Sugarcane Bagasse as An Alternative Medium for Removal of Hexavalent Chromium from Aqueous Solution

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ABSTRACT

Perlis has long been known to have the largest plantation of sugar cane in Malaysia for sugar production. The production of sugar, however, produced enormous quantity of unwanted bagasse. This by product of sugar production will be used as an alternative medium for adsorption of toxic heavy metals from industrial wastewater. The bagasse was initially modified by simple acid treatment to improve its adsorptive capacity. In order to determine its effectiveness, a study of the adsorption mechanism was conducted on the removal of 50-300 mg/L range of haxavalent chromium from aqueous solution at 30, 40 and 50 ℃.

Keywords: *Adsorption, hexavalent chromium, sugarcane bagasse*

Introduction

Toxic pollutants, either organic or inorganic in nature, can enter the environment through various means. Most of the organic compounds eventually degrade, regardless of the rate and the level of decomposition. Inorganic materials present harder challenges; especially those that are metal elements with little else bound to them. Chromium as an example is an element, and cannot be degraded to a substance lesser than its elemental form.

The health effects of chromium are partially related to the valence state of the metal at the time of exposure. Metallic chromium and chromium alloys are essentially inert and do not cause any adverse health effects (ICDA, 2003). However, Cr (III) and Cr (VI) compounds are thought to be the most biologically significant to human health (ASTDR, 2000). Cr (III) is an essential dietary mineral in low doses required to potentiate insulin for normal glucose metabolism. Soluble Cr (III) substances can be irritating to the eyes and skin, but this effect is usually related to their acidic nature. Insufficient evidence exists to determine whether Cr (III) can be a human carcinogen (EPA, 1998), however Cr (VI) was classified as a known human carcinogen based on studies of workers in chromium processing factories who developed lung cancer after chronic inhalation exposures (EPA, 1998 and IARC, 1997). Apart from that, there is no scientific evidence for any adverse acute or chronic health effects caused by exposures at typical environmental concentrations.

Chromium has various industrial applications; namely in steel and alloys making, electroplating, wood treatment, textile dyeing, paint production and leather tanning (Browning, 1969), thereby large quantities of chromium-bearing wastewater are generated. It is therefore, essential to provide a systematic discharge and treatment method to conserve the environment from chromium contamination.

Adsorption on activated carbon is a well-developed method for the treatment of water and wastewater. However, the price of activated carbon made of charcoal, coconut shell and oil palm shell is getting more costly, thereby limiting its use in wastewater treatment, especially for small industries in developing countries. In the recent years, researchers are extensively searching for low-cost and abundantly available adsorbents for Cr adsorption, such as residue of olive mill products (Gharaibeh et al., 1998); straw (Kumar et al., 2000); crab shell (Kim, 2003); wheat bran (Farajzadeh & Monji, 2004); carrot residues (Naserjad et al., 2005) and oil palm fibre (Isa et al., 2008).

Perlis has long been known to have the largest plantation of sugar cane in Malaysia for sugar production. The production of sugar, however, produced enormous quantity of unwanted bagasse. This by product of sugar production will be used as an alternative medium for adsorption of hexavalent chromium from a synthetic industrial wastewater.

Materials and Methods

Chemicals and Raw Material Preparation

All primary chemicals used were of analytical reagent grade. Potassium dichromate ($K_2Cr_2O_7$), sulphuric acid (H_2SO_4) and sodium hydroxide (NaOH) were used without further purification. Aqueous solutions were prepared with distilled water. A 1000mg/L Cr(VI) stock solution was prepared using $K_2Cr_2O_7$. This solution was used to prepare the desired working solutions for batch experiments, simulating chromium-bearing industrial wastewater.

Sugarcane bagasse obtained from a local sugar industry in Perlis was activated with simple sulphuric acid and heat treatment according to the method used by Garg et al. (2004) for further use in the adsorption experiments. One part of air-dried adsorbent was mixed with one part of concentrated sulphuric acid in a ceramic crucible and heated in a muffle furnace for 24 hours at 150°C. The heated material was cooled and washed with a copious quantity of water until the pH was that of distilled water. After that, the bagasse was dried in an oven for 24 hours at 105°C. The resulting adsorbent was then ground and seived to an average size of 1.18cm.

Batch Adsorption Method

Previous studies showed that adsorption of Cr (VI) was favourable at acidic initial pH (Brown et al., 2000; Ajmal et al., 2001; Yu et al., 2003 and Isa et al., 2008), thus test for pH were carried out using 6 conical flasks, each containing 50 mL of 50 mg/L of Cr (VI) and adjusted to pH 1.0-6.0. In a separate test, adsorbents were mixed with solutions of Cr (VI) ranging from 50-300 mg/L (at optimum pH) for adsorption equilibrium study; each done at 3 different temperatures (i.e. 30, 40 and 50°C). Thus, the effect of temperature on adsorption equilibrium could be assessed.

Initial pH adjustment was done using 1N sulphuric acid or 1N sodium hydroxide solutions. Contact time allowed for each flask; filled with 500 mg adsorbent and 50 mL of adsorbate was 2 hrs. After being agitated, the supernatant was filtered out using filter paper. Following filtration, the filtrate was then analysed using Hach DR 2800 Spectrophotometer for Cr (VI) final concentration.

Results and Discussion

Optimum pH

Cr (VI) ions adsorbed per mass of adsorbent (mg/g) was at maximum in initial pH range of 1.0 to 2.0, and reducing as the pH values of Cr (VI) solutions were increased (Figure 1). The results obtained were in accordance with previous studies on the uptake of Cr (VI) from aqueous solution by agricultural waste biomass, hazelnut shell activated carbon and powdered activated carbon (Garg et al., 2007; Kobya et al., 2004; Isa et al., 2008).

Optimum adsorption of Cr (VI) by the sugarcane bagasses treated with sulphuric acid at lower pH range may be due to abundantly available positive ions for neutralization of the negatively charged adsorbent sites, thus increase the adsorption of Cr (VI) anions onto the bagasse (Rao et al., 2002).

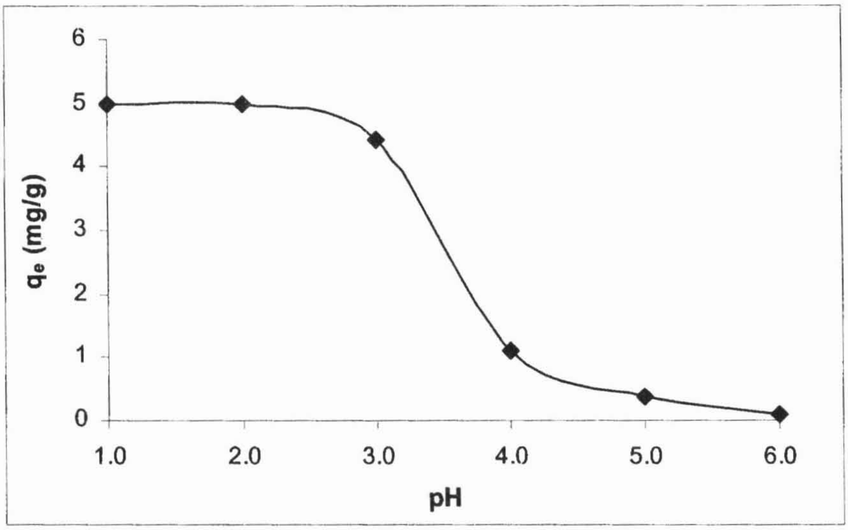

Figure 1: Effect of pH on the Removal of Cr (VI) by Sugarcane Bagasse

Adsorption Isotherms

The Langmuir and Freundlich isotherms were employed to describe the adsorption equilibrium (Figures 2 and 3). Theoretically derived Langmuir model assumes adsorption energies are uniform and independent of surface coverage and complete coverage of the surface by a monolayer of adsorbate indicates maximum adsorption. On the other hand, Freundlich mode is an empirical equation encompasses the heterogeneity of the adsorbent surface, the exponential distribution sites and their energies (Weber, 1985). The linear form of Langmuir and Freundlich isotherm is expressed as the following:

$$\frac{1}{q_e} = \frac{1}{Q_0} + \frac{1}{Q_0 b C_e} \tag{1}$$

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{2}$$

where q_e is the amount of Cr (VI) adsorbed per unit weight of adsorbent (mg/g) and C_e is the equilibrium concentration of Cr (VI) in solution (mg/L).

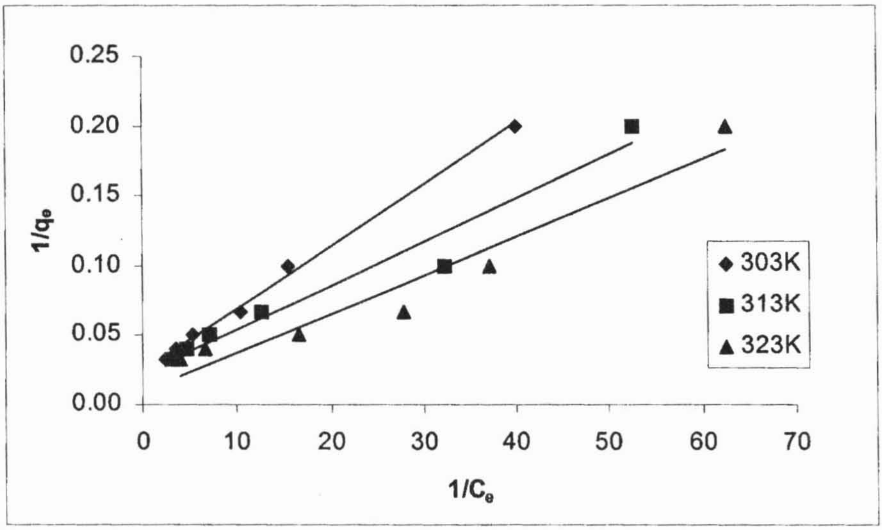

Figure 2: Linearized Langmuir Isotherms at Different Temperatures

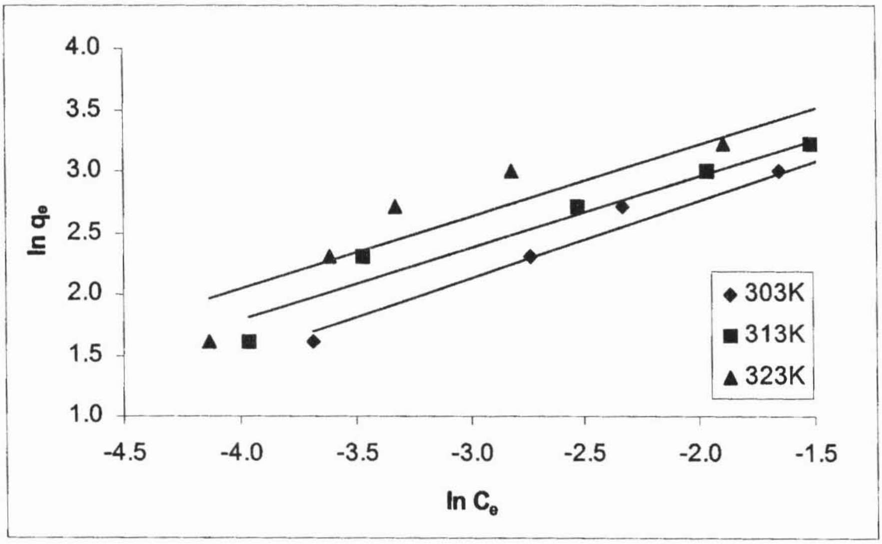

Figure 3: Linearized Freundlich Isotherms at Different Temperatures

Table 1 lists the values of Q_0, maximum adsorption capacity of Cr (VI) adsorbed onto treated EFB; calculated from Equation 1 and *b*, a constant related to the affinity of binding sites with Cr (VI) ions (Goel *et al.*, 2005). Q_0 is highest at 50°C, thus the adsorption process was considered as endothermic; where increasing temperature increases the Cr (VI) adsorbed.

Table 1: Langmuir Isotherm Model Constants and Correlation Coefficients for Adsorption of Cr (VI) onto EFB

Temperature	Langmuir constants		
T (°C)	b (L/mg)	Q_0 (mg/g)	R^2
30	5.7500	39.53	0.9961
40	7.5806	42.55	0.9605
50	3.6429	98.04	0.9401

The plot of ln q_e versus ln C_e yields K_F and n as shown in Table 2. K_F (L/g) or the quantity of Cr (VI) adsorbed onto adsorbent at equilibrium concentration increases with temperature rise from 30 to 50°C. The n (dimensionless) is a measure of adsorption intensity or surface heterogeneity. Adsorption of Cr (VI) is favourable at situation where $0.1 < 1/n < 1.0$ (McKay et al., 1982).

Table 2: Freundlich isotherm model constants and correlation coefficients for adsorption of Cr (VI) onto EFB

Temperature	Freundlich constants			
T (°C)	K_F	n	$1/n$	R^2
30	55.53	1.5893	0.6292	0.9825
40	61.83	1.7126	0.5839	0.9587
50	80.17	1.7044	0.5867	0.8639

Based on R^2 values summarized in Tables 1 and 2, it is concluded that both Langmuir and Freundlich isotherm models can adequately describe the adsorption of Cr (VI) onto sugarcane bagasse. However, experimental data shows a slightly better fit to the Langmuir equation than that of Freundlich.

Adsorption Thermodynamics

Adsorption standard free energy changes ($\Delta G°$) can be determined from:

$$\Delta G° = -RT \ln K_C \tag{3}$$

$$K_C = \frac{q_e}{C_e} \tag{4}$$

where the universal gas constant, R equals to 8.314J/mol.K; q_e is the amount of Cr (VI) adsorbed (mg) on the oil palm EFB per litre of solution at equilibrium; C_e is the equilibrium concentration (mg/L) of Cr (VI) in solution; T is the temperature in K; K_d is the observed equilibrium constant of adsorption process. K_d was calculated with respect to temperature according to the method used by previous researchers (Khan and Singh, 1997); by plotting ln (q_e/C_e) versus q_e and extrapolating to zero q_e (Figure 4).

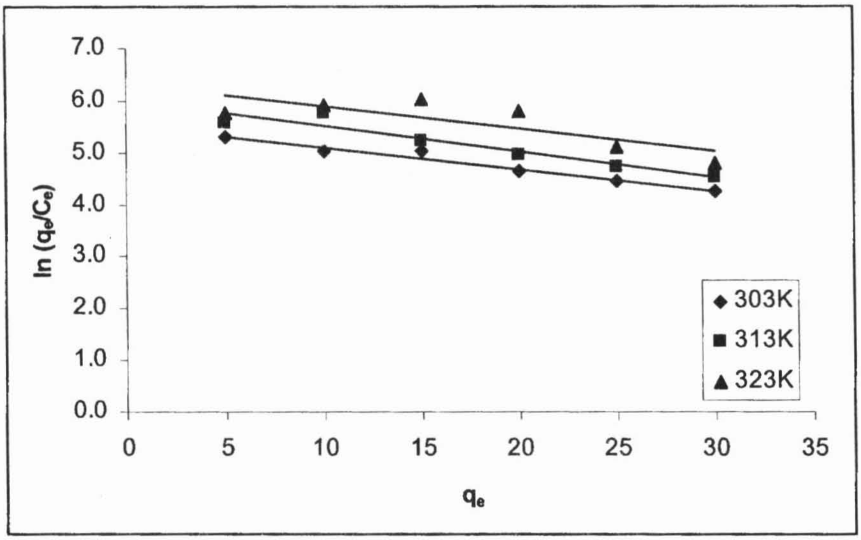

Figure 4: Plots of ln (q_e/C_e) versus q_e for Cr (VI) Adsorption onto Sugarcane Bagasse at Different Temperatures.

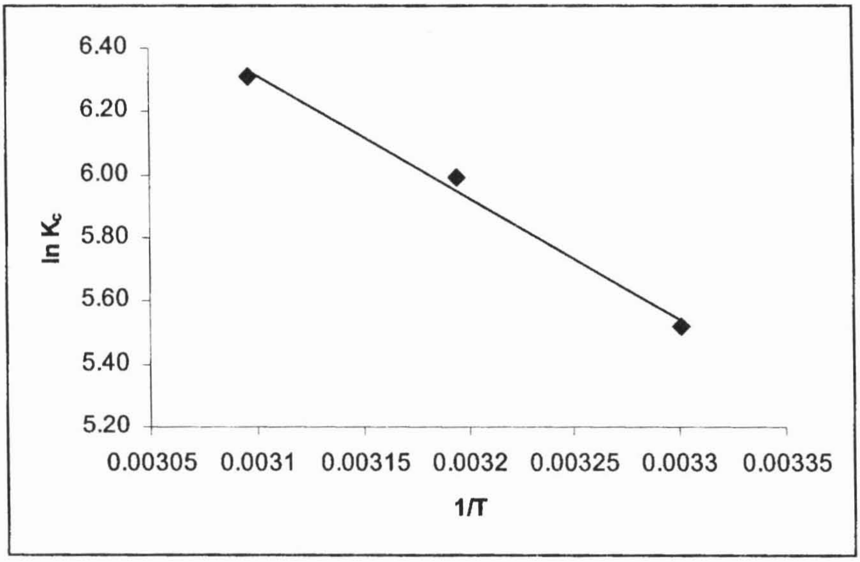

Figure 5: Van't Hoff Plot for Cr (VI) Adsorption onto Sugarcane Bagasse

Thermodynamic parameters; standard enthalpy change (ΔH°) and entropy (ΔS°) for the adsorption of Cr (VI) onto sugarcane bagasse were derived from the plot of ln K_C versus $1/T$ (Figure 5) based on Van't Hoff equation:

$$\ln K_C = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (5)$$

As shown in Table 3, a positive enthalpy change obtained suggests that the adsorption process of Cr (VI) onto sugarcane bagasse is endothermic. The free energy of the process at all temperatures is negative and changes with the rise in temperature, indicating that the adsorption process is spontaneous in nature, and the spontaneity increases with the rise in temperature (Lyubchik et al., 2004). The entropy change is a positive value, representing the affinity of sugarcane bagasse for

Cr (VI) and the increasing randomness at solid-solution interface during adsorption process.

Table 3: Thermodynamic Parameters of Cr (VI) Pdsorption onto EFB at Different Temperatures

T (°C)	K_C	$\Delta G°$ (kJ/mol)	$\Delta S°$ (J/mol K)	$\Delta H°$ (kJ/mol)
30	249.46	-13.90	152.13	32.14
40	400.57	-15.60		
50	548.84	-16.94		

Conclusions

The adsorption of Cr (VI) onto sugarcane bagasse was highest at pH below 2.0, thus suitable for applications in treatment of electroplating effluents which is normally acidic in nature. Both Freundlich and Langmuir isotherm models were applicable to describe the adsorption process with respect to temperature based on their R^2 values, however experimental data is better fitted to the latter model. Maximum adsorption capacity of Cr (VI) adsorbed onto treated sugarcane bagasse, Q_0 as calculated using Langmuir isotherm at 50°C is 98.04 mg/g. Thermodynamics parameters studied were used to partly explain the adsorption mechanism. The adsorption process of Cr (VI) onto sugarcane bagasse was endothermic and spontaneously occurred.

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References

Ajmal, M., Rao, R.A.K, Ahmad, R., Ahmad, J. & Rao, L.A.K. (2001). Removal and recovery of heavy metals from electroplating wastewater by using Kyanite as an adsorbent. *Journal of Hazardous Materials*, vol. B87, pp. 127-137.

Agency for Toxic Substances and Disease Registry (ATSDR). (2000). *Toxicological profiles for chromium*. Public Health Service, U.S. Department of Health and Human Services, Atlanta. [Online]. [Accessed on 5th February 2005]. URL: http://www.astdr.cdc.gov/toxprofiles/tp7.html.

Brown, P.A., Gill, S.A. & Allen, S.J. (2000). A review paper: Metal removal from wastewater using peat. *Water Research*, vol. 34 (16), pp. 3907-3916.

Browning, E. (1969) *Toxcity of Industrial Metals*. 2nd ed. London: Butterworths. Pp. 119-131.

Environmental Protection Agency (1998). *Human Health Fact Sheet: Chromium*. [Online]. [Accessed on 15th January 2005]. URL: http://www.epa.gov/ttn/atw/hlthef/chromium.html

Farajzadeh, M.A. and Monji, A.B. (2004). Adsorption characteristics of wheat bran towards heavy metal cations. *Sep. Purif. Technol,38*, 197-207.

Garg, V.K., Gupta, R., Kumar, R. & Gupta, R.K. (2004). Adsorption of chromium from aqueous solution on treated sawdust. *Bioresource Technology*, *92*, pp. 79-81.

Garg, U.K., Kaur, M.P., Garg, V.K. & Sud, D. (2007). Removalof hexavalent chromium from aqueous solution by agricultural waste biomass. *Journal of Hazardous Materials*, vol. 140, pp. 60-68.

Gharaibeh, S.H., Abu-el-Sha'r, W.Y. and Al-Kohafi, M.M. (1998). Removal of selected heavy metals from aqueous solutions using processed solid residue of olive mill products. *Wat. Res., 32* (22), 498-502.

Goel, J., Kadirvelu, K., Rajagopal, C. & Garg, V.K. (2005). Removal of lead (II) by adsorption using treated granular activated carbon: batch and column studies, *Journal of Hazardous Materials*, vol. B125, pp. 211-220.

International Agency for Research on Cancer (IARC). (1997). *Chromium and Chromium Compounds*. [Accessed online on 13th February 2005]. URL: http://www-cie.iarc.fr/htdocs/monographs/vol49/

International Chromium Development Association (ICDA). (2003). *Chromium*. [Online]. [Accessed 4th March 2005]. Available at URL: www.chromium-asoc.com/

Isa, M.H., Ibrahim, N., Aziz, H.A., Md.N., Sabiani, N.H.Md., Zinatizadeh, A.A.L, & Kutty, S.R.M. (2008). Removal of chromium (VI) from aqueous solution using treated oil palm fibre. *Journal of Hazardous Materials*, vol. 152, pp. 662–668.

Khan, A.A. & Singh, R.P. (1997). *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, vol. 242, pp. 151-158.

Kim, D.S. (2003). The removal by crab shell of mixed heavy metal ions in aqueous solution. *Bioresour. Technol., 87,* 355-357.

Kobya, M. (2004). Adsorption, kinetic and equilibrium studies of Cr (VI) by hazelnut shell activated carbon. *Adsorption Science Technology*, vol. 22 (1), pp. 51-64.

Kumar, A., Rao, N.N. and Kaul, S.N. (2000). Alkali-treated straw and insoluble straw xanthate as low cost adsorbents for heavy metal removal-preparation, characterization and application. *Bioresour. Technol., 71*, 133-142.

Lyubchik, S.I., Lyubchik, A.I., Galushko, O.L., Tikhonova, L.P., Vital, J., Fonseca, I.M. & Lyubchik, S.B. (2004). Kinetic and thermodynamics of the Cr (III) adsorption on the activated carbon from co-mingled wastes. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, vol. 242, pp. 151-158.

McKay, G., Blair, H.S. & Garden, J.R. (1982). *Journal of Applied Polymer and Sciences*, vol. 27 p. 3043.

Naserjad, B., Zadeh, T.E., Pour, B.B., Bygi, M.E. and Zamani, A. (2005). Comparison for biosorption modeling of heavy metals (Cr (III), Cu (II), Zn (II) adsorption from wastewater by carrot residues. *Process Biochem., 40*, 1319-1322.

Rao, M., Parwate, A.V. & Bhole, A.G. (2002). Removal of Cr^{6+} and Ni^{2+} from aqueous solution using bagasse and fly ash. *Waste Management*, vol. 22, pp. 821-830.

Weber, W.J. (1985). Adsorption Theory, Concepts and Models in Adsorption Technology: A Step-by-Step Approach to Process Evaluation and Application. (Slejko, F.L., Editor). New York: Marcel Dekker, Inc., pp. 1-32.

Yu, L.J., Shukla, S.S., Dorris, K.L., Shukla, A. & Margrave J.L. (2003). Adsorption of chromium from aqueous solutions by maple sawdust. *Journal of Hazardous Materials*, vol. B100, pp. 53-63.

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