris trichiura</i>		0
	<i>Taenia sp</i>		50
	<i>Hymenolepis nana</i>		0
	<i>Fasciola hepatica</i>		0

The results shown in Table 1 show that some metals present in the sludge are found in high concentrations. These values could cause concern when using sludge as adsorbent material. However, according to the

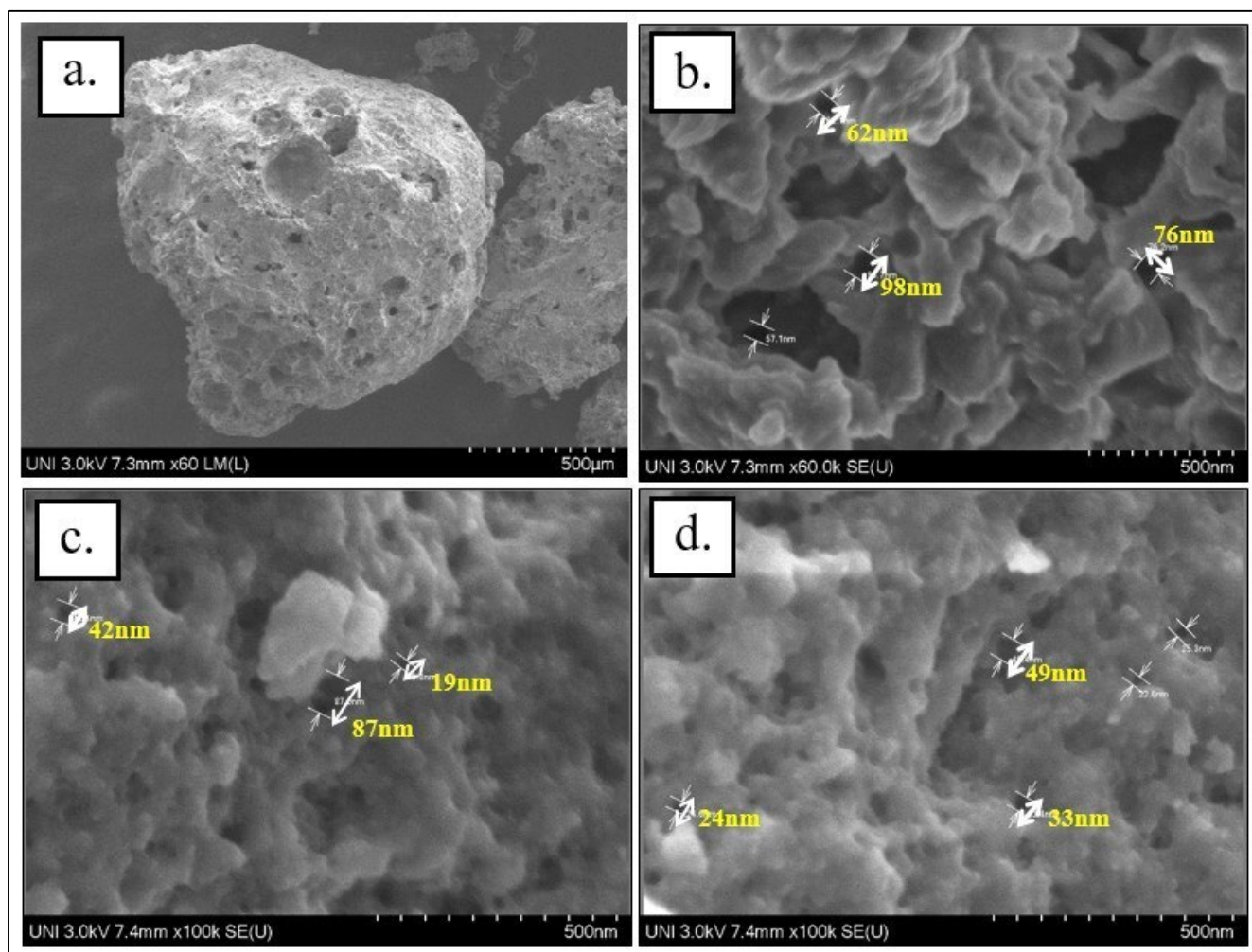
studies carried out by Park, Kang and Kim (2008) indicate that converting the sludge to activated carbon through the pyrolysis process would allow the metals to be concentrated in the activated carbon, avoiding their subsequent leaching in the adsorption process. On the other hand, the concentration of the different microbiological organisms shown in Table 2 show the presence of fecal coliforms, *Strongyloides stercoralis* and *Taenia sp.* Nevertheless, according to Rojas, Gutiérrez and Colina (2016), the conversion of sludge to activated carbon through the pyrolysis process also allows the total elimination of pathogenic microorganisms. Therefore, it can be inferred that the metals and coliforms present in the composition of the sludge shown in Tables 1 and 2 would not represent harm to people's health.

## **Characterization of nanoporous activated carbon**

### **Morphological analysis of activated carbon by scanning electron microscopy (SEM)**

Figure 1 shows the presence of pores on the activated carbon surface, which shows the effect of the activating agent ( $\text{ZnCl}_2$ ) on the structure of the material. This is done due to the washing process of the raw material with the applied chemical activator that helps create new cavities or craters that contribute to the porous structure of the activated carbon and therefore guarantees a greater removal of metals. Likewise, Rio, Faur-Brasquet, Le-Coq, Courcoux y Cloirec (2005) affirm the importance of the

use of an activating agent, since tests carried out by these authors showed that the use of sludge as an adsorbent material without an activation process presents a lower efficiency in the removal of metals due to the smooth structure of the material.



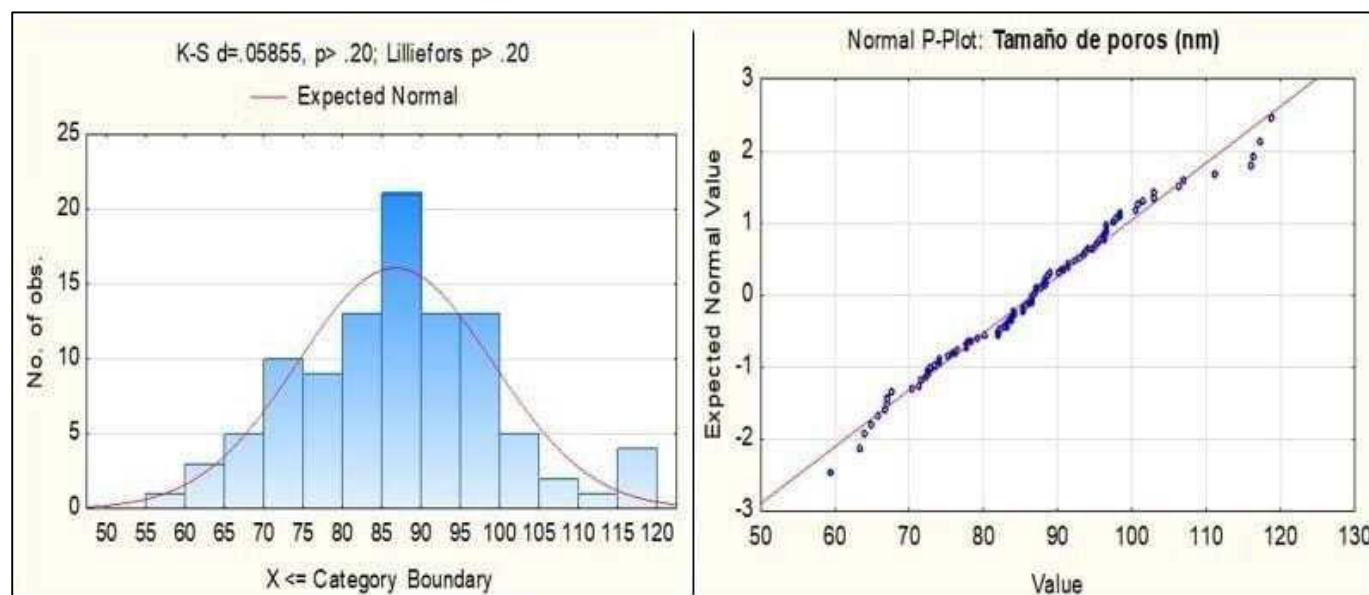
**Figure 1.** Microphotography of activated carbon using the SEM technique with magnifications of (a) 60x, (b) 60,000x, (c) 100,000x and (d) 100,000x.



In Figure 1a, with a magnification of 60x, the presence of some pores on the surface of the activated carbon is observed. Magnification at 60000x in Figure 1b allows observing the presence of pores of size 57 to 98 nm. With a magnification of 100000x it is clearly seen in Figures 1c and 1d the formation of pores of 19, 24, 49 and 87 nm. Therefore, the scanning microscopy analysis shows that the nanopores found on the surface are smaller than 100 nm.

On the other hand, the images obtained from the Scanning Microscopy analysis were submitted to the IMAGE-J program to calculate the pore size of a certain area and determine if their size follows a normal distribution.

Figure 2 shows that the pore sizes present on the activated carbon surface follow a normal distribution. Likewise, the average pore size according to the Gaussian distribution is 86.7 nm and most of the samples have a size between 70 and 95 nm. Murray (2008) corroborates indicating that nanopores are cavities of manometric size between 1 and 100 nm. Therefore, with these data it is stated that the activated carbon made from sludge from a WWTP has nanopores.



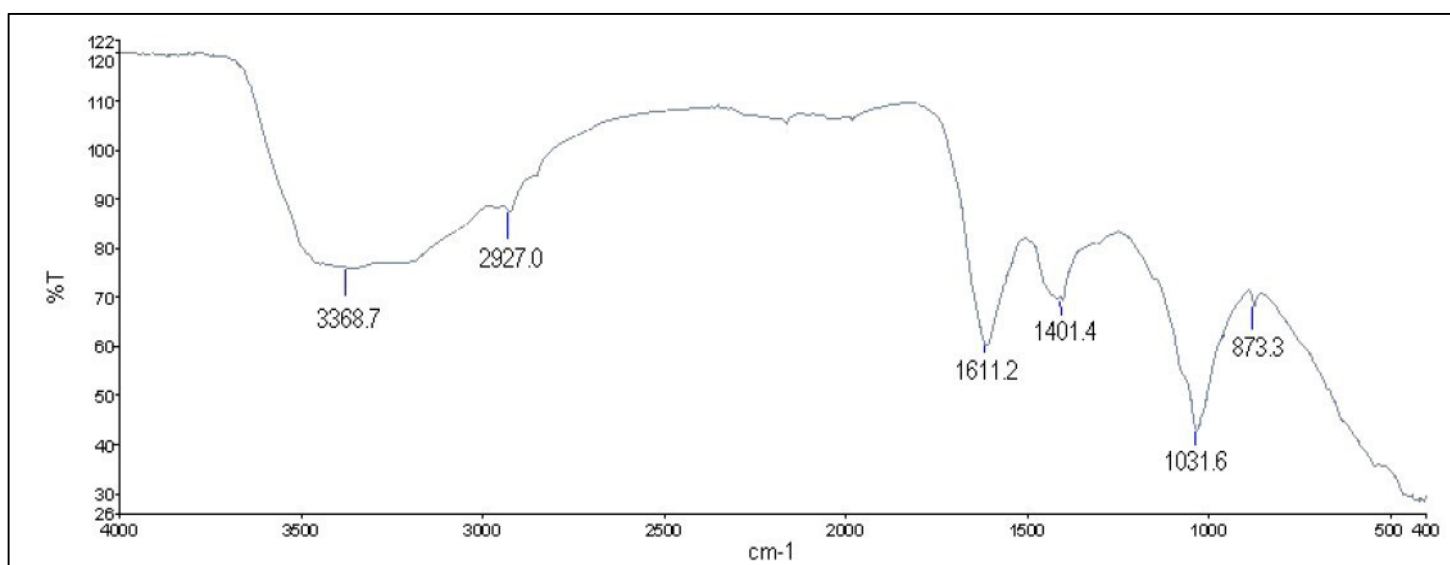
**Figure 2.** Normality distribution for the pore size of activated carbon.

## Surface chemical analysis of activated carbon by Fourier Transform Infrared Spectroscopy (FTIR)

The results of the surface chemical analysis of activated carbon based on organic sewage sludge are shown in Table 3 and Figure 3.

**Table 3.** Identification of functional groups found in activated carbon.

Characteristic peak (cm <sup>-1</sup> )	Functional group	Vibrational mode	Theoretical absorption range (cm <sup>-1</sup> )
3368.7	O-H	Tension	3700-3200
2927.0	O-H	Tension	3200-2700
1611.2	C=C	Tension	1620-1610
1401.4	O-H	Bending	1440-1395
1031.6	C-O	Tension	1050-1000
3368.7	O-H	Tension	3700-3200



**Figure 3.** Chemical analysis of activated carbon by Fourier transform spectroscopy.

Figure 3 shows the presence of peaks in the IR electromagnetic spectrum, the peaks being at  $3368.7\text{ cm}^{-1}$ ,  $1611.2\text{ cm}^{-1}$  and  $1031.6\text{ cm}^{-1}$  the most pronounced. Likewise, these peaks indicate the existence of functional groups such as: hydroxyl and carboxyl, which will have a crucial role in the adsorption of heavy metals, in this case As (III). Therefore, these results affirm that activated carbon made from sludge from a WWTP has adsorption properties.

### Effect of As (III) concentration on adsorption

Table 4 shows that the adsorption percentage of As (III) decreases when the concentration increases due to the limited availability of adsorption sites on the surface of activated carbon in the face of a higher concentration of the metal. While at lower concentrations of As (III), the percentage of adsorption increases due to the existence of a greater number of active sites per gram of adsorbent available for the deposition of metal ions at lower concentrations.

**Table 4.** Adsorption tests at different initial concentrations of As (III).

$C_0$ As (mg/l)	$C_e$ As (mg/l)	Adsorption of As (III) (%)	$q_e$ (mg/g)
0.247	0.004	98.4	0.02
0.406	0.007	98.3	0.02
0.564	0.038	93.3	0.03
0.683	0.05	92.6	0.04
0.801	0.063	92.1	0.05

Likewise, the results show the efficiency of activated carbon from organic wastewater sludge, since this adsorbent managed to reduce the concentration of As (III) to 0.004 mg/l, a value that is below the Maximum Permissible Limit (MPL) of As (III) established by the WHO. Likewise, studies carried out by Wongrod *et al.* (2018), also demonstrated the adsorption efficiency of WWTP sludge as activated carbon, obtaining an adsorption percentage of 72 % for As (III). However, this percentage was lower than that found by the present investigation, where a maximum efficiency of 98.4 % was obtained.

On the other hand, there are similar studies that show the efficiency of sludge as activated carbons, reaching high percentages of adsorption on other metals Yang *et al.* (2010), who showed that activated sludge has an adsorption efficiency of 89 % for Zn (II).

### **As (III) adsorption kinetics**

The application of the kinetic models to the experimental data of the adsorption of As (III) as a function of time, was carried out in order to evaluate which of the proposed models is the one that best describes the kinetics and the limiting step in the adsorption of the ion. Metal in the adsorbent.

Table 5 shows the values calculated for the first-order adsorption kinetics model from the tests carried out with the variation of the contact or agitation time.

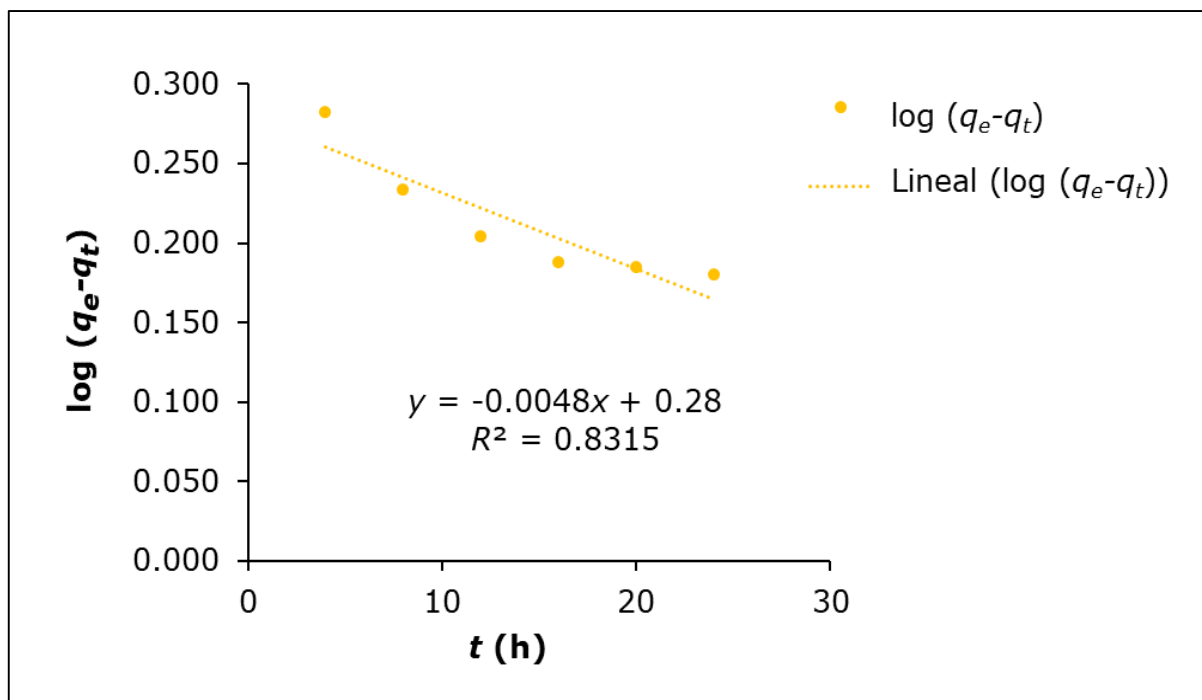
**Table 5.** Values for first-order adsorption kinetics.

t (h)	C <sub>o</sub> As(III) (mg/l)	C <sub>e</sub> As(III) (mg/l)	q <sub>e</sub> (mg As III/g adsorbent)	q <sub>t</sub> (mg As III/g adsorbent)	Log (q <sub>e</sub> -q <sub>t</sub> )
4	0.56	0.37	0.012	-1.905	0.283
8	0.56	0.24	0.020	-1.694	0.234
12	0.56	0.14	0.027	-1.574	0.204
16	0.56	0.07	0.031	-1.512	0.188
20	0.56	0.06	0.032	-1.500	0.185
24	0.56	0.04	0.033	-1.481	0.180

The graph shown in Figure 4 details the application of the pseudo-first order model to the experimental data of the adsorption kinetics of As (III). From this graph, the pseudo-first order linear equation can be obtained, which is:

$$\text{Log } (q_e - q_t) = 0.2802 - 0.0048 t \quad (6)$$

From which it follows that the pseudo first order constant ( $K_1$ ) is  $0.01 \text{ h}^{-1}$  and the equilibrium adsorption capacity  $y$  for a time  $t$  ( $q_1$ ) is 1.91.



**Figure 4.** Pseudo-first order kinetics for As (III).

On the other hand, Table 6 shows the values calculated for the second-order adsorption kinetics model from the tests carried out with the variation of the contact time or agitation.

**Tabla 6.** Values for second order adsorption kinetics

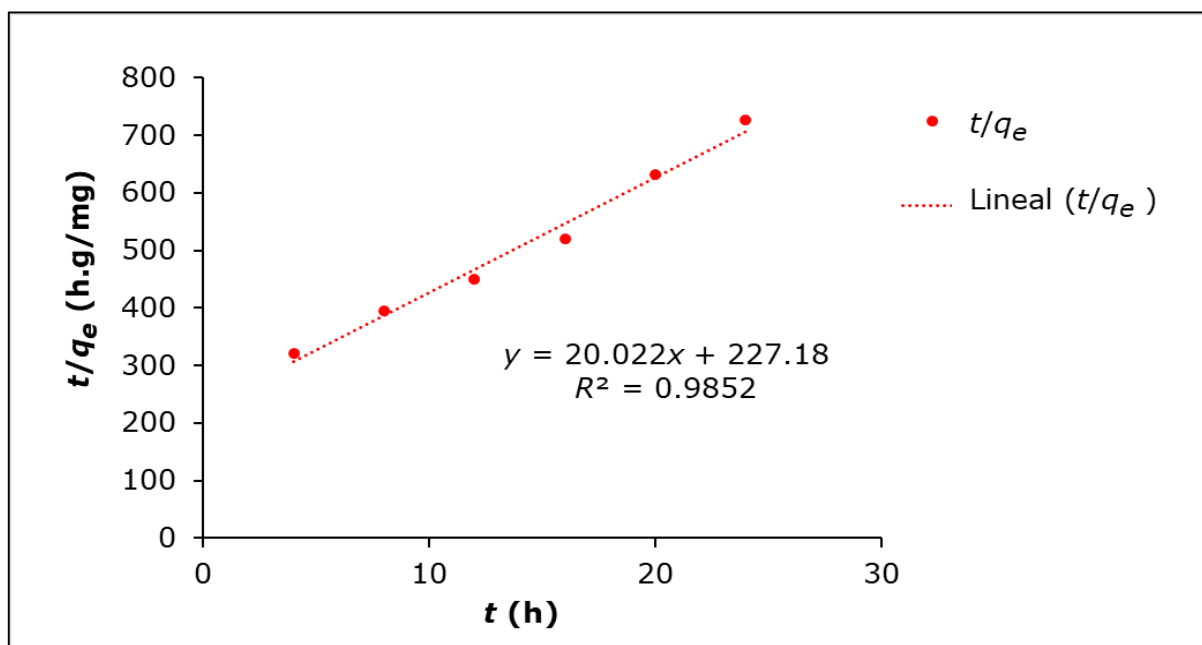
<b>t (h)</b>	<b>C<sub>o</sub> As(III) (mg/l)</b>	<b>C<sub>e</sub> As(III) (mg/l)</b>	<b>q<sub>e</sub> (mg As III/g adsorbent)</b>	<b>t/q<sub>e</sub> (h.g adsorbent /mg As III)</b>
4	0.56	0.37	0.012	321.61
8	0.56	0.24	0.020	395.06
12	0.56	0.14	0.027	450.18
16	0.56	0.07	0.031	519.80
20	0.56	0.06	0.032	632.41
24	0.56	0.04	0.033	725.90

Figure 5 shows the application of the pseudo-second order model to the experimental data of the adsorption kinetics of As (III). From this graph, the pseudo-second order linear equation can be obtained, which is:

$$t/q_t = 227.18 + 20.022 t \quad (7)$$

From which it follows that the pseudo second order constant ( $K_2$ ) is 0.05 g/mg.h and the equilibrium adsorption capacity ( $q_2$ ) is 1.91.





**Figure 5.** Pseudo second order kinetics for As (III).

Table 7 presents the pseudo-first and pseudo-second order adsorption kinetic constants obtained for As (III). Likewise, it is observed that the results present a high fit with respect to the pseudosecond order model ( $R^2 > 0.99$ ). Taking into account that the pseudo-second order model is based on the assumption that the reaction rate is controlled by a chemisorption, we can say that the As (III) adsorption mechanism of the present study is determined by a phenomenon chemical, where the exchange of ions between the adsorbent and adsorbate takes place (Agrofioti, Kalderis, & Diamadopoulos, 2014; Bjorklund & Li, 2017).

**Table 7.** Pseudo first and second order kinetic constants for As (III).

Metal	Pseudo first order			Pseudo second order		
	$q_1$	$k_1$	$R^2$	$q_1$	$k_1$	$R^2$
As (III)	1.91	0.01	0.83	0.05	1.76	0.99

The kinetics obtained for the adsorption process of the present investigation is similar to the adsorption kinetics of As found by Wongrod *et al.* (2018), since when using KOH as an activator for the transformation of wastewater sludge to activated carbon, they were able to determine that the adsorption kinetics that best fit the process was pseudosecond order with an  $R^2$  of 0.96. Likewise, the value of the rate constant ( $k_2$ ) found by these authors was 1.91 g/mg.h, a value similar to that found in the present investigation.

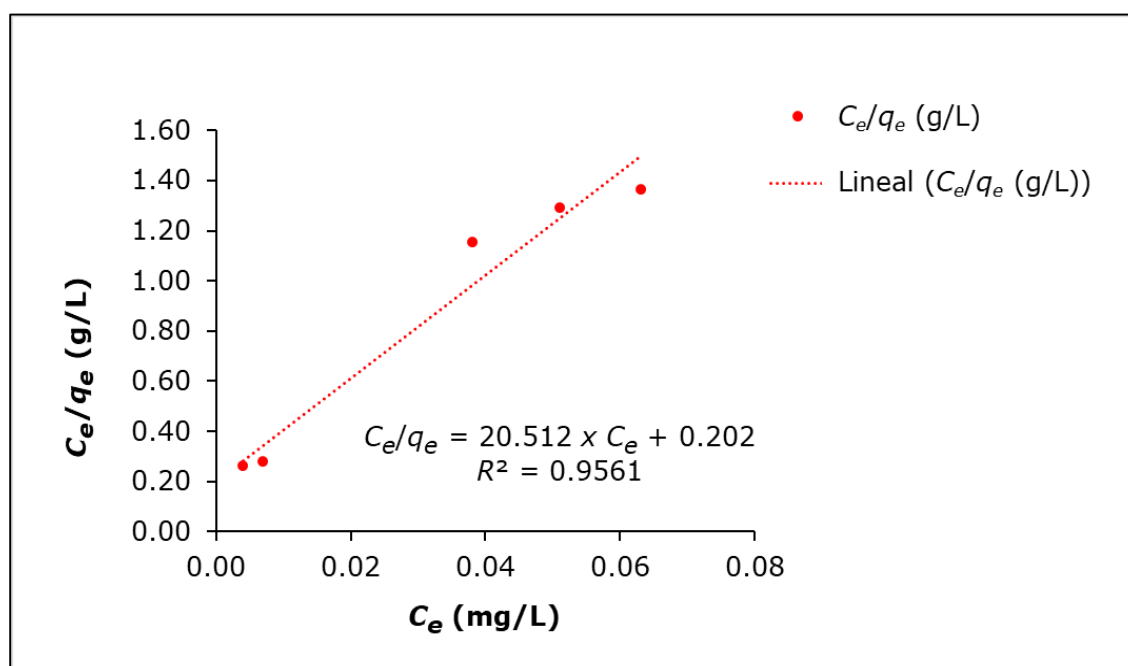
In the same way, the results of the present study agree with what was found by Tavares *et al.* (2012), who also determined that the adsorption kinetics of As (III) followed the pseudo-second order model, obtaining an  $R^2$  of 0.96.

### As (III) adsorption isotherm

Experimental data on arsenic ion adsorption equilibrium were evaluated using Langmuir and Freundlich adsorption isotherm models.

Figure 6 shows the graph of the experimental values of the specific adsorption ( $C_e/q_e$ ) as a function of the concentration of the metal ion in equilibrium ( $C_e$ ) and the linear form of the Langmuir equation it is:

$$\frac{C_e}{q_e} = 20.51 C_e + 0.202 \quad R^2 = 0.96 \quad (8)$$



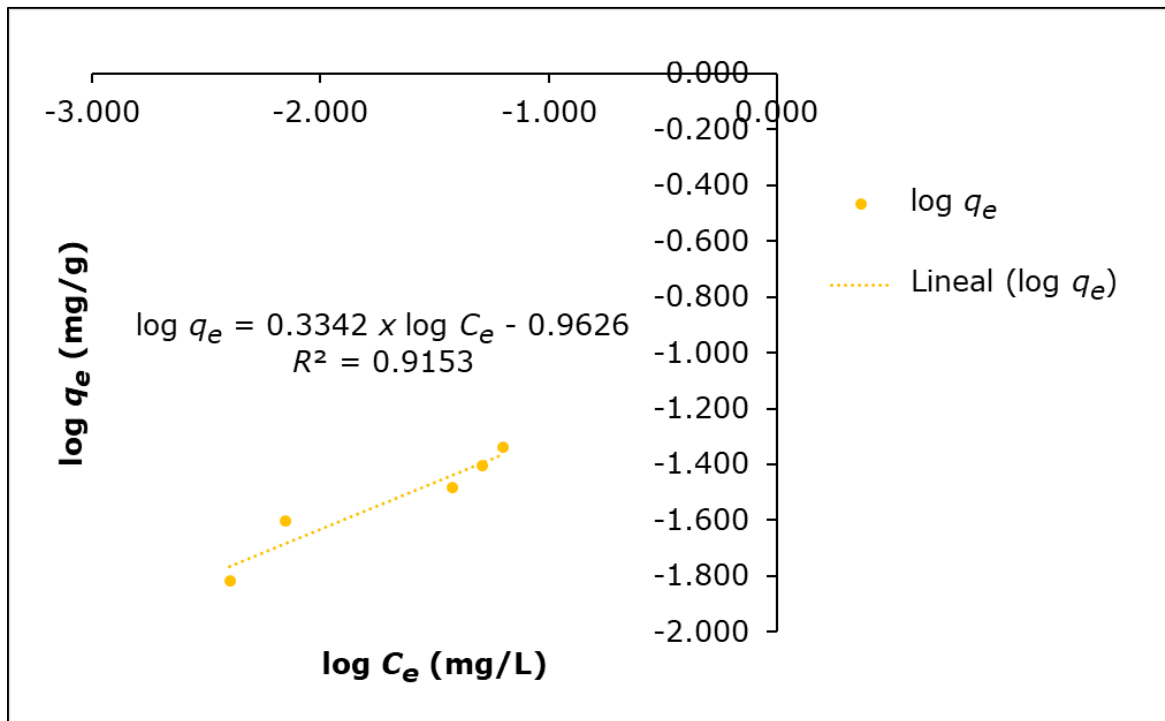
**Figure 6.** Langmuir isotherm for the adsorption of As (III) with activated carbon.

From the data obtained, it is determined that the maximum adsorption capacity ( $q_{e \text{ max}}$ ) is 0.05 mg/g and the adsorption equilibrium constant ( $b$ ) is 101.54 l/mg. Likewise, these results show that the

adsorption of As (III) on activated carbon fits the Langmuir model because the value of  $R^2$  is 0.96.

Figure 7 shows the graph of  $\log q_e$  as a function of  $\log C_e$  and the linear form of the Freundlich equation, which is:

$$\log q_e = 0.3342 \log C_e - 0.9626 \quad R^2 = 0.92 \quad (9)$$



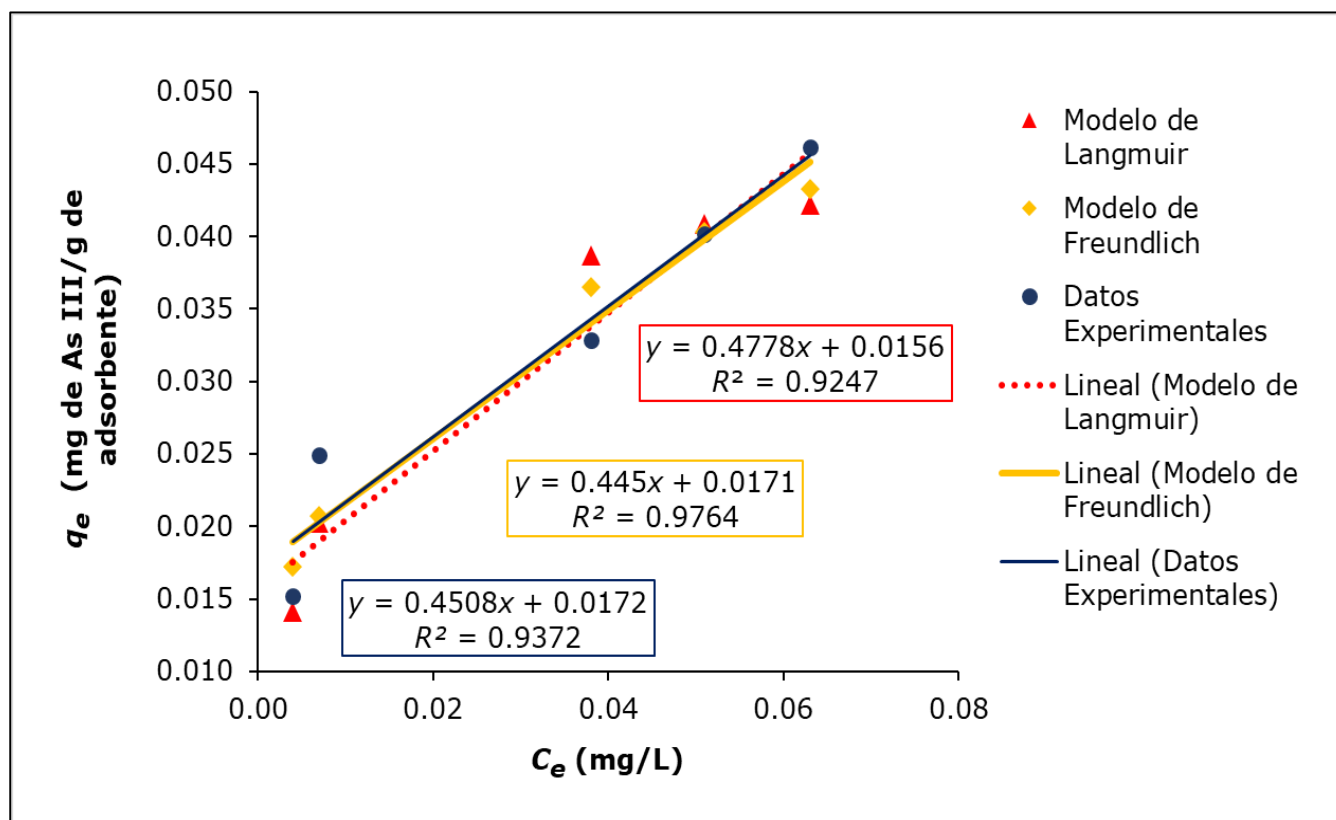
**Figure 7.** Freundlich isotherm for the adsorption of As (III) with activated carbon.

From the data mentioned above, it is determined that the Freundlich equilibrium constant ( $K_F$ ) is 0.11 (mg<sup>1-n</sup>·Ln/g), the intensity of the equation ( $1/n$ ) is 0.33, and the Freundlich exponent ( $n$ ) is 2.99.

In relation to the data obtained from the equation, it is determined that the Freundlich isotherm is favorable since the value of  $n$  is greater than 1. Likewise, the value of the slope ( $1/n < 0.5$ ) of figure 7 demonstrates the validity of the Freundlich isotherm over the range of As (III) concentration studied and states that the isotherm is favorable (Obregón, 2012). These values are attributed to the heterogeneous nature of the adsorbent surface with an exponential distribution of the energy of the adsorption sites. Likewise, these results show that the adsorption of As (III) on activated carbon fits the Freundlich model because the value of  $R^2$  is 0.918.

## Comparison between Langmuir and Freundlich isotherm

The graph in Figure 8 shows the fit of the experimental data with the Langmuir and Freundlich isotherm models. Observing a better fit of the Freundlich model with the experimental data ( $R^2 = 0.98$ ).



**Figure 8.** Adjustment of the experimental data of the adsorption of As (III) on activated carbon to the Langmuir and Freundlich models.

Likewise, Table 8 shows that there is a significant difference ( $p < 0.05$ ) between the adsorption capacities of As (III) ( $q_e$ ) of the experimental data and the Langmuir Isotherm. However, there is no significant difference ( $p > 0.05$ ) between the experimental data between the adsorption capacity of As (III) ( $q_e$ ) of the experimental data and the Freundlich Isotherm. Therefore, it can be stated that the Freundlich model presents a better fit to the experimental data. That is the adsorption of As (III) can be by multilayer (Freundlich, 1907).

**Table 8.** T-test of independent variables for the adsorption capacity of the Langmuir and Freundlich isotherms.

Groups 1, 2	Media Group 1	Media Group 2	t-value	Df	P
E vs. L	0.031850	0.047715	-2.89470	8	0.020054
E vs. F	0.031850	0.023244	0.77484	8	0.460722

## Conclusions

The synthesized activated carbon has a nanoporous surface with an average size of 86.7 nm with the presence of functional groups such as hydroxyl and carboxyl. That could indicate the existence of covalent bonds, and these could show that the adsorption of As (III) ions was a chemical process.

From the kinetic study it was determined that the adsorption process fits the pseudo-second order model, which allows establishing that the adsorption of As (III) ions is the result of the physical and chemical interaction of the metal on the carbon surface activated.

According to the correlation of the experimental data with the Langmuir and Freundlich models, it was shown that the experimental data fit both models. However, according to the statistical analysis, it can be shown that since there is no significant difference between the

experimental data of the adsorption capacities of As (III) ( $q_e$ ) and the Freundlich Isotherm, the best data fit would be with the Freundlich model. Therefore, based on the assumptions of the Freundlich Isotherm, the adsorption process of As (III) would be carried out in energetically heterogeneous centers, where the adsorption sites with the same energy of interaction between adsorbate and adsorbent are grouped in small areas.

The activated carbon made from organic sewage sludge presented an efficiency of 98.4 % in the adsorption of As (III) ions, reducing the concentration of this metal to 0.004 mg/l, a value that is below of LMP the established by the WHO for drinking water.

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