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Adsorption of Cr (VI) by Activated Carbon from Oil Palm Endocarp: Adsorption Isotherm and Kinetic Analysis

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Through different scientific researches and empirical cases, it has been shown that compounds of Cr (VI), which are widely used in the tanning industry, are lethal, even at low concentrations. This situation arises the need to make effective treatments to effluents from the process and the activated carbon (AC) may be useful for treating the wastewater with low chromium concentration. The main objective of this work was to evaluate the behaviour of three different shapes of an AC obtained from the endocarp Colombian palm oil. Batch experiments were conducted based on specific experimental parameters, and the studies included an analysis of the kinetics of adsorption, Freundlich and Langmuir adsorption isotherms, pseudo-first and pseudo-second order kinetic, and a diffusion mechanism. The adsorbed amount of hexavalent chromium until the equilibrium was related with the surface area and pore size, which were obtained by BET analysis. The equilibrium data fitted well to Freundlich isotherm model, suggesting that the removal of hexavalent chromium is performed because of the energy distribution of the adsorption active sites and absence of monolayers. Finally, kinetic studies showed a better fit to the pseudo-second order model.

1. Introduction

Heavy metals in wastewater, like Chromium, have a detrimental impact on the ecosystem and public health. Chromium compounds are usually released from steelworks, chromium electroplating, leather tanning, and chemical manufacturing (Cecen, 2011). In aquatic systems, chromium is usually encountered in the form of Cr(III) and Cr(VI). The hexavalent form Chromium, which is primarily present as chromate (CrO^{-}_{4}) and dichromate ($Cr2O^{-}_{7}$), is generally considered more toxic than the trivalent form, since its salts are very soluble and can be easily absorbed and accumulated in the human body, causing skin irritation, lung cancer, and kidney, liver or gastric damage. Therefore, it is necessary to reduce the concentration of Cr(VI) to acceptable levels before discharging it into aquatic environments (Yang et al, 2014). Activated carbon (AC) is widely used to remove contaminant molecules that cause colour, odour or flavours (Erto et al, 2013), due to its high specific surface area and pore volume, high efficiency and relatively low cost. Removal of Chromium (VI) from wastewaters by using AC depends on the initial concentration of Cr (VI), the contact time, temperature and pH of the water (Silgado et al, 2014). The literature reports a significant number of research about the use of biomass and waste biomass as a source to prepare AC, since any material with high carbon content and low inorganics can be used as a raw material for the production of AC. This is why the studies are focused on obtaining and evaluating low cost, non-conventional adsorbents to develop an economically feasible and effective way to treat water contaminated with Cr(VI) and other contaminants. It has been found that oil palm endocarp yields activated carbon with high developed porosity, due to the high carbon content. This technology not only solves the problems of waste disposal, but also converts it into a product that can be employed as an adsorbent for wastewater treatment. On the other hand, there is a growing interest to develop new carbon materials from biomass to make carbon composites and carbon nanotubes that can also be used to protect the environment.

As a previous stage of this research, the basic characterization of three shapes (pellets, granular, and powder) of an AC obtained from oil palm endocarp was presented together with a kinetic analysis of the Cr(VI)

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adsorption from aqueous solutions (Silgado et al, 2014). This paper reports the adsorption isotherms, which illustrate the amount of contaminant metal adsorbed on a solid surface at different pressures but at the same temperature, for the three samples of AC prepared from oil palm endocarp (granular, powder and pellets). For that purpose, the Langmuir and Freundlich isotherm models were used. The results showed that both models fitted the data reasonably, but the Freundlich adsorption isotherm model fitted better in the time range studied. Since the adsorption capacity of activated carbons can be evaluated from their physical characteristics, such as porosity, surface area and pore size, a BET (Brunauer-Emmett-Teller) analysis was conducted for each sample (granular, powder and pellets). The results showed that the activated carbons studied here have a lower surface area and pore volume than others reported in the literature (Ahmad et al, 2007). According to these results, it is possible to apply some changes in the activation process, in order to obtain AC with better porous structure.

2. Experimental

2.1 Adsorbent and BET surface area

The activated carbon was provided in granular, powder and pellets samples, produced by a Colombian company. In a previous paper, a basic characterization was reported, which included granulometric analysis, determination of moisture content, apparent density, pH measurement, ash content and methylene blue index (Silgado et al, 2014). The surface area for each shape of activated carbon was determined by gas adsorption analysis, and the specific surface areas were calculated by the BET method. Pore volume for each sample was determined as the volume of nitrogen that was kept in the sample at the highest relative pressure.

2.2 Kinetics Test and Adsorption Isotherm

According to the adsorption kinetic (Silgado et al, 2014), batch experiments with various concentrations were conducted to determine the parametric effects of initial adsorbate concentration on Cr(VI) removal. Chromium samples were prepared by dissolving 141.4 mg of potassium dichromate ($K_2Cr_2O_7$) in distilled water. This solution was used as a stock one and diluted to the required initial concentration (Al-Sou'od, 2012). For 100 mL Cr (VI) solution was employed stock solution (5 mL, 10 mL, 15 mL), acetone and 1,5-Diphenylcarbazide in an acid medium for the different initial concentrations (0.75 ppm, 1 ppm, 1.25 ppm). Then, was added 1.0 g of activated carbon and the mixture was stirred at 500 $r•min^{-1}$ at a controlled temperature. Finally, each 20 min a sample of the solution was measured, filtered and determined the absorbance with a spectrophotometer (UV Spectronic 20D) at 540 nm. Each procedure was done in triplicate with each shape of AC (granular, powder and pellets).

3. Results and discussions

3.1 Surface area, pore volume and pore diameter

Table 1 shows the results for the BET surface area, total pore volume, and average pore diameter for granular, powder and pellets active carbon. BET surface area refers to the area of the surface pores developed in the coal: a greater surface area means a greater number of available adsorption sites (Hidayu et al, 2013). Sun (2013) reported that large surface area and surface active adsorption sites are important physical properties in the AC as a conventional adsorbent to be applied on Cr (VI) adsorption.

Table 1: BET surface area and porosity of granular, powder and pellets AC

Carbon	BET Surface Area, m^2g^{-1}	Pore Volume, cm^3g^{-1}	Pore Diameter, nm
Granular	20.35	0.006098	3.2903
Powder	135.94	0.159552	6.2750
Pellets	570.85	0.278235	3.6999

Based on Table 1, pellets AC type has an area of 570.85 m^2/g, followed by the granular and powder. It is also observed that the surface area is directly related to the pore volume and pore diameter. Active carbons have pores with different sizes, ranging from less than a nanometer, to several thousand nanometers. The pores size determine the adsorptive properties of AC; for example, small pores will not trap adsorbates that have a large molecular size, and large pores will not trap adsorbates that have a small molecular size; also, a higher degree of mesoporosity in highly porous structure promotes diffusion and adsorption of larger adsorbates. According to the results, and the classification established by the IUPAC, it is observed that the powder sample has a mesoporous structure (pore volume between 0.1 and 0.2 cm^3g^{-1}, and effective dimensions in the

2 to 50 nm range), while the pellets sample has an enhanced mesoporosity, since the pore volume is in the range from 0.2 to 0.65 cm^3g^{-1}, the effective dimensions are between 2 and 50 nm and the surface area is above 200 m^2g^{-1}. The pore diameter in granular sample suggests a mesoporous structure, although it has a small pore volume and surface area, which would make it less suitable for pollutants adsorption. In the synthesis of AC, the activation process determines the classification of the final material. This suggests that the manufacture process to obtain the granular sample needs to be optimized in the activation step (for instance, by increasing the activation temperature), in order to yield a porous structure for an efficient adsorption of Cr(VI). Also, as a complement for the BET analysis, a FTIR analysis would provide information about the surface oxygen functional groups that are formed during the physical activation.

3.2 Effect of contact time

Figure 1 shows the experimental results for the amount of adsorbed Cr(VI) with time, for the three samples of AC (granular, powder and pellets), together with the fitting for the pseudo-first order model, the pseudo-second order model and the intraparticle diffusion model.

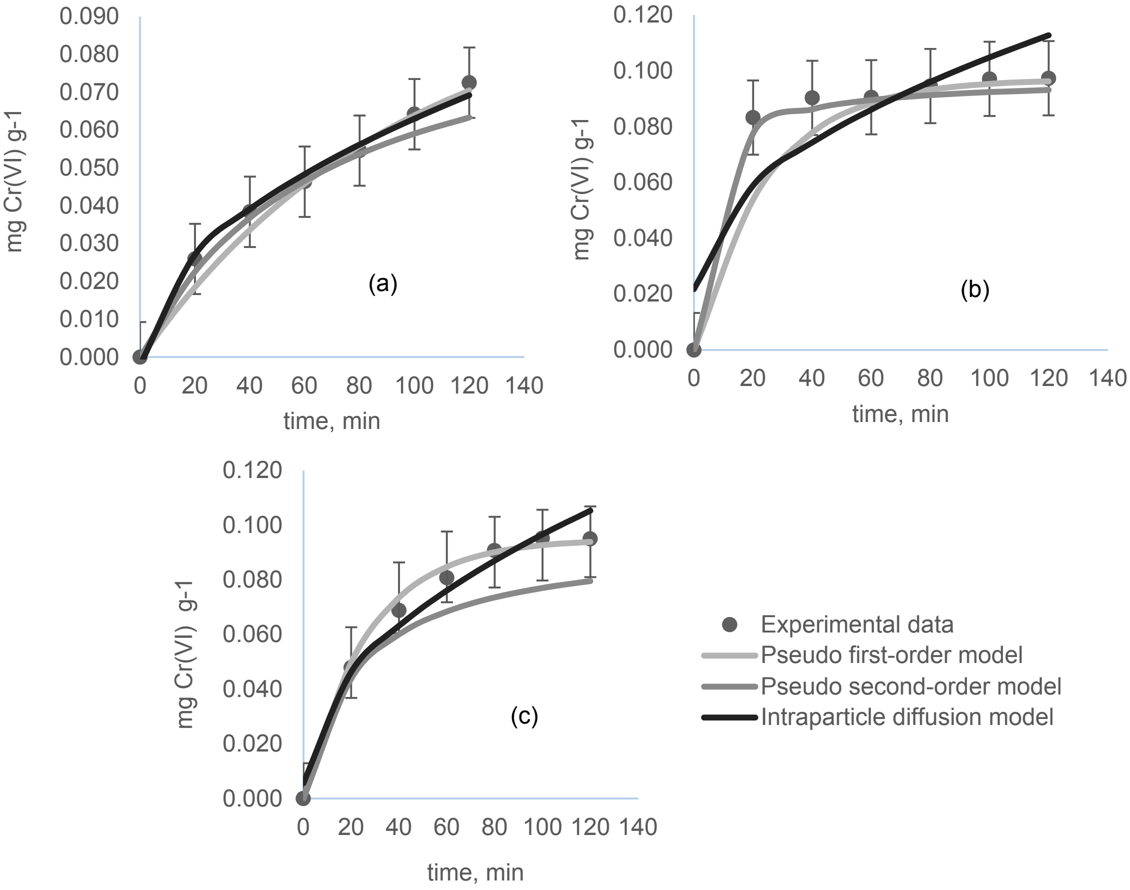

Figure 1: Experimental results and model fitting for Cr(VI) adsorption kinetics: a) Granular b) Powder c) Pellet activated carbon

It is observed in Figure 1 that the amount of adsorbed Cr (VI) increases gradually with the contact time, in the presence of activated carbon. It is also observed that the equilibrium is reached around 100 min for pellets, and 60 min for powder AC. Granular AC did not reach equilibrium at the experiment time, which is probably due to the low internal surface area (20.35 m^2g^{-1}), that is related to the adsorption rate. Extrapolation of the data for granular AC was made, in order to estimate the time for reaching equilibrium, and it was found to be about 180 min.

The adsorption phenomenon has been illustrated by the three stages of adsorbate diffusing into the interior of the structures, where the rate-limiting step is the gradual adsorption process in the second stage (Mak et al, 2009). The fitting of the experimental data was done by linearizing the three models (pseudo-first order, pseudo-second order and intraparticle diffusion), in order to determine the values for the coefficient of determination (R^2); the R^2 obtained for pseudo-first order, pseudo-second order and intraparticle diffusion models were, at 1 ppm, respectively: granular (0.98, 0.95, 0.99), powder (0.87, 0.99, 0.78), and pellets (0.97, 0.99, 0.97). These results suggest that the kinetics of Cr(VI) adsorption can be described suitably by the three models, although there is a better fit depending on the type of AC; in other words, the kinetics of Cr(VI) adsorption on granular AC can be described better by the intraparticle diffusion model, while on powder and pellets samples, the kinetics can be described better by the pseudo-second order model. This second-order kinetic behaviour suggests that the adsorption mechanism is the rate-controlling step. There is a difference between the results of R^2 for pellets and what is observed in Figure 1.c, since it seems that the pseudo-first order and intraparticle diffusion models fit better to the experimental data for pellets; this difference probably arises when plotting the data that were fitted previously to a linearized model.

3.2 Adsorption Isotherm

Adsorption equilibrium can be described by adsorption isotherms. The adsorption isotherm represents the relationship between the amount adsorbed by a unit weight of solid adsorbent and the amount of solute remaining in the solution at equilibrium. Two different adsorption isotherms were used in order to correlate the equilibrium adsorption data, as described by Al-Sou'od, 2012. The adsorption isotherms used here were the Langmuir and Freundlich, since these are commonly used for describing adsorption equilibrium in water and wastewater treatment.

The Langmuir model is commonly expressed as Eq(1).

$$\frac{C_e}{q_e} = \frac{1}{Q_m k_l} + \frac{C_e}{Q_m} \tag{1}$$

Where C_e is the equilibrium concentration of Cr(VI) remaining in the solution (mg L^{-1}). q_e is the amount of adsorbate adsorbed per mass unit of adsorbent at equilibrium (mg g^{-1}). Q_m is the amount of contaminant metal to form a monolayer on the surface (mg g^{-1}), that is, the maximum value of q_e that can be obtained as the equilibrium concentration of the solute is increased, and k_l is Langmuir constant, which is related to the heat of adsorption. This constant k_l increases with the strength of the adsorption bond (Pure Water Lab). All of the constants in Lagmuir and Freundlich model are specific to test conditions and the adsorbent type (Uddin, 2007). The Freundlich model has the following linear form, as in Eq (2):

$$\log q_e = \log k_f + \frac{1}{n}\log C_e \tag{2}$$

Where C_e and q_e have the same meaning; and k_f and n^{-1} are constants that are considered to be relatively indicators of adsorption capacity and adsorption intensity. The constants from Freundlich equation have substantial importance when characterizing the adsorption system. The constant k_f is a function of the adsorption capacity of the adsorbent, and the value of n^{-1} is a measure of the strength of the adsorption. When holding all other variables constant, the value of solute adsorbed will increase with increasing k_f (Pure Water Lab). Figure 2 shows the amount of Cr(VI) adsorbed per gram of activated carbon q_e, versus the concentration of Cr(VI) remaining in the solution C_e. As seen in Figure 2, the adsorption capacity at equilibrium C_e increases as a function of the concentration in the solution q_e. These results are in agreement with the results of the fitting showed in Table 2, where isotherm constants and coefficients of determination for the three types of activated carbon are reported. These values in Table 2 were determined by least squares regression. From Table 2, it is observed that for the granular AC, the R^2 value is higher for the Freundlich model, which suggests that adsorption equilibrium for granular AC can be more effectively described by the Freundlich isotherm. This means that the removal of Cr(VI) is due to the energy distribution on active sites that are available for the adsorption (Sun et al, 2013). As illustrated in Table 2 and Figure 2, a high value for the coefficient of determination (R^2=0.999) indicates that the equilibrium data for Langmuir describes better the adsorption for powder and pellets samples. According to Yang et al (2013), this means that there is a monolayer surface adsorption that occurs on specific homogeneous sites. The results showed that removing Cr (VI) by activated carbon from oil palm endocarp requires moderate temperatures, acid pH (<2), stirring speed to 500 rpm and the range concentration between 0.75 and 1.25 ppm.

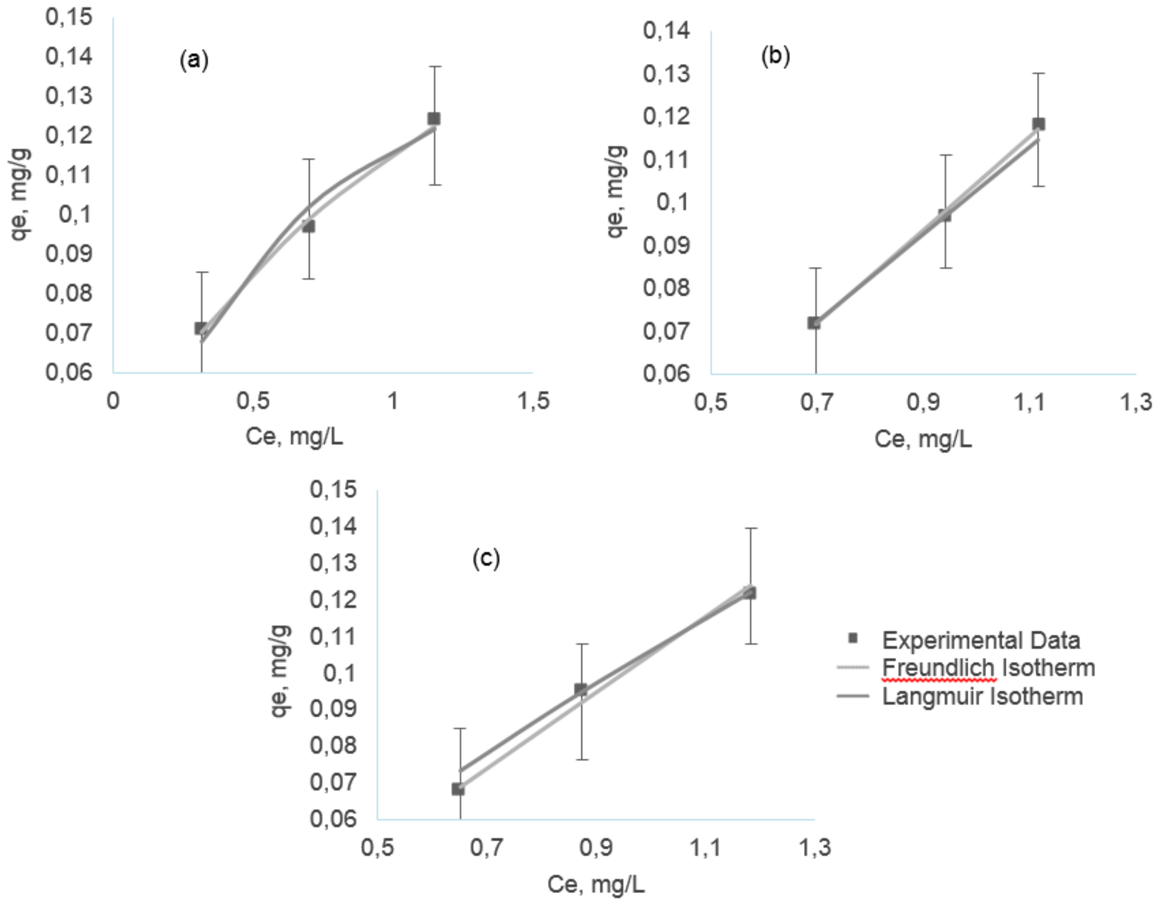

Figure 2: Experimental results and model fitting for Cr (VI) adsorption isotherms: a) Granular b) Powder c) Pellet activated carbon

Table 2: Freundlich and Langmuir isotherm constants and coefficients of determination for AC

Carbon	Adsorption Isotherm					
	Freundlich			Langmuir		
	$k_{f,}$ L g^{-1}	n	R^2	Q_m mg g^{-1}	k_{L}, L g^{-1}	R^2
Granular	0.115	2.330	0.996	0.174	2.021	0.983
Powder	0.104	0.961	0.998	0.955	0.013	0.999
Pellets	0.105	1.204	0.992	0.625	0.205	0.999

4. Conclusions

The characterization of granular, powder and pellets activated carbon obtained from oil palm endocarp was analysed in terms of the surface area, pore volume, average pore diameter and adsorption isotherms. This work shows that adsorption of Cr (VI) by activated carbon from oil palm endocarp is a cheap and easily available way for treatment which can be successfully used as alternative adsorbent for wastewater treatment process. The surface area, pore volume and average pore diameter showed that the three samples powder sample have a mesoporous structure; the granular sample showed a low surface area and small pore volume, which suggests that improving the conditions at the activation step will enhance its porous structure for an efficient adsorption of Cr(VI). FTIR analysis is suggested for future studies, since it will provide information about the functional groups that are present at the surface of the AC.

Kinetic analysis showed that the adsorption equilibrium is reached in 120 min in the pellets and powder shapes of activated carbon, however the granular carbon is reached after 120 min. It was also observed that the adsorption kinetics depend on the shape, the internal surface area and porosity of the activated carbon.

The Chromium (VI) adsorption in pellets and powder shapes, follows a pseudo-second order kinetics, while the adsorption in the granular carbon can be described by intraparticle diffusion. Regarding to the adsorption at the equilibrium, this is well described by the Freundlich isotherm model for the granular sample, while in powder and pellets sample, it can be described by Langmuir isotherm model.

Any of the three samples of activated carbon studied (granular, powder and pellets) can be used to remove Cr (VI) in aqueous systems, at different levels of efficiency. The pellets sample removed 89.7 % of Cr(VI), powder sample removed 92.1 % and granular sample removed 68.1 %.

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