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Study of Chromium Adsorption in Angelim Vermelho Sawdust (AVS)

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Angelim Vermelho is a characteristic tree of central region of Brazil, known for its high resistance. This paper investigated the AVS as an adsorbent of chromium ions from water waste of many industries such as tanneries. The combined influence of pH, initial concentration of chromium and adsorbent concentration were analyzed using a central composite design (CCD). The kinetic curves of chromium adsorption were determined for five different initial concentrations. All the kinetics experiments were conducted at pH= 2.75, T=30°C using 5g of AVS. The kinetics models of Michaelis-Menten and Largergren were used to correlate the experimental kinetics data. All the models were able to describe the observed behavior.

1. Introduction

Heavy metals are non biodegradable pollutants whose release in the environment is mainly related to industrial waste waters discharged from industrial and mining activities (Cruz et al. 2009). Chemical precipitation, membrane filtration, ion exchange, reverses osmosis, evaporation, electrolysis and adsorption are some these methods (Shen et al. 2010). Water purification processes, based on rather severe chemical conditions, particularly oxidation, have a tendency to produce dangerous by-products. Among chemicals that undergo this transformation there are phenolic compounds which are quite usual contaminants in industrial wastewaters (Sambenedetto et al. 2007). Adsorption has been used to remove several kinds of pollutants from waste water. An abundant source of potentially metal-sorbing biomass is cellulosic agricultural wastes. Although their sorption capacity is usually lower than activated carbons these materials could be an inexpensive substitute for the heavy metal laden wastewater's treatment (Erdem et al. 2005). Table 1 presents, the adsorption capacity of some solids used in the removal of Chromium from waste water.

The present investigation is devoted to study the removal of chromium (VI) by using AVS as adsorbent. The AVS sawdust used in this investigation was obtained in Uberlândia´s carpentry (Brazil).

Table1. Literature references about use of adsorption in removal of Cr(VI).

Adsorbent	Adsorption Capacity [mg/g]	Reference
Sugarcane bagasse pith	13.4	Sharma & Forster 1994
Sugarcane bagasse pith	5.75	Garg at al. 2007
Modified sugarcane bagasse	103	Wartelle & Marshall 2005
Sargassum sp	298.5	Carmona, Silva & Leite 2005
Modified sugarcane bagasse	30.74	Garg et al. 2009
Activated Carbon, yield from biomass	28.44	Fahim et al. 2006

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2. Experiments

2.1. Materials e Reagents

The AVS used in this study was collected from a carpentry located in Uberlândia (Brasil). The sawdust collected was washed under running water and dried under sun. The material used had diameter of 0.5 ±0.02mm.

Solutions of chromium were prepared by dissolving potassium dichromate in double distilled water to yield the desired concentrations. pH of the solutions was adjusted using 0.2N H_3PO_4, using Orion 420A pH meter. The Cr(VI) concentration was determined spectrophotometrically [Thermo Spectronic Genesys 10 UV,], by method APHA, (APHA-1998).

2.2 Experimental Planning – Central Composite Design

In order to investigate the influence of the variables: Cr (VI) initial concentration, dose of adsorbent and pH of solution, under adsorption capacity of AVS it was done a Central Composite Design (CCD). The Table 2 presents the matrix of Central Composite design used. The statistical calculation was implemented in the *Software Statistica® 7.*

2.3 Adsorption Experiments

2.3.2 CCD experiments

For each run from experimental planning (Table 2), 250 ml of chromium solution at the conditions established were put in 500mL Erlenmeyer flask at 25±1 °C temperature, and submitted to agitation by 2 hours. After that time the samples were separated by vacuum filtration in a Buchner number 2 funnel. The chromium concentration in the solution was determined as given in Section 2.1. All experiments were replicated thrice. The amount of Chromium adsorbed per gram of AVS (*qads*) was determined by:

$$qads = \frac{(C_i - C_f)V_s}{m_a} \tag{1}$$

In the Equation 1, C_i and C_f are the concentration of Cr(VI) in the solution in the beginning and in the end of the experiment. V_s is the volume of solution (250mL) and m_a is the mass (in gram) of adsorbent used in the experiment.

2.3.3 Kinetics curves experiments

The kinetics curves for five different initial concentration of Cr(VI) were determined, in order to evaluate the effect of contact time under the adsorption capacity of AVS. 250mL of solution, with the Cr(VI) concentration of 80, 110, 150, 170 and 200 mg/L and 5 g of AVS were placed in 500mL Erlenmeyer flask and subjected to agitation. In all experiments the pH used was 2.75. The Cr(VI) concentration was measured after contact times of: 5min, 15min, 30min, 45min and 60min. In the end of each time, for each experiment, the samples were filtered under vacuum using a number 2, Buchner funnel, sealed. The amount of Chromium adsorbed per gram of Angelim (*qads*) was determined by Equation 1.

3. Results e Discussion

3.1. Central Composite Design (CCD)

The experimental results obtained in the conditions of CCD tested, using the following variables: pH (X_1), Cr(VI) concentration(X_2 [mg/L]) and adsorbent dose (X_3 [gram]). The adsorbed amount of Cr(VI) varied from 0.107 mg/g to 6.131 mg/g. The bigger values of adsorbed amount were obtained in the bigger rates of initial concentration of Cr(VI) by mass of Angelim (experiments 3, 7 and 13). Using the hypothesis testing Student's t, an equation correlating the independents variables (X_1, X_2, X_3) with the adsorbed amount, was built (Equation 2).

$$qads = 7.5894 + 6.2428.X_2 - 4.7776.X_3 - 0.7595.X_1^2 + 3.1578.X_3^2 - 3.1379.X_2X_3 \quad (2)$$

Table 2- Conditions and Results of CCD

run	pH	Cr(VI) Concentration [mg/L]	Dose of Adsorbent [g]	Adsorbed amount [mg/g]
1	1.5	25	5	0.941
2	1.5	25	15	0.329
3	1.5	140	5	6.131
4	1.5	140	15	2.083
5	4	25	5	1.051
6	4	25	15	0.398
7	4	140	5	5.561
8	4	140	15	2.170
9	1.06	82.5	10	1.760
10	4.44	82.5	10	1.590
11	2.75	4.7	10	0.107
12	2.75	160.3	10	3.711
13	2.75	82.5	3.2	5.259
14	2.75	82.5	16.8	1.077
15	2.75	82.5	10	1.854
16	2.75	82.5	10	1.865
17	2.75	82.5	10	1.590

The adsorption capacity, expressed by mass of solute adsorbed/mass of adsorbent, is the maximum adsorbed amount for a given condition of temperature and pH. The determination coefficient (R^2) of Equation 2 was 0.98, indicating the 98% of experimental data fitted the equation. The data, as well as the equation 2, shows that pH did not have a strong influence in the adsorption of Cr(VI) by AVS.

3.2. Kinetic Curves

The experimental data obtained for each kinetic curve at the initial concentration of Cr(VI) of 80, 110, 150, 170 and 200mg/L are presented in the Figure 1. The high slope of the curve at time zero indicates that the process is favorable. The equilibrium is reached before 60 minutes of contact. It can be observed that the adsorbed amount of Cr(VI) was almost 8mg/g for high initial concentration of Cr(VI) in the water solution.

To determined, the adsorptive capacity of AVS is necessary to determine the adsorbed amount for bigger concentration of Cr(VI).

The experimental data were correlated by the kinetics models of Michaelis and Largergren. The first order model of Largergren, presented in 1898, is one of the most used models to describe the kinetic curves of adsorption of solute in liquid phase (Ayyappan et al. 2005). The equation is written by:

$$\log(q_{eq} - q) = \log(q_{eq}) - \frac{kt}{2,303} \tag{3}$$

In this equation q_{eq} is the adsorbed amount in the equilibrium (maximum), k is the rate constant and q is the adsorbed amount in time t.

According to Bailey & Ollis (1986) the Michaelis-Menten kinetic model was initially proposed by Henry in 1902 to represent mathematically the experimental behavior of some enzymatic reaction expressed in terms of rate of reaction *(v)* versus concentration of free substrate (S). The original equation is written as:

$$v = \frac{v_{\max} S}{K_m + S} \text{ Where } v_{\max} = \alpha e_0 \tag{4}$$

In that equation e_0 is the concentration of total amount of enzyme present in both free and combined form (Bailley & Ottis 1986). The same shape of the Michelis-Menten model is observed in many adsorptive processes when you plot adsorbed amount (q) versus time (t). Therefore, making an analogy between the enzymatic reaction and the adsorption process it is possible to get an adaptable model to adsorption, which is written as:

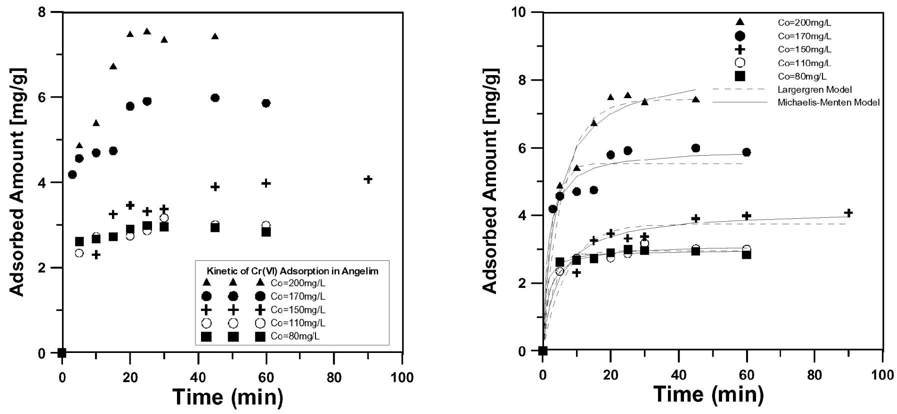
$$q = \frac{q_{\max} t}{K + t} \tag{5}$$

In Equation 5 q_{max} is the maximum adsorbed amount, relative to adsorbent saturation, k is a parameter of the model. The *Software Statistica® 7* was used to correlate the kinetic models to the experimental data. The parameters fitted are presented in Tables 3 e 4.

The Figure 1 presents the experimental data and the fitted models of Largergren and Michaelis-Menten for initial concentration of Cr(VI) in the solution of 80, 110, 150, 170 and 200mg/L.

Table 3. Parameters fitted by Largergren Kinetic model

Parameters	**Initial Concentration of Cr(VI) in the solution C_i[mg/L]**				
	80	110	150	170	200
$q_{max} \pm \sigma$	2.87±0.04	2.95±0.06	3.74±0.18	5.53±0.22	7.43±0.23
$K \pm \sigma$	0.46±0.08	0.30±0.04	0.14±0.03	0.40±0.09	0.17±0.02



(a) (b)

Figure 1. Kinetic Curves of Cr (VI) adsorption in . (a) Experimental data: (b): correlated models.

Table 4. Parameters fitted by Michaelis-Menten Kinetic model

Parameters	**Initial Concentration of Cr(VI) in the solution C_i[mg/L]**				
	80	110	150	170	200
$q_{max} \pm \sigma$	2.97±0.05	3.12±0.07	4.16±0.21	5.97±0.22	8.40±0.37
$K \pm \sigma$	0.76±0.22	1.63±0.37	4.63±1.23	1.57±0.43	3.99±0.88

σ=Standart deviation

As can be observed, in the Figure 1, both models present a similar performance in the correlation of experimental data. The Table 5 presents the Mean Relative Deviation (MRD) calculated by each model tested in each initial concentration condition. The MRD is calculated by:

$$MRD = \frac{\sum_{i=1}^{Np} \left| q^{cal} - q^{exp} \right|}{Np} 100\% \qquad (6)$$

In that equation, *Np* is the number of experimental point and q^{exp} and q^{cal} are the adsorbed amount determined experimentally and that calculated by the model, respectively.

Table 5. Mean Relative Deviation presented by the models

Model	**Mean Relative Deviation MRD (%)**				
	C_i=80mg/L	**C_i=110mg/L**	**C_i=150mg/L**	**C_i=170mg/L**	**C_i=200mg/L**
Largergren	3.08	3.57	10.00	8.57	4.54
Michaelis	2.48	2.51	7.46	5.61	4.97

4. Conclusions

Based on the results shown it can be concluded that AVS presents a high adsorptive capacity in the removal of Cr(VI) from water solution. For initial concentration of Cr(VI) of 200mg/L the adsorbed amount was around 8mg/g. That value is bigger than some values reported in literature (Table1). The results show too that pH did not have a strong influence in the adsorption of Cr(VI) by AVS.

A favorable aspect in the use of AVS is related to kinetic of adsorption. In all experiments conducted in this work the equilibrium was reached up to 60 minutes. The experimental results were well correlated by the kinetic models of Largergren and Michaelis-Menten.

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