



Removal of chromium (VI) from aqueous solution by adsorption using *Cousinia eryngioides* Boiss and activated carbon

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Abstract

Adsorption capacity of Cr (VI) onto *Cousinia eryngioides* Boiss, activated carbon 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 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: Removal of chromium, Adsorption isotherm, Low cost absorbent, Waste water, Chromium

1. Introduction

The pollution by heavy metals has received widespread attention in the recent years (Bishnoi, et al., 2004), due to the toxicological importance in the ecosystem, agriculture and human health (Malkoc, et al., 2006). 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 (Acar and Malkoc, 2004). Chromium exists in either +3 or +6 oxidation states, as all other oxidation states are not stable in aqueous systems. Chromium (VI) is 100-1000 times more toxic to organisms than Cr (III) and more readily transported in soils (Low, et al., 1999). Strong exposure of Cr (VI) causes cancer in the digestive tract and lungs and may cause epigastric pain, nausea, vomiting, severe diarrhea, and hemorrhage. It is therefore, essential to remove Cr (VI) from wastewater before disposal (Mohanty, et al., 2005). The allowable limit of hexavalent chromium for the discharge to surface water is 0.1 mg/L (Aliabadi, et al., 2006). A wide list of methods is available for the removal of chromium from wastewaters.

Some of the well-established methods are chemical coagulation, ion exchange, reverse osmosis, electro-dialysis, solvent extraction, electroflotation and adsorption (Verma, et al., 2006).

However, these high-technology processes have significant disadvantages, including incomplete metal removal, requirements for expensive equipment and monitoring systems, high reagent or energy requirements or generation of toxic sludge or other waste products that require disposal (Malkoc, et al., 2006).

Natural materials that are available in large quantities, or certain waste products from industrial or agricultural operations, may have potential as inexpensive sorbents. Therefore, there is need to explore low cost sorbent having high contaminant sorption capacity.

Consequently, numerous low cost alternatives have been studied including Beech sawdust (Bishnoi, et al., 2004), eucalyptus bark (Sarin and Pant, 2006), green algae (*Ulothrix zonata*) (Malkoc and Nuhoglu, 2003), seaweeds (Vijayaraghavan, et al., 2005), coirpith (Kadirvelu, et al., 2001), peanut husks carbon (Ricordel, et al., 2001), zeolite tuff (Al-Haj and El-Bishtawi, 1997), activated carbon derived from agricultural waste material and activated carbon fabric cloth (Mohan, et al., 2005), bagasse fly ash (Gupta, et al., 1999), activated slag (Srivastava, et al., 1997), etc.

In this study, *Cousinia eryngioides* Boiss and activated carbon as adsorbent for Cr (VI) was used to determine adsorption efficiency as a function of contact time, initial concentration, adsorbent dose, particle size, pH, temperature, agitation speed and constants of the adsorption isotherm.

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2. Materials

Cousinia eryngioides boiss were collected from fields in around Birjand, Iran. Activated carbon, Potassium dichromate and other chemicals used were of analytical reagent grade and were obtained from standard sources.

3. 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°C). 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 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 wave length of 540 nm (Arthur and vogel, 1998).

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.

4. Results and discussion

Various mechanisms and steps in adsorption phenomena can control the kinetics. Four major rate-limiting steps are generally cited (Jia-Yu, et al., 2003): (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:

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

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:

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

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 linearization 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:

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

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

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:

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

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

4.1. Effect of contact time

Figure 1 shows the adsorption of Cr(VI) by *Cousinia eryngioides* Boiss and activated carbon as a function of time. Initial Cr(VI) concentration 5 mg/l and adsorbent dose of 2 g/100ml were used. Fig. 1 shows rapid adsorption in the initial 15 min for all biosorbent. Basically, the removal of Cr(VI) is rapid but it gradually decreases with time until it reaches equilibrium. The necessary time to reach this equilibrium is about 15 min. Further increase in contact time did not show 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 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. For example in changing the initial concentration from 0.5 to 5 mg/l, the percentage removal decreased from 68.52 to 29.05 percentage for *Cousinia eryngioides* Boiss adsorbent and for a time period of 30 min. The results indicate that within a certain range of initial metal concentration, the percentage of metal adsorption on adsorbent is determined by the sorption capacity of the adsorbent.

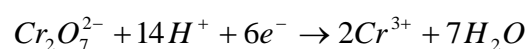
4.3. Effect of adsorbent dose

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. Experimental results showed that the percentage removal Cr (VI) increases with the increasing amount of adsorbent up to 3 g for activated carbon. After this dose of adsorbent no significant change was observed but for *Cousinia eryngioides* Boiss percentage removal Cr (VI) increases with the increasing amount of adsorbent (Fig. 3).

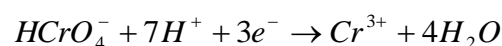
The phenomenon of increase in percent chromium removal with increase in adsorbent dose was due to the availability of more and more adsorbent surfaces for the solutes to adsorb. Never the less, very slow increase in removal beyond an optimum dose may be attributed to the attainment of equilibrium between adsorbate and adsorbent at the operating conditions. This effect had been termed as "solid concentration effect", i.e. overcrowding of particles, (Bishnoi, et al., 2004).

4.4. Effect of PH

It was observed that the adsorption capacity of the prepared adsorbent was highly dependent on the pH of the solution. As results show, the optimum initial pH was observed at pH 2.0. Fig.4 shows the effect of pH of the solution on adsorption capacity. The results indicate that the adsorption capacity of the prepared adsorbent increases with decreasing the pH of the solution. The improved removal of Cr at low pH is probably due to reduction of hexavalent Cr to trivalent Cr. At low pH:



At moderate pH:



At low pH, there is presence of a large number of H^+ ions, which in turn neutralizes the negatively charged adsorbent surface thereby reducing hindrance to diffusion of dichromate ion. It is anticipated that the effect of pH on adsorption is also governed by the development of an electrical double layer on the adsorbent. The polarity of the double layer at the adsorbent surface may be changed from positive to negative as the H^+ -ion concentration changes from acidic to basic with the increase of pH. It was found that at lower pH the system attained equilibrium faster and the percentage of chromium adsorbed increased.

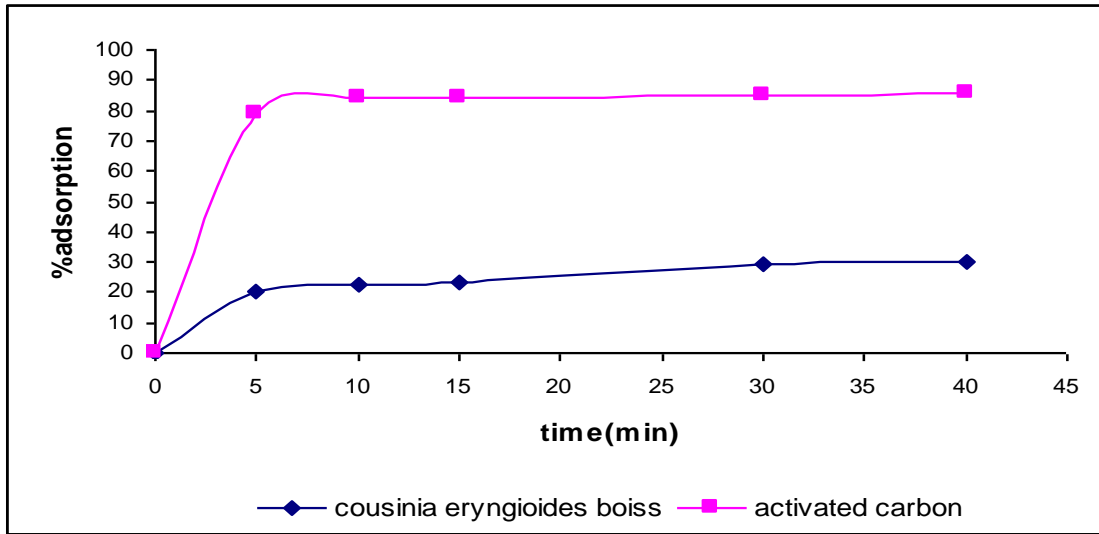


Fig. 1. Percent removal of Cr (VI) (5ppm) Vs. time

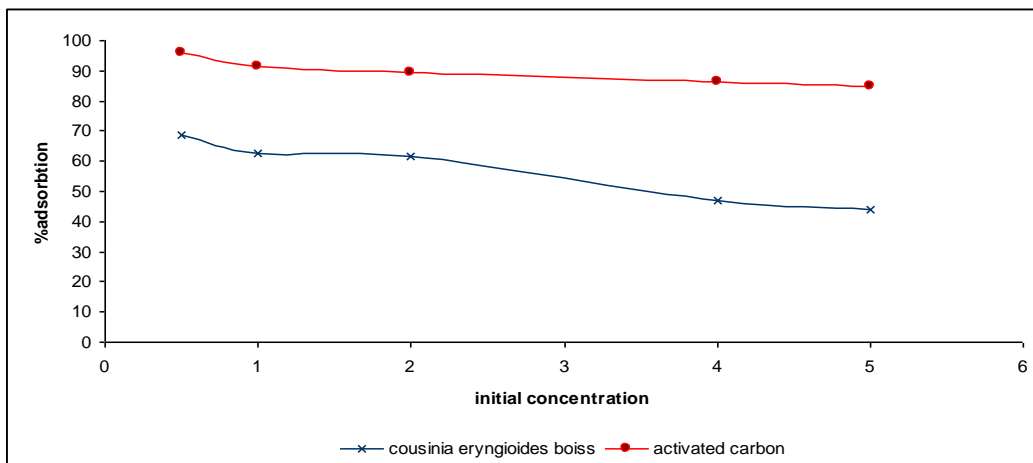


Fig. 2. Effect of initial Cr (VI) concentration

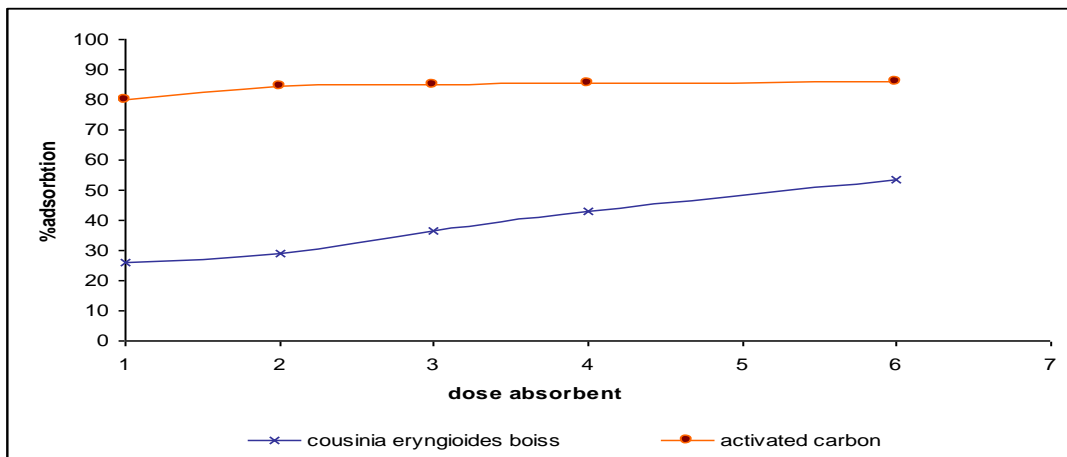


Fig. 3. Effect of dose on Cr (VI) adsorption

4.5. Effect of temperature

Adsorption is considered as an exothermic process; therefore, it is expected that the equilibrium concentration will increase (i.e., amount of adsorbed material decreases) with increasing temperature. But some chemical adsorption processes are endothermic processes; thus, 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 adsorbents 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 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 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

$$\Delta G^0 = -RT \ln K_c \quad (8)$$

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

$$K_c = \frac{C_{Ae}}{C_e} \quad (9)$$

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 equations:

$$\ln K_c = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (10)$$

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 figure 5.

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.

4.6. Effect of particle size

The mass transfer is found to be dependent on particle size. The results of these experiments are given in figure 7. The percentage removal curves indicate that the mass transfer rate and the extent of adsorption are higher in case of the smaller particle than that of bigger size of particles. The larger particles contribute more diffusional resistance to mass transfer than the smaller one. Since adsorption is a surface phenomenon, the particles with higher surface area have greater adsorption capacity in comparison with the particles with lower surface area. Moreover, greater diffusional resistances with the larger particles reduce the rate of mass transfer.

4.7. Effect of agitation speed

The rate of mass transfer from the solution to the solid surface depends to some extent on the degree of mixing. The result of this experiment is shown in Fig. 8. The chromium removal curve presented in the figure indicates that at lower degree of agitation the effect of mass transfer is pronounced. But the effect becomes insignificant at the higher degree of agitation. At higher degree of agitation, the effect of mass transfer is present at the beginning of the process while it becomes nullified with passage of time.

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 as (Aliabadi, et al., 2006):

$$\frac{C_e}{x/m} = \frac{1}{KV_m} + \frac{C_e}{V_m} \quad (11)$$

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:

$$K = K_0 = \exp\left(\frac{q}{RT}\right) \quad (12)$$

where q is the heat of adsorption.

Freundlich isotherm describes the heterogeneous surface energies by multilayer adsorption and is expressed in linear form as (Aliabadi, Morshedzadeh and Soheyli 2006):

$$\text{Log} \frac{x}{m} = \text{Log} K_f + \frac{1}{n} \text{Log} C_e$$

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 $\text{log}(x/m)$ can be plotted against $\text{log} C_e$ with slope $1/n$ and intercept $\text{log} K_f$.

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 (Karthikeyan, Rajgopal and Miranda 2005):

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

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

Where A (l/g) and B are Temkin constants. The theoretical parameters of isotherms along with regression coefficient are listed in Table 1.

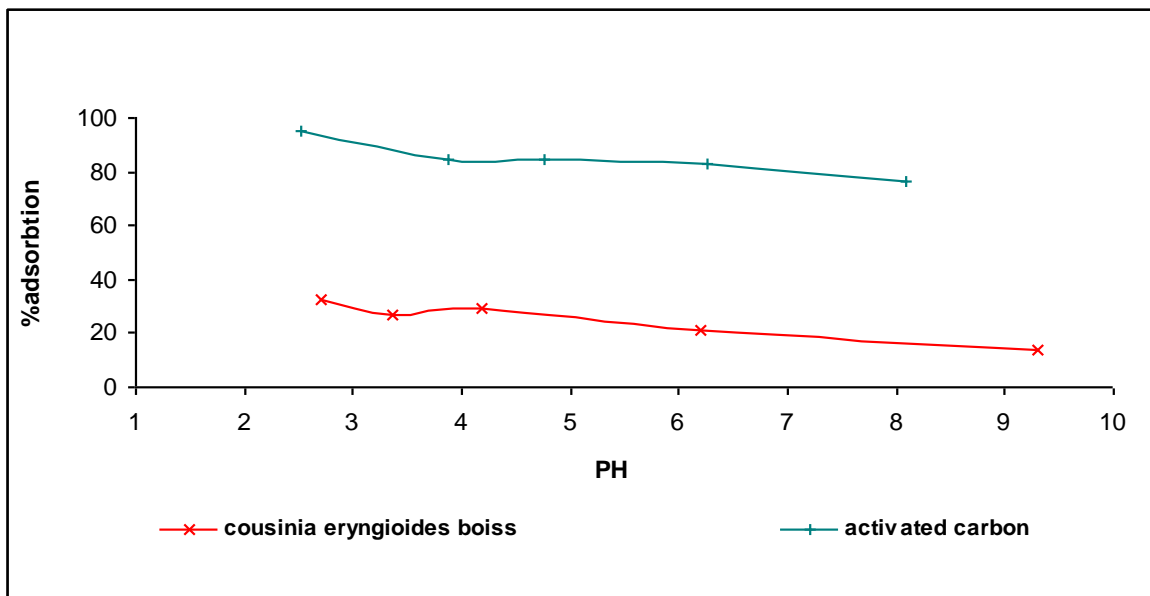


Fig. 4. Effect of PH on Cr (VI) adsorption

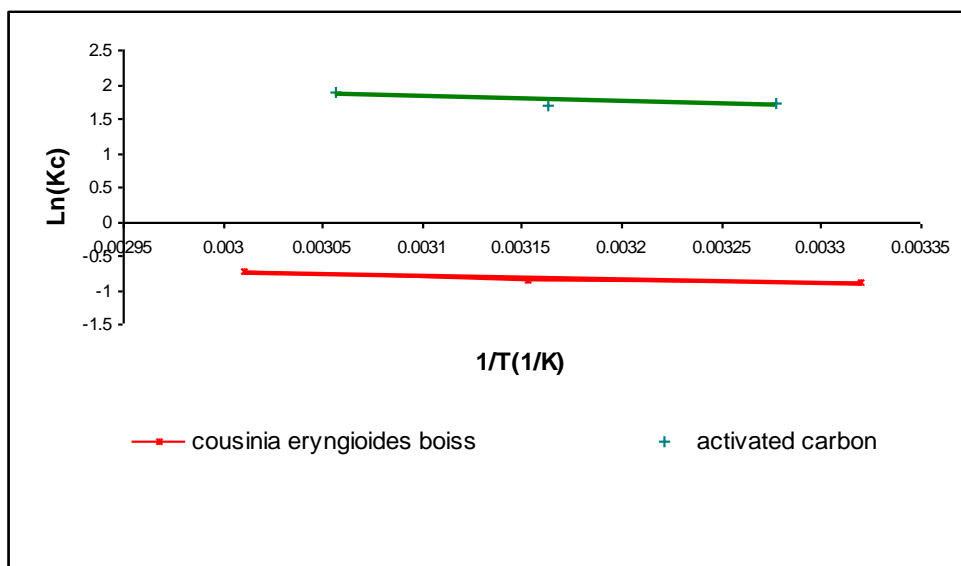


Fig. 5. Vant Hoff's plot at ambient temperature

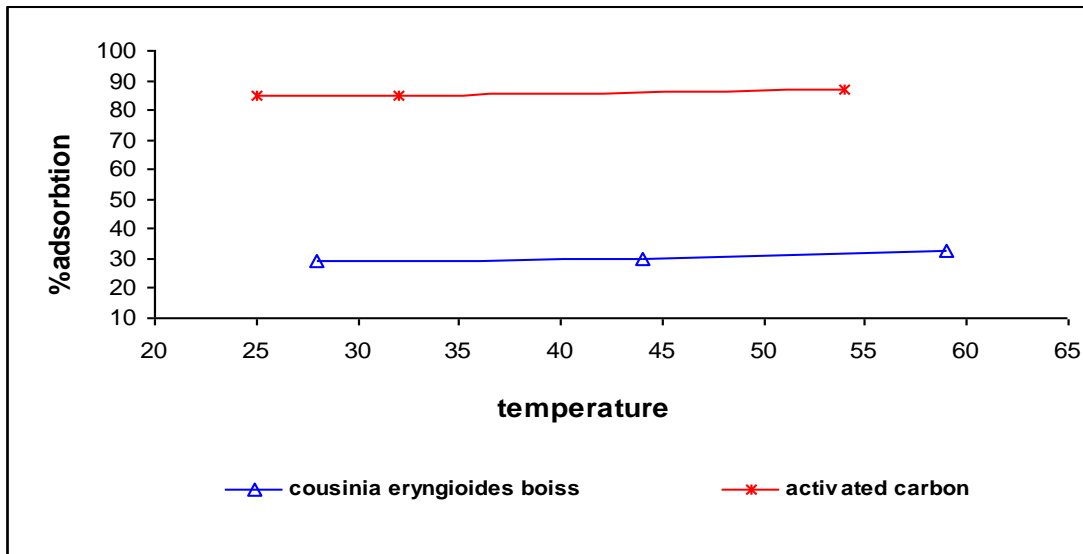


Fig. 6. Effect of temperature on Cr (VI) adsorption

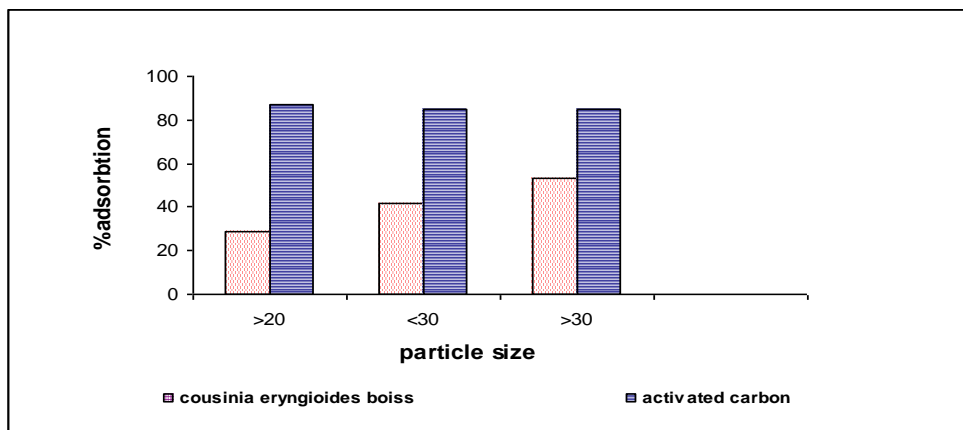


Fig. 7. Effect of particle size on Cr (VI) adsorption

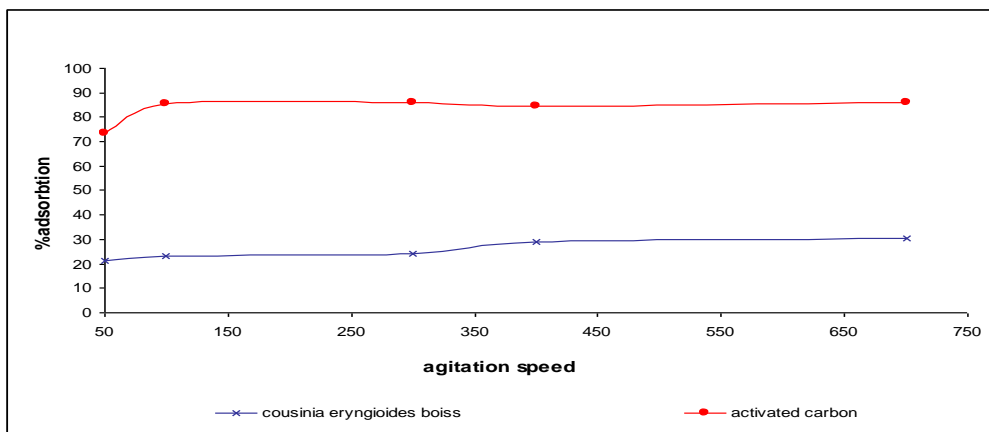


Fig. 8. Effect of agitation speed on Cr (VI) adsorption

5. Conclusions

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, adsorbent 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 *Cousinia eryngioides* boiss used in this investigation are freely, abundantly and locally available, the resulting biological wastes are expected to be economically viable for wastewater treatment.

Table1. Adsorption isotherm

Adsorbent name	Langmuir constants		
	V_m (mg/g)	K (l/mg)	R^2
<i>Cousinia eryngioides</i> boiss	0.0900	2.003	0.9362
Activated carbon	0.3101	2.4700	0.8856
Adsorbent name	Freundlich constants		
	$1/n$	K_f (mg/g)	R^2
<i>Cousinia eryngioides</i> boiss	0.5101	0.0522	0.8649
Activated carbon	0.6109	0.2400	0.9875
Adsorbent name	Temkin constants		
	B	A (l/gr)	R^2
<i>Cousinia eryngioides</i> boiss	0.0224	14.629	0.835
Activated carbon	0.0515	48.594	0.885

Since the value of $1/n$ is less than 1 at Freundlich isotherm, it indicates a favourable adsorption.

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