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Effect of Activated Carbon Made from Cocoa (Theobroma Cacao L.) Shells on the Adsorption of Iron in Aquifer Water

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This research aims to determine the effect of activated carbon obtained from cocoa husks (*Theobroma cacao L.*) on the adsorption of iron (II) present in water of an aquifer for human consumption. Charcoal was prepared at different carbonization temperatures (500, 600 and 700 °C) for 30 minutes and activated with phosphoric acid in the proportions of 1:1. Iron (II) adsorption was determined as a function of variations in mixing speed, contact time, charcoal dosage and stirring speed. It was determined that, over the range considered, agitation speeds had no significant effect on the percentage of iron (II) removal, being the dose of activated carbon and temperature, the most influential variables. The water samples had an initial iron concentration of 3.15 mg/L and 4 mg/L. The best iron (II) adsorption result was obtained with activated carbon at the carbonization temperature of 700 °C, with a mass of 1.5 g of carbon, with efficiencies of 93 % and 98 % for both samples considered. Based on the results, it was concluded water for human consumption is treatable with activated carbon derived from *Theobroma cacao L*. for the adsorption of iron (II), considering that this parameter is below the maximum limit of 0.3 mg/L allowed by current regulations.

1. Introduction

Water is the main natural element of planet Earth, it is a limited renewable natural resource and is what allows the development of plant, animal and human life (Baquerizo et al., 2019), however, in many regions of the world, water has become an increasingly scarce resource due to population growth and the consequent domestic, industrial, agricultural, livestock, mining and other activities (Gastañaga, 2018). As a result, despite the fact that water is the most valuable liquid on earth and an essential component of all living things, it has never received as much attention as other issues (Bolaños-Alfaro et al., 2017). Therefore, the management of water resources in rural areas becomes important, where it depends largely on the participation of communities in the administration and the use of the resource (Delgado-García et al., 2017). In this regard, Chaturvedi and Dave (2012), consider universal access to safe drinking water as a challenge for the scientific community, which has a responsibility to develop appropriate technologies.

Water pollution is the presence of chemical, physical or biological constituents or factors that produce an impaired condition of a given mass of water with respect to some beneficial use (Schweitzer and Noblet, 2018). Thus, water quality in rivers and lakes is critical for human and economic development, and accurate assessment and estimation of water quality levels has become essential, since even minimal changes in water quality characteristics can endanger lives and industries that depend on water (Li and Liu, 2019).

Iron is the fourth most abundant element on Earth (Khatri et al., 2017) and is found naturally in water in various forms (ref), is a vital mineral nutrient that acts as a cofactor for many enzymes, and plays a role in maintaining energy metabolism. The permissible limit established by the World Health Organization for iron in drinking water is 0.3 mg/L; despite not being thought to pose a health risk to people, its presence in drinking water is somewhat unpleasant due to the offensive odors it emits, its rusty taste and color, how it feels on skin and hair, and its

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propensity to stain clothing (Ityel, 2011). However, Matsiyevska et al. (2020) consider the fact that drinking water with a high iron content over an extended period of time can lead to liver disorders, allergic reactions, and other conditions, as well as having a bad impact on the skin and blood composition.

Activated carbon is purified, powdered charcoal, which is physically or chemically treated to generate microcracks, which greatly increase its adsorption surface area. It has a large surface area (500-1500 m^2/g) and electrical charge that effectively adsorbs a wide range of polar compounds (Marsh and Rodriguez-Reinoso, 2006; Jackson, 2020).

Previously, the raw material for activated carbon synthesis was coal and charcoal, however, it can nowadays be obtained from a variety of materials (Isemin et al., 2021). As a result, lignocellulosic and charcoal materials can be utilized as feedstocks to make activated carbon, which can then be made from environmental wastes with a high carbon content (Ahmad and Azam, 2019).

Commercial activated carbon is one of the most widely used adsorbent materials, however while having a high surface area, a good volume of pores, and a variety of surface active functional groups, it is expensive to produce. Therefore, it has chosen to look for more affordable alternatives to traditional adsorbents, such as agricultural waste, whose use is environmentally friendly because it lowers the cost of waste disposal. (Ramírez et al., 2017).

With the use of an environmentally friendly method of adsorption with activated carbon employing cocoa (*Theobroma cacao L*.) shells as the activating carbon, this study effort is provided as an alternative to standard treatments to reduce the concentration of iron (II) in an aquifer.

The aim of the research was to evaluate the effect of activated carbon made from cocoa shells on the adsorption of iron (II) present in water from an aquifer in the district of Yantaló in the province of Moyobamba, located in the department of San Martín, in northern Peru.

2. Materials and methods

The following steps were taken in conducting the investigation: gathering, drying, crushing, and sieving cocoa shells; impregnating the sample with phosphoric acid in a 1:1 ratio (15 grams of sample to 15 ml of phosphoric acid) for 24 hours; anaerobic carbonization in the muffle for 30 minutes at a temperature of 700 °C; grinding; neutralization with 1M sodium hydroxide; and washing with distilled water. The American Public Health Association's analytical methods were used to determine the amount of iron in the water.

2.1 Materials

Turbidimeter Turbiquant 1100 IR, Magnetic Hotplate Stirrer equipment (Model 984 VW7CHSEUA), Colorimeter DR 1900, Muffle Furnace FO110CR, Cooker Memmert UF75, Analytical Balance PGW 753i, pH meter pHC 101 are the instruments and materials utilized in the research.

2.2 Reagents

Cocoa (*Theobroma cacao L*.) shell charcoal treated with 85 % phosphoric acid (H_3PO_4) was used.

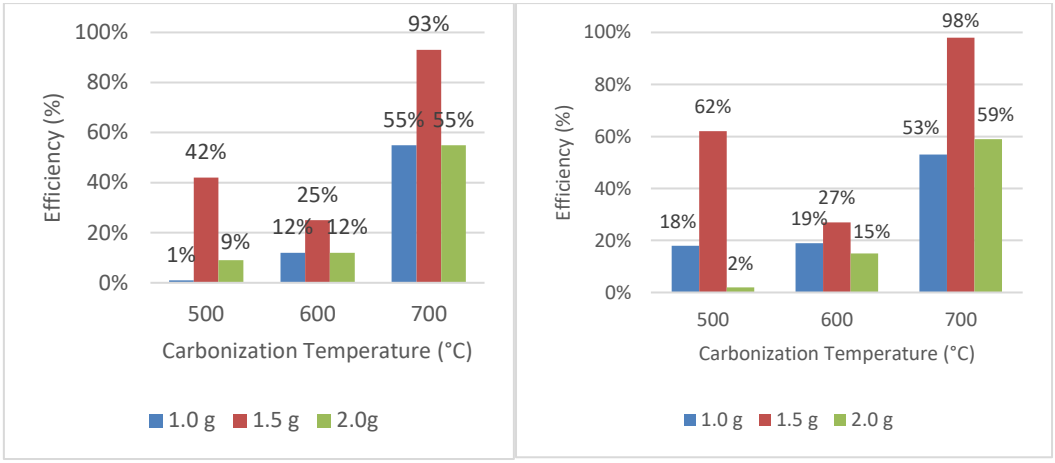
2.3 Statistical analysis

With the goal of determining whether there is a significant difference between the treatments, a completely randomized design was constructed, with the basic assumptions being checked, the test for normality and homogeneity of variance conducted, and the ANOVA completed. For this purpose, the variance of the treatment was compared to the variance of the error, and it was determined whether the first one was high enough in accordance with the distribution F. There are established treatments that will be used on the experimental units. The treatments for each case were determined by the parameter Iron (II).

3. Results and discussion

Palisoc et al (2019) obtained the removal of Zn^{2+}, Cd^{2+} and Pb^{2+} between 24 and 81 %, using 10 mg of activated cocoa carbon with $ZnCl_2$ at 800 °C in 100 mL of sample, after 72 hours of treatment. Maita et al. (2020) removed 68.36 % of Cu^{2+} with activated carbon from the cocoa husk (5 g/100 mL water) at 500 °C of a 10 g/L copper sulfate solution for 2 hours. These investigations confirm the high adsorption capacity, high surface area and porous structure (micro and mesoporous) that is achieved in this material. Figure 1 shows the iron (II) removal efficiency using different amounts of activated carbon per 100 mL of treated sample and different activation temperatures (500, 600 y 700 °C). When using 1.5 g of activated carbon, it is observed that the removal efficiency at 600 °C decreases to 25 % for sample of 3.13 mg/L Fe (II) and 27 % for sample of 2.34 mg/L Fe (II), in contrast to the 1 g and 2 g masses where the removal efficiency increases for the three given temperatures. A similar behaviour is observed for hardness removal with coconut shell activated carbon by Shemeera et al. (2019), where the removal decreases for doses of 12, 13 and 14 g of activated carbon per 100 ml of treated

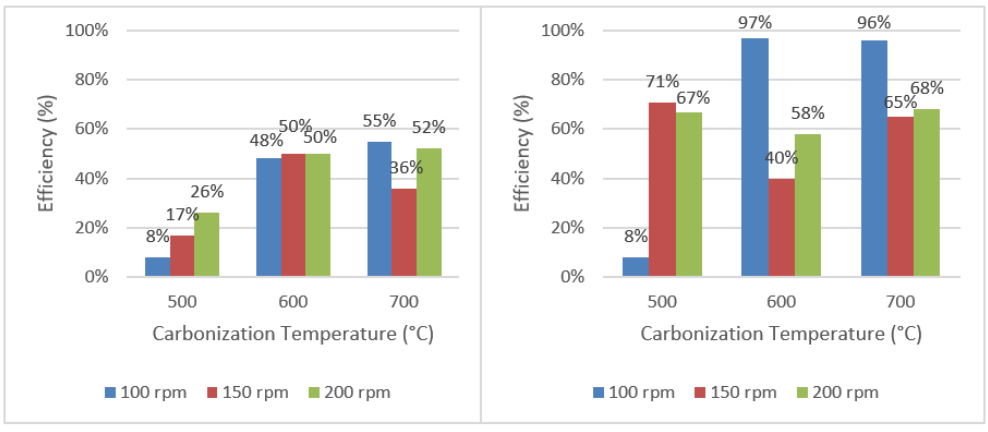
water. Removal of a specific ion present in the water may decrease with increasing doses of activated carbon, especially when other ions are present, as reported by Kaveeshwar et al. (2018) on the removal of Ba (II) and Sr (II) with pecan shell activated carbon. The presence of other ions in the aquifer and the pore size of the activated carbon were combined so that at 1.5 g activated carbon and 600 °C, the adsorption of iron (II) decreased.



(a) (b)

Figure 1: Removal efficiency of Iron (II) versus carbonization temperature (°C) and mass (g) of activated carbon. (a) Sample with 3.13 mg/L of Iron (II) (b) Sample with 2.34 mg/L of Iron (II)

Using a 50 % phosphoric acid solution as an activating agent for 1 hour, Yetril et al (2019), refer in their research that the functional groups OH, CO and CH are responsible for the adsorption, the first two are part of the cellulose and hemicellulose respectively and the third is part of aromatic groups. Eletta et al (2020) reviewed research on the adsorption of pollutants with activated carbon from cocoa, specifying that removals above 90 % of most water pollutants are achieved, with some exceptions. The acid treatment and the temperature are fundamental for the pore size, morphology and the type of functional groups that the activated carbon will present (Ahmad et al, 2013; Eletta et al, 2020). These antecedents explain the adsorption of iron (II) in this investigation.



(a) (b)

Figure 2: Removal efficiency of Iron (II) versus carbonization temperature (°C) and stirring rate (rpm). (a) Sample with 3.13 mg/L of Iron (II) (b) Sample with 2.34 mg/L of Iron (II).

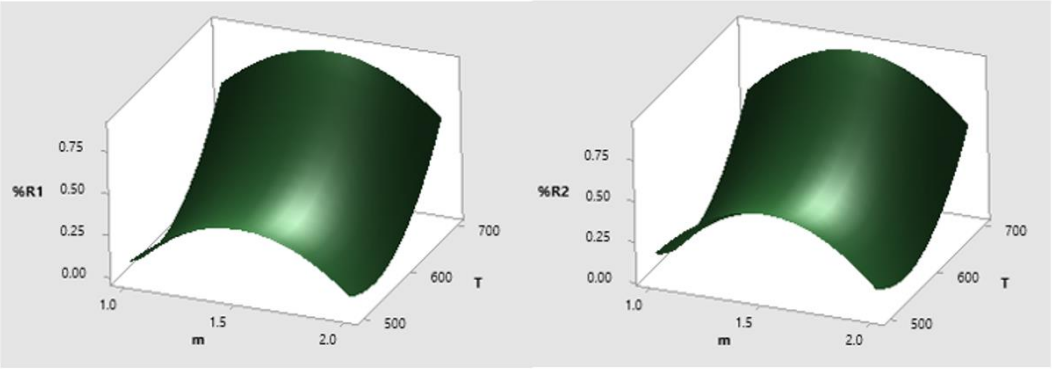
Figure 2 shows the removal of iron (II) using 1.5 g of activated carbon for every 100 mL of sample at 500 °C, 600 °C and 700 °C but at different stirring speeds of 100 rpm, 150 rpm and 200 rpm. If we perform an analysis of variance on the data, the parameter P is greater than 0.05 for the variable stirring rate and temperature

multiplied by stirring rate, resulting only as a significant variable the temperature. Although in the present research the stirring rate has been varied; in the proposed values the changes have not been statistically significant; however, Yetril et al (2020) report that working with an activated carbon column and with water flows of 5 and 10 L/min, greater removal of the contaminant is achieved with the lowest flow rate.
Table 1 shows that significant difference test of Tukey Multiple Comparisons for stirring rate factor indicates that the mean differences (in percentage of Iron (II) removal) are very similar because they belong to only one common group A, so this proves that the stirring rate is not a factor that affect significantly for the percentage of Iron (II) removal.

Table 1. HSD Tukey Multiple Comparisons for Stirring rate

Stirring rate	Sample 3.13 mg/L			Sample 2.34 mg/L		
	N	Media	Group	N	Media	Group
100	3	37.00	A	3	67.00	A
150	3	34.33	A	3	58.67	A
200	3	42.67	A	3	64.33	A

Figure 3 shows response surface graphs for the two treated samples considering the mass of activated carbon used per 100 mL of sample and the activation temperature; likewise, the mathematical models for both treatments in the evaluated ranges, corresponding to these graphs, are shown in Table 3.



(a) (b)

Figure 3: Removal percentage of Iron (II) (%R1, %R2) versus carbonization temperature (T) and mass of activated carbon (m). (a) Sample with 3.13 mg/L of Iron (II) (b) Sample with 2.34 mg/L of Iron (II).

Table 2: Parameters of the sample water to be treated with activated carbon

Origin of variations	Sample 3.13 mg/L					Sample 2.34 mg/L				
	Degrees of freedom	Sum of squares	Mean squares	F	P	Degrees of freedom	Sum of squares	Mean squares	F	P
Model	3	0.689	0.230	38.39	0.001	3	0.674	0.225	14.12	0.007
Lineal	1	0.380	0.380	63.52	0.001	1	0.273	0.273	17.16	0.009
T	1	0.380	0.380	63.52	0.001	1	0.273	0.273	17.16	0.009
Squared	2	0.309	0.155	25.83	0.002	2	0.400	0.200	12.59	0.011
m*m	1	0.172	0.172	28.77	0.003	1	0.240	0.240	15.10	0.012
T*T	1	0.137	0.137	22.89	0.005	1	0.161	0.161	10.09	0.025
Error	5	0.030	0.006			5	0.080	0.016		
Total	8	0.719				8	0.754			

Table 2 shows the ANOVA or analysis of variance, to analyze the results of the investigation fulfilling the assumptions of the normality test with the Shapiro-Wilk statistic (for small samples) with a P value > 0.05 for the

Iron (II) adsorption percentage data, for which it is assumed that the data present a normal distribution, in the same way the test of homogeneity of variances was carried out, the Levene statistic having a significance greater than 0.05, this means that the variances of the independent variable in the groups that are compare are approximately the same, because they do not differ significantly. Likewise, it can be seen in the variables temperature (T) and mass of activated carbon (m), there is a significant difference in the percentage reduction of iron in water for human consumption, with a P value < 0.05; which contrasts the interaction of both factors on the dependent variable Iron (II) adsorption, on the other hand it is evident that the values of P are less than 0.05, therefore, the linear and quadratic models selected for temperature (T) and mass of activated carbon (m) are significant.

Table 3 shows the two models of response surface for both percentage of removal of Iron (II) which depend linearly only on temperature and is a quadratic function of mass and temperature at the same time. The stirring rate was discarded from the modeling since it was not statistically significant in the evaluated range.

Table 3: Models of response surface for the percentage of removal of Iron (II) versus temperature (T) and mass of activated carbon (m) for both samples.

mg/L Iron (II)	Models of response surface
3.13	%R1 = 0.3589 + 0.2517 T - 0.2933 m*m + 0.2617 T*T
2.34	%R2 = 0.4344 + 0.2133 T - 0.3467 m*m + 0.2833 T*T

Table 4 shows the R squared values for both models of removal of Iron (II). For the first sample (a) the squared R indicates the variance of common factors, that is, the percentage of the variation of one variable due to the variation of the other variable and vice versa, therefore, the incidence between the mass of coal activated and the temperature is explained in 89.44 %. On the other hand, the predicted R square drops significantly at 31 %. For the second sample the squared R indicates the variance of common factors, the percentage of the variation of one variable due to the variation of the other variable and vice versa, the incidence between the mass of activated carbon and the temperature is explained in 95.84 %, while the predicted R square falls by 13 %. The second model is more sustainable, with the ability to predict responses for new observations.

Table 4: R squared values for both models of removal of Iron (II) obtained

S	R- squared	R-squared (adjusted)	R- squared (predicted)
0.126	89.44 %	83.10 %	58.18 %
0.077	95.84 %	93.34 %	82.95 %

4. Conclusions

This research consisted of the search for the best conditions of mass of activated carbon per 100 mL of sample, activation temperature and stirring speed for the removal of iron (II).

The optimal conditions of carbonization temperature and carbon weight to reduce the iron (II) content, is 700 ºC of carbonization with 1.5 g of carbon, having a removal efficiency of 93 % and 98 % for both samples of water. The speed with which iron (II) is removed is not a factor that influences the reduction of the iron (II) content of the aquifer. The mathematical models obtained for both samples of water from the aquifer show a linear dependence on temperature, as well as a quadratic dependence on mass and also on temperature with the highest correlation coefficient for the sample being 2.34 mg/L of iron (II). It is recommended to characterize the activated carbon from cocoa with SEM microphotographs to analyze the pore size, as well as the evaluation of other raw materials from the region for the removal of other heavy metals.

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