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Adsorption of Chromium (VI) by Activated Carbon Produced from Oil Palm Endocarp

Karen J. Silgado, Greisly D. Marrugo, Juliana Puello*

Univ.de San Buenaventura, School of Chemical Engineering, Cartagena de Indias, Colombia
jpuello@usbctg.edu.co

Chromium (VI) compounds are harmful when ingested, and even low concentrations of these compounds are lethal. Chromium is a carcinogenic chemical that is widely used in tanning industry. The effluents from this process require efficient treatments, and activated carbon (AC) can be useful to treat the waste waters where the chromium concentration is low. This work presents the basic characterization and Cr (VI) adsorption capacity of three different shapes of an AC obtained from oil palm endocarp, produced by a company located in Colombia, South America. Moisture, apparent density, ashes, pH, and methylene blue index were measured for pellets, granular and powder shapes of AC. Kinetics of adsorption were evaluated for the three shapes of AC for a time of 2 hours, pH less than 2, and room temperature. It was found that for pelletized and powder AC, the adsorption of Cr (VI) follows pseudo-second order kinetics, while in granular AC the adsorption of Cr (VI) is predominantly of intra-particle diffusion type. Results from adsorption kinetics also suggest that the three shapes of AC can be used to remove heavy metals such as Cr (VI) from waste waters, in order to meet the country environmental standards. The results show that in general, the granular AC performs the best among the three shapes, and an optimization procedure is required to lower moisture and ash contents, especially for the pellets and powder AC, so these carbons can provide a suitable alternative for environmental applications.

1. Introduction

Activated carbon (AC) is a carbonaceous and crystalline material with a high surface area that makes it appropriate for adsorbing chemical substances that contaminate water or air, depending on its structure. The contamination from waste waters is considered a significant source of environment and human health deterioration. Among the contaminants, heavy metals like Chromium (VI) are a concern due to the detrimental effects that it causes on the environment and human health (Jung et al., 2013). AC is a widely used technique to remove contaminant molecules that cause color, odor or flavors, due to the surface atoms that are available to fix pollutant substances, at a reasonable cost and simplicity (Belgacem et al., 2013). Removal of Chromium (VI) from waste waters by using AC depends on the initial concentration of Cr (VI), the contact time, the temperature and pH of the water. AC is produced from a variety of raw materials, and oil palm endocarp (or oil palm shell) is an abundant agricultural solid waste from palm-oil processing mills in many tropical countries such as Malaysia, Indonesia and Thailand. While relatively small compared to those, the Colombian palm oil industry is the fourth largest in the world. Oil palm is currently the third most important crop in Colombia, and the residual biomass from palm-oil processes can be used for several applications, such as the production of activated carbons. However, just a few facilities in Colombia produce AC from oil palm endocarp, and research is needed in order to obtain a suitable product that meets the standards for environmental applications. As an initial stage of research, the basic characterization of three shapes (pellets, granular, and powder) of an AC obtained from oil palm endocarp is presented together with a kinetic analysis for adsorption of Cr (VI) from aqueous solutions. There are Colombian standards for activated carbons, however, ASTM standards were considered for measuring moisture, ashes, pH, particle size, apparent density and methylene blue index of the AC obtained from oil palm endocarp.

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2. Experimental

Samples of AC from oil palm endocarp were provided in pellets, granular and powder shape. Granulometric analysis was done to determine the average particle size and its uniformity coefficient. Standard methods were followed to characterize the three shapes of activated carbon from oil palm endocarp. The tests included determination of moisture content, apparent density, pH measurement, ash content and methylene blue index. High moisture content is undesirable, since this will add to transport and storage costs. Moisture content is also important because it affects the ability of adsorbents to perform against certain substances. Adsorption efficiency decreases as moisture content increases, since some adsorption sites within the pores are filled with water. However, in the case of impregnated h carbons, higher moistures generally result in an increase in efficiency, since the mechanisms of contaminant removal are chemical reactions that occur in the reagent solutions contained in the pores. The moisture content was determined using the “oven drying method” described in ASTM D2867-09. A clean empty porcelain capsule was oven dried at 105 °C, then cooled in a desiccator, and then 1 to 2 g of the sample were weighed. The content was then oven dried at 110 °C to a constant weight for 3 h. The percentage moisture content was calculated using the Eq (1):

$$\%\ Moisture = \frac{Weight\ loss}{Sample\ weight}\ x\ 100 \tag{1}$$

Apparent density is essential for mass to volume conversions required for designing and filling equipment, such as filter trays, cartridges, and adsorber vessels (Shawabkeh and Abu-Nameh, 2007). According to ASTM 2854-09, 10 g of sample were weighed, then carefully transferred to a test tube; the top layer was then flattened by tapping the side of the test tube. The apparent density is given by Eq (2):

$$Apparent\ density = \frac{(Sample\ mass,\ g)x(100\text{-}\%\ moisture)}{(Sample\ volume,\ cm^3)x100} \tag{2}$$

The pH value of activated carbon is a measure of whether it is acidic or basic. This is important since reactions may take place between the activated carbon, its noncarbonaceous constituents, and the fluid that contains the contaminants (Madu and Lajide, 2013). According to ASTM 3838-05, 2.22 g of the sample were weighed and dissolved in 100 ml of deionized water. The mixture was heated and stirred for 2 minutes to ensure proper dilution. The solution was then filtered at room temperature, using a Whatman No. 2 filter paper (medium rate). The pH of the filtered solution was determined using a digital pH meter.

The ash content indicates inactive matter present in the carbon, and can be an indication of a low grade carbon. Therefore the amount of ash present in activated carbon should be limited (Shrestha et al., 2012). Ash content determination was done according to the ASTM D2866-11 method. For each sample, a crucible was placed in a furnace at 650 ° C for 1 h, cooled down in a desiccator, and weight was recorded. The sample of activated carbon was placed in the crucible and transferred into a preheated muffle furnace set at a temperature of 650 °C for 3 hours. Ashes were cooled to room temperature in a desiccator, and weight was recorded. The ash content was calculated using the Eq (3):

$$\%\ Ash\ content = \frac{Mass\ of\ crucible\ plus\ ashed\ sample,\ g - Mass\ of\ empty\ crucible,\ g}{Mass\ of\ crucible\ plus\ dried\ sample,\ g - Mass\ of\ empty\ crucible,\ g}\ \text{x}\ 100 \tag{3}$$

The methylene blue index reveals the adsorptive properties of a carbon towards a larger molecule, and can give an indication of the internal surface area of the carbon. This value is useful for evaluating consistency between production batches of carbon (Okibe et al., 2013). According to the CEFIC Test Method (European Council of Chemical Manufacturers’ Federation), as a preliminary step, a blue methylene test solution was prepared by dissolving the equivalent to 1,200 mg of pure methylene blue to 1000 mL of water. This methylene blue test solution was verified by diluting 5 mL of it, with 0.25 % (v/v) acetic acid to 1 L, and measuring the absorbance at 620 nm (the absorbance had to be 0.840 ± 0.01). Then, 25 mL of the blue methylene test solution were put in contact with 0.1 g of pulverized and dried activated carbon, in a glass stoppered flask. This set was then shaken until decolorization. Then, another 5 mL of the methylene blue test solution were added to the mixture, and this was shaken again until decolorization. The volume of methylene blue test solution in ml that is decolorized was recorded as the methylene blue index.

The procedure describe by Turegano (2012) was followed to measure the Cr (VI) adsorption potential of the activated carbon. First, a calibration curve is prepared, using a set of solutions of known concentration of Cr (VI). Each solution is added with some drops of a sulphuric acid solution (1:1), in order to reach a pH below 2. Then, 2 mL of a solution of 1,5 diphenylcarbazide in acetone were added to each solution of Cr

(VI). Each solution was then left to rest during 10 min, until it developed a red-violet color. The color intensity of this red-violet complex is proportional to the concentration of Cr (VI). Absorbance of the red-violet solution was measured with a spectrophotometer (UV Spectronic 20D) at 540 nm, calibrated with target solutions. After preparing the calibration curve, a solution of 1 mg L^{-1} Cr (VI) was prepared, following the same procedure, until the solution developed the red-violet color. The 1 mg L^{-1} concentration was chosen because some studies have shown that, in Colombia, this is an average concentration of Cr (VI) in effluents. Then, 1 g of activated carbon was added, and the solution was stirred at 500 rpm for 120 min and room temperature (25 °C). 10 mL samples were taken each 20 min. Each sample was filtered to remove any particle of activated carbon, and absorbance was measured with the spectrophotometer to determine the actual concentration of Cr (VI). Each procedure was done in triplicate.

3. Results and discussions

3.1 Basic properties of activated carbon

Table 1 shows the basic properties of the activated carbon. It can be observed that moisture values are significantly high, compared to what is reported in literature (Evbuomwan et al., 2013). Some commercial carbons report moisture below 5 %, this indicates that the carbons provided for this study require of appropriate packaging, transportation and storage conditions for moisture control. The pH values were found to be 6.2 for pellets, 8.82 for granular, and 7.56 for powder shapes. A carbon of pH 6-8 is acceptable for most application such as sugar decolorization and water treatment (Ahmedna et al., 2000), although some commercial carbons may have a pH of 9-10. Apparent density values are in agreement with results reported in the literature (Ahmedna et al., 2000). Regarding to ash content, this value must also be low (some companies offer activated carbons from palm residue with 5 – 7 % ash content), since its presence inhibits surface area development. According to this, the granular shape would be the only suitable carbon for environmental applications, if the moisture is controlled.

Table 1: Physicochemical properties of the activated carbon obtained from Oil palm Endocarp

Test	Units	Carbon		
		Pellets	Granular	Powder
Moisture content	%	28.20	11.00	25.81
pH of water extract	Adimensional	6.20	8.82	7.56
Apparent density	kg m^{-3}	0.44	0.64	0.46
Ash content	%	16.21	3.32	14.75
Effective particle size	mm	1.40	0.80	0.10
Coefficient of uniformity	Adimensional	1.20	2.10	4.00
Particle size range	Standard grid	14x20	20x30	< 100
Methylene blue index	mL g^{-1}	2.18	1.99	2.20

Particle size distribution is important to provide proper contact of gases or liquid in a packed bed of the AC, and it is also related to the pressure drop and the rate of adsorption across the bed (Erto et al., 2013). Granular activated carbon (GAC) is generally more expensive than pulverized activated carbon (PAC), but it is also more effective than PAC in removing organic compounds, since GAC is usually preceded by pre-treatment, which reduces the load on the carbon. On the other side, PAC represents low capital cost and it can be applied only when it is needed, which is convenient in countries where outbreaks of taste and odour compounds are usually seasonal and intermittent (Freese et al., 2003). However, when carbon addition is required over extended periods of time, GAC is better, since it can be regenerated, while PAC is not regenerated as a rule, making it costly when used for long periods; PAC also provides a lower rate of natural organic material removal than GAC, creates more sludge disposal problems, and difficulties are often experienced in removing the PAC particles from the water (Freese et al., 2003). Finally, it is observed that pellets and powder shapes showed the highest adsorption capacity for methylene blue.

3.2 Analysis of adsorption kinetics

Eq (4) and Eq (5) are used to calculate the amount of Cr (VI) removed from the solution by the AC at a zero time and a specific time, respectively.

$$\left(\frac{mg\ Cr(VI)}{g}\right)_0 = \frac{C_0\, V_0 - C_0\, V_0}{g} \tag{4}$$

$$\left(\frac{mg\ Cr(VI)}{g}\right)_n = \frac{[\ (CV)_{n-1} - (CV)_n\ ]}{g} + \left(\frac{mg\ Cr(VI)}{g}\right)_{n-1} \tag{5}$$

C_0 is the initial Cr (VI) concentration in mg L^{-1}, V_0 is the initial volumen of the solution in L, C is the remaining Cr (VI) concentration at a time t in mg L^{-1} (calculated with Eq (5)), V is the remaining solution volume at a time t in L, and n is the number of data that have been taken at a time t. A plot of Cr (VI) removed versus time, allows identifying the time when the equilibrium is reached, and the corresponding adsorption capacity q_e. Figures 1, 2 and 3 show the experimental data, together with the model fitting, which will be discussed later.

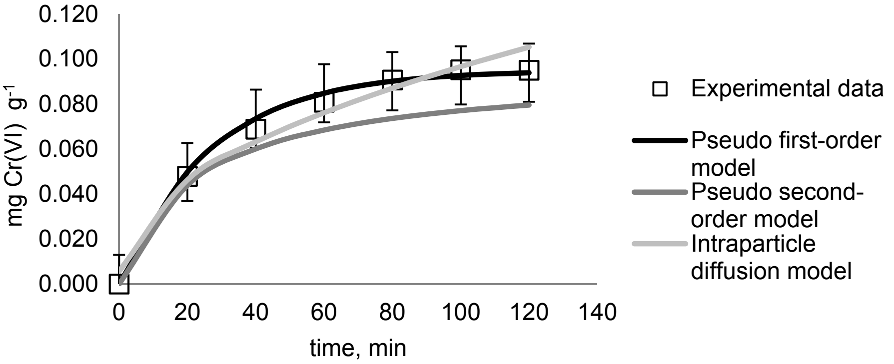

Figure 1: Pellet AC, experimental results and model fitting for Cr (VI) adsorption kinetics

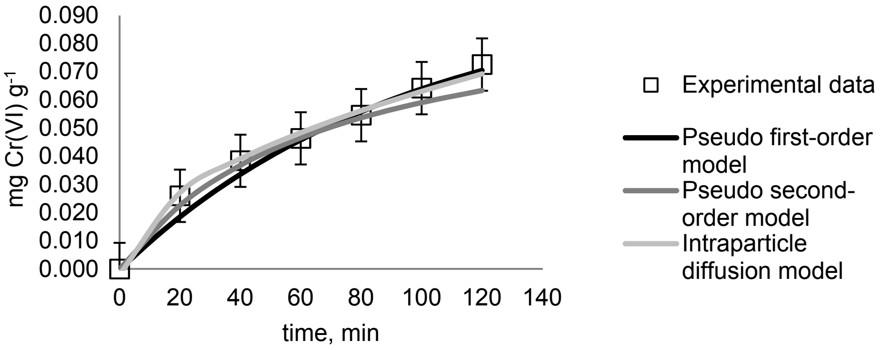

Figure 2: Granular AC, experimental results and model fitting for Cr (VI) adsorption kinetics

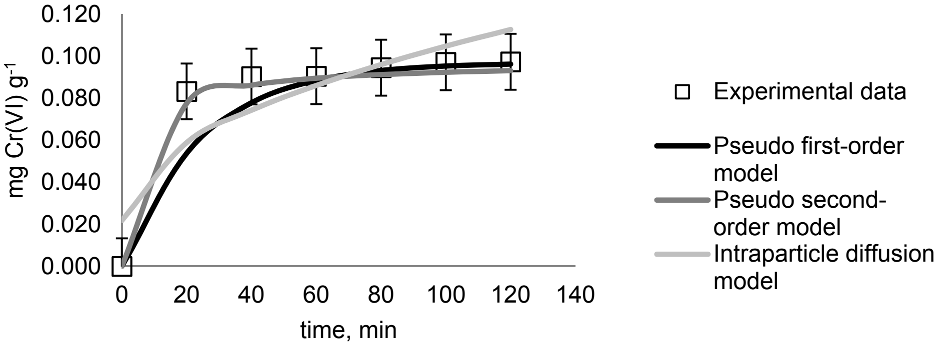

Figure 3: Powder AC, experimental results and model fitting for Cr (VI) adsorption kinetics

Based on the Figures 1, 2, and 3, it is observed that equilibrium is reached at approximately 120 min for pellets and powder AC; granular AC does not reach equilibrium at 120 min, suggesting that it still has active sites available for adsorption. For comparison purposes, and as a preliminary result, equilibrium was considered at 120 min for the three shapes of AC.

The analysis of the adsorption kinetics provides information about the transport mechanisms associated to the elimination of contaminants from the aqueous systems (Iovino et al., 2013). To estimate the adsorption rate for Chromium (VI), two kinetic models and one adsorption mechanism were considered. The conformity between the experimental work and the kinetic model was analyzed by the R^2 values.

The pseudo-first-order kinetic model was proposed by Lagergren, and it is expressed as in Eq (6), where q_e and q_t are adsorption capacity (mg g^{-1}) at equilibrium and at time t, respectively, and k_1 is the rate constant of pseudo-first-order model (min^{-1}).

$$\log\left(q_e - q_t\right) = \log q_e - \frac{k_1}{2.303}\, t \tag{6}$$

The pseudo-second-order kinetic model is given by Eq (7), where q_e and q_t are defined in the pseudo-first-order model, and k_2 is the rate constant of pseudo-second-order model (g $mg^{-1}min^{-1}$)

$$\frac{t}{q_t} = \frac{1}{k_2\, q_e^2} + \frac{1}{q_e} t \tag{7}$$

The intra-particle diffusion model is represented by Eq (8), where q_t is the amount of substance adsorbed (mg/g) at a contact time t ($min^{1/2}$), k_{id} is the intra-particle rate constant (mg min^{-1} $t^{-0.5}$) and C_i is the intercept for the *i*-stage, which is an indicator of the boundary layer thickness.

$$q_t = k_{id}\, t^{0.5} + C_i \tag{8}$$

Table 2 shows the parameters values for the two kinetic models and the diffusion model, for the three shapes of activated carbon from oil palm endocarp. It is observed that for pelletized and powder AC, the adsorption of Cr (VI) follows pseudo-second order kinetics. This result is in agreement with that one reported by Rashidi et al. (2013). In granular AC the adsorption of Cr (VI) is better described as intra-particle diffusion. Also, the q_e values indicate that after 2 hours, the three shapes adsorb enough Cr (VI) to meet the Colombian environmental standard (maximum 0.5 mg L^{-1} of Cr (VI)).

Table 2: Kinetic and diffusion parameters for three shapes of activated carbon from oil palm endocarp

Carbon	q_e experimental mg g^{-1}	Kinetic models						Adsorption mechanism		
		Pseudo first-order			Pseudo second-order			Particle diffusion		
		q_e mg g^{-1}	k_1 x 10^2, min^{-1}	R^2	q_e mg g^{-1}	k_2, g mg^{-1} min^{-1}	R^2	q_e mg g^{-1}	k_{id} x10^3, mg g^{-1} $min^{-0.5}$	R^2
Pellets	0.095	0.103	3.708	0.97	0.121	0.4512	0.99	0.105	9.1	0.97
Granular	0.072	0.095	1.036	0.98	0.114	0.1493	0.95	0.121	6.5	0.99
Powder	0.097	0.054	4.053	0.87	0.101	2.0532	0.99	0.113	8.3	0.78

4. Conclusions

This study presented a basic characterization of three shapes of an activated carbon obtained from oil palm endocarp. Moisture, apparent density, ashes, pH, and methylene blue index were measured for pellets, granular and powder shapes of AC. Moisture content and ashes must be carefully considered in order to obtain an acceptable product that can be used for environmental applications, especially in the pellets and powder carbons. Kinetic analysis showed that adsorption equilibrium is reached at approximately 120 min by the pellets and powder shapes of activated carbon, while in granular carbon equilibrium is reached after 120 min. Results also showed that the three shapes can be used to remove Cr (VI) from aqueous systems, since at 120 min the concentration of Cr (VI) is lower than the maximum concentration allowed by local environmental standards. It was also found that adsorption kinetics depends on the shape of the activated carbon. Adsorption of Cr (VI) on pellets and powder AC shows pseudo-first order kinetics, while in granular carbon it is better described as intra-particle diffusion. Results showed that in general, the granular active carbon has the best performance among the three shapes.

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