

Removal of hexavalent chromium from industrial effluents by natural ion exchanger

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In this study, removal of chromium (VI) from aqueous solution using *Tamarindous indicia* seeds has been investigated. The effects of pH, contact time, exchanger dose, have been studied at ambient temperature ($25^{\circ}\text{C} \pm 2^{\circ}\text{C}$). The equilibrium process has been described by the Langmuir isotherm model with adsorption capacity for chromium (VI). The *Tamarindous indica* seeds are subjected to different modification methods (pulverization, formaldehyde and sulphuric acid treatment) and adsorption capacity of modified *Tamarindous indica* seeds for metal ion is obtained. The maximum exchange level have been attained 99% at pH 6.5 with exchanger dose 3.5 g and contact time 30 min. Method is applied for removal of chromium from industrial effluents.

Keywords: Chromium (VI), Natural ion exchange, Industrial effluents, Isothermal model, *Tamarindous indica*

Rapid industrialization affects the rise up in disposal of heavy metals in environment. The exceeding increase in the use of heavy metals leads to environmental as well as public health problems¹. Toxic heavy metal ions discharge in waste water through various industrial activities as mining, refining of ores, fertilizer industries, tanneries, batteries, paper industries, pesticides, nuclear power plant and textile industries².

The electroplating and metal finishing plants discharge waste water contains hexavalent and trivalent chromium. Hexavalent chromium requires high cost chemicals for reduction, so was usually treated with ion exchange resin which offers greater advantages³. Trivalent chromium is essential in human nutrition (glucose metabolism). Most of the hexavalent compounds are toxic cause's lungs cancer. Chromium (VI) moves readily through the soil and aquatic environment which was strong oxidizing agent, being absorbed through the skin. The maximum concentration limits for chromium (VI), discharge in to ground water is 0.1 mg L^{-1} and in potable water is 0.05 mg L^{-1} (Ref 4). A number of technologies have been developed over the years to remove heavy metals from industrial waste water. The most important technology includes adsorption and

coagulation⁵, ion exchange⁶, electro coagulation⁷, adsorption⁸, bio sorption⁹ and zeolite¹⁰. Ion exchange can be used to remove heavy metals from waste water using an ion exchange resin as synthetic ones derived from Dowex HCR-S (Ref 11), D-151 weak acid resin¹², amberlite 200 (Ref 13). The natural ion exchangers are Attapulgate¹⁴, Kudzu (*Pueraria Lobata Ohwi*)¹⁵, activated carbon¹⁶, coconut husk¹⁷, fly ash¹⁸, coffee husk¹⁹, fungal biomass²⁰, *Tamarindous indica* seeds²¹, Tendu (*Diospyros melanoxylan*)²², rice husk²³, *Lactobacillus bulgaricus*²⁴.

In the present study, adsorption of chromium (VI) by naturally occurring *Tamarindous indica* seeds powder is examined. The purpose of the study is to examine heavy metal removal by natural ion exchanger. The parameters that influence adsorption viz. pH, ion exchanger dose, temperature, contact time were investigated.

Experimental Section

Seed powder

Tamarindous indica seeds were pulverized after drying in sunlight and open air for one week. Small size pieces of dried seeds were ground and passed through the mesh size 200 unit. This powder was

treated with 39% formaldehyde and 0.1 mol L⁻¹ sulphuric acid at 80°C, for 30 min. After cooling and washing with double distilled water, substrate was allowed to dry for overnight in open air. Dried powder was used for adsorption studies (Scheme 1). The properties of resin were reported in Table 1.

Sorbent

For adsorption study stock solution of chromium (1000 mg L⁻¹) was prepared by dissolving 4.8 g of chromium sulphate [Cr₂ (SO₄)₃.6H₂O] in double distilled water (DDW). The various concentrations were then obtained by diluting the stock solution with double distilled water.

Method for Separation of Chromium

Chromium solution [Cr₂ (SO₄)₃.6H₂O] having concentration 1.0 mg L⁻¹ (25 mL) was transferred to a beaker. pH of this solution was adjusted to 6.5 ± 0.1 and was transferred to a 250 mL conical flask. In this solution 3.5 g natural adsorbent was added with successive shaking for 30 min. Solution was filtered using Whatman filter paper no. 41 and concentration of chromium remain in solution was determined using Shimadzu UV-visible spectrophotometer by standard method²⁵. In this method, 0.6 mL of 7.0 mol L⁻¹ hydrogen peroxide solution, 0.2 mL of 10⁻⁴ mol L⁻¹ potassium cyanide and 5.5 mL of buffer solution (pH 6.5) were transferred in 25 mL standard volumetric flask. This solution was warmed at 60°C in a water

bath for 10 min. The effluent from column was transferred in it after mixing the solution, absorbance were measured at 360 nm. The initial concentration C_o (mg L⁻¹) and equilibrium concentration at various time intervals C_e (mg L⁻¹) were determined and metal uptake q_e (mg L⁻¹) was calculated from the mass balance equation as:

$$q_e = (c_o - c_e) \frac{V}{m} \quad \dots(1)$$

where, C_o and C_e are the initial and equilibrium concentration of chromium solution (mg L⁻¹), v is the solution volume (mL), and m is the adsorbent weight (g). The adsorption capacity was calculated using the equation 2.

$$\text{adsorption capacity} = \frac{(c_o - c_e)}{c_o} \times 100 \quad \dots (2)$$

The sorption equilibrium data for chromium on *Tamarindous indica* seeds powder was analyzed in terms of the Freundlich and Langmuir isotherm models. The Langmuir isotherm equation could be written as:

$$\frac{q_e}{q_m} = \frac{K_L C_e}{1 + K_L C_e} \quad \dots (3)$$

Where

q_e = the equilibrium concentration on adsorbent (mg g⁻¹)

C_e = equilibrium concentration in solution (mg L⁻¹)

q_m = maximum adsorption capacity (mg L⁻¹)

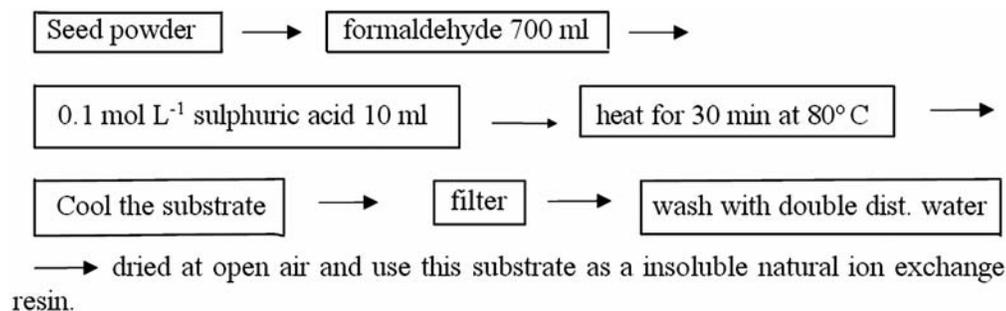
K_L = adsorption equilibrium constant (mg L⁻¹)

This method is based on the assumption that the forces of interaction between adsorbed molecules are negligible and once a molecule occupies a site no further sorption take place.

Also, the logarithmic form of Freundlich equation may be written as:

Table 1—Properties of ion exchange resin

Parameters	Value
Physical form	Spherical
Bulk density	0.15 gm./cm ³
Ash content	10.4%
Moisture content	8.7%
Matter soluble in water	8.4%
Matter soluble in acid	18%
Water holding capacity	80.32%



Scheme 1

$$q_e = K_F C_e^{1/n} \quad \dots(4)$$

where,

q_e = the equilibrium concentration of adsorbent (mg g⁻¹)

C_e = equilibrium concentration in solution (mg L⁻¹)

K_F = adsorption capacity

n = reaction energy

The Freundlich equation can be described by assuming a heterogeneous surface with adsorption on each class of sites. Although this expression is empirical, $1/n$ reflects the curvature in the isotherm and may represent the energy distribution of adsorption sites.

The liberalized form of Freundlich sorption isotherm is:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad \dots(5)$$

By plotting $\ln q_e$ versus $\ln C_e$ K_F and n can be determined, if a straight line is obtained.

To study the effect of important parameters like contact time, resin amount, pH, initial metal concentration and temperature on the removal of Cr (VI) by natural ion exchanger, experiments were conducted at room temperature except those in which the effect of temperature. The parameters chosen in the experiments were reported in Table 2.

Results and Discussion

FTIR Analysis

The FTIR spectra of raw seeds powder, formaldehyde treated resin and Cr (VI) adsorbed resin have been studied. The fact that broad peak in between 3462 and 3281 cm⁻¹ indicates presence of phenolic -OH group in both resin. IR absorption at 2924 cm⁻¹ also indicates presence of =C-H group on the benzene ring. The 1600-1500 cm⁻¹ absorption peak clearly indicates the presence of aromatic double bonds in both resin. The IR bonds in the region of 1149-1066 cm⁻¹ indicate C-O bond in raw resin. One characteristic peak at 1739-1743 cm⁻¹ indicates presence of ester group in both resins. Some peaks in the region of 1670-1612 cm⁻¹ also are of due to olefinic bonds in raw and treated resin. The

IR frequency at 2924 cm⁻¹ is due to stretching vibration of -CH₂- group in alkane. IR absorption at 2022 cm⁻¹ in treated resin also suggest presence of -CH₂- group in between two phenolic rings which is lower frequency than that of raw seeds powder. Hence due to adsorption of Cr (VI) ion color of product change because of d-d transition²⁷.

SEM and EDX Analysis

The morphological analysis of phenol formaldehyde resin was performed by SEM as shown in Figs 1(a)-1(c). Many small pores and particles >5µm diameter are observed on the surface of resin. Pores are does not observed in Fig. 1(c), clearly indicates that biosorption of chromium on phenol formaldehyde resin. EDX spectrum from Fig. 2(c), also showed a peak at 0.5 KeV, which confirmed that Cr (VI) was adsorbed on phenol formaldehyde resin, which was absent in Figs 2(a) and 2(b). It supports

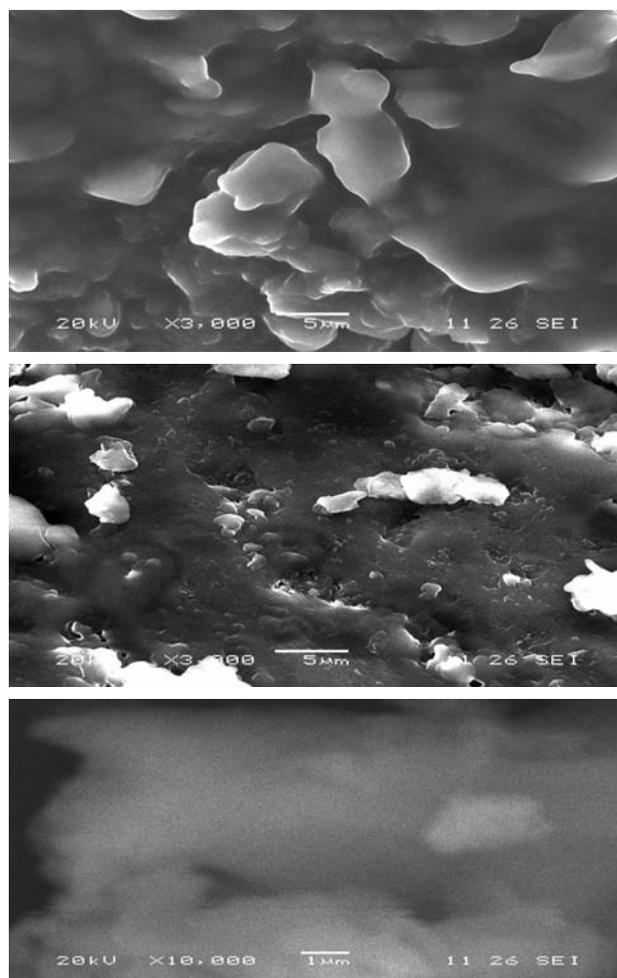


Fig. 1(a-c)—SEM Image of (a) raw seed powder; (b) phenol-formaldehyde resin and (c) phenol-formaldehyde resin after Cr (VI) adsorption

Table 2—Experimental parameter

Parameters	Studied ratio
Initial metal concentration (mg/L)	25, 50, 100, 250 and 500
pH	1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0, 5.5, 6.0 and 6.5
Solution temperature (K)	273, 298, 323 and 348

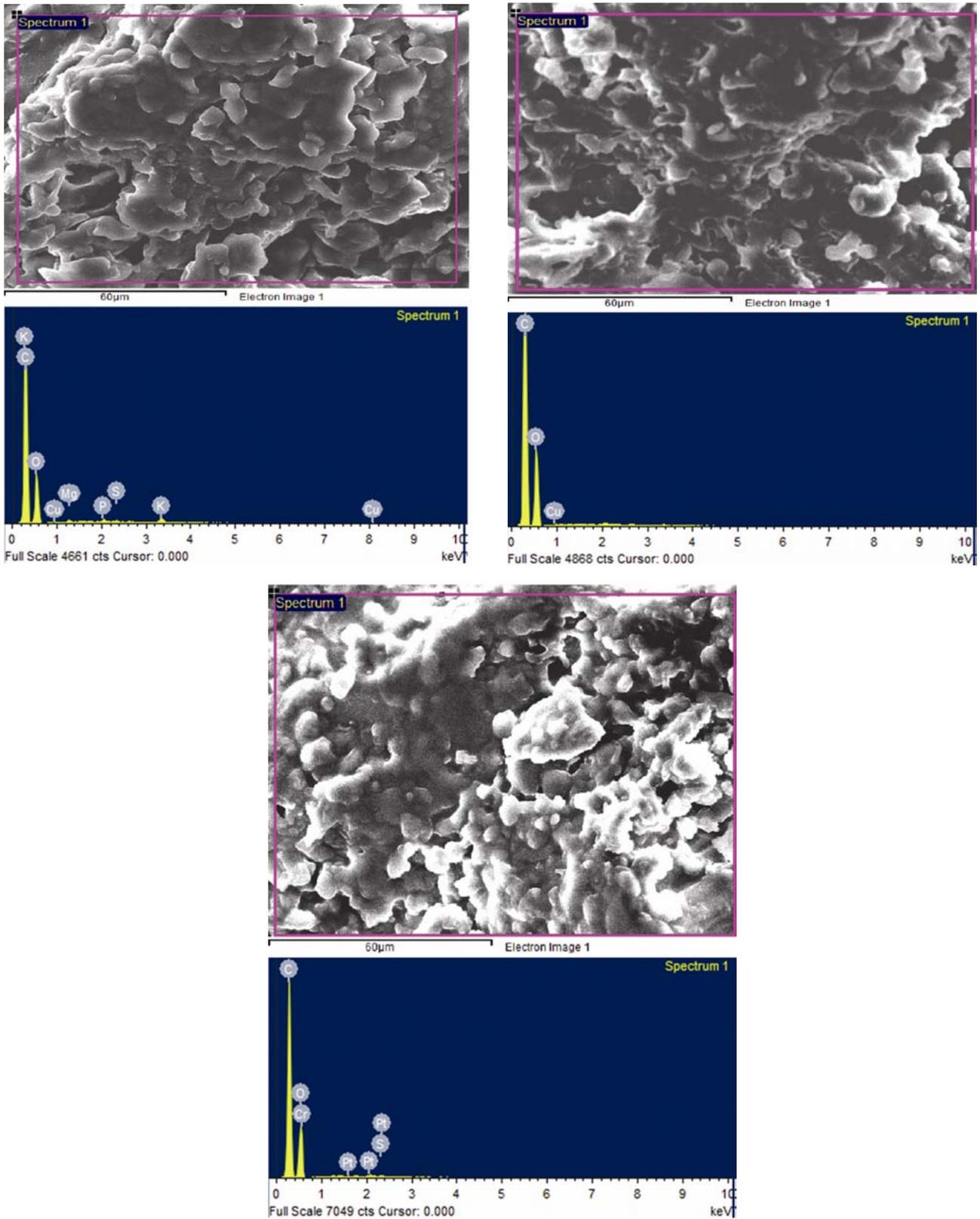


Fig. 2(a-c)—EDX spectrum of (a) raw seed powder; (b) phenol-formaldehyde resin and (c) chromium adsorbed resin

that the reaction of metal ion and phenolic –OH group on phenol formaldehyde resin surface may be partly ion exchange or complexation²⁸.

Effect of pH on ion exchange process

In order to establish the effect of pH on the ion exchange of chromium (VI) ion on natural resin, the batch equilibrium studies at different pH values were carried out in the range of 1.0-7.0 for a constant ion exchanger of 3.5 g L⁻¹ and initial metal concentration of 25 mg/L at 298 K. The high values of pH were not studied because of precipitation of metal ion take place. Figure 3 shows the change in metal up take by natural ion exchange resin at different pH levels. It can be seen from Fig. 3, the pH of the aqueous solution is important control parameter in the ion exchange process²⁹. The percentage removal of metal increased with pH 1.0-7.0 with maximum binding at pH 6.5. At this pH 99% removal of chromium was observed.

Effect of initial metal concentration on ion exchange process

The chromium (VI) metal solution (25 mL) of different concentrations ranging from 25 to 250 mg L⁻¹ with 3.5 g of ion exchanger was stirred with ambient temperature (298 K) for a contact period of 30 min. The result obtained is shown in Fig. 4. It was also realized that the capacity of metal removed by natural ion exchanger at the equilibrium increased with the initial concentration of metal but the percent removal decreased with the increase in initial metal concentration. Apparently, the initial heavy metal ion concentration played an important role in affecting the capacity of metal exchange on natural resin. The higher the heavy metal concentration, stronger the driving forces of the concentration gradient and therefore the higher the adsorption capacity³⁰.

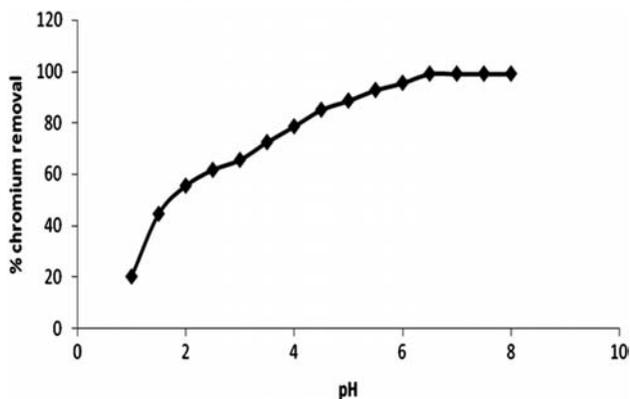


Fig. 3—Effect of pH on ion exchange process (293 K solution temperature, 1mg L⁻¹ initial metal concentration and 3.5g resin dose)

Effect of solution temperature on ion exchange process

The effect of solution temperature on to chromium (VI) metal removal is shown in Fig. 5. The removal of metal ion increased slightly increasing temperature from 273 K to 348 K. It is seen from Fig. 5, when natural ion exchanger used for chromium (VI) removal with an increase in temperature from 273 K to 348 K, the ion exchange capacity increased from 52.36 to 99% with initial metal concentration. This indicated that the exchange reaction was endothermic and ion exchange mechanism favours high temperature. An increase the removal with the rise in temperature may be explained by active site on natural ion exchanger being more active at high temperature³¹.

Effect of resin dose on ion exchange process

The percentage efficiency of chromium (VI) ion at different doses of ion exchanger was strongly acidic and shown in Fig. 6. The degree (%) of removal efficiency increased as the resin dose was increased. It might be concluded that by increasing the resin dose, the removal efficiency of heavy metal ion increased, while ion exchange density decreased with increase in resin dose. The decrease in ion exchange density may be due to the fact that some adsorption

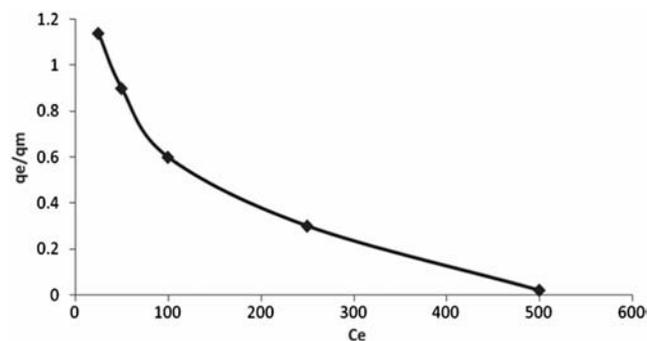


Fig. 4—Effect of initial metal concentration on ion exchange process (pH 6.5, 293 K solution temperature and 3.5 g resin dose)

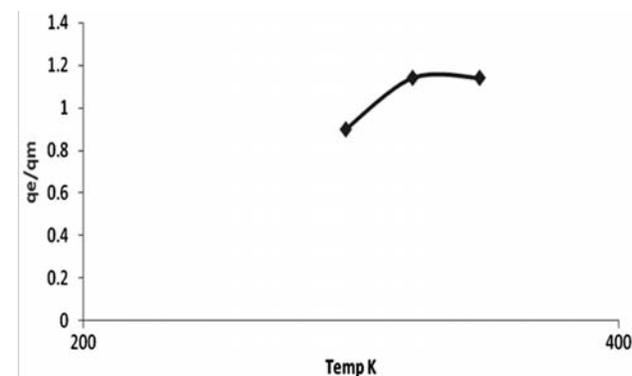


Fig. 5—Effect of solution temperature on ion exchange process (pH 6.5, 1 mg L⁻¹ initial metal concentration, 3.5g resin dose)

site may remain unsaturated during the adsorption process, where as the number of sites available for adsorption increased by increasing the resin dose and that results in the increase of removal efficiency³². When increased resin dosage from 0.5 to 3.5 g, removal efficiency increased from 80.55 to 99 % for chromium (VI).

Effect of contact time on ion exchange process

The removal efficiency increased with increase in contact time. Other parameter such as adsorbent dose, pH and temperature of solution was kept optimum. It can be seen that chromium removal efficiency increased from 60.00 to 99%, when contact time increased from 10 to 30 min, the result obtained are shown in Fig. 7. Optimum contact time for chromium (VI) removal was found to be 30 min. Hence the ion exchanger requires shorter contact time. Greater availability of various functional groups on the surface of resin, which are required for interaction

- 1- 0.1 mol/dm³ sodiumtetraborate
- 2- 1x10⁻⁴ mol/dm³ Cl⁻
- 3- 1x10⁻³ mol/dm³ Cl⁻
- 4- 1x10⁻² mol/dm³ Cl⁻
- 5- 5x10⁻² mol/dm³ Cl⁻

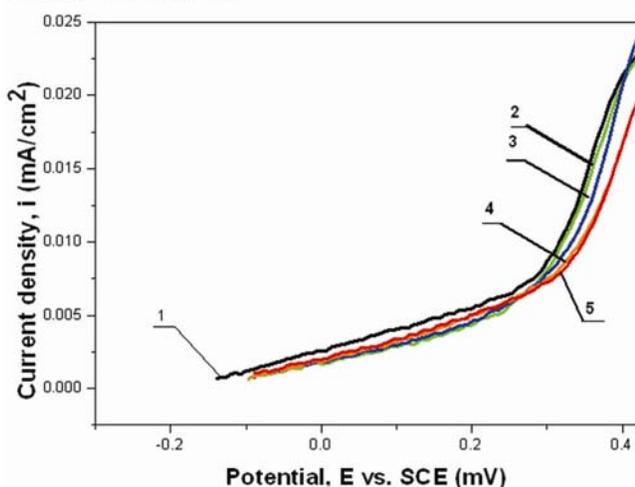


Fig. 6—Effect of adsorbent dose on ion exchange process (pH 6.5, 293 k solution temperature, 1 mg L⁻¹ initial metal concentration)

with anions and cations, significantly improved the binding capacity and the process proceeded rapidly. The result is important as equilibrium time is one of the important parameters for an economical wastewater treatment³³.

Sorption isotherm

The sorption isotherm for the removal of Cr from effluent on ion exchanger are found to be regular, positive and concave with respect to the concentration axis. The results show efficiency of ion exchanger for chromium removal from effluent. The sorption studies are carried out at 323 K to determine the sorption isotherms.

The isotherm parameters were evaluated using Langmuir and Freundlich isotherm models. The straight line obtained for two sorption isotherms indicated that the sorption of chromium (VI) fit to investigate isotherm models. The corresponding Langmuir and Freundlich parameters along with correlation coefficient are given in Table 4. The slope of the Freundlich isotherm was more linear than Langmuir isotherm, hence sorption isotherm fit better with Freundlich model.

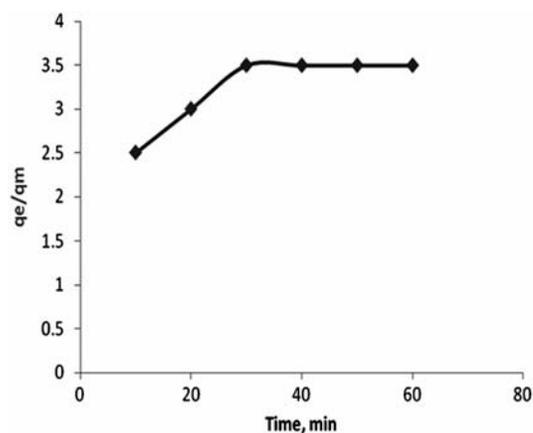


Fig. 7—Effect of contact time on ion exchange process (pH 6.5, 293 K solution temperature, 1 mg L⁻¹ initial metal concentration, 3.5 g resin dose)

Table 3—Concentration of Cr (VI) in industrial effluent before and after treatment of ion exchange resin of 3.5 gm at pH 6.5, time 30 min and temperature 25°C

Industrial Sample	Effluent (mL)	Concentration before treatment (mg L ⁻¹)	Concentration after treatment (mg L ⁻¹)	%Removal
1	25	5.0	0.03	99.40
2	25	4.5	0.02	99.55
3	25	4.5	0.02	99.55
4	25	2.2	0.01	99.54
5	25	3.5	0.01	99.70

Table 4—Isothermal parameters of Cr (VI) adsorption

Langmuir Isotherm			Freundlich Isotherm			
q_m (mg L ⁻¹)	K_L (mg L ⁻¹)	R^2	1/n	K_F m mg g ⁻¹	R^2	
3.94	0.018	0.85	1	0.5	0.99	

Application

Removal of chromium (VI) from industrial effluents

In order to assess the practical performance of natural ion exchanger for removal of hexavalent chromium from industrial effluent, an experiment was carried out after adjusting the pH 6.5 at which the maximum adsorption of hexavalent chromium can be achieved. Developed method was applied for removal of hexavalent chromium, from 5 different Pharmaceutical industrial effluents. The concentration of hexavalent chromium from these effluents was determined before treatment and after treatment with natural ion exchanger. It was observed that more than 99% of hexavalent chromium was removed from effluents. The results are reported in Table 3.

Conclusion

The purpose of this work is to study the possibility of removing hexavalent chromium from effluent through sorption by modified natural ion exchanger. The data reported here, show that *Tamarindous indica* seed powder is an effective sorbent for removing Cr from effluent. The sorption capacity of natural adsorbent is higher than the reported value of other adsorbents. Equilibrium studies are conducted for the adsorption of chromium from effluent by surface modified natural ion exchanger. The equilibrium data have been analyzed using Langmuir and Freundlich isotherm models, and results show that the sorption of hexavalent chromium occur at pH 6.5, which fits better to Freundlich isotherm model. It could be planned to use natural ion exchanger to economic polluted water treatment.

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