Application of nut shells for chromium removal from wastewater

M.T. Hamed Mosavian[1*], I. Khazaei[2], M. Aliabadi[3], J. Sargolzaei[1]

[1]*Department of Chemical Engineering, Ferdowsi University of Mashhad, Mashhad, Iran*
(Email: mosavian@um.ac.ir; Email: sargolzaei@um.ac.ir)
[2]*Islamic Azad University, Ghouchan Branch, Ghouchan, Iran*
(Email: Imane_khazaei@yahoo.com)
[3]*Islamic Azad Univerisity, Birjand Branch, Birjand, Iran (Email:majid.aliabadi@gmail.com)*

Abstract Adsorption capacity of Cr (VI) onto activated carbon, almond and apricot shells was investigated in a batch system by considering the effects of various parameters like contact time, initial concentration, pH, temperature, agitation speed, absorbent dose and particle size. Cr (VI) removal is pH dependent and found 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. A contact time of 30 min was found to be optimum. Experimental results show low cost biosorbent were 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, Low-Cost Biological Wastes, Adsorption, Biosorbent, Agricultural Solid Wastes

Introduction

Due to the toxicological importance in the ecosystem, agriculture and human health, pollution by heavy metals has received wide spread attention in the recent years. The main sources of chromium pollution are mining, leather tanning and cement industries, use in dyes, electroplating, production of steel and other metal alloys, photographic material and corrosive paints [1]. Once chromium is introduced in to the environment it exists in two stable oxidation states, Cr(III) and Cr(VI). The trivalent form is relatively innocuous, but hexavalent chromium is toxic, carcinogenic, and mutagenic in nature, highly mobile in soil and aquatic system and also is a strong oxidant capable of being adsorbed by the skin [2].The permissible limit for hexavalent chromium in industrial wastewaters is 0.1 mg/l. In order to reduce Cr(VI) in these effluents to the standard level, an efficient and low cost method needs to be developed. The various methods of removal of Cr(VI) from industrial wastewater include filtration, chemical precipitation, adsorption, electrodeposition and membrane systems or even ion exchange process.

These techniques use a lot of treatment chemicals and the residual Cr(VI) concentration required in the treated wastewater is not achieved because of the structure of the precipitates. The application of membrane systems for the wastewater treatment has major problems like membrane scaling, fouling and blocking. The drawback of the ion exchange process is the high cost of the resin while the electrodeposition method is more energy intensive than other methods. Among these methods adsorption is one of the most economically favorable and a technically easy method [3].
Natural materials that are available in large quantities, or certain waste products from industrial or agricultural operations, may have potential as inexpensive sorbents. Due to their low cost, after these materials have been expended, they can be disposed of without expensive regeneration. Most of the low cost sorbents have the limitation of low sorptive capacity and thereby for the same degree of treatment, it generates more solid waste (pollutant laden

sorbent after treatment), which poses disposal problems. Therefore, there is need to explore low cost sorbent having high contaminant sorption capacity [4].The other limitations of the technology include that large-scale production of effective biosorbent materials has not been established and that the technology has only been tested for limited practical applications [5].

Several recent publications utilized locally available adsorbents e.g. fly ash, microbial biomass [4], leaf mould , moss peat [6], bark, walnut shell, straw and plant root [7], peanut hull [8], baggage pith [9], tea dust leaves [10], paddy straw [11], coir pith [12], sawdust and pine leaves [13]. This study aims at comparative evaluation of agrobased materials, namely activated carbon, almond and apricot shells, for removal of Cr(VI) from aqueous solution. The effects of various operating parameters were investigated on the synthetic sample of Cr(VI).

Materials
Adsorbents
We could find that using of the natural absorbents compared with industrial absorbents are low cost. Natural(biological) absorbents were too cheap to use in this research. For example almond and apricot shells are biological waste which usually are used as fuel. Thus, only cost for this absorbents is preparing of them such as to powder. Therefore, it is important that using of the natural (biological) absorbents can decrease cost of matter. Samples were dried (sun or mechanical) at the sources of collection dried and then pulverized. Potassium dichromate and other chemicals used were of analytical reagent grade and were obtained from standard sources.

Method
A known weight (e.g. 2.0 g of absorbent) was equilibrated with 100 ml of the chromium solution of known concentration in 250 ml glass flask at room temperature (25^0C) .Chromium solution was prepared by dissolving the potassium dichromate ($K_2Cr_2O_7$) in distilled water. Fresh dilutions were used for each study. The pH of Chromium solution was adjusted with a 0.1M HCL/0.1M NaoH solution. Time of each experimental was kept at 30 min. These flasks then were shaken on the shaker at 400 rpm. The samples were filtered through filter paper. The concentration of the samples was analyzed in a spectrophotometer (JENWAY 6305 UV/Vis model) using 1,5-diphenylcarbazide as the complexing agent at the wavelength of 540 nm [14].

 The Cr(VI) loadings on sorbents were computed 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 and intensity were calculated by the Langmuir, Freundlich and Temkin isotherm.

Results and discussion
Various mechanisms and steps in adsorption phenomena can control the kinetics. Four major rate-limiting steps are generally cited [15]: (1) mass transfer of solute from solution to the boundary film; (2) mass transfer of metal ions from boundary film to surface; (3) sorption of ions onto sites; and (4) internal diffusion of solute. The third step is assumed to be very rapid and non-limiting in this kinetic analysis: sorption is a rapid phenomenon. The first and the second steps are external mass transfer resistance steps, depending on various parameters

such as agitation and homogeneity of solution. The fourth one is an intraparticle diffusion resistance step.

The model used to calculate the external mass transfer rate is described by the following equation:

$$\frac{dC_t}{dt} = -\beta_L S(C_t - C_s) \qquad (1)$$

where β_L is the external mass transfer coefficient, S the specific surface, C_t the metal ion concentration in solution, and C_s the surface concentration of solute on the adsorbent. According to complementary hypotheses such as a surface concentration of solute on the sorbent ($C_s \rightarrow 0$) negligible at time $t = 0$, and the intraparticle diffusion rate also negligible, Eq. (1) can be simplified to:

$$\frac{d(C_t/C_0)}{dt} = -\beta_L S \qquad (2)$$

according to boundary conditions and the hypothesis formulated:
$C_t \rightarrow C_0$
when
$t \rightarrow 0$

So the external mass transfer rate, $-\beta_L S$, is approximated by the initial slope of the C_t/C_0 graph and is obtained by the derivative (at $t = 0$) of the polynomial linerarization of $C_t/C_0 = f$ (t), where C_0 is the initial metal concentration in solution. Theoretical treatments of intraparticle diffusion rates yield rather complex equations differing in form for different shapes of particle. Fick's laws of diffusion through solids are expressed by:

$$J = -D\left(\frac{dC}{dX}\right) \qquad (3)$$

$$\frac{dC}{dt} = D\left(\frac{d^2C}{dX^2}\right) \qquad (4)$$

where J is the rate of transfer per unit area of the section, X the space co-ordinate and D the diffusion coefficient. The sorption rate (q_e) is calculated according to the conversion:

$$q_e = \frac{(C_0 - C_t)V}{m} = \left(\frac{1 - C_t}{C_0}\right)\frac{VC_0}{m} \qquad (5)$$

where q_e (mg/g) is the equilibrium adsorption capacity, C_0 and C_e are the initial and equilibrium concentration (mg/l) of Cr(VI) ions in solution, V(l) is the volume and M (g) is the weight of the adsorbent.

The adsorption kinetics of the experiment is influenced by various factors. The main parameters influencing metal sorption were investigated: initial metal ion concentration, amount of adsorbent, contact time, temperature and pH value of solution.

Effect of contact time
Fig. 1 shows the adsorption of Cr(VI) by activated carbon, almond and apricot shells, 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 necessary time to reach this equilibrium is about 30 min.
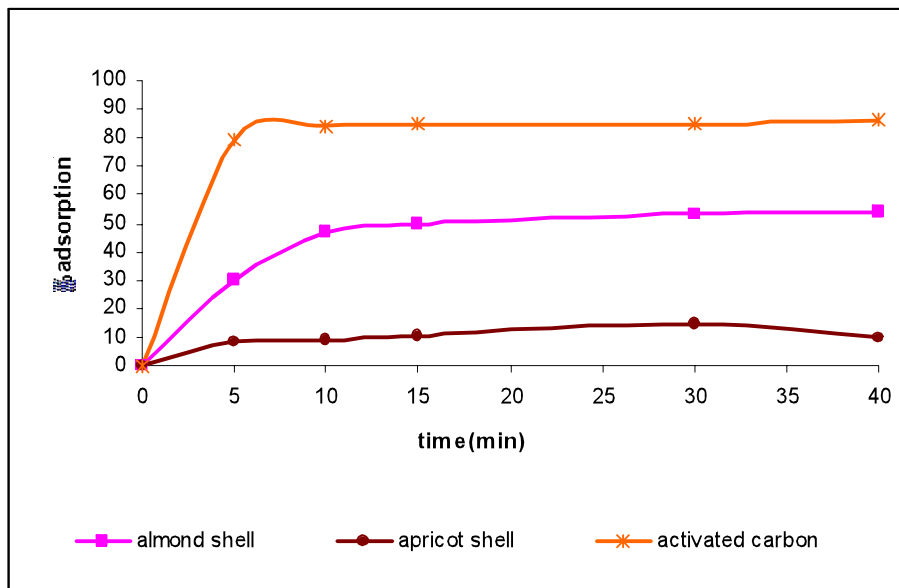
Fig.1. percent removal of Cr(VI)(5ppm)Vs. time

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 time interval 30 min show in Fig. 2. The percentage removal was decreased with increase in Cr(VI) concentration. At low concentrations the ratio of available surface to the initial Cr(VI) concentration is larger, so the removal becomes independent of initial concentrations. However, in the case of 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 .
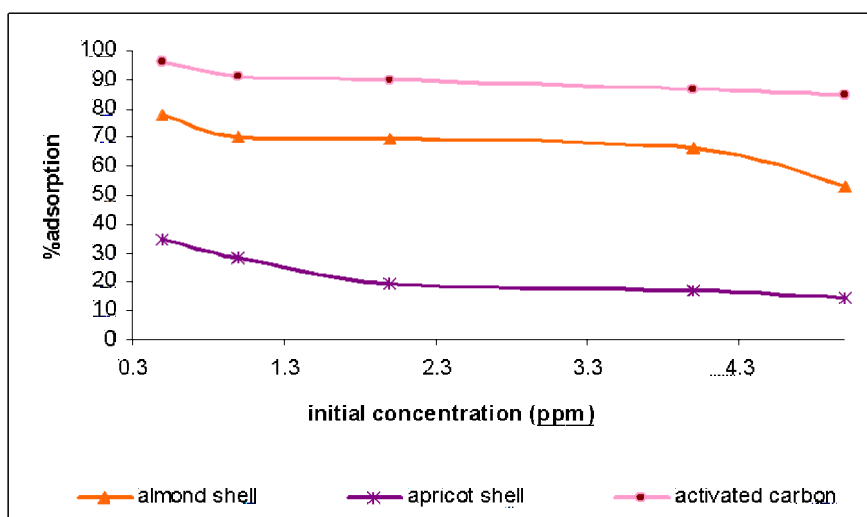

Fig. 2. Effect of initial Cr (VI) concentration

Effect of absorbent 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 30 min. Activated carbon almond and apricot shells percentage removal Cr(VI) increases with the increasing amount of adsorbent.

4

The phenomenon of increase in percent chromium removal with increase in adsorbent dose was due to the availability of more and more adsorbent surfaces for the solutes to adsorb. However very slow increase in removal beyond an optimum dose may be attributed to the attainment of equilibrium between adsorbate and adsorbent at the operating conditions. This effect had been termed as "solid concentration effect" i.e. overcrowding of particles, by Mehrotra et al. [2].
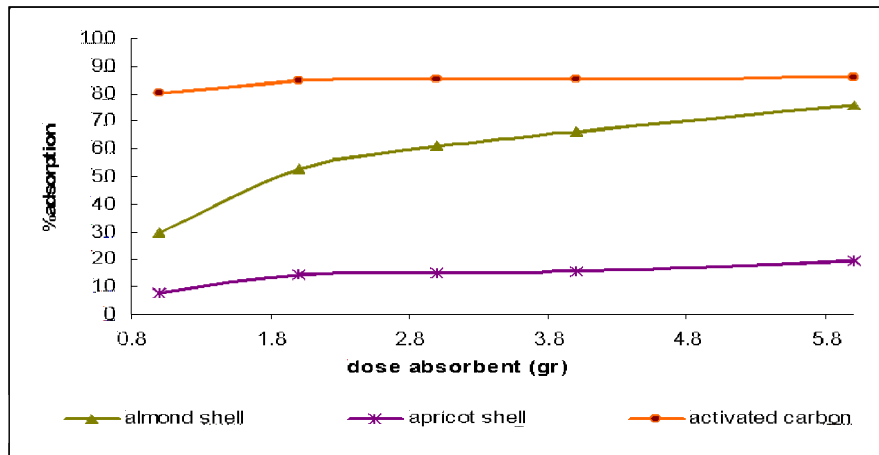

Fig.3. Effect of dose on Cr (VI) adsorption

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). As results show, The optimum initial pH was observed at pH 2.0. The dominant chromium compound within the solution at pH=2 is $HCr\,O_4^-$ ($Cr\,O_4^{-2}$ 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 pH of the solution is 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 HCrO4⁻ ions;

$$\equiv OH_2^{\pm} \pm HCrO_4 \leftrightarrow OH_2^{\pm}(HCrO_4^-) \tag{6}$$
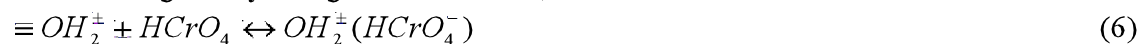
At low pH values active sites are positively charged. Therefore negative metals adsorption increases significantly. When pH value increases, surface of the adsorbent becomes the neutral and a decrease in the adsorption is observed. When adsorbent surface is negatively charged, adsorption decreases significantly. This behavior is specific for the chromium ions and it is different for the divalent metals. Chromium ions release hydroxide ions to the solution instead of proton [16].
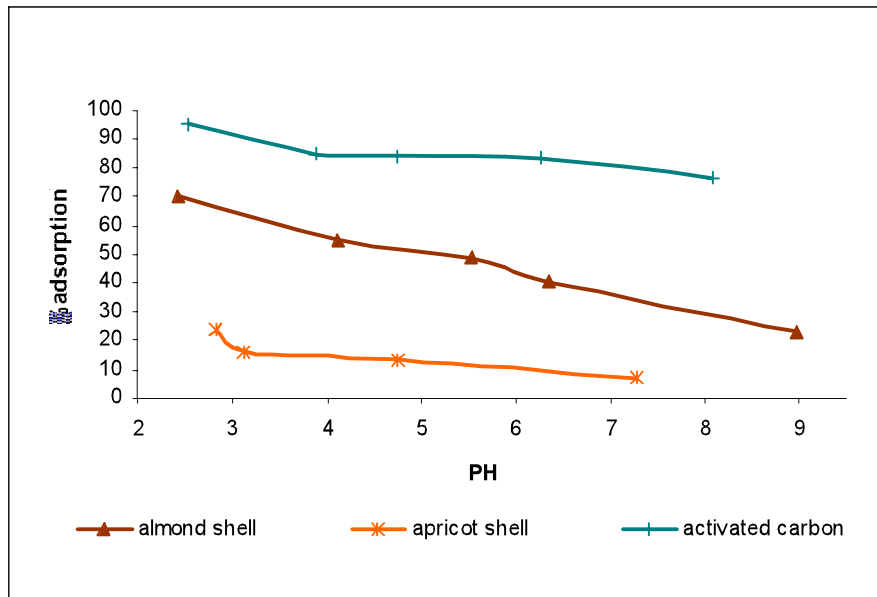
Fig.4. *Effect of PH on Cr (VI) adsorption*

Effect of temperature

Adsorption is considered as an exothermic process; therefore it is expected that the equilibrium concentration increases (i.e amount of adsorbed material decreases) with increasing temperature. But some chemical adsorption processes are endothermic processes; therefore increase in temperature leads to increase both in adsorption rate and amount of adsorbed materials. Since this trend was observed in this study, adsorption of Cr(VI) is possibly a chemical adsorption process. The adsorption of Cr(VI) at different temperatures shows an increase in the adsorption capacity when the temperature is increased (Fig.6). This indicates that the adsorption reaction is endothermic in nature. The enhancement in the adsorption capacity may be due to the chemical interaction between adsorbates and adsorbent, creation of some new adsorption sites or the increased rate of intraparticle diffusion of Cr(VI) ions into the pores of the adsorbent at higher temperatures .

Kinetic energies of chromium ions were low at low temperatures. Therefore it is 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 further increased, the kinetic energies of chromium ions become higher than the potential attractive forces between active sites and ions .

The standard Gibb's energy was evaluated by
$$\Delta G^0 = -RT \ln K_C$$
The equilibrium constants Kc was evaluated at each temperature using the following relationship

$$K_C = \frac{C_{Ae}}{C_e} \tag{7}$$

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^o) and standard entropy (ΔS^o) were determined using the following equations

$$\ln K_C = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \qquad (8)$$

ΔH^o and ΔS^o were obtained from the slope and intercept of the Van't Hoff's plot of $\ln Kc$ versus $1/T$ as shown in Fig. 5.

Positive value of ΔH^o indicates that the adsorption process is endothermic. The negative values of ΔG^o 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.
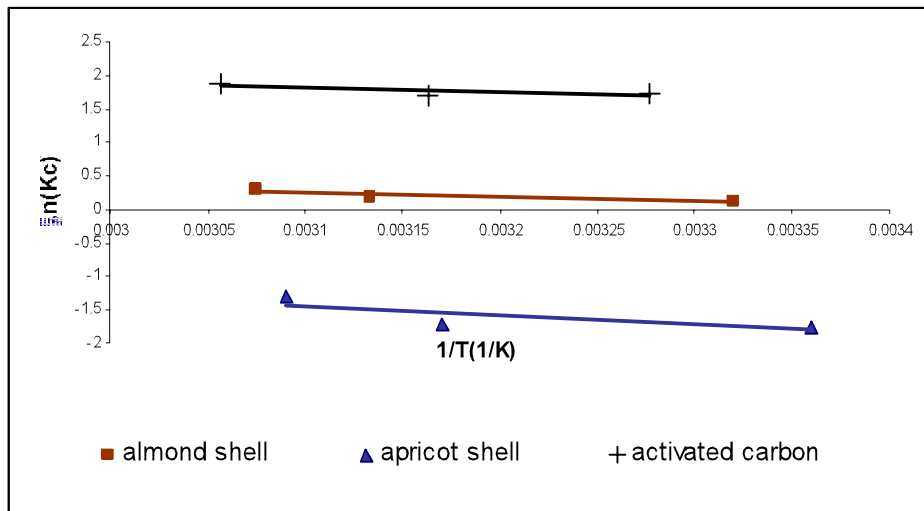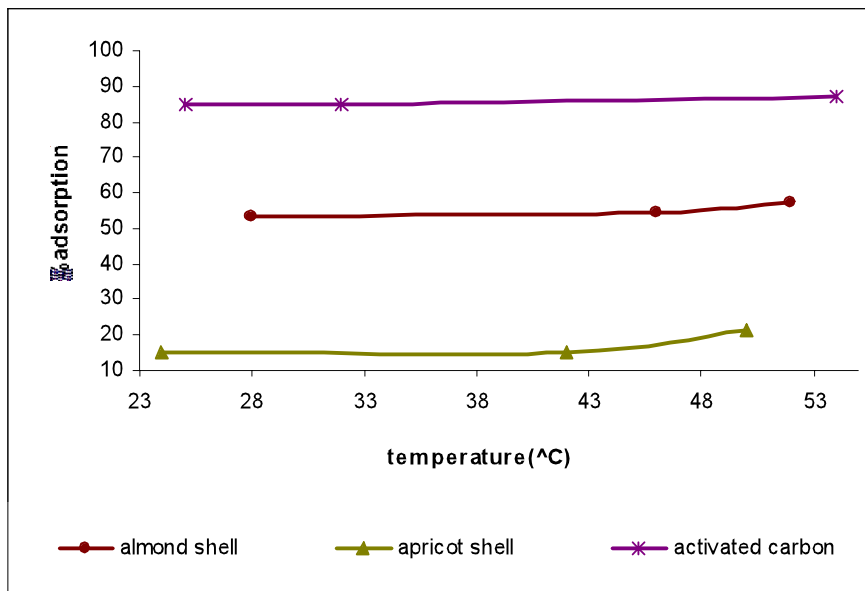

Fig.5. Vant Hoff' s plot at ambient temperature

Fig.6. *Effect of temperature on Cr (VI) adsorption*

Effect of particle size

Effect of particle size on Cr(VI) sorption capacity of activated carbon, almond and apricot shells in Fig.7. It is evident from the Fig.7. that particle size of sorbents has a significant effect on Cr(VI) sorption. The larger sorbent size showed lesser Cr(VI) removal as compared

to the smaller sorbent size. The reason may be that surface area available for adsorption decreases with the increase of particle size for the same dose of sorbent, providing less active surface sites for adsorption of sorbate. The reduction in Cr(VI) removal capacity with increase in sorbent size gives an idea about the porosity of sorbent i.e., if the sorbent is highly porous then it would not have significant effect on Cr(VI) removal at equilibrium.
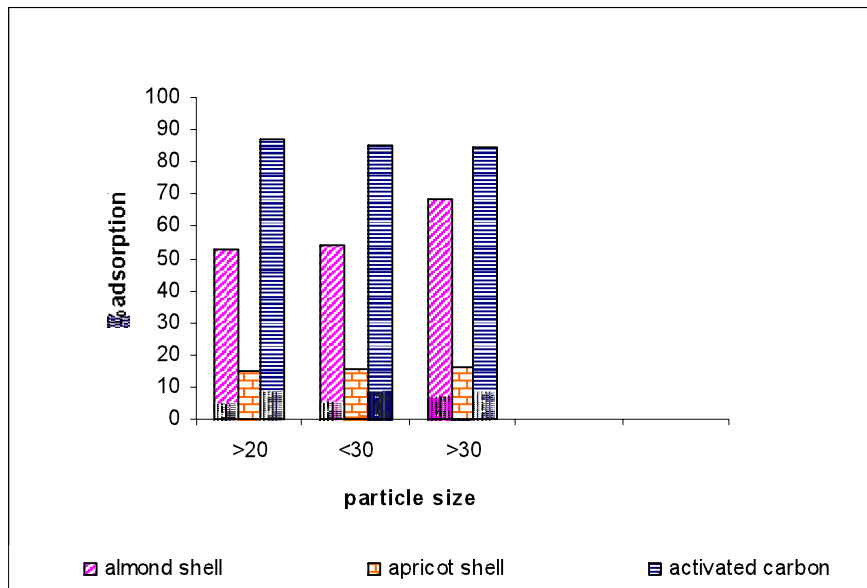

Fig.7. Effect of particle size on Cr (VI) adsorption

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 increase agitation speed and perecent removal of Cr(VI) of solutions were not change after 400 rpm therefore Cr(VI) adsorption efficiency was maximal at 400 rpm.
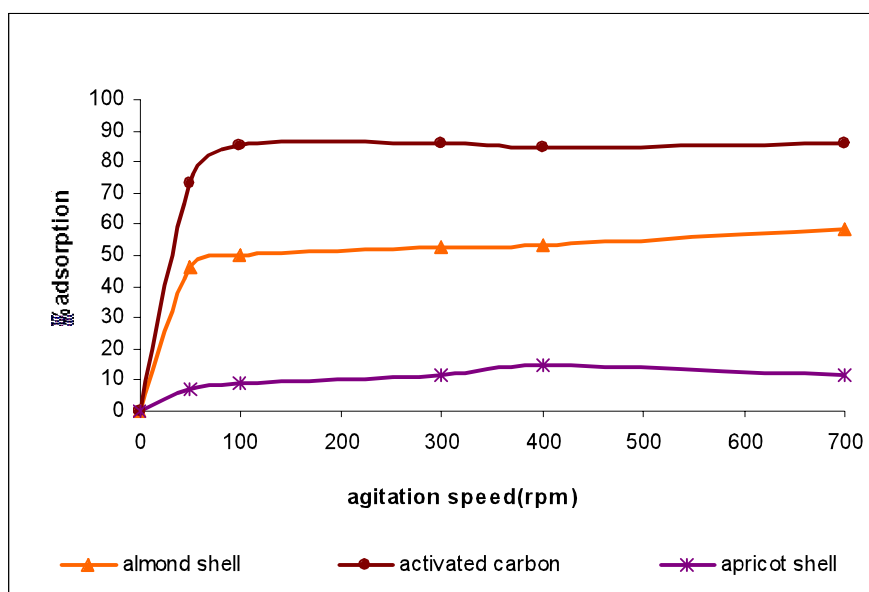
Fig.8. Effect of agitation speed on Cr (VI) adsorption

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 absorbent sites and is expressed in the linear form as [13]

$$\frac{Ce}{x/m} = \frac{1}{KV_m} \pm \frac{Ce}{V_m} \qquad (9)$$

where Ce 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:

$$K = K_0 = \exp(\frac{q}{RT}) \qquad (10)$$

where q is the heat of adsorption.

Freundlich isotherm describes the heterogeneous surface energies by multilayer adsorption and is expressed in linear form as [13]

$$Log\frac{x}{m} = LogK_f \pm \frac{1}{n}LogCe$$

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 $\log Ce$ 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 [3]

$$\frac{x}{m} = (\frac{RT}{b})LnA \pm (\frac{RT}{b})LnCe$$

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

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

The theoretical parameters of isotherms along with regression coefficient are listed in Table 1.

Table 1: Adsorption isotherm

Adsorbent name	Langmuir constants		
	V_m (mg/g)	K (1/mg)	R^2
Apricot shell	0.05357	0.4845	0.9336
Almond shell	0.20988	0.84567	0.9238
Activated carbon	0.3101	2.4700	0.8856
Freundlich constants			
	1/n	K_f (mg/g)	R^2
Apricot shell	0.5579	0.01644	0.9898
Almond shell	0.6798	0.0889	0.9692
Activated carbon	0.6109	0.2400	0.9875
Temkin constants			
	B	A(1/gr)	R^2
Apricot shell	0.0111	5.488	0.9406
Almond shell	0.042	11.129	0.9274
Activated carbon	0.0515	48.594	0.885

Conclusion

The biosorbents evaluated can remove hexavalent chromium from aqueous phase. The adsorption process is a function of the contact time, initial concentration, pH , temperature, agitation speed, absorbent dose and particle size.

The amounts of Cr(VI) adsorbed increased with increase in dose of both adsorbents and their contact time. A contact time of 30 min was found to be optimum. 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 rise in temperature reveals that the adsorption is chemical in nature and the process is endothermic, which is confirmed by the thermodynamical parameters evaluated. Removal of Cr(VI) increased with increasing adsorbent dose.

The Freundlich isotherm fits the data better than the Langmuir and Temkin isotherms. Since all agricultural solid wastes used in this investigation are freely, abundantly and locally available, the resulting biological wastes are expected to be economically viable for wastewater treatment.

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