Available online www.jocpr.com

Journal of Chemical and Pharmaceutical Research

ISSN No: 0975-7384
CODEN(USA): JCPRC5

J. Chem. Pharm. Res., 2011, 3(6):73-87

Equilibrium and kinetic studies for biosorption system of chromium ions from aqueous solution using *Ficus benghalensis* L. powder

L. Nageswara Rao[a] and G. Prabhakar[b]

[a]*Department of Chemical Engineering, R. V. R & J. C. College of Engineering, Guntur*
[b]*Department of Chemical Engineering, S. V. U. College of Engineering, Tirupati*

ABSTRACT

In the present investigation, the biosorption is carried out to test the suitability of abundantly available plant based material Ficus Benghalensis L. Leaf powder as an adsorbent for removal of chromium ions from aqueous solution. The equilibrium studies are systematically carried out in a batch process, covering various process parameters that include contact time, adsorbent size and dosage, initial chromium ion concentration and pH of the aqueous solution. It is observed that there is a significant increase in percentage removal of chromium ions as pH increases from 2 to 6 and attain maximum when pH is 6. The contact time is to be 10 minutes. The Langmuir isotherm is more suitable for biosorption followed by Temkin and Freundlich isotherms. The biosorption of chromium ions follows second order kinetic model having a correlation coefficient of 0.9987.

Key words: Biosorption; *Ficus Benghalensis* L.; Adsorption isotherms; Kinetic studies.

INTRODUCTION

The effects of heavy - metal ions on human health have received great attention in the last decades. As a consequence, methods to remove metal species from waste water have been the subject of interest of researchers, in order to improve the water quality. The removal of toxic metal ions and recovery of valuable ions in mine waste waters, soils and waters have been important in economic and environmental problems [1-4]. Heavy metals and other metal ions exist as contaminants in aqueous waste streams of many industries, such as metal plating, electro plating, mining, ceramic, batteries and pigment manufacturing [5, 6].

Heavy metals like lead, mercury, arsenic, copper, chromium and cadmium are highly toxic when adsorbed into the body [7]. Chromium is often found in effluents discharged from industries involved in acid mine drainage, galvanizing plants, natural ores and municipal waste water treatment plants and is not biodegradable and travels through the food chain via bioaccumulation. Therefore, there is significant interest regarding chromium removal from waste waters [8] since its toxicity for humans is 100-500 mg/day [9]. World health organization (WHO) recommended the maximum acceptable concentration of chromium in drinking water as 0.05 mg/L [10].

Conventional methods of removing toxic heavy metal ions include chemical precipitation, chemical oxidation or reduction, filtration, ion exchange, electrochemical treatment, application of membrane technology and evaporation recovery. However, these processes have considerable disadvantages such as incomplete metal removal, expensive equipment and monitoring system, high reagent or energy requirements, generation of toxic sludge and other waste products that require disposal [11-14]. Therefore, there is need for an alternative technique, which is efficient and cost effective. Biosorption, based on living or non living microorganisms or plants could be such an alternative method of treatment. Which describes the removal of heavy metals by the passive binding to non-living biomass from an aqueous solution [15]. Kuyucak indicated that the cost of biomass production is the crucial factor in determining the over all cost of a biosorption process [16].

The present work investigates the potential use of untreated *Ficus Benghalensis L.*biomass as metal sorbent for chromium from aqueous solution. *Ficus Benghalensis L.*was chosen as a biosorbent because of the relative lack of information about its sorption ability. Environmental parameters affecting the biosorption process such as pH, contact time, metal ion concentration, biosorbent dosage and biosorbent sizes were evaluated. The equilibrium adsorption data were evaluated by Langmuir, Freundlich and Temkin isotherm models. The kinetic experimental data were correlated by first and second order kinetic models.

EXPERIMENTAL SECTION

2.1. Preparation of biosorbent

The *F. Benghalensis L.*leaves were collected from R.V.R. & J. C College of Engineering campus of Guntur, Andhra Pradesh, India. Leaves were washed with deionized water several times to remove dirt and dried. Then the dried leaves were powdered using domestic grinder to the powder size of 75-212 µm. and used as biosorbent without any pretreatment for chromium adsorption.

2.2 Chemical

Analytical grades of $K_2Cr_2O_7$, $Cr_2(SO_4)_3$, HCl and NaOH were purchased from Merck (Mumbai, Maharastra, India). Chromium ions were prepared by dissolving its corresponding sulphate salt in distilled water. The pH of solutions was adjusted with 0.1 N HCl and NaOH.

All the experiments were repeated five times and the average values have been recorded. Also, blank experiments were conducted to ensure that no adsorption was taking place on the walls of the apparatus used.

2.3 Biosorption experiments

Biosorption experiments were performed at room temperature (30 ± 1^0C) in a rotary shaker at 180 rpm containing 30 mL of different chromium concentrations using 250 mL Erlenmeyer flasks. After one hour of contact (according to the preliminary sorption dynamics tests), with 0.1 g *F. Benghalensis L.*leaves biomass, equilibrium was reached and the reaction mixture was centrifuged for 5 min. The metal content in the supernatant was determined using Atomic Absorption Spectrophotometer (GBC Avanta Ver 1.32, Australia) after filtering the adsorbent with 0.45 µm filter paper. The amount of metal adsorbed by *F. Benghalensis L.*leaves was calculated from the differences between metal quantity added to the biomass and metal content of the supernatant using the following equation:

$$q = \left(C_0 - C_f\right)\frac{V}{M} \quad (1)$$

Where q is the metal uptake (mg/g); C_0 and C_f the initial and final metal concentrations in the solution (mg/L), respectively; V the solution volume (mL); M the mass of biosorbent (g).The pH of the solution was adjusted by using 0.1N HCl and 0.1N NaOH.

The Langmuir [17] sorption model was chosen for the estimation of maximum chromium sorption by the biosorbent. The Langmuir isotherm can be expressed as

$$q = \frac{Q_{\max} bC_{eq}}{1 + bC_{eq}} \quad (2)$$

Where Q_{max} indicates the monolayer adsorption capacity of adsorbent (mg/g) and the Langmuir constant b (L/mg) is related to the energy of adsorption. For fitting the experimental data, the Langmuir model was linearized as

$$\frac{1}{q} = \frac{1}{Q_{\max}} + \frac{1}{bQ_{\max}C_{eq}} \quad (3)$$

The freundlich [18] model is represented by the equation:

$$q = KC_{eq}^{\frac{1}{n}} \quad (4)$$

Where K (mg/g) is the Freundlich constant related to adsorption capacity of adsorbent and *1/n* is the Freundlich exponent related to adsorption intensity (dimensionless). For fitting the experimental data, the Freundlich model was linearized as follows:

$$\ln q = \ln K + \frac{1}{n}\ln C_{eq} \quad (5)$$

The Temkin [19] isotherm has generally been applied in the following form:

$$q = \frac{RT}{b_T} \ln\left(A_T C_{eq}\right) \quad (6)$$

Where A_T (L/mg) and b_T are Temkin isotherm constants.

2.4. Biosorption Kinetics

The kinetic studies were carried out by conducting batch biosorption experiments with different initial chromium concentrations. Samples were taken at different time periods and analyzed for their chromium concentration.

RESULTS AND DISCUSSION

3.1. The effect of contact time

The data obtained from the biosorption of chromium ions on the *F. Benghalensis L.*showed that a contact time of 10 min was sufficient to achieve equilibrium and the adsorption did not change significantly with further increase in contact time. Therefore, the uptake and un -adsorbed chromium concentrations at the end of 10 min are given as the equilibrium values (q_e, mg/g; C_{eq}, mg/L), respectively (Fig. 1) and the other adsorption experiments were conducted at this contact time of 10 min (pH 6).

3.2. Effect of pH

We know that the pH of the medium affects the solubility of metal ions and the concentration of the counter ions on the functional groups of the biomass cell walls, so pH is an important parameter on biosorption of metal ions from aqueous solutions [20–24].

*F. Benghalensis L.*presents a high content of ionizable groups (carboxyl groups from mannuronic and guluronic acids) on the cell wall polysaccharides, which makes it very liable to the influence of the pH. As shown in Fig. 2, the uptake of chromium increased with the increase in pH from 2.0 to 6.0. Similar results were also reported in literature for different biomass systems [25–27]. At pH values lower than 2.0, chromium removal was inhibited possibly as a result of the competition between hydrogen and chromium ions on the sorption sites, with an apparent preponderance of hydrogen ions, which restricts the approach of metal cations as in consequence of the repulsive force. As the pH increased, the ligands such as carboxylate groups in *F. Benghalensis L.*would be exposed increasing the negative charge density on the biomass surface, which in turn increases the attraction of metallic ions with positive charge and allowing the biosorption onto the cell surface.

In this study, the chromium cations at around pH 6 were expected to interact more strongly with the negatively charged binding sites in the adsorbent. As a result, the optimum pH for chromium adsorption was found as 6 and the other adsorption experiments were performed at this pH value.

3.3. Effect of metal ion concentration

Fig. 3 shows the effect of metal ion concentration on the adsorption of chromium by *Ficus Benghalensis L.* The data shows that the metal uptake increases and the percentage adsorption of chromium decreases with increase in metal ion concentration. This increase (5.31–14.54 mg/g) is a result of increase in the driving force, i.e. concentration gradient. However, the percentage

adsorption of chromium ions on *F. Benghalensis L.*was decreased from 82.29 to 72.93%. Though an increase in metal uptake was observed, the decrease in percentage adsorption may be attributed to lack of sufficient surface area to accommodate much more metal available in the solution. The percentage adsorption at higher concentration levels shows a decreasing trend whereas the equilibrium uptake of chromium shows an opposite trend. At lower concentrations, all chromium ions present in solution could interact with the binding sites and thus the percentage adsorption was higher than those at higher chromium ion concentrations. At higher concentrations, lower adsorption yield is due to the saturation of adsorption sites. As a result, the purification yield can be increased by diluting the wastewaters containing high metal ion concentrations.

3.4. Effect of adsorbent size

The effect of different adsorbent particle sizes on percentage removal of chromium is investigated and shown in Fig. 4. It reveals that the adsorption of chromium on *F. Benghalensis L.*decrease from 82.29 to 51.64% with the increased particle size from 75 to 212 µm at an initial concentration of 20 mg/L. The smallest size obtained was 75µm due to the limitation of available grinder configuration. It is known that decreasing the average particle size of the adsorbent increases the surface area, which in turn increases the adsorption capacity.

3.5. Effect of adsorbent dosage

Fig. 5 shows the effect of adsorbent dosage on the % removal at equilibrium conditions. It was observed that the amount of chromium adsorbed varied with varying adsorbent dosage. The amount of chromium adsorbed increases with an increase in adsorbent dosage from 0.1 to 0.5 g. The percentage chromium removal was increased from 82.29 to 91.61% for an increase in adsorbent dosage from 0.1 to 0.5 g at initial concentration of 20 mg/L. The increase in the adsorption of the amount of solute is obvious due to increasing biomass surface area. Similar trend was also observed for chromium removal using *Azadirachta indica* as adsorbent [28].

4. Biosorption equilibrium

The equilibrium biosorption of chromium on the *F. Benghalensis L.*as a function of the initial concentration of chromium is shown in Fig. 6-9. There was a gradual increase of adsorption for chromium ions until equilibrium was attained. The Langmuir, Freundlich and Temkin models are often used to describe equilibrium sorption isotherms. The calculated results of the Langmuir, Freundlich and Temkin isotherm constants are given in Table 1.

It is found that the adsorption of chromium on the *F. Benghalensis L.*was correlated well with the Langmuir equation and Temkin as compared to Freundlich equation under the concentration range studied. Examination of the Freundlich data shows that this isotherm was not modeled as well across the concentration range studied.

5. Kinetics of adsorption

The prediction of adsorption rate gives important information for designing batch adsorption systems. Information on the kinetics of solute uptake is required for selecting optimum operating conditions for full-scale batch process. Fig.10 shows the plottings between amount adsorbed, q_e (mg/g) versus time, *t* (min) for an initial concentration of 20 mg/L. The adsorption rate within the first 5 min was observed to be very high and there after the reaction proceeds at a slower rate till

equilibrium and finally a steady state was obtained after equilibrium. The saturation time was found to be 10 min based on the initial metal concentration. The kinetics of the adsorption data was analyzed using two kinetic models, pseudo-first- and pseudo-second-order kinetic model. These models correlate solute uptake, which is important in predicting the reactor volume. These models are explained below

5.1. The pseudo-first-order equation

The pseudo-first-order equation of Lagergren [29] is generally expressed as follows:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \qquad (7)$$

where q_e and q_t are the sorption capacities at equilibrium and at time *t*, respectively (mg/g) and k_1 is the rate constant of pseudo first-order sorption (min^{-1}). After integration and applying boundary conditions, q_t =0 to $q_t = q_t$ at *t* = 0 to *t* = *t*; the integrated form of Eq. (7) becomes:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303}t \qquad (8)$$

The pseudo-first-order rate constant k_1 can be obtained from the slope of the graph between $\log(q_e\text{-}q)$ versus time, *t* (Fig.11). The calculated k_1 values and their corresponding linear regression correlation coefficient values are shown in Table 2. The linear regression correlation coefficient value R_1^2 found to be 0.9648, which shows that this model cannot be applied to predict the adsorption kinetic model.

5.2. The pseudo-second-order equation

If the rate of sorption is a second-order mechanism, the pseudo-second-order chemisorption kinetic rate equation is expressed as [30]:

$$\frac{dq_t}{dt} = k(q_e - q_t)^2 \qquad (9)$$

Where q_e and q_t are the sorption capacity at equilibrium and at time *t*, respectively (mg/g) and *k* is the rate constant of pseudo-second-order sorption (g/(mg min)). For the boundary conditions q_t =0 to $q_t = q_t$ at *t* = 0 to *t* = *t*; the integrated form of Eq. (9) becomes:

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e}t \qquad (10)$$

where *t* is the contact time (min), q_e (mg/g) and q_1 (mg/g) are the amount of the solute adsorbed at equilibrium. Eq. (10) does not have the problem of assigning an effective q_e. If pseudo-second-order kinetics is applicable, the graph t/q_t against *t* of Eq. (10) should give a linear relationship, from which q_e and *k can* be determined from the slope and intercept of the plot (Fig. 12) and there is no need to know any parameter beforehand.

The pseudo-second-order rate constant k_2, the calculated q_e value and the corresponding linear regression correlation coefficient value R_2^2 are given in Table 2. At an initial chromium

concentration of 20 mg/L, the linear regression correlation coefficient R_2^2 value was higher. The higher R_2^2 value confirms that the adsorption data were well represented by pseudo-second order kinetic model.

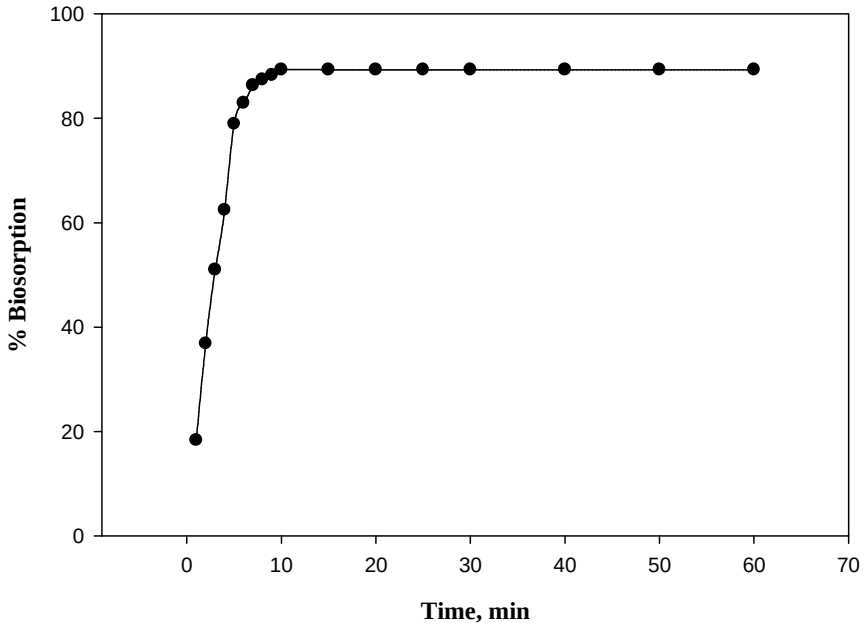

Fig.1. Effect of contact time on biosorption of chromium by *Ficus Benghalensis* L. for 20 mg/L of metal and 0.1 g/30 mL of biosorbent concentration.

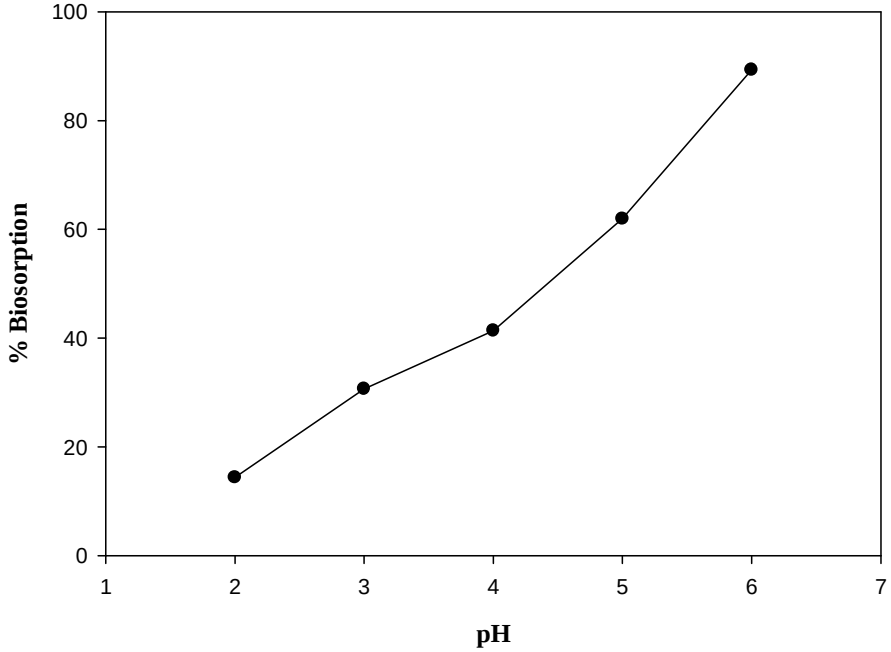

Fig.2. Effect of pH on chromium biosorption by *Ficus Benghalensis* L. for 20 mg/L metal and 0.1 g/30 mL of biosorbent concentration.

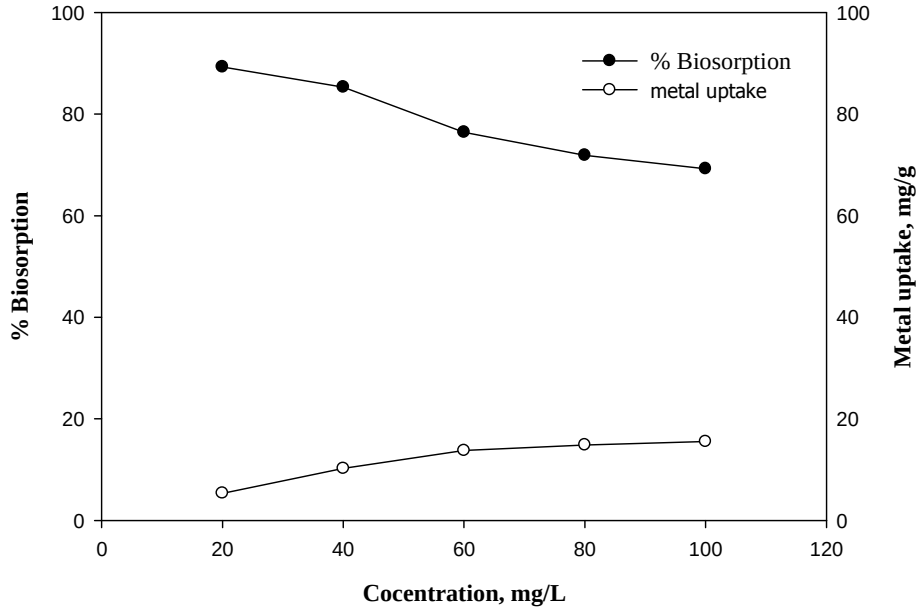

Fig.3. Effect of metal concentration on the biosorption of chromium by *Ficus Benghalensis* at 0.1 g/30 mL of biosorbent concentration.

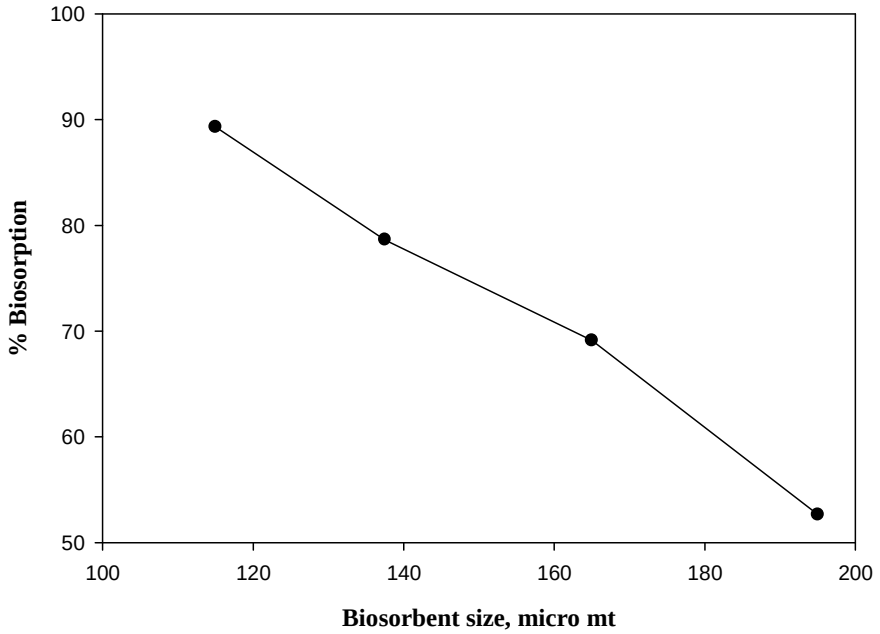

Fig.4. Effect of *Ficus Benghalensis* L. particle size on biosorption of chromium for 20 mg/L of metal and 0.1 g/30 mL of biosorbent concentration.

A comparison of the maximum capacity Q_{max} of *F. Benghalensis L.*with those of some other adsorbents reported in literature is given in Table 3. Differences of metal uptake are due to the properties of each adsorbent such as structure, functional groups and surface area.

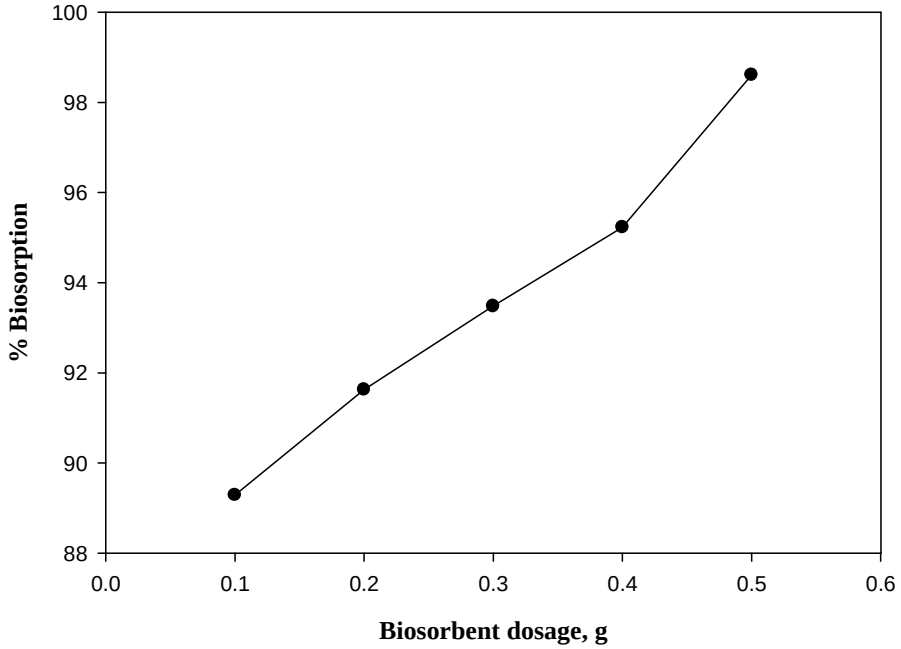

Fig.5. Effect of *Ficus Benghalensis* L dosage on biosorption of chromium for 20 mg/L of metal concentration.

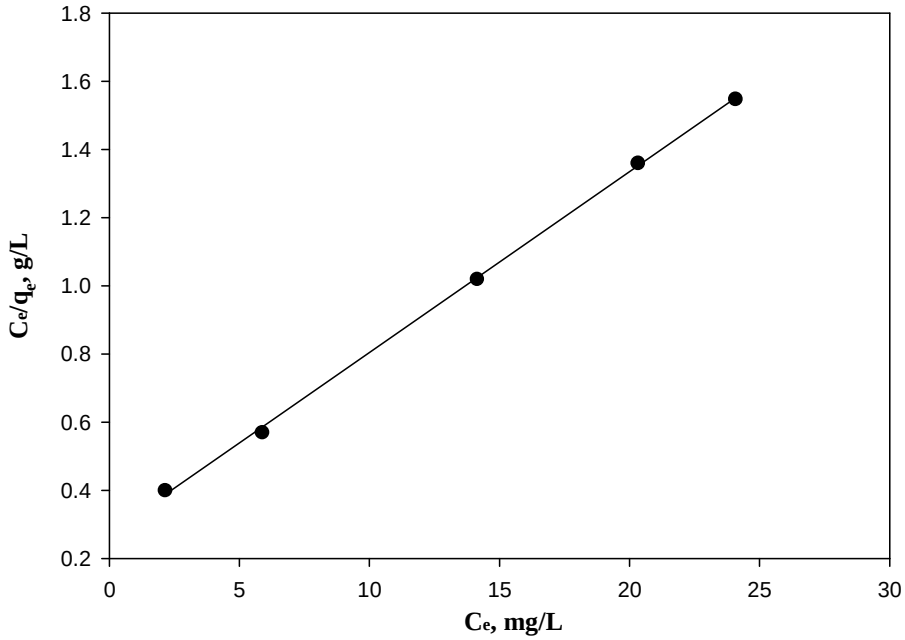

Fig.6. Langmuir biosorption isotherm for chromium at 0.1 g/30 mL of biosorbent concentration.

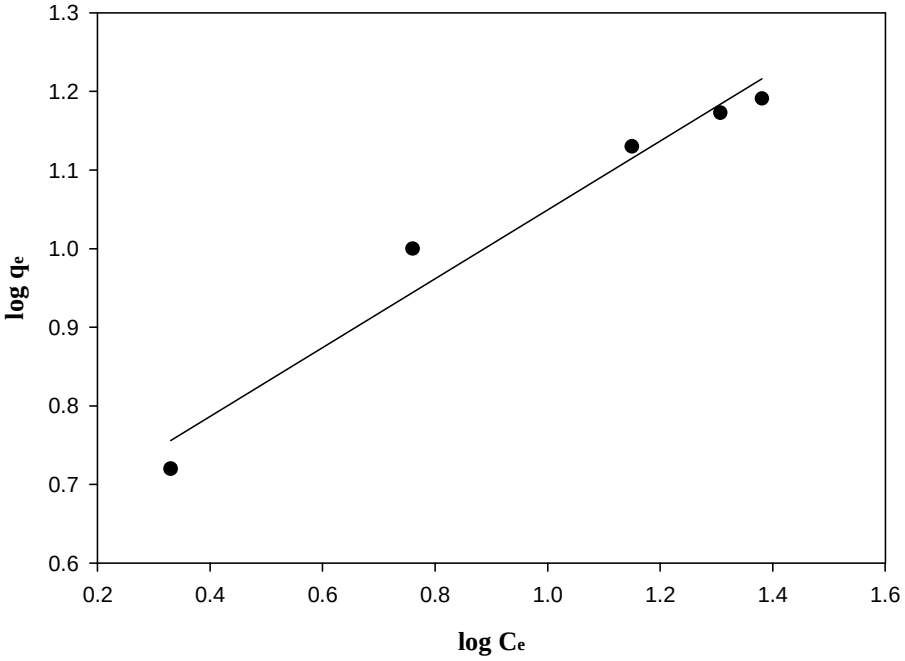

Fig.7. Freundlich biosorption isotherm for chromium at 0.1 g/30 mL of biosorbent concentration.

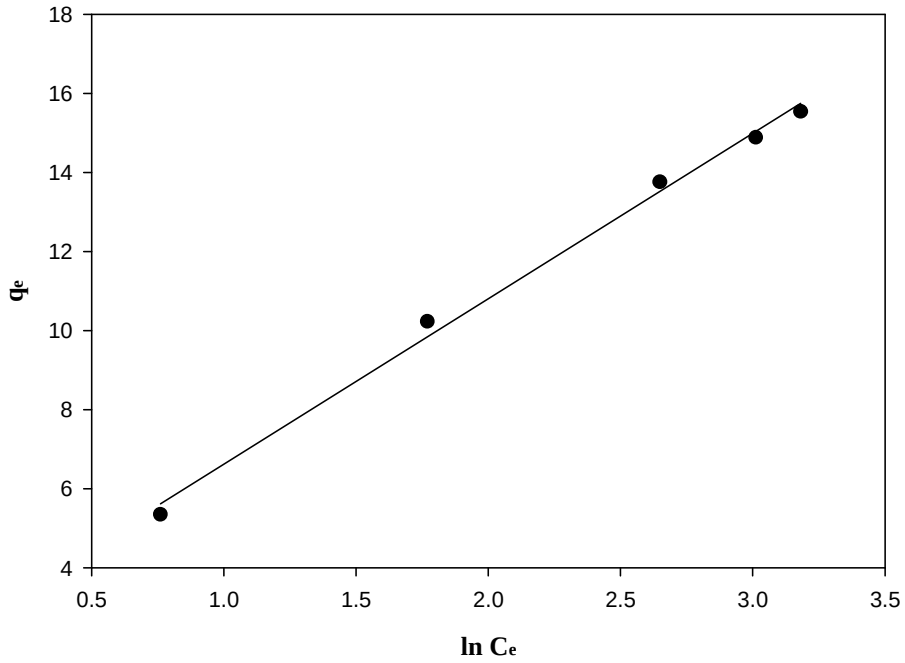

Fig.8. Temkin biosorption isotherm for chromium at 0.1 g/30 mL of biosorbent concentration.

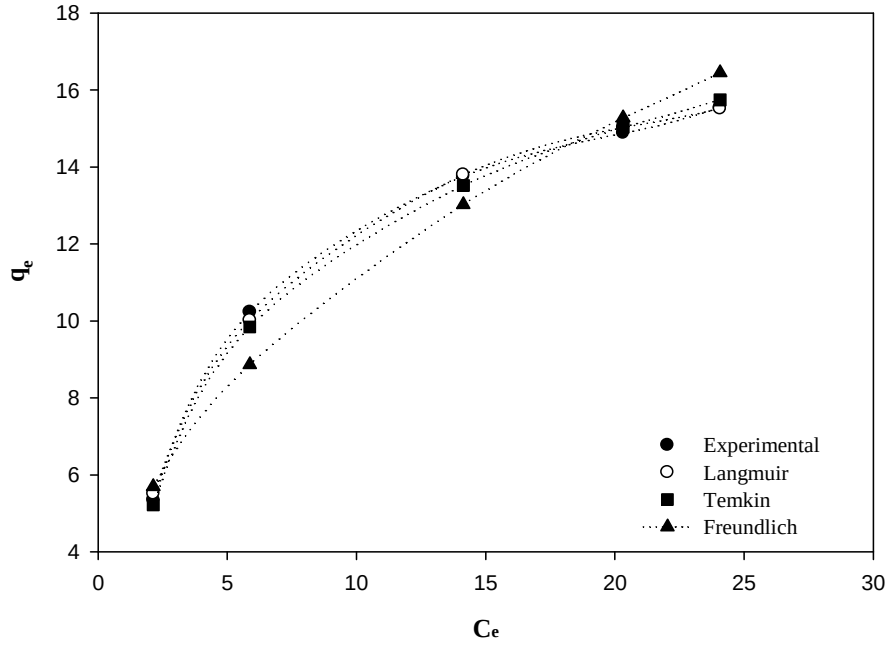

Fig.9. Equilibrium curves for chromium onto .Ficus Benghalensis.L

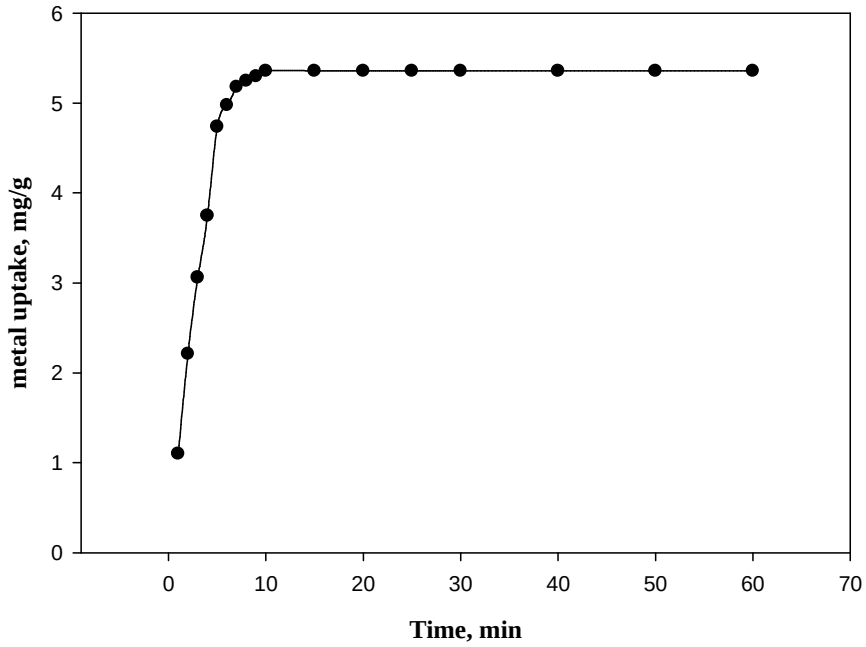

Fig.10. Effect of contact time on chromium uptake by *Ficus Benghalensis* L. for 20 mg/L metal and 0.1 g/30mL of biosorbent concentration.

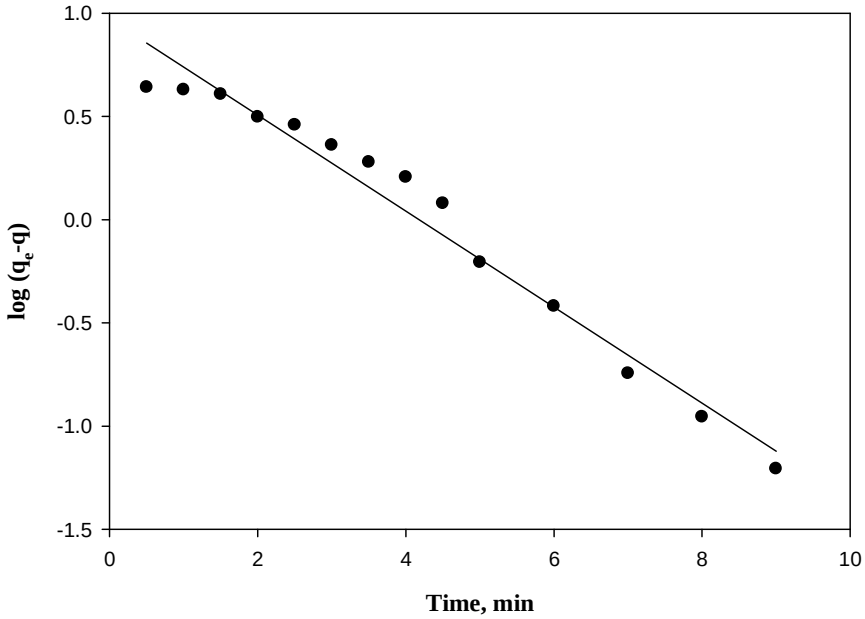

Fig.11. Pseudo-first-order biosorption of chromium by *Ficus Benghalensis* L. for 20 mg/L metal and 0.1 g/30 mL of biosorbent concentration.

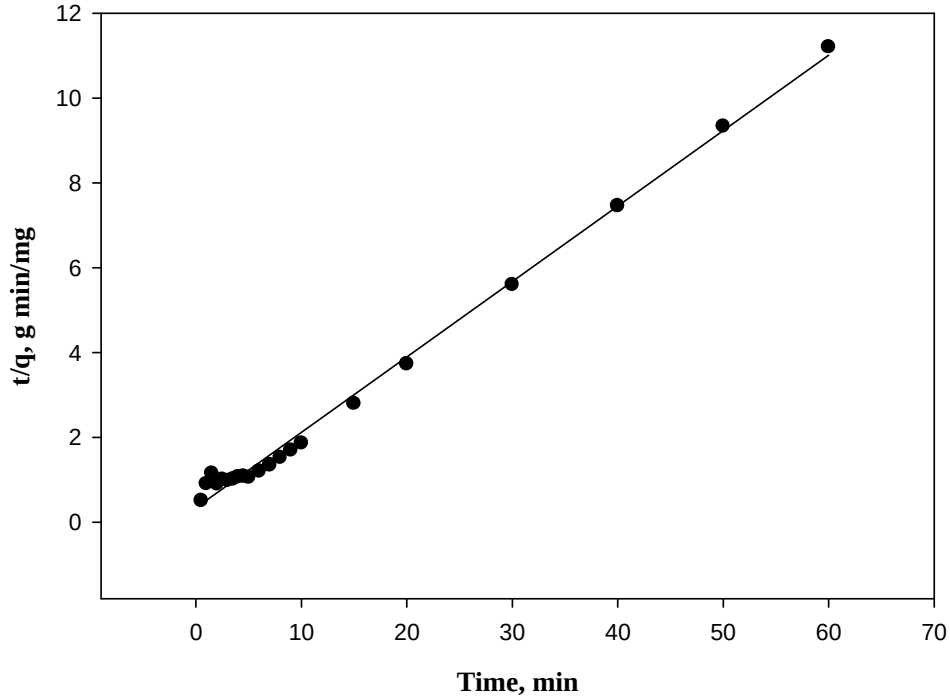

Fig.12. Pseudo-second-order biosorption of chromium by *Ficus Benghalensis* L. for 20 mg/L metal and 0.1 g/30 mL of biosorbent concentration.

Table 1: Langmuir, Freundlich and Temkin isotherm constants and correlation coefficients

Metal ion	Freundlich isotherm			Langmuir isotherm			Tempkin isotherm		
	K_f (mg/g)	n	R^2	b (l/mg)	Q (mg/g)	R^2	A_T (L/mg)	b_T	R^2
Chromium	4.085	0.4379	0.9648	0.1813	17.81	0.9985	1.7922	596.21	0.9951

Table 2: Kinetic constants for chromium onto *Ficus Benghalensis L.*

Initial Concentration (mg/L)	Pseudo – first – order			Pseudo second order		
	$k_1(\min^{-1})$	q_e (mg/g)	R_1^2	$k_2(\min^{-1})$	q_e (mg/g)	R_2^2
20	0.5354	9.3583	0.9669	0.1604	5.711	0.9987

Table 3:Maximum adsorption capacities for chromium adsorption to different adsorbents

Adsorbent material	Adsorption Capacity (mg/L)	pH	References
Na-Mont morillonite	3.61	5	[31]
Crushed concrete fines	33	5.5	[32]
Coir	8.6	5.5	[33]
Barley straw	5.3	5.5	[33]
Peat	11.71	5.5	[33]
Coniferous bark	7.4	5.5	[33]
Sil/PE1/$GA_{0.5}$	32.79	5-6	[34]
Fontinalis antipyretica	14.7	5.0	[35]
Activated carbon	31.11	4.5	[10]
Streptoverticillium cinnamoneum	21.3	5.5	[6]
Aspergillus niger 405	4.70	5.0	[36]
Penicillium digitatum	9.7	5.5	[37]
Streptomyces noursei	1.6	5.8	[38]
Mucor rouxii (live)	4.89	5.0	[39]
Mucor rouxii (Na_2CO_3 pretreated)	3.26	5.0	[39]
Mucor rouxii (NaOH pretreated)	5.63	5.0	[39]
Mucor rouxii ($NaHCO_3$ pretreated)	6.28	5.0	[39]
Pseudomonas syringae	8.0	n.a	[40]
Rhizopus arrhizus	13.5	6-7	[41]
Citrobacter strain MCMB-181	23.62	6.5	[42]
Sargassum sp.	24.35	4.5	[43]
F.Benghalensis.L	18.86	6	Present study

CONCLUSION

1) The present study shows that the *F. Benghalensis L.*was an effective biosorbent for the adsorption of chromium ions from aqueous solution.
2) The effect of process parameters like pH, metal ion concentration, adsorbent dosage and adsorbent size on process equilibrium was studied.
3) The Percentage biosorption of chromium ions by *F. Benghalensis L.*was increased by increasing the pH up to 6
4) The uptake of chromium ions by *F. Benghalensis L.*was increased by increasing the metal ion concentration.
5) The Percentage biosorption of chromium ions by *F. Benghalensis L.*was increased with increasing the adsorbent dosage.

6) The Percentage biosorption of chromium ions by *F. Benghalensis L.*was decreased with increase in the adsorbent size.
7) The adsorption isotherms could be well fitted by the Langmuir equation followed by Temkin equation.
8) The biosorption process could be best described by the second-order equation.

REFERENCES

[1] B. Thomson, W. Turney, *Water Environ. Res.* 67 (**1995**) 527-529.
[2] K. Seki, N. Saito, M. Aoyama, *Wood Sci.Technol*. 31 (**1997**) 441-447.
[3] A. Hong, T. Chen, R. Okey, *Water Environ. Res*. 67 (**1995**) 971-978.
[4] J. Monteagudo, M. Ortiz, *J. Chem. Technol. Biotechnol*. 75 (9) (**2000**) 767-772.
[5] M. Iqbal, R.G.J. Edyvean, *Miner. Eng*. 17 (**2004**) 217-223.
[6] P.R. Puranik, K.M. Paknikar, *J. Biotechnol*. 55 (**1997**) 113-124.
[7] L. Friberg, G.F. Nordberg, B. Vouk. (Eds.), Hand book on the toxicology of Metals, Elsevier, North- Holland, Biomedical Press, Amsetrdam **1979**.
[8] L.Norton, K.Baskaran, S.T. Mckenzie, *Adv. Environ. Res*. 8 (**2004**) 629-635.
[9] K.H. Chong, B. Volesky, *Biotechnol. Bioeng*. 47 (**1995**) 461-460.
[10] D. Mohan, K.P. Singh, *Water. Res*. 36 (**2002**) 2304-2318.
[11] Aksu Z, Gonen, F Demircan. Z., *Process Biochem,* 38 (**2002**) 175-186.
[12] Benguella B, Benaissa H, *Colloid Surf. A: Physicochem Eng. Aspects* 201 (**2002**) 143-150.
[13] Bai, R.S., Abraham, E., *Bioresour. Technol*, 87 (**2003**) 17-26.
[14] Veglio, F., Beolchini, F., *Hydrometallurgy* 44 (**1997**) 301-316.
[15] T.A.Davis. B.Volesky, A.Mucci, *Water Res* 37 (**2003**) 4311-4330.
[16] N. Kuyucak, feasibility of biosorbents application, in: B. Volesky (Ed), Biosorption of heavy Metals, CRC Press, Boca Raton, (**1990**) 371-378.
[17] I. Langmuir, *J. Am. Chem. soc.* 40 (**1916**) 1361-1368.
[18] H.M.F. Freundlich, *J. Phys. Chem*. 57 (**1906**) 385-470.
[19] C. aharoni, M. Ungarish, *J. Chem. Soc. Faraday Trans*. 73 (**1977**) 456-464.
[20] R. Gong,Y.D. Ding, H. Liu, Q. Chen, Z. Liu, *Chemosphere* 58 (**2005**) 125–130.
[21] F.A. Abu Al-Rub, M.H. El-Naas, F. Benyahia, I. Ashour, *Process. Biochem*. 39 (**2004**) 1767–1773.
[22] P.X. Sheng, Y.P. Ting, J.P. Chen, L. Hong, *J. Colloid Interface Sci*. 275 (**2004**) 131–141.
[23] G. Ozdemir, N. Ceyhan, T. Ozturk, F. Akirmak, T. Cosar, *Chem. Eng. J*. 102 (**2004**) 249–253.
[24] A. Iyer, K. Mody, B. Jha, *Mar. Pollut. Bull*. 49 (**2004**) 974–977.
[25] Y. Sag, A. Kaya, T. Kutsal, *Hydrometallurgy* 50 (3) (**1998**) 297–314.
[26] J.L. Zhou, P.L. Huang, R.G. Lin, *Environ. Pollut*. 101 (1) (**1998**) 67–75.
[27] J.T. Matheickal, Q. Yu, *Bioresour. Technol*. 69 (**1999**) 223–229.
[28] K.G. Bhattacharyya, A. Sharma, *J. Hazard. Mater*. B113 (**2004**) 97–109.
[29] S. Lagergren, S. Kungliga Svenska Ventenskapsakademiens, Handlingar, Band 24(4) (**1898**) 1.
[30] Y.S. Ho, E. McKay, *Can. J. Chem. Eng*. 76 (**1998**) 822–827.
[31] O. Abollino, M. Aceto, M. Malandrino, C. Sarzanini, E. Mentasti, *Water Res*. 37 (**2003**) 1619–1627.
[32] N.J. Coleman, W.E. Lee, I.J. Slipper, *J. Hazard. Mater*. B121 (**2005**) 203–213.

[33] C. Kathrine, H.C.B. Hansen, *Bioresour. Technol*. (**2006**).
[34] M. Ghoul, M. Bacquet, M. Morcellet, *Water Res.* 37 (**2003**) 729–734.
[35] R.J.E. Martins, R. Pardo, R.A.R. Boaventura, *Water Res.* 38 (**2004**) 693– 699.
[36] Z. Filipovic-Kovacevic, L. Sipos, F. Briski, *Food Technol*. 38 (**2000**) 211–216.
[37] M. Galun, E. Galun, B.Z. Siegel, P. Keller, H. Lehr, S.M. Siegel, *Water Air Soil Pollut*. 33 (**1987**) 359–371.
[38] B. Mattuschka, G. Straube, *J. Chem. Technol. Biotechnol*. 58 (**1993**) 57–63.
[39] G. Yan, T. Viraraghavan, *Water SA* 26 (**2000**) 119–123.
[40] J.P.S. Cabral, *Microbios* 71 (**1992**) 47–53.
[41] E. Fourest, J. Roux, *Appl. Microbiol. Biotechnol*. 37 (**1992**) 399–403.
[42] P.R. Puranik, K.M. Paknikar, *Biotechnol. Prog*. 15 (**1999**) 228–237.
[43] A.J.P. Esteves, E. Valdman, S.G.F. Leite, *Biotechnol. Lett*. 22 (**2000**) 499–502.