

Adsorption of chromium (VI) on chemically activated saw dust

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Asian Journal of Environmental Science (June to November, 2009) Vol. 4 No. 1 : 29-33

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SUMMARY

Bioremediation of heavy metal pollution remains a major challenge in environmental biotechnology. The ability of chemically activated sawdust to remove chromium from aqueous solution was investigated. Experiments were carried out as a function of adsorbent dosage, initial concentration of chromium and contact time. The mechanism of metal sorption by chemically activated sawdust gave good fits for Langmuir, Freundlich and Lagergren models. The bioadsorption efficiency of chromium to the sawdust was decreased as the initial concentration of metal ions increased. The percentage removal was increased (79% to 97%) with an increase in contact time (20 to 100 min) at an initial Cr (VI) concentration of 20 mg/L. According to Langmuir isotherm, the monolayer saturation capacity (Q_0) was 33.55mg/g. The study showed that chemically activated sawdust was more favourable for the adsorption of chromium (VI) from the aqueous solutions.

Key words :

Sawdust,
Kinetics,
Adsorption,
Hexavalent
chromium, Low
cost adsorbents

Due to various human activities like ore mining and industrial processes, the natural biogeochemical cycles is disrupted causing increased deposition of heavy metals in terrestrial and aquatic environment. Heavy metals can be extremely toxic as they damage nerves, liver, kidney and bones and also block functional groups of vital enzymes. Release of these pollutants without proper treatment poses a significant threat to both environment and public health, as they are non biodegradable and persistent in nature. Through a process of biomagnifications, they further accumulate in food chains. (Martins *et al.*, 2006). Hexavalent chromium compounds are toxic, several can even cause lung cancer. Chromium and its compounds are widely used in electroplating, leather tanning, cement, dyeing, metal processing, wood preservatives, paint and pigments, textile, steel fabrication and canning industries. These industries produce large quantities of toxic wastewater effluents (Raji and Anirudhan, 1997). The maximum concentration limit for Cr (VI) for discharge into inland surface waters is 0.1 mg/l and in potable water is 0.05mg/l. Procedures for the removal of toxic metals from contaminated environments have been developed and most of them are based on ion exchange and/or precipitation. Physico-chemical methods have several disadvantages such as unpredictable metal ion removal, high reagent requirements and formation of sludge and its disposal, in addition to high installation and operational costs (Deepa *et al.*, 2006). Natural

materials that are available in large quantities or certain waste from agricultural operations may have potential to be used as low cost adsorbents, as they represent unused resources, widely available and are environmentally friendly (Deans and Dixon, 1992). In the present study, saw dust, which is a milling agro-waste available in plenty in a tropical country like India, is used for the removal of Cr (VI) ions from aqueous solutions.

MATERIALS AND METHODS

Preparation of adsorbent:

Saw dust was procured from local market and was chemically activated by 50% sulphuric acid. It was washed with distilled water to remove the residual acid. Then that was dried in hot air oven and sieved.

Preparation of stock and adsorbate solution:

A stock solution of chromium (VI) was prepared by dissolving 2.8287 g of potassium dichromate ($K_2Cr_2O_7$) in 1000 ml of distilled water. This solution was diluted as required to obtain standard solutions containing 5, 10, 15, 20, and 25 mg/L of chromium (VI).

Batch mode adsorption studies:

Contact time:

1g of chemically activated sawdust was added in a 50ml of various adsorbate solutions at a constant pH of 2.0 and was agitated in a horizontal bench shaker at room temperature ($27 \pm 2^\circ C$). The flasks were withdrawn at

Accepted :
February, 2009

predetermined time intervals of 20 minutes. The adsorbent and adsorbate were separated by centrifugation at 3000 rpm for 5 minutes. The remaining adsorbate concentration in the supernatant was determined spectrophotometrically at 540 nm.

Adsorbent dosage:

50mL of adsorbate solutions (20 to 100mg/L) at a constant pH of 2.0 were agitated with various dosages of adsorbent (1.0g to 5.0g/50ml) at equilibrium period. The adsorbent and adsorbate were separated and the amount of adsorbate adsorbed was determined.

Adsorption isotherms:

Any adsorption study is incomplete without mentioning of adsorption isotherm. They are useful for estimating the amount of adsorbent needed to adsorb a given adsorbate from the solution. Langmuir, Freundlich and Lagergren isotherms were used to determine the adsorption capacity and the adsorption rate constant respectively.

RESULTS AND DISCUSSION

Physical characteristics of activated carbon:

The efficacy of the chemically activated sawdust was depending on its physical characters that are presented in Table 1.

Table 1: Physical characteristics of chemically activated saw dust	
Physical characters	Percentage (%)
Ash content	98.05
Moisture content	4.438
Matter soluble in water	1.293
Matter soluble in acid	3.59
Bulk density	0.68965g/l

Effect of contact time and initial chromium concentration:

Equilibrium time and adsorbent uptake varied with adsorbates, which may be due to difference in affinity of various adsorbents for adsorbates. Time required by the activated sawdust to reach adsorption equilibrium was 80 minutes. Equilibrium time is one of the important considerations for economical water and wastewater treatment (Shekinaah *et al.*, 2002). The adsorption was very rapid initially and a large fraction of the total concentration of chromium was removed in the first 60 minutes (Fig.1). Though it was observed that adsorption of chromium decreased with an increase in chromium

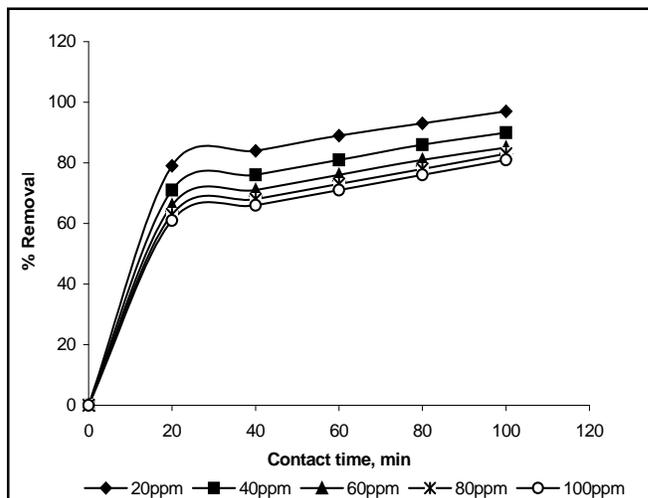


Fig. 1 : Effect of contact time for the adsorption of chromium using activated saw dust

concentration in the solution, which showed that removal of chromium was dependent upon the concentration of the chromium solution. The time variation adsorption increased continuously and seemed to be smooth which was indicative of the formation of monolayer coverage on the surface of adsorbent (Desai *et al.*, 1997).

Effect of adsorbent dosage:

The study was carried out with different adsorbent dosages (1.0 to 5.0g/50ml) up to an equilibrium time. Increase in adsorbent dosage increased the percentage removal of chromium ions (Fig.2). The optimum adsorbent dosage for chromium was found to be 3.0 g. Availability of more surface area of the adsorbent could be the reason for the increase in percentage removal of adsorbate with the increase in adsorbent dosage (Kadirvelu *et al.*, 2000).

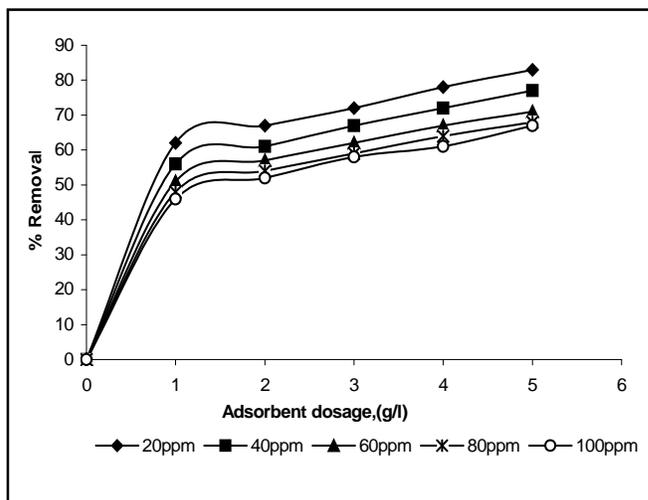


Fig. 2 : Effect of adsorbent dosage for the adsorption of chromium using activated saw dust

Adsorption isotherms:

Langmuir isotherm:

This isotherm relates adsorption density q_e (uptake of adsorbate per unit weight of adsorbent) to equilibrium adsorbate concentration in the bulk fluid phase, C_e . It was valid for monolayer adsorption onto a surface containing a finite number of identical sites (Namasivayam and Ranganathan, 1993). The model assumes uniform energies of adsorption onto the surface and no transmigration of adsorbate in the plane of surface (Langmuir, 1918).

The Langmuir isotherm is represented by the following equation:

$$C_e/q_e = 1/Q_0b + C_e/Q_0 \tag{1}$$

where,

C_e is the equilibrium concentration (mg/l)

q_e is the amount adsorbed at equilibrium time (mg/g)

Q_0 and b is Langmuir constants related to adsorption capacity and energy of adsorption, respectively.

In Langmuir plots for adsorption, the linear plots of C_e/q_e vs C_e confirmed that the adsorption followed the Langmuir isotherm model (Fig. 3). Langmuir constants, Q_0 and b were 33.55mg/g and 0.0089, respectively. The Q_0 values for the adsorption of chromium in the present study were compared with other reports (Table 2).

Freundlich isotherm:

Freundlich equation can be derived by assuming that the free energy of adsorption decreases logarithmically as adsorption density increases. It is used for heterogenous

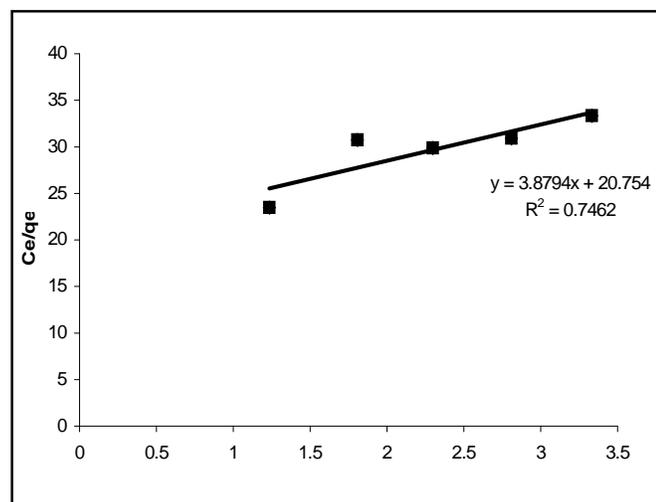


Fig. 3 : Langmuir plot for the adsorption of chromium using activated saw dust

Table 2 : Adsorbent capacity for chromium removal with various adsorbents

Adsorbent	Adsorbent capacity, Q_0 (mg/g)	References
Palm pressed-fibres	15.0	Tan <i>et al.</i> , 1993.
Maize cob	13.8	Sharma and Forster, 1994.
Sugar cane bagasse	13.4	Sharma and Forster, 1994.
Biomass residual slurry	5.87	Namasivayam and Yamuna, 1995.
Waste tea	1.55	Orhan and Buyukgungur, 1993.
Fe (III)/Cr (III) hydroxide	1.43	Namasivayam and Ranganathan, 1993.
Walnut shell	1.33	Orhan and Buyukgungur, 1993.
Coconut tree sawdust	3.60	Selvi <i>et al.</i> , 2001.
Treated saw dust of Indian rose wood	10.0	Garg <i>et al.</i> , 2004.
Cement kiln dust	33.0	Karthikeyan <i>et al.</i> , 2005.
Neem leaf powder	7.43	Venkateswarlu <i>et al.</i> , 2007.
Sulphuric acid treated sawdust	33.55	Present study

surface energies in which the energy term, Q_0 , in the Langmuir equation varies as a function of the surface coverage, q_e , strictly due to variation in the heat of adsorption.

$$q_e = K_f C_e^{1/n} \tag{2}$$

Rearranging the equation (2) gives

$$\log_{10} X/m = \log K_f + 1/n \log_{10} C_e \tag{3}$$

where, C_e is the equilibrium concentration (mg/l)

X/m is the amount adsorbed at equilibrium time (mg/g)

K_f and n are Freundlich constants.

n gives an indication of favourability and K_f [mg/g (L/mg)ⁿ], the capacity of the adsorbent. Linear plots of $\log C_e$ Vs $\log X/m$, Freundlich plots, (Fig.4) showed that the adsorption of adsorbates onto the sawdust follows Freundlich isotherm model, suggesting that the average energy of adsorption decreases with increasing adsorption density. From the slope and intercept of the plots, the values of n and K_f were calculated as 0.820 and 1.398mg/g.

Adsorption rate constant:

The adsorption rate constant was determined from

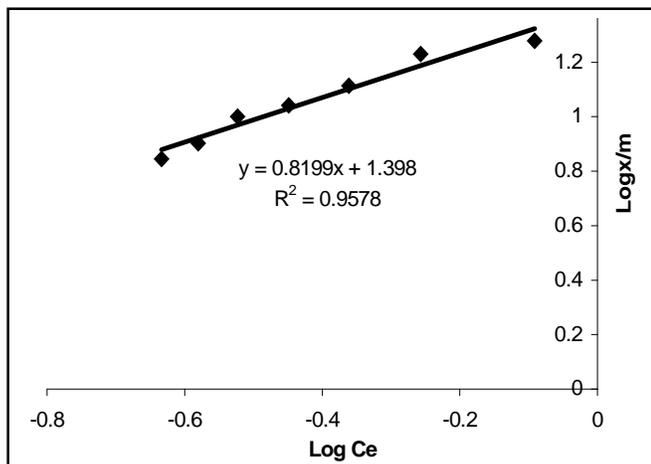


Fig. 4 : Freundlich isotherm for the adsorption of chromium using activated saw dust

the following first order rate expression (Lagergren and Svenka, 1898).

$$\text{Log}(q_e - q) = \text{log } q_e - \text{Kad} / 2.303 \times t \quad (4)$$

where,

q and q_e are amounts of adsorbate adsorbed (mg/g) at time, t (min) and at equilibrium, respectively.

K_{ad} is the adsorption rate constant (l/min).

The straight-line plots of $\text{log}(q_e - q)$ Vs contact time (Fig.5) showed the applicability of the above equation. The K_{ad} values were calculated from the slope of the linear plots and were observed to be in the range of 0.012 to 0.035 l/min at 30°C respectively for adsorption of chromium using activated sawdust (Table 3).

The use of agricultural residues such as sawdust or

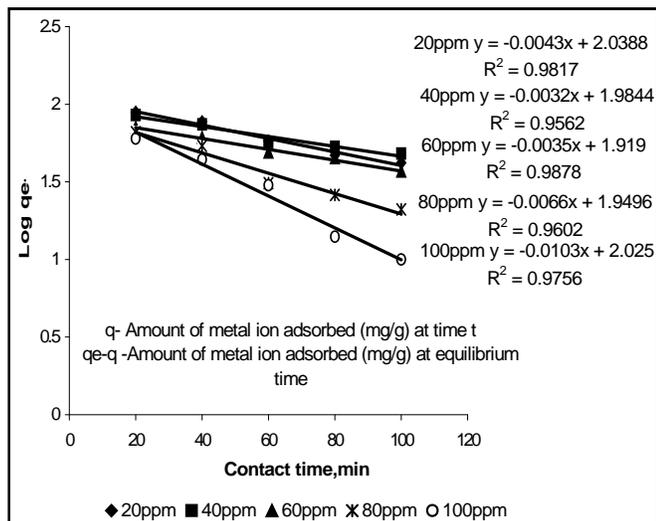


Fig. 5 : Freundlich isotherm for the adsorption of chromium using activated saw dust

Table 3: Lagergren constant for chromium removal using activated sawdust

Initial chromium concentration (mg/l)	Adsorption rate constant [K_{ad} (l/min)]
20	0.012
40	0.015
60	0.019
80	0.030
100	0.035

industrial by-products like bagasse have received considerable attention (Achari and Anirudhan, 1995; Gaghate *et al.*, 1990; Siddique *et al.*, 1999; Haribabu, 1992) Therefore, there is a need to produce activated carbon from cheaper and readily available materials, which can be used economically on a large scale. Activated carbons prepared from rice husk, groundnut husk, fertilizer waste slurry, peanut hull, jute stick, moringa olefera seed husk, coconut husk and sawdust have been used for wastewater treatment and the potential of their ultimate usage may be determined by their adsorption capacity, regeneration characteristics and physical properties of the subsequent product. In recent years, adsorption has emerged as a cost-effective and efficient alternative for the removal of heavy metals from low strength wastewaters (Manju and Anirudhan, 1997; Raji and Anirudhan, 1997; Warhursta *et al.*, 1997).

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