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Equilibrium Studies for Biosorbtion of Cr(III) by Roots of *Calotropis procera*

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Chromium is present in different types of industrial effluents, being responsible for environmental pollution. Traditionally, the chromium removal is made by chemical precipitation. However, this method is not completely feasible to reduce the chromium concentration to levels as low as required by environmental legislation. Biosorption is a process in which solids of natural origin are employed for binding heavy metals. It is a promising alternative method to treat industrial effluents, mainly because of its low cost and high metal binding capacity. The aim of the present study is to utilize the locally available wild plant material for heavy metal removal from industrial wastewater. The wastewater containing trivalent chromium was treated with biomass prepared from roots of *Calotropis procera*. These studies were carried out in order to determine some operational parameters of chromium sorption such as the time required for the metal-biosorbent equilibrium, the effects of change in biomass quantity and pH. It was found that a time of 50 min is sufficient enough to attain equilibrium. The optimum pH was found to be 4 for chromium. The biosorption data was well fitted to Langmuir and freundlich adsorption model. It is concluded that adsorbent prepared from *Calotropis procera* roots can be used for treatment of heavy metals in waste waters.

Key Words: Cr(III), Biosorption, Wastewater, *Calotropis procera*.

INTRODUCTION

The application of biosorption in environmental treatment has become a significant research area in the past 10 years. Heavy metal ions are reported as priority pollutants, due to their mobility in natural water ecosystems and due to their toxicity. The discharge of heavy metals into surface waters has become a matter of concern in Pakistan over the last two decades. These contaminants are introduced into surface waters through various industrial operations. The pollutants of concern include lead, chromium, zinc and copper. Heavy metals such as zinc, lead and chromium have number of applications in basic engineering works, paper and pulp industries, leather tanning, petrochemicals fertilizers, *etc*. The hexavalent and trivalent chromium is often present in electroplating wastewater[1]. Other sources of chromium pollution are leather tanning, textile, metal processing, paint and pigments, dyeing and steel fabrication.

According to Pakistan standards the maximum discharge limits for chromium in wastewater is 1.0 mg L^{-1}. Maximum limit in drinking water is 0.05 mg L^{-1}. In fact there is no safe level of chromium in drinking water and even a very dilute content can cause adverse health effects.

The conventional methods for treatment of chromium wastes include: lime and soda ash precipitation, adsorption with activated carbon, ion exchange, oxidation and reduction, fixation or cementation. These methods are economically unfavourable or technically complicated and are used only in special cases of wastewater treatment[1].

Biosorption of heavy metals from aqueous solutions is a relatively new technology for the treatment of industrial wastewater. Adsorbent materials derived from low cost agricultural wastes can be used for the effective removal and recovery of heavy metal ions from wastewater streams. The major advantages of biosorption technology are its effectiveness in reducing the concentration of heavy metal ions to very low levels and the use of inexpensive biosorbent materials[2,3].

Removing metals from wastewater requires development of new sorbents. A wide range of commercial sorbents including chelating resins and activated carbon are available for metal sorption, but they are relatively expensive. In recent years, numerous low cost natural materials have been proposed as potential biosorbents. These include moss peat, algae, leaf mould, sea weeds, coconut husk, sago waste, peanut hull, hazelnut, bagasse, rice hull, sugar beet pulp, plants biomass and bituminous coal[4-12].

The aim of this research is to use abundantly available wild plant material for treatment of chromium wastes. Roots of *Calotropis procera* are used as biosorbent to remove chromium from known amount of solution. The present work deals with equilibrium studies and operating conditions of process of adsorption of chromium like pH, initial metal concentration, effect of biosorbent dose.

EXPERIMENTAL

Biomass preparation: *Calotropis procera* roots were collected from local environment of Old Kahna near Lahore. These roots were washed with distilled water to remove any soil or debris.The washed samples were oven dried at a temperature of 333 K for 2 d. Dried roots were ground and sieved to 100 mesh sizes. This biomass was stored in air tight glass bottles to protect it from humidity.

FTIR spectroscopy was used to identify the chemical groups present in roots. The samples were examined using Midac FTIR 2000 spectrometer within range 7800-406 cm^{-1} KBr was used as background material in all the analysis. 0.0035 g roots powder was mixed with 0.5 g KBr and pressed to form a pellet. FTIR spectra of roots before and after adsorption was compared.

Batch studies: Adsorption studies on this adsorbent were carried out using chromium(III) stock solution of 1000 mg L^{-1} (± 0.5 %) as $Cr(NO_3)_3·9H_2O$ in 1 M HNO_3 of Applichem was bought. This was further diluted to get solutions of various known concentrations of chromium. For equilibrium studies (to obtain adsorption isotherms), a series of flasks (250 mL, as batch sorption reactors) were prepared containing chromium solutions (50 mL) of known concentrations (C_0) varying from 10 mg L^{-1} to 30 mg L^{-1}. Experiments conditions were as follows: addition of *Calotropis procera* roots into each flask (dose varying from 5 g biomass L^{-1} to 30 g L^{-1}), agitating mixtures using variable speed shaker (125 rpm, GFL 3033) for 3 h as the adsorption time at temperatures 303 K. The pH for the experiments was taken as original pH of solutions. The biomass was removed at last by filtration through a vacuum filter assembly having Pyrex filter funnel of porosity grade 4 and the filtrate was analyzed for ion content (C_e) by flame atomic absorption spectrophotometry (Hitachi Z-5000). All experiments were performed 3 times and average values were used in all calculations.

RESULTS AND DISCUSSION

Fourier transform infrared spectroscopy (FT-IR) investigation: The FT-IR spectra before and after adsorption of *Calotropis procera* roots showed various functional groups and the corresponding infrared absorption bands. The spectra display a number of absorption peaks, indicating the complex nature of *Calotropis procera* roots. These band shifts indicated that especially the bonded -OH groups and/or -NH stretching and carboxyl groups were especially played a major role in chromium(III) biosorption on *Calotropis procera* roots.

Effect of contact time: The rate at which sorption takes place is of most importance, especially when designing batch sorption systems. Consequently it is important to establish the time dependency of such systems for various pollutant removal processes. Therefore, the required contact time for sorption to be completed is important to give insight into a sorption process. This also provides information on the minimum time required for considerable adsorption to take place and the possible diffusion control mechanism between the metal ion as it moves from the bulk solution towards the adsorbent surface. The kinetic behaviour of Cr(III) ion sorption onto the *Calotropis procera* roots was examined using agitation times of 10-50 min.

The metal sorption capacity (qt) of the *Calotropis procera* roots was calculated from the relationship using eqn. 1:

$$q_t = \frac{(C_i - C_t)}{m} \times V \qquad (1)$$

Also, the percentage of Cr(III) ions removed (% RE) from the aqueous solution was calculated using eqn. 2:

$$\% \text{ RE} = \frac{(C_i - C_t)}{C_i} \times 100 \qquad (2)$$

whereas the fraction of Cr(III) ions removed by the two adsorbents was determined from the following relationship:

$$Y_T = \frac{(C_i - C_t)}{(C_i - C_e)} \tag{3}$$

where q_t is the metal sorption capacity of the adsorbent (mg g^{-1}), C_i is the initial metal ion concentration (mg L^{-1}), C_t is the metal ion concentration in solution at time t (mg L^{-1}), Y_T is the fraction of the metal adsorbed at time t, m is the weight of the adsorbent (g), V is the volume of the metal ion solution used for sorption (dm^3) and C_e is the concentration of metal ion, when sorption is completed, *i.e.*, infinity sorption [$C_\infty = C_e$].

The removal efficiency of the *Calotropis procera* roots for Cr(III) ions is illustrated in Fig. 1, while the variation of sorption capacity (qt) of Cr(III) with contact time for the adsorbent is shown in Fig. 2. It can be seen from the figures that 80 % of the Cr(III) ions were removed in first 10 min. Thus, the rate of Cr(III) removal was quite rapid initially, but it gradually becomes slower with passage of time reaching a maximum in 50 min. The initial faster rate may be due to the availability of the uncovered surface area of the adsorbent initially, since adsorption kinetics depends on the surface area of the adsorbent. In addition, the variation in the amount of Cr(III) ion removed by the adsorbent could be related to the nature and concentration of the surface groups (active sites) responsible for interaction with the chromium ions.

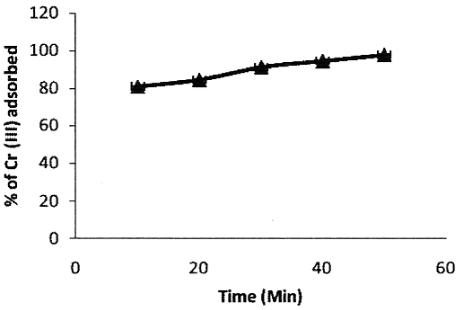

Fig. 1. Percentage removal of Cr(III) ions on *Calotropis procera* roots with increasing contact time

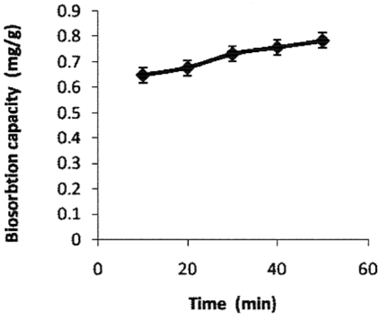

Fig. 2. Cr(III) sorption capacity (q_t) variation with contact time

Fig. 3 depicts the time-dependence of the fraction of adsorption of Cr(III) ions. It can be seen from the figure that as $T^{1/2}$ increases, the rate fraction of adsorption (Y_T) also increases. This indicates that with passage of time, a higher fraction of the Cr(III) ions migrates from the bulk solution through the adsorbent boundary layer onto the active sites of the adsorbent and is adsorbed.

Effect of adsorbent dose: The removal of chromium(III) by *Calotropis procera* roots at different adsorbent doses (5-25 g L^{-1}) for the chromium concentration 20 mg L^{-1} is investigated. The results are shown that the per cent removal of Cr(III) increases rapidly with increase in the dose of *Calotropis procera* roots as shown in

Fig. 4. The increase in adsorbent dosage from 5.0 to 25 g L^{-1} resulted in an increase from 40.48 to 97.89 % in adsorption of Cr(III) ions. This is due to the larger number of available adsorption sites favouring the enhanced uptake of the metal ion.

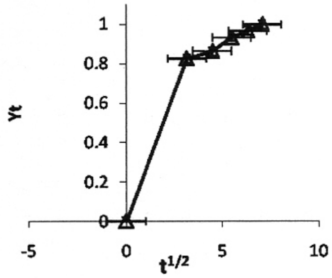

Fig. 3. Time-dependence of the fraction of adsorption of Cr(III) on *Calotropis procera* roots

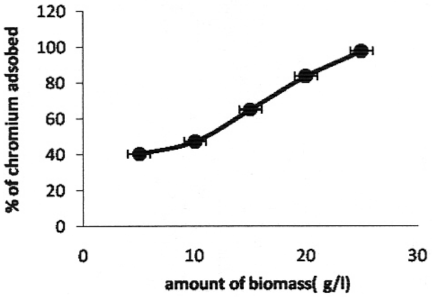

Fig. 4. Percentage removal of Cr(III) ions with increasing adsorbent dose

However, uptake of Cr(III) showed a reverse trend to the removal percentage adsorptions. With increasing adsorbent dosage from 5.0 to 25 g L^{-1}, the adsorption of Cr(III) ion per unit weight of adsorbent decreased from 1.619 to 0.783 mg g^{-1}. This was due to metal concentration shortage in solution at high dose rates (Fig. 5).

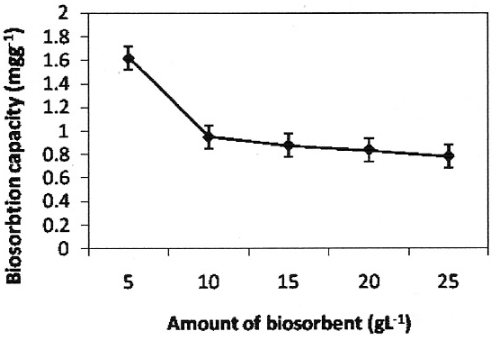

Fig. 5. Sorption capacity variation with adsorbent dose

Effect of pH: Aqueous phase pH governs the speciation of metals and also the dissociation of active functional sites on the sorbent. FT-IR spectra shows that the carboxyl functional groups play a major role in the uptake of the metal cations[13]. At pH in the range 3.5-5.5 these groups generate a negatively charged surface and electrostatic interactions between cationic species and this surface can be responsible for metal biosorption. Hence, metal sorption is critically linked with pH. Not only different metals show different optimum pH for their sorption but may also vary from one kind of biomass to the other[14].

The effect of pH on the removal of Cr(III) is investigated by testing four values of pH 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0 and 8.0 at a temperature of 25 ± 1 °C. The contact time has been fixed to 50 min for all the experiments. The experimental results are presented in Fig. 6. It was found that sorption of chromium was in the range of 3 to 5 pH.The optimal pH for chromium was found to be 4. This pH dependence suggests a competition of metallic ions and protons by the same binding sites, since in this pH range chromium ion is present as a cation.

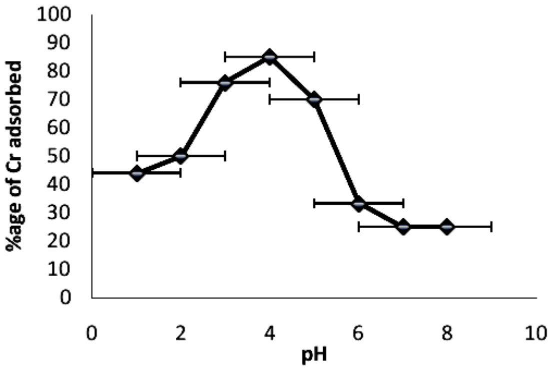

Fig. 6. Effect of pH on biosorption of Cr(III) on *Calotropis procera* roots

Sorption isotherms: Equilibrium studies that give the capacity of the adsorbent and adsorbate are described by adsorption isotherms, which is usually the ratio between the quantity adsorbed (qe) and the remaining in solution (Ce) at fixed temperature at equilibrium[15]. Several isotherm models are available to describe this equilibrium sorption distribution. Freundlich and Langmuir adsorption isotherm models were applied to the system, studied with different dose of adsorbent.

Freundlich isotherm: The Freundlich model is used to estimate the adsorption intensity of the sorbent towards the adsorbate and is given by:

$$qe = K_F \, Ce^{1/n} \tag{4}$$

where K and n are the Freundlich constants which determines the curvature and steepness of the isotherm[16]. Also the value of n indicates the affinity of the adsorbate towards the biomass. The above equation is conveniently used in linear form as:

$$\ln qe = \ln K_F + (1/n) \ln Ce \tag{5}$$

A plot of ln Ce against lnqe yielding a straight line indicates the conformation of the Freundlich adsorption isotherm.

Batch adsorption isothermal data, fitted into the linear form of the Freundlich isotherm is shown in Fig. 7. The adsorption capacity, K and the adsorption intensity, 1/n are directly obtained from the slopes and the intercepts of the linear plot, respectively and the data are provided in Table-1.

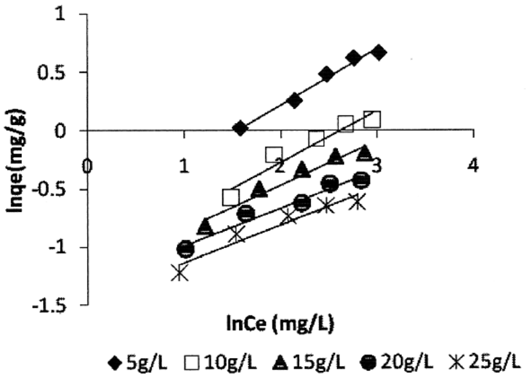

Fig. 7. Freundlich plots for chromium adsorbtion at 300 K using different amount of biomass

The adsorption capacity, K and the adsorption intensity, 1/n are directly obtained from the slopes and the intercepts of the linear plot, respectively and the data are provided in Table-1.

TABLE-1
FREUNDLICH ADSORPTION PARAMETERS FOR CHROMIUM(III) ADSORPTION ON *Calotropis procera* ROOTS

Amount of biomass (g/L)	K_F (mg g^{-1})	n (gL^{-1})	R^2
5	0.530	2.23260	0.9542
10	0.312	2.23910	0.934
15	0.285	2.54971	0.9491
20	0.258	2.86600	0.9539
25	0.231	3.05000	0.9365

The K, which is a measure of adsorption capacity, decreased from 0.530 to 0.231 with increasing adsorbent dose. The magnitude of the exponent, n increased from 2.236 to 3.050 with increasing the adsorbent dose from 5 to 25 g L^{-1} (Table-1). This is due to metal concentration shortage in solution at high dose rates.

The plot of ln qe *versus* ln Ce for various initial concentrations is linear indicating the applicability of Freundlich adsorption isotherm ($R^2 > 0.955$). Fitting of the data to the Freundlich model indicate that the forces of adsorption by *Calotropis procera* roots are governed by physio-sorption.

Langmuir isotherm: The Langmuir equation is used to estimate the maximum adsorption capacity corresponding to complete monolayer coverage on the adsorbent surface and is expressed by:

$$qe = (q_{max} K_L Ce) / (1 + K_L Ce) \quad (6)$$

This equation was rearranged to get:

$$\frac{Ce}{qe} = \frac{1}{q_{max} b} + \frac{Ce}{q_{max}} \quad (7)$$

where q_{max} is the maximum possible amount of metal ion adsorbed per unit weight of biomass and b is the equilibrium constant related to the affinity of the binding sites for the metals, lower is b more is the affinity of metal to biomass.

Equilibrium concentration Ce and equilibrium capacity qe were calculated for each initial metal concentration. Ce was plotted against Ce/qe and a straight line was fitted in the data.

The value of correlation coefficient ($R^2 > 0.9905$) (Table-2) indicates that there is a strong positive relationship for the data and that sorption data of the Cr(III) ion onto *Calotropis procera* roots follows the Langmuir isotherm.

TABLE-2
LANGMUIR ADSORPTION PARAMETERS FOR CHROMIUM(III) ADSORPTION ON *Calotropis procera* ROOTS

Amount of biomass (g/L)	q_{max} (mgg^{-1})	b (Lmg^{-1})	R^2
5	2.950	0.132	0.985
10	1.501	0.150	0.989
15	1.045	0.228	0.997
20	0.782	0.298	0.992
25	0.643	0.358	0.998

The Q_{max} for Cr(III) on *Calotropis procera* roots was decreased from 2.95 to 0.64 mg g^{-1} with the increase in adsorbent dose from 5 to 25 g L^{-1} (Table-2). The decreasing trends observed in Q_{max} and b provided in the table are due to metal concentration shortage in solution at high dose rates. All these results showed that Langmuir isotherm model fitted the results quite well suggesting that the surface of the sorbent is homogenous. Each binding site accepts only one Cr(III) molecule, that sorbed molecules are organized as a monolayer and all sites are energetically equivalent and there is no interaction between sorbed molecule[17].

Equilibrium parameter: The essential characteristics of Langmuir equation can be expressed in terms of a dimensionless separation factor or equilibrium parameter, R_L.

The dimensionless adsorption intensity (R_L) is calculated using the following formula:

$$R_L = 1/1 + bC_0$$

These values indicate the shape of the isotherm to be either unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$) or irreversible ($R_L = 0$).

The values of R_L obtained for the Cr (III)-*Calotropis procera* roots system are provided in Table-3. The calculated average R_L value for different initial metal concentrations 10-30 mg/L of chromium ions in the solution, lying between 0 and 1, indicate favourable adsorption for all 5 adsorbent doses.

TABLE-3
DIMENSIONLESS SEPARATION FACTOR R_L FOR CHROMIUM ADSORBTION ON *Calotropis procera* ROOTS USING DIFFERENT AMOUNT OF BIOMASS

Amount of biomass (g/L)	R_L
5	0.294
10	0.270
15	0.202
20	0.159
25	0.137

Conclusion

The objective of this work is to study the dependence of adsorption on adsorbent and adsorbate (chromium) characteristics by means of batch and column studies. Conclusions from the present study are as follows: (a) *Calotropis procera* roots can be successfully used for Cr(III) removal from aqueous solutions. (b) The removal of Cr(VI) from aqueous solutions strongly depends on the pH of the solution, adsorbent mass and contact time. The maximum adsorption capacity was obtained at pH 4.0. (c) The percentage of adsorption of Cr(III) increased with increasing contact time. Increase in the mass of the adsorbent leads to increase in Cr(III) adsorption owing to corresponding increase in the number of adsorption sites. (d) Langmuir and Freundlich adsorption models were used to represent the experimental data fitted very well to the Langmuir isotherm model. (e) The employed adsorbent is quite economic than commercially available adsorbents.

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