



Use of Sawdust of Aspen Tree for the Removal of Chromium (VI) from Aqueous Solution

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Abstract

Adsorption capacity of Cr (VI) onto sawdust of aspen tree and activated sawdust, was investigated in a batch system by considering the effects of various parameters like contact time, initial concentration, pH, temperature, agitation speed, adsorbent dose and particle size. Cr (VI) removal is pH dependent and caused to be maximum at pH 2.0. The amounts of Cr(VI) adsorbed increased with increase in dose of both adsorbents and their contact time. Experimental results show that the low cost biosorbent was effective for the removal of pollutants from aqueous solution. The Langmuir, Freundlich and Temkin isotherm were used to describe the adsorption equilibrium studies of agrowaste. Freundlich isotherm shows better fit than Langmuir and Temkin isotherm in the temperature range studied.

Keywords: Chromium, Aqueous, Lignocellulosic solid wastes, Adsorption, Sawdust.

1. Introduction

Hexavalent chromium is present in the effluents produced during the electroplating, leather tanning, cement, mining, dyeing and fertilizer and photography industries and causes severe environmental and public health problems. Hexavalent chromium has been reported to be toxic to animals and humans and it is known to be carcinogenic [3].

The permissible limit for hexavalent chromium in industrial wastewaters is 0.1 mg/l and in potable water is 0.05 mg/l [7]. In order to decrease Cr(VI) in these effluents to the standard amount, an efficient and low cost method must be expanded. The different methods of removal of Cr(VI) from industrial wastewater consist of filtration, chemical precipitation, adsorption, electrodeposition and membrane systems or even ion exchange process.

These techniques apart from being economically expensive have disadvantages such as deficient metal removal, high reagent and energy requirements, and generation of toxic sludge or other waste products that need disposal. Efficient and environment friendly methods are thus needed to be employed to reduce heavy metal content. In this context, considerable attention has been focused in recent years upon the field of sorption by lignocellulosic solid wastes such as straw, coconut husks, exhausted coffee [4], waste tea [13], seeds of *Ocimum Basilicum*, bark, walnut shell, straw and plant root [15], defatted rice bran, rice hulls, soybean hulls and cotton seed hulls [14, 20], wheat

bran, pea pod, cotton and mustard seed cakes [10], paddy straw [18], coir pith [11], sawdust and pine leaves [1].

2. Materials

2.1 Adsorbents

Sawdust of Aspen tree was prepared from agricultural solid wastes as adsorbents (major agricultural wastes of Birjand, Iran). Sawdust were soaked with 1 M HCL solutions for 30 min, rinsed several times with deionised water, oven dried at 100°C and used as activated sawdust. Samples were pulverized before taking them for further experiments. Potassium dichromate and other chemicals used for these tests were of analytical reagent grade and were obtained from standard sources.

3. Method

A known weight (e.g. 2.0 g of adsorbent) was equilibrated with 100 ml of the chromium solution of known concentration in 250 ml glass flask at room temperature (25°C). Chromium solution was prepared by dissolving the potassium dichromate ($K_2Cr_2O_7$) in distilled water. Fresh dilutions were applied for each research.

The pH of Chromium solution was adjusted with a 0.1M HCL/0.1M NaOH solution. The time of each experimental was kept at 30 min. These flasks then were shaken on the shaker at 400 rpm. The samples were filtrated. The concentration of the samples was analyzed in a spectrophotometer (JENWAY 6305

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UV/V is model) using 1,5-diphenylcarbazide as the complexing agent at the wavelength of 540 nm [2].

The Cr(VI) loadings on sorbents were calculated based on mass balance through loss of metal from aqueous solution. Effect of various pH; temperature; dose 1, 2, 3, 4 and 6 g/100 ml of solution ; contact time 5, 10, 15, 30, 40 min; initial concentration 0.5,1,2,4,5 ppm; particle size mesh>30, mesh<30, mesh>20; agitation speed 50, 100, 300, 400, 700 rpm were studied. The adsorption capacity was calculated by the Langmuir, Freundlich, and Temkin isotherm.

4. Results and Discussion

4.1. Effect of contact time

Fig. 1 shows the adsorption of Cr(VI) by sawdust and activated sawdust, as a function of time. The experiments were carried out under the conditions of 25°C, particle size of <30 mesh, with 2 g of adsorbent in 100 ml of chromium solution and Initial Cr(VI) concentration 5 mg/l. The experiments showed that the removal rate take place urgently, seemly reaching balance within the first fifteen minutes of adsorption. More increase in contact time did not indicate an increase in biosorption.

4.2. Effect of initial Cr (VI) concentration

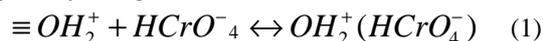
The effect of Cr (VI) concentration on the sorbent by varying the initial Cr(VI) concentration (0.5, 1, 2, 4 and 5 mg/l) for a time interval of 30 min has been indicated in Fig. 2. The percentage removal was reduced with increase in Cr(VI) concentration. At low concentrations the ratio of available surface to the initial Cr(VI) concentration is larger, as a result the removal becomes independent of initial concentrations. But, in order to higher concentrations this ratio is low, the percentage removal then depends upon the initial concentration. From the results, it is revealed that within a certain range of initial metal concentration, the percentage of metal adsorption on absorbent is determined by the sorption capacity of the absorbent.

4.3. Effect of Adsorbent Dose

The effect of adsorbent dose on Cr (VI) uptake was investigated by varying the adsorbent dose (1, 2, 3, 4 and 6 g/100 ml) for a time interval of 30 min (Fig. 3). Experimental results showed that the percentage removal Cr (VI) increases with the increasing amount of adsorbent up to 3g. This can be explained by the fact that the more the mass increases, the more the contact surface offered to the adsorption of chromium becomes important.

4.4. Effect of pH

The pH of the aqueous solution is an important controlling parameter in the adsorption process. As results show, adsorption of Cr (VI) was higher at lower pH and decreased with increasing pH (Fig. 4). And the optimal initial pH was observed at pH 2.0. The dominant chromium compound within the solution at pH=2 is $HCrO_4^-$ (CrO_4^{2-}) and also $Cr_2O_7^{2-}$ exists). Removal of Cr (III) at pH=2 is zero while its removal percentage is very high at pH=5 where as removal percentage of Cr(VI) is significantly low. This shows that the pH of the solution is a very important parameter for the removal of Cr(VI) which is the toxic form of the chromium metal. At pH=2, due to the excess amount of H^+ ions within the medium, the active site on the absorbent positively charged. This causes a strong attraction between these sites and negatively charged $HCrO_4^-$ ions;



At low pH values active sites are positively charged. As a result negative metals adsorption increases considerably. When pH value becomes more, surface of the adsorbent becomes the neutral and a reduction in the adsorption is noticed. When the adsorbent surface is negatively charged, adsorption decreases significantly. This behavior is specific to the chromium ions and it is different for the divalent metals. Chromium ions release hydroxide ions to the solution instead of proton [17].

4.5. Effect of Temperature

The adsorption of Cr(VI) at different temperatures shows an increase in the adsorption capacity when the temperature is increased (Fig.5). This shows that the adsorption reaction is endothermic in nature. The increase in the adsorption capacity may be because of chemical interaction between adsorbates and adsorbent, creation of some new adsorption sites or the increased rate of intraparticle spread of Cr(VI) ions into the pores of the adsorbent at higher temperatures .

At low temperatures kinetic energies of chromium ions were low. As a result, it is a very difficult and time-consuming process for ions to reach the active sites on the adsorbent. Increase in temperature causes increase in the mobility of the ions. If temperature is increased more, the kinetic energies of chromium ions become more than the potential attractive forces between active sites and ions.

The standard Gibb's energy was evaluated by

$$\Delta G^0 = -RT \ln K_c \quad (2)$$

The equilibrium constants K_c was evaluated at each temperature using the following relationship:

$$K_C = \frac{C_{Ae}}{C_e} \quad (3)$$

where C_{Ae} is the amount adsorbed on solid at equilibrium and C_e is the equilibrium concentration. The other thermodynamic parameters such as change in standard enthalpy (ΔH^0) and standard entropy (ΔS^0) were determined using the following equation:

$$\ln K_C = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (4)$$

ΔH^0 and ΔS^0 were obtained from the slope and intercept of the Van't Hoff's plot of $\ln K_C$ versus $1/T$ as shown in Fig. 6.

Positive value of ΔH^0 indicates that the adsorption process is endothermic. The negative values of ΔG^0 reflect the feasibility of the process and the values become more negative with increase in temperature. Standard entropy determines the disorderliness of the adsorption at solid-liquid interface.

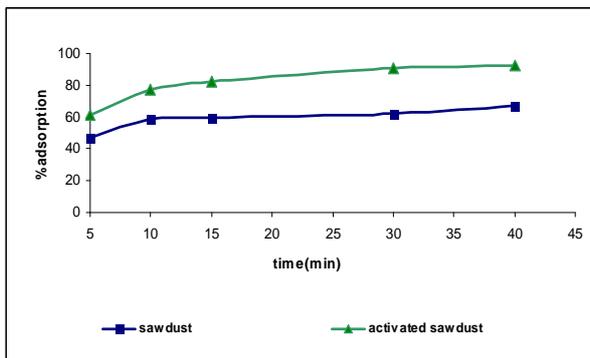


Fig.1. percent removal of Cr(VI)(5ppm) Vs. time.

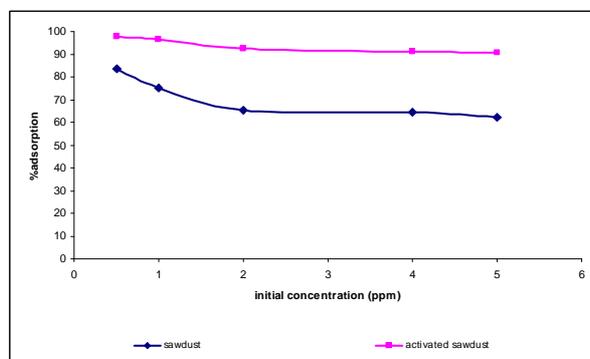


Fig. 2. Effect of initial Cr (VI) concentration.

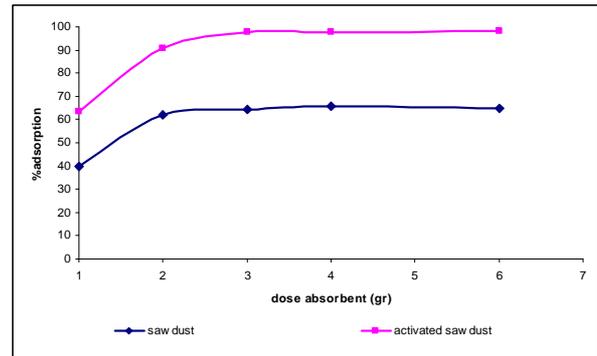


Fig.3. Effect of dose on Cr (VI) adsorption.

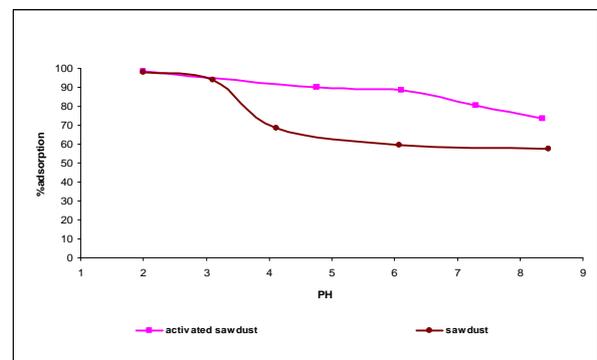


Fig.4. Effect of pH on Cr (VI) adsorption.

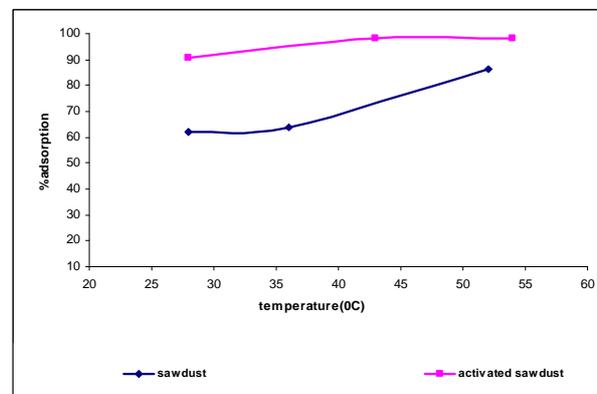


Fig.5. Effect of temperature on Cr (VI) adsorption.

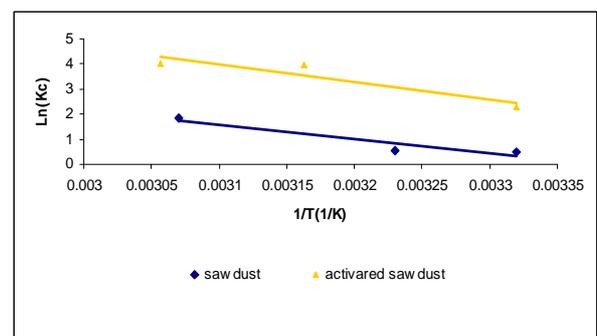


Fig.6. Vant Hoff's plot at ambient temperature.

4.6. Effect of Particle Size

The effect of particle size on Cr(VI) sorption capacity of sawdust and activated sawdust of aspen has been shown in Fig.7. The eradication of Cr(VI) ions at different particle sizes indicated that the capacity of chromium adsorption at the equilibrium increased with the decrease in particle sizes. The relatively higher adsorption with smaller adsorbent particle may be attributed to the fact that smaller particles yield large surface areas and indicate that chromium ion adsorption occurs through a surface mechanism. It was also noticed that there is a tendency for a smaller particle to produce shorter time to equilibration.

4.7. Effect of Agitation Speed

Biosorption studies were carried out with a magnetic shaker at ambient temperature. Cr(VI) solution was 5 ppm. The agitation speed varied from 50 to 700 rpm. The biosorption rate increased because of increasing kinetic energy of Cr(VI) particles (Fig. 8). Basically, the removal of Cr(VI) is rapid but it gradually decreases with the increase of agitation speed, and the percent removal of Cr(VI) of solutions were not changed after 300 rpm; therefore, Cr(VI) adsorption efficiency was maximal at 300 rpm.

4.8. Adsorption Isotherm

Adsorption equilibrium data were fitted to the Langmuir, Freundlich and Temkin isotherms. Langmuir isotherm is based on the monolayer adsorption of chromium ions on the surface of adsorbent sites and is expressed in the linear form[1].

$$\frac{C_e}{x/m} = \frac{1}{KV_m} + \frac{C_e}{V_m} \quad (5)$$

where C_e is the equilibrium solution concentration, x/m the amount adsorbed per unit mass of adsorbent, m the mass of the adsorbent, V_m the monolayer capacity, and K is an equilibrium constant related to the heat of adsorption by equation:

$$K = K_0 \times \exp\left(\frac{q}{RT}\right) \quad (6)$$

where q is the heat of adsorption. Freundlich isotherm describes the heterogeneous surface energies by multilayer adsorption and is expressed in linear form as[1]

$$\text{Log} \frac{x}{m} = \text{Log} K_f + \frac{1}{n} \text{Log} C_e \quad (7)$$

where K_f and $1/n$ are Freundlich constants related to adsorption capacity and intensity of adsorption, and

other parameters are the same as in the Langmuir isotherm. The term $\log(x/m)$ can be plotted against $\log C_e$ with slope $1/n$ and intercept $\log K_f$. Temkin isotherm based on the heat of adsorption of the ions, which is due to the adsorbate and adsorbent interactions taken in linear form, is given by[12]:

$$\frac{x}{m} = \left(\frac{RT}{b}\right) \text{Ln} A + \left(\frac{RT}{b}\right) \text{Ln} C_e \quad (8)$$

$$\frac{RT}{b} = B$$

where A (l/g) and B are Temkin constants.

The data obtained from the adsorption experiments conducted at $25(\pm 2)^\circ\text{C}$ were fitted to Eqs. (5), (7) and (8), linear plot (not shown) were obtained for $C_e/(x/m)$ versus C_e , $\text{Log}(x/m)$ versus $\text{Log}(C_e)$ and x/m versus $\text{Ln} C_e$. The theoretical parameters of isotherms together with regression coefficient are shown in Table 1. The isotherms are compared based on the parameter values with experimental data at 298K as shown in Fig. 9 and Fig. 10. The results indicate that the data better fit to Freundlich equation than Langmuir and Temkin equations. The adsorption capacity of Cr(VI) onto sawdust of aspen tree was compared with other adsorbents mentioned in literature and is listed in Table 2. It can be noticed that a pH of 2.0 was realized to be an optimum in almost all cases whatever be the method of activation.

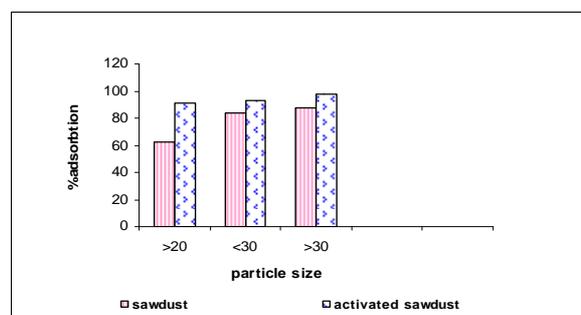


Fig.7. Effect of particle size on Cr (VI) adsorption.

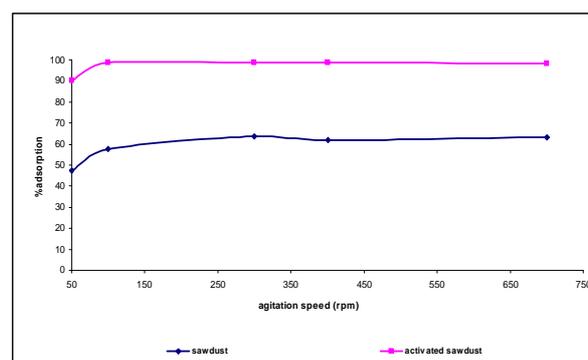


Fig.8. Effect of agitation speed on Cr (VI) adsorption.

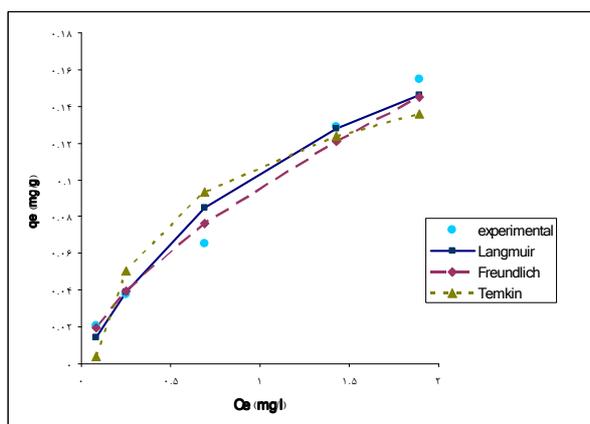


Fig.9. Equilibrium isotherms of Cr (VI) on to sawdust.

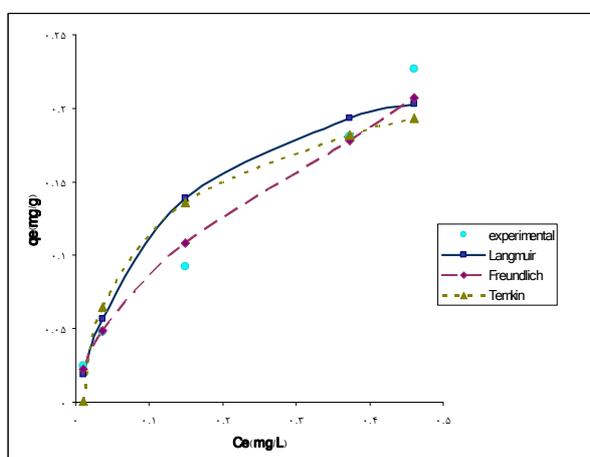


Fig.10. Equilibrium isotherms of Cr (VI) on to activated sawdust.

Table 1. Adsorption isotherm.

Adsorbent name	Langmuir constants		
	V_m (mg/g)	K (l/mg)	R^2
Sawdust	0.2476	0.7535	0.8007
Activated sawdust	0.2615	7.6158	0.7890
	Freundlich constants		
	$1/n$	K_f (mg/g)	R^2
	0.6398	0.0965	0.9860
	0.5737	0.3237	0.9894
	Temkin constants		
B	A (l/gr)	R^2	
0.0419	13.515	0.8783	
0.0506	98.970	0.8712	

Table 2. Comparison of adsorption capacities of Cr(VI) with other adsorbents.

Adsorbents	Adsorption Capacity (mg/g)	pH	C_0 (mg/l)	Reference
Leather	459.00	2.0	1000	[16]
Tyres activated carbon	58.50	2.0	60	[19]
F400	48.54	2.0	60	[19]
Leaf mould	43.10	2.0	1000	[6]
Coconut shell carbon	20.00	2.0	-	[9]
HSAC	17.70	2.0	30	[8]
Sugarcane bagasse	13.40	2.0	500	[5]
RAC	44.05	2.0	200	
sawdust of aspen tree	0.093	2.0	5	Present study
activated sawdust of aspen tree	0.078	2.0	5	Present study

5. Conclusion

- The present study showed that lignocellulosic solid wastes such as sawdust can be used as effective adsorbents for removal of Cr(VI) from wastewater. These natural wastes are available in large quantity and can be used as an alternative to existing commercial adsorbents for removal of Cr(VI).
- The adsorption process is a function of the contact time, initial concentration, pH, temperature, agitation speed, adsorbent dose and particle size.
- The level of Cr(VI) adsorbed increased with increase in amount of both adsorbents and their contact time. Adsorption of Cr(VI) is found to be effective in the lower pH and found to be maximum at pH 2.0. Increase in adsorption capacity with increase in temperature reveals that the adsorption is chemical in nature and the process is endothermic, which is approved by the thermodynamical parameters evaluated. Removal of Cr(VI) rised with increasing adsorbent amount.

In conclusion, the Freundlich isotherm fits the data better than the Langmuir and Temkin isotherms.

Notation

- ΔG° : standard Gibbs energy of adsorption (kJ/mol)
- T : temperature ($^\circ\text{K}$)
- K_c : equilibrium constant
- CA_e : amount adsorbed on solid at equilibrium (mg/l)
- C_e : equilibrium concentration (mg/l)
- ΔH° : standard enthalpy of adsorption (kJ/mol)
- ΔS° : standard entropy of adsorption (J/mol k)
- x/m : amount adsorbed per unit mass of adsorbent
- m : mass of the adsorbent (gr)
- V_m : monolayer capacity (mg/g)
- K : equilibrium constant (l/mg)
- q : heat of adsorption
- K_f : Freundlich constant (mg/g)
- $1/n$: Freundlich constant
- A : Temkin constant (l/g)
- B : Temkin constant

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