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RESEARCH ARTICLE

Adsorption Efficiency of Sawdust in Activated and Surface-Modified Forms - A Comparative Study

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Abstract: Two different forms of sawdust, *viz*., acid-activated sawdust in powder form (ASDP) and surface-modified sawdust in bead form (SDCCB) were prepared and used as adsorbents for the removal of chromium(VI) from aqueous solution. Batch experiments were carried out to investigate the potential efficiency of the two forms of sawdust to remove Cr(VI) ions from aqueous solution as a function of the initial Cr(VI) concentration, pH, contact time, agitation speed and temperature. Based on Langmuir isotherms, the maximum adsorption capacity was found to be 45.5 mg/g for ASDP and 125 mg/g for SDCCB. Equilibrium was found to be attained at about 120 min and 150 min respectively for ASDP and SDCCB. Various isotherms and kinetic models were fitted to describe the solid–solute interaction and the activation parameters were evaluated in both the cases. Based on the results, it has been suggested that the sorption of Cr(VI) on surface of both sawdust adsorbents is an endothermic, a spontaneous and a nonspecific-chemisorption process.

Keywords: Sawdust, Adsorption capacity, Adsorption isotherms, Kinetics, Thermodynamic parameters

Introduction

Despite the availability of numerous techniques for the treatment of effluents with heavy toxic metals, adsorption is constantly viewed as the highly effective technique. Agricultural by-products are mostly composed of lignin and cellulose as well as other polar poly functional groups like alcohols, aldehydes, ketones, carboxylate, phenols and ethers. These groups are able to bind heavy metals through replacement of hydrogen ions with metal ions in solution or by donation of an electron pair to form complexes with the metal ion in solution[1,2]. Therefore, biomass like rice husk, seaweeds, sawdust, chitosan *etc*. have been recognised as effective, eco-friendly low-cost adsorbents because of their remarkable properties such as hydrophilic character, sufficient flexibility of linear chain, cationic properties of polysaccharides, presence of polar poly functional groups, bio degradability and bio comparability. But in recent years, surface modification is being done chemically, physically or biologically to enhance their ion-exchange properties through the creation of surface functionality[3,4].

Hexavalent chromium is one of the harmful heavy metals because of its carcinogenetic nature and also wide application in industries such as electroplating, leather tanning, mining, dyes and pigments, steel fabrication, canning industries *etc*. Due to its severe toxicity, Environmental Protection Agency, Cincinaati, USA set the tolerance limit for the discharge of Cr(VI) ions into surface water as 0.1 mg/L and in potable water as 0.05 mg/L. Thus the removal of Cr(VI) ions is mandatory.

Hence in the present study, sawdust (ligno cellulose polysaccharide) has been chosen as the precursor and its two surface-modified forms, activated sawdust powder (ASDP) and sawdust-chitosan composite bead (SDCCB) have been employed in separate experiments for the adsorption of Cr(VI) ions from aqueous solution. Results from these studies have been compared to decide which of these two forms is better in removing Cr(VI) from toxic effluents.

Experimental

Saw dust was collected from the local saw mill. Potassium dichromate (AR) was used for the preparation of Cr(VI) stock solution. Chemicals such as sulphuric acid, hydrogen peroxide and nitric acid were purchased from Merck India. The pH of the solutions was maintained by hydrochloric acid - potassium chloride for the range of pH 1-3, acetic acid - sodium acetate for the range of pH 4-6 and boric acid - sodium hydroxide for the range of pH 8-10. Sigma Aldrich analytical grade reagents of 1,5-diphenyl carbazide and acetone were used for analyzing the chromium ions. Double distilled water was used for preparing all the solutions.

Preparation of ASDP

Sawdust was charred thoroughly by the careful addition of conc. H_2SO_4, washed with sodium carbonate and distilled water and dried in hot air oven at 100 ^{o}C. The dried sample was treated with H_2O_2 (10 mL) in a water bath at 50 ^{o}C for 30 minutes and then 10% conc. HNO_3 was added with constant stirring at 70 ^{o}C for about 40 minutes. The sample was then washed and dried to get the activated sawdust powder.

Preparation of SDCCB

Saw dust was treated with sulphuric acid for 2 h Then it was neutralized with distilled water and dried in a hot air oven at 100 ^{o}C. Chitosan gel was prepared by dissolving 3 g of chitosan in 100 mL of 2% acetic acid. 3 g of acid treated saw dust was added to the chitosan gel and kept in a rotary shaker for 12 h at 200 rpm. Then this solution was dropped into 0.5 mol/L NaOH solution which was kept for 12 h. The composite beads thus obtained were washed with distilled water to remove excess NaOH. Cross linking was done by immersing the beads in ethanolic 7.5% glutaraldehyde solution for 24 h. The beads were then washed and dried to get the sawdust chitosan composite beads.

Both ASDP and SDCCB were characterized by using BET analyzer (Micromeritics), and FTIR spectrophotometer (Perkin Elmer, spectrum RXI) to identify the presence of activation in the adsorbents.

Method

Batch adsorption studies were conducted by shaking 25 mL of desired quantity of aqueous Cr(VI) solution with 0.1 g adsorbent and pH 2.0 at 200 rpm speed to determine the equilibrium time. The supernatant liquid samples were filtered periodically and then analyzed by using Jasco UV spectrophotometer at 540 nm to calculate the adsorption capacity and percentage removal efficiency. The amount of adsorption, q_t (mg/g) and percentage removal were calculated using Eqs. (1) and (2).

$$q_t = (C_o - C_t)V/m \tag{1}$$

$$\text{Percentage removal} = \left[(C_o - C_F)/C_o\right] \times 100 \tag{2}$$

Where C_o and C_t are the initial concentration and concentration at any instant (mg/L), V is the volume of solution (l), q_t is the adsorption capacity (mg/g) at time t, *m* is the weight of adsorbent (g) and C_F is the solution concentration at the end of the adsorption process (mg/L).

Results and Discussion

Adsorption usually depends on the surface area available on the adsorbent. The BET analysis shows the specific surface area of ASDP and SDCCB to be 321 m^2/g and 30 m^2/g respectively.

FTIR results confirm the presence of polar poly functional groups in ASDP and SDCCB (Figures 1 and 2). The significant changes of functional groups are visible due to the different mode of activation carried out in the two adsorbents. The successive acid treatment in the case of ASDP hydrolyzes the amides and esters of ligno cellulosic polymer into acid, alcohol and amines which are confirmed by their corresponding absorbance peaks in FTIR spectrum (Figure 1).

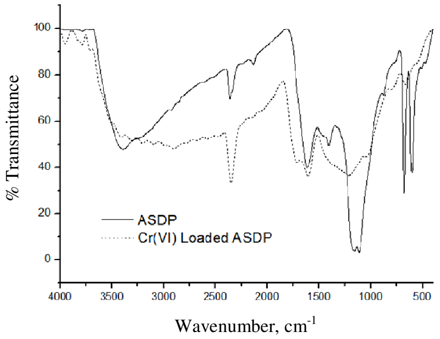

Figure 1. FTIR spectra of raw and Cr-loaded ASDP

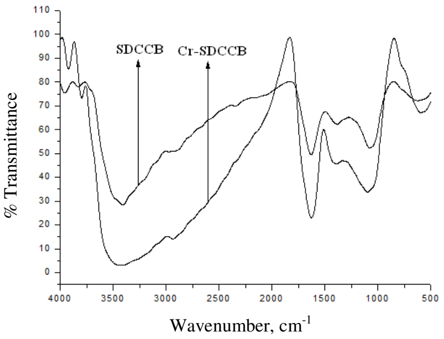

Figure 2. FTIR spectra of raw and Cr-loaded SDCCB

Table 1 lists the functional groups and shift in the functional group of dominant peaks of SDCCB on Cr(VI) adsorption. These shifts in the wave number indicate the adsorption of Cr(VI) ion on the surface of the SDCCB.

Table 1. Functional groups present in SDCCB and Cr-loaded SDCCB

Functional groups	Functional group frequencies, cm^{-1}	
	SDCCB	Cr-loaded SDCCB
O-H (H bonded) and NH stretching	3408.36	3412.3
N-H bending vibrations	1631.10	1627.48
C-O and O-H bending	1383.62	1385
C-N stretching	1075.08	1097
NH_2 and NH wagging	622.70	594.5

The studies of effect of contact time, agitation speed and pH on the adsorption capacity of Cr(VI) ions reveal that equilibrium is reached at nearly 120 min in the case of ASDP and 150 min in the case of SDCCB and maximum adsorption occurs at 200 rpm and pH 2.0 with respect to both the adsorbents.

The amount of chromium adsorbed for different initial concentration onto ASDP and SDCCB is shown in Figure 3. For ASDP (Figure 3a), the adsorption capacity increases from 6.1 mg/g to 42.4 mg/g and percentage removal decreases from 98% to 68% in the initial concentrations ranging from 25 ppm to 250 ppm. For SDCCB (Figure 3b), the adsorption capacity increases from 11.1 mg/g to 101.1 mg/g and % removal decreases from 95% to 80.9% in the initial concentrations ranging from 100 ppm to 500 ppm.

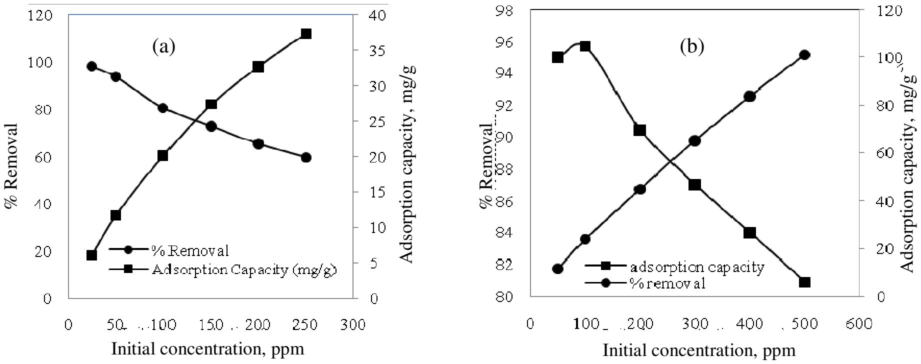

Figure 3. Effect of initial concentration on adsorption of Cr(VI) ions on (a) ASDP and (b) SDCCB (m = 0.1g, pH = 2, V = 25 mL, Speed = 200 rpm)

In adsorption process, the initial Cr(VI) concentration acts as a driving force to overcome the mass transfer between the adsorbent and Cr(VI) ions. In general, at lower concentrations of Cr(VI) there are sufficient active sites to occupy. However in higher concentration of Cr(VI), they are left unadsorbed due to the saturation of binding sites of the adsorbent[5,6]. For the initial Cr(VI) concentration value of 180 ppm, the optimum values (the point of intersection in the Figure 3) of percentage removal and adsorption capacity are found to be 77% and 33.5 mg/g respectively for ASDP (C_o = 180 ppm) and 87.85 & 65.3 mg/g respectively for SDCCB (C_o = 300 ppm).

The effect of temperature on adsorption of Cr(VI) ions was investigated for ASDP (C_o = 100 ppm) and SDCCB (C_o = 200 ppm) by varying the temperature from 30 ºC to 70 ºC (Figure 4). The maximum adsorption capacity was observed at 70 °C. The increase in adsorption capacity with increase in temperature may be due to the formation of some new adsorption sites on the surface of the adsorbent, the enlargement of the pores and also the increased rate of intra-particle diffusion of Cr(VI) ions into the pores of adsorbent.

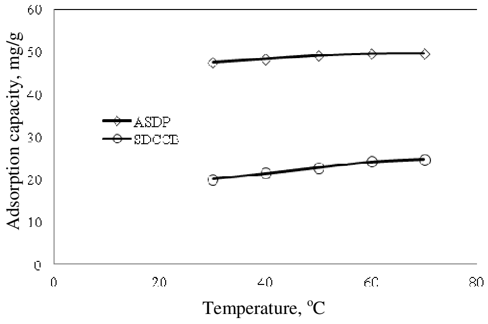

Figure 4. Effect of temperature on adsorption of Cr(VI) on ASDP and SDCCB (m = 0.1 g, pH = 2, V = 25 mL, Speed = 200 rpm)

Various isotherm equations like Langmuir, Freundlich and Temkin were used to describe[7] the equilibrium characteristics of adsorption of chromium by SDCCB and ASDP. The linearised form of isotherms and the constants obtained from the slope and intercept are listed in Table 2.

Table 2. Summary of parameters for various isotherm models

Isotherm Model	Equation	Constants for SDCCB	Constants for ASDP
Langmuir	$\frac{C_e}{q_e} = \frac{1}{b\theta} + \frac{C_e}{\theta}$ $K_L = \theta \cdot b$ $R_L = \frac{1}{1+bC_o}$	$\theta = 125$ mg/g b = 0.04 L/mg $K_L = 5$ L/g $R_L = 0.2$ $R^2 = 0.967$	$\theta = 45.5$ mg/g b = 0.13 L/mg $K_L = 5.9$ L/g $R_L = 0.13$ $R^2 = 0.979$
Freundlich	$\ln q_e = \ln K_F + \frac{1}{n} C_e$	n = 1.8 L/mg $K_F = 8.74$ L/g $R^2 = 0.974$	n = 2.7 L/mg $K_F = 8.63$ L/g $R^2 = 0.991$
Temkin	$q_t = B \ln K_T + B \ln C_e$	B = 22.9 $K_T = 0.58$ L/g $R^2 = 0.960$	B = 7.05 $K_T = 3.39$ L/g $R^2 = 0.967$

Based on R^2 values the order of isotherm in both the surfaces are Freundlich > Langmuir > Temkin (*i.e.*) multilayer lateral adsorption is possible. So the adsorption mechanism is same whereas the maximum adsorption capacity ($\theta = 125$ mg/g) is greater in the composite bead form than powder form of sawdust (45.5 mg/g).

The pseudo first order, pseudo second order, intra particle diffusion and simple Elovich kinetic models were tested to investigate the rate of adsorption of Cr(VI) by SDCCB and ASDP. The linearised form of adsorption kinetics and their constants are given in Table 3.

Table 3. Summary of parameters for various kinetic models

Kinetic model	Linear equation	Constants for SDCCB	Constants for ASDP
Pseudo first order	$\ln(q_e - q_t) = \ln q_e - K_{1ad} t$	$K_{1ad} = 0.034$ min^{-1} $R^2 = 0.877$	$K_{1ad} = 0.019$ min^{-1} $R^2 = 0.955$
Pseudo second order	$\frac{t}{q_t} = \frac{1}{K_{2ad} \cdot {q_e}^2} + \frac{t}{q_e}$	$q_e = 25$ mg/g $K_{2ad} = 0.0043$ g/mg/min h = 2.7 mg/g/min $R^2 = 0.994$	$q_e = 23.3$ mg/g $K_{2ad} = 0.0084$ g/mg/min h = 4.6 mg/g/min $R^2 = 0.999$
Simple Elovich	$q_t = \beta \ln t + \beta \ln(\alpha\beta)$	$\alpha = 1.2$ mg/g/min $\beta = 3.62$ g/mg $R^2 = 0.984$	$\alpha = 614$ mg/g/min $\beta = 1.85$ g/mg $R^2 = 0.978$
Intraparticle diffusion	$q_t = K_{id} t^{1/2} + C$	$K_{id} = 0.867$ mg/g.min$^{0.5}$ $R^2 = 0.958$	$K_{id} = 0.550$ mg/g.min$^{0.5}$ $R^2 = 0.963$

Therefore based on R^2 values, pseudo second order kinetics is the suitable one in both the surfaces. This adsorption occurs through chemisorption. From the data obtained at different temperatures, the thermodynamic parameters for the adsorption process have been evaluated and shown in Table 4.

Table 4. Thermodynamic parameters

Adsorbent	ΔG^o, kJ/mol	ΔH^o, kJ/mol	ΔS^o, J/K/mol
SDCCB	−3.95	+45.98	164.78
ASDP	−1.31	−55.04	185.98
Suggestion[8]	Feasible, spontaneous, non-specific diffusion of ions into pores	Endothermic due to diffusion on the adsorbents	Driving forces of non-specific chemisorptions at the surface

Adsorption mechanism

The adsorption of Cr(VI) on ASDP and SDCCB occurs in a same kind of multistep process. Initially ion-exchange occurs rapidly due to electrostatic force of attraction between solid-solute interfaces. The Cr(VI) ions then diffuse slowly into the pores due to specific chemisorptions with active sites of adsorbents. This is the rate-controlling step. This is supported by the effect of pH, and activation parameters. Finally equilibrium is reached due to chelation with chromium binding centres such as O^-, N^- or S^{2-} containing the surface functionality of both the adsorbents[9].

Conclusion

Results reveal that both the modified forms of saw dust (*i.e.* ASDP and SDCCB) can be used as effective, economic and eco-friendly adsorbents to the maximum removal of Cr(VI) ion (>90% removal at pH 2.0) from aqueous solutions. The feasibility of this adsorption on both the modified surfaces is spontaneous, non-specific, endothermic and the multi-layer chemisorption suitably obeys the pseudo second order on the energetic heterogeneous surface.

On comparing the efficiency of these two surfaces, adsorption isotherm, kinetic models and activation parameters indicate that the modified surface of saw dust behaves as a superior adsorbent in its composite bead form rather than raw powder form because of its maximum adsorption capacity (θ = 125 mg/g) and higher negative ΔG^o value.

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References

1. Gupta S and Babu B V, *Chem Eng J.,* 2009, **150(2-3)**, 352-365.
2. Ansari R and Mosayebzadeh Z, *J Iran Chem Soc.,* 2010, **7(2)**, 339-350.
3. Sud D, Mahajan G and Kaur M P, *Bio Resource Technol.,* 2008, **99(14)**, 6017-6027.
4. Crini G, Robert C, Martel B and Badot P M, *J Hazard Mater.,* 2008, **153(1-2)**, 96-106.
5. Karthiheyan T, Rajagopal S and Miranda L R, *J Hazard Mater.,* 2005, **B124(1-2)**, 192-199.
6. Hamadi N K, Chen X D, Farid M M and Lu M G Q, *J Chem Eng.,* 2001, **84(2)**, 95-105.
7. EI- Ashtoukhy E S I, Amin N K and Abdel Wahab O, *Desalination*, 2008, **223**, 162-173
8. Cestari A R, Vieria E F S and Mota J A, *J Hazard Mater.,* 2008, **160(2-3)**, 337-343.
9. Shukla A, Zhang Y, Dubey P, Margrave J L and Shukla S, *J Hazard Mater.,* 2002, **B95(1-2)**, 137-152.