ISSN: 0975-8585

Research Journal of Pharmaceutical, Biological and Chemical Sciences

Biosorption of Cd (II) and Pb (II) ions from Aqueous Solutions Using *Carissa carandus*

Amrita Tanwar*, Goswami SP, Arora SK, Mathur SP

Material Research Laboratory, Department of Chemistry, Government College, Ajmer. M.D.S. University, Ajmer-305001, Rajasthan, India.

ABSTRACT

In the present work an attempt has been made to remove Cd (II) and Pb (II) from aqueous solution by using *Carissa carandus* Stem Bark (CcSB) as an inexpensive biosorbent. Various parameters such as initial metal concentration (5-25mg/L), biosorbent dosages (1-3g/L), pH (2-8) and contact time (30-240min.) having an impact on adsorption efficiency were studied. Equilibrium contact time was found to be 150 minutes in the case of Cd (II) while in the case of Pb (II) it was attained after 210 minutes. The pH (6) was found optimum for adsorption of Cd (II) and Pb (II). These metals show maximum removal capacity at 2.0g/L (adsorbent dosage) and 10-15mg/L (initial metal concentration). The adsorption data were modeled by using both Langmuir and Freundlich classical adsorption isotherm. The data are better fitted by the Freundlich isotherm as compared to Langmuir and the adsorption capacity (Q_m) was found to be 32.84 mg/g and 80.99 mg/g for Cd(II) and Pb(II) respectively.

Keywords: Biosorption, *Carissa carandus* stem bark, Cd(II) and Pb(II) removal, Adsorption isotherm

Corresponding author

INTRODUCTION

Environmental contamination by heavy metals is a serious growing problem throughout the world. Human exposure to heavy metals has risen dramatically in the last 50 years as a result of an exponential increase in metallic substance in aquatic environment [1]. Heavy metal ions such as Zn, Cd, Hg, Cu, Pb etc. are highly toxic and can cause damaging effects even at very low concentration. They tend to bioaccumulate in the food chain and can be highly dangerous to human health [2]. Cd(II) accumulates mainly in the kidney and liver. It is carcinogenic and an endocrine disruptor. Long-term exposure to Cd leads to several morphopathological- changes in the kidneys. Ca excretion increased by Cd exposure in animals and humans [3]. Cd is more toxic to bone metabolism of women [4]. Cadmium enters into the aqueous environment through wastewater from cadmium plating industries, Cd-Ni batteries, control rods within nuclear reactors and television phosphors. Cd(II) is a common impurity in phosphate fertilizers [5].

Pb is a cumulative tissue poison and gets stored in bones, liver, kidney and brain. Direct ingestion of lead leading to increased blood lead levels, accumulated lead acts as a significant source of blood lead burden [6]. There are various sources of lead such as storage batteries, plumbing, cable coverings, X-ray equipment etc.

Various physio-chemical methods have been developed for removal of heavy metals from contaminated water, which include chemical precipitation, membrane processes (reverse osmosis, nanofiltration, etc.), solvent extraction, ion exchange, electrofloatation [7,8]. However, these processes may be ineffective or expensive, especially when the heavy metal ions are in solution containing in the order of 1-100 mg/L [9]. Adsorption is the most widely used process and present in many natural, physical, biological and chemical systems. Commercial Activated Carbon (CAC) has been widely used adsorbent for treatment of waste water [10,11]. However, it is an expensive adsorbent and need to complexing agents to improve its removal efficiency. This problem has lead to investigate various low-cost adsorbents including chitosan [12], zeolites [13], fly ash [14], clay [15], bone char [16], peat moss [17] etc.

Bioadsorption [18] has become familiar for many researchers as an alternative pathway for heavy metal removal. The various biosorbents were evaluated includes bacteria [19], fungi [20], algae [21], plant products (papaya wood [22], sunflower stem [23], rice husk [24], black tea leaves [25] etc.). These have shown adequate capacity for heavy metal removal from contaminated water at low cost.

In the present investigation, stem bark of *Carissa carandus* has been used as biosorbent for removal of Cd(II) and Pb(II) from aqueous solution. Various experimental conditions such as initial metal concentration, biosorbent dosages, pH and contact time were studied and the isotherms were tested for Langmuir and Freundlich equations.

Experimental

Preparation of Adsorbent

The stem bark of *Carissa carandus* was obtained from Foysagar Telephone Exchange, Ajmer, Rajasthan, India. It was washed by double-distilled water to remove dust and particulate materials from its surface. The substance was dried at room temperature in shade for 10 days and then in an air oven at 120^{o} C for 72 hours. It was grinded into fine powder in a mechanical grinder and sieved to a particle size of 0.3-0.5 mm. The adsorbent was stored in polypropylene jars for further experiments.

Illustration.1 *Carissa carandus* Stem Bark (CcSB)-Particle size of (0.3-0.5 mm)

Preparation of Stock solution

The stock solutions of Cd(II) (1000ppm) and Pb(II) (1000ppm) were prepared by dissolving $CdSO_4$ and $PbSO_4$ respectively in double distilled water. The analytical grade salts were used for analysis. The desired solutions were obtained by diluting the stock solution in double distilled water. The pH of the solution was adjusted using M/10 HCl and M/10 NaOH.

Biosorption experiments

The biosorption studies were conducted by using desired quantities of the bio adsorbent (stem bark powder of *Carissa carandus*) added to 100 mL of heavy metal solution in a 250 mL conical flask at room temperature. The samples were placed on a rotary shaker at 300 rpm and taken at regular intervals. The adsorption experiments were carried out by varying contact time (30-240 minutes), metal –ion concentration (5-25 mg/L), pH (2-8) and also the biosorbent dosages (1-3 g/L).

The samples were filtered through Whatman No.42 and the concentration of the residue heavy metal solution was determined by using ECIL Atomic Absorption Spectrophotometer.

All the experiments were performed triplicate to assess reproducibility.

Adsorption equilibrium [26] was calculated by using

$$q_e = (C_0 - C_e)\,V \,/\, W \qquad (1)$$

Where:

q_e = metal concentration retained in the adsorbent phase (mg/g)

C_0 = initial concentration of metal ion in solution (mg/L)

C_e = equilibrium concentration of metal ion in solution (mg/L)

V = volume of liquid (L)

W= weight of the adsorbent (g)

RESULTS AND DISCUSSION

Effect of Contact Time

The effect of contact time on the uptake of the studied cations onto the biosorbent is shown in the Fig. 1. This was achieved by varying the contact time from 30 – 240 minutes at room temperature (298K).

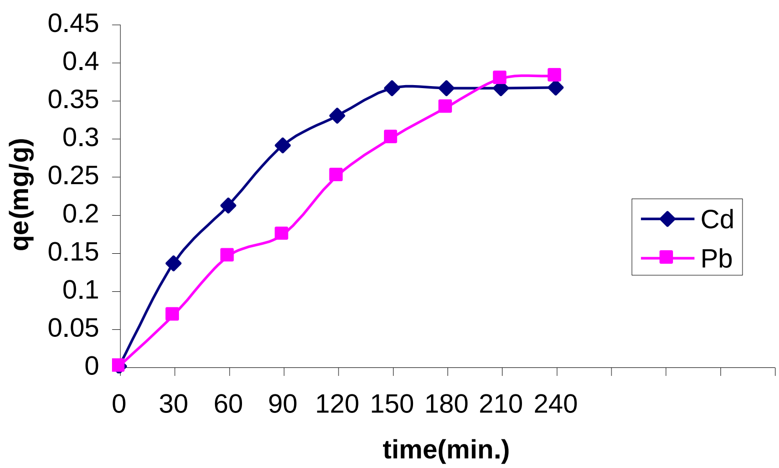

Fig. 1 Effect of contact time

Equilibrium contact time was found to be 150 minutes in the case of Cd(II) while in the case of Pb(II) it was attained after 210 minutes. The removal efficiency for Cd and Pb at these contact times was 73.01% and 75.65% respectively. Fig. 1 shows that biosorption of Cd and Pb increased with increase in contact time to some extent due to vacant sites on biosorbent. The rate of adsorption of metals gradually decreased with increase in contact time due to decrease of sorption sites.

Effect of pH

The pH of the metal solution was a key parameter for biosorption of Cd(II) and Pb(II). Optimization of pH was done at pH range (2-8). According to Fig. 2 at a low pH<=2 adsorption of metals is negligible with increasing pH in the range of 4.0 to 6.0 metal uptake on biosorbent also increases but different proportion depending on the metals until reaching a plateau.

At lower pH the H^+ ions are much more than metal ions so they compete powerfully with metal ions for active sites of biosorbent, thus resulting their adsorption decrease. At higher pH the effect of competition from H^+ ions decreases and the metal ions get adsorbed on surface of adsorbent, resulting an increase in the metal uptake. For the rest of experiments the optimum pH of 6.0 was chosen for adsorption of Cd(II) and Pb(II).

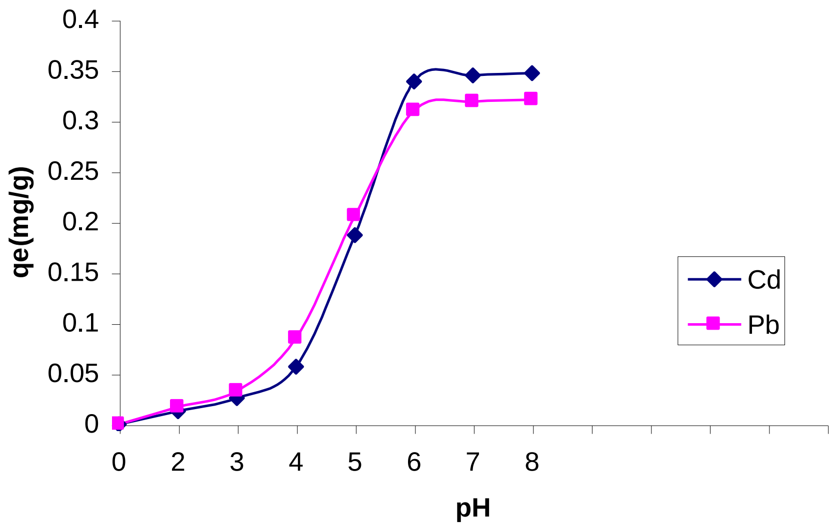

Fig. 2 Effect of pH

Effect of Adsorbent Dosages

The effect of adsorbent dosages on removal of Cd(II) and Pb(II) has been presented in Fig. 3. The experiments were carried out by varying the biosorbent dosages from (1.0-3.0g/L). The sorption capacity of biosorbent increases with increasing the adsorbent dosages. This is due the availability of more functional groups and surface area at higher dosages. It was observed that Cd(II) shows 40.63% adsorption at an adsorbent dosage of 1.0g/L but at a higher dosage of 2.0g/L a removal efficiency of 70.91% is achieved.

On further increasing the adsorbent dosage to 3.0g/L an increasing trend in removal efficiency is observed but it is slightly higher than that obtained at an adsorbent dose of 2.0g/L. In case of Cd(II) and Pb(II) maximum removal was attained at 2.0g/L of adsorbent weight.

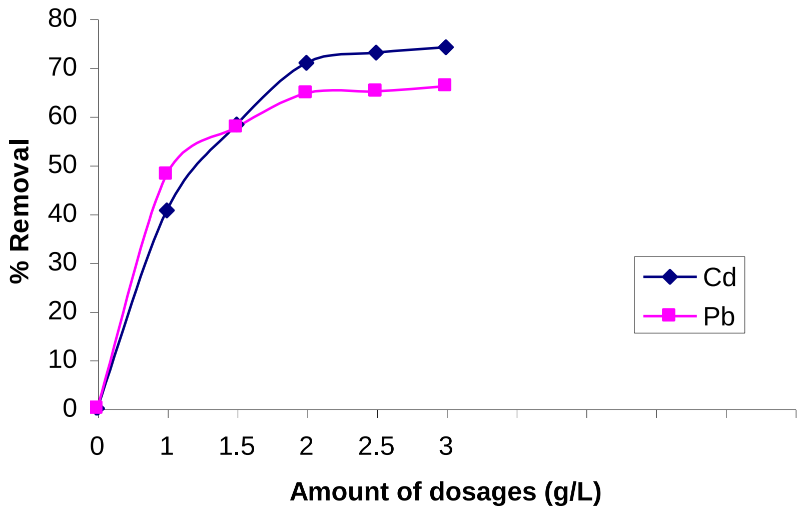

Fig. 3 Effect of adsorbent dosages

Effect of Adsorbate Initial Concentration

Studies were performed with Cd(II) and Pb(II) with initial concentrations ranging from 5 to 25 mg/L at a pH of 6.0, with a biosorbent dosage of 2.0 g/L. It was observed that there is a decrease of the removal percentage with increase in initial metal concentrations from 5 to 25 mg/L. (Fig. 4). It may be explained on the basis that at lower concentrations of metal ions more adsorption sites are available on adsorbent but at higher concentration competing metal ions are increased for the available adsorption sites [9]. The percentage removal of Cd(II) and Pb(II) remained constant at initial metal concentrations of 15-25mg/L

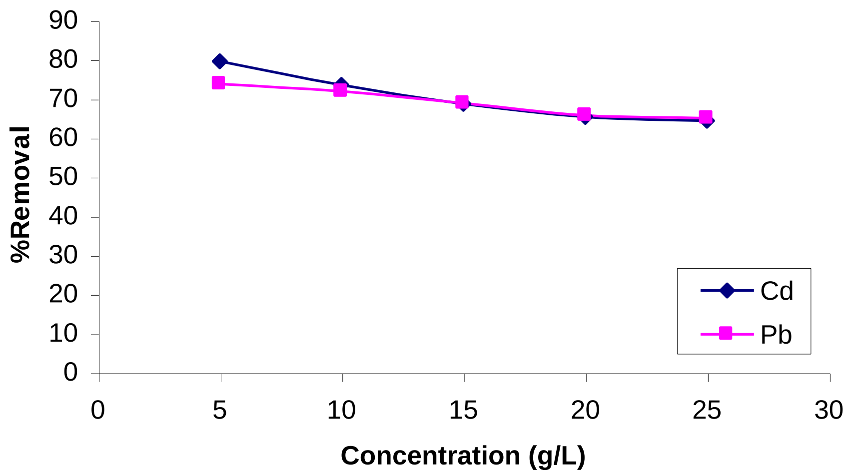

Fig. 4 Effect of adsorbate initial concentration

Adsorption Isotherm Models

Langmuir Isotherm

The Langmuir isotherm [27] is represented by the following equation

$$C_e / q_e = C_e / Q_m + 1 / Q_m b \qquad (2)$$

Where

C_e = equilibrium concentration of solute (mg/L)

q_e = the amount of solute adsorbed at equilibrium time (mg/g)

Q_m = adsorption capacity (mg/g)

b = free energy of adsorption

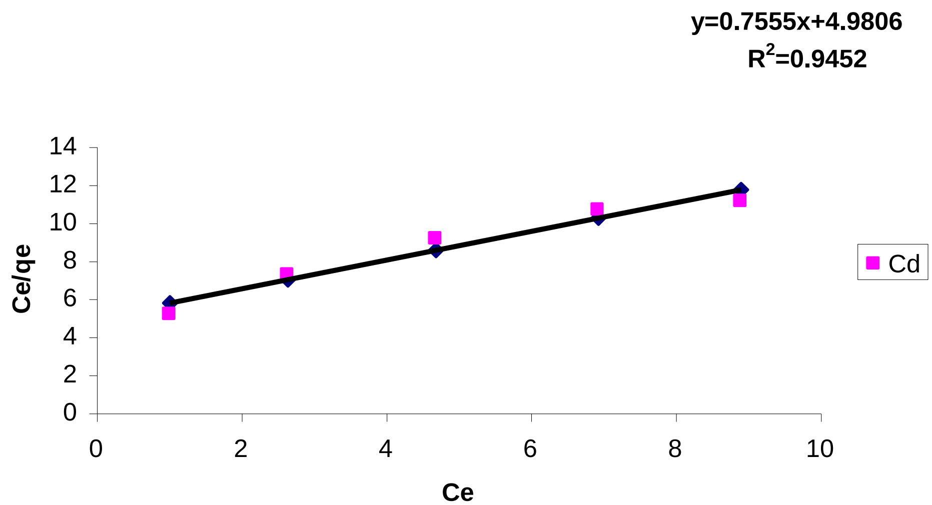

Fig 5 Langmuir Adsorption Isotherm of Cd

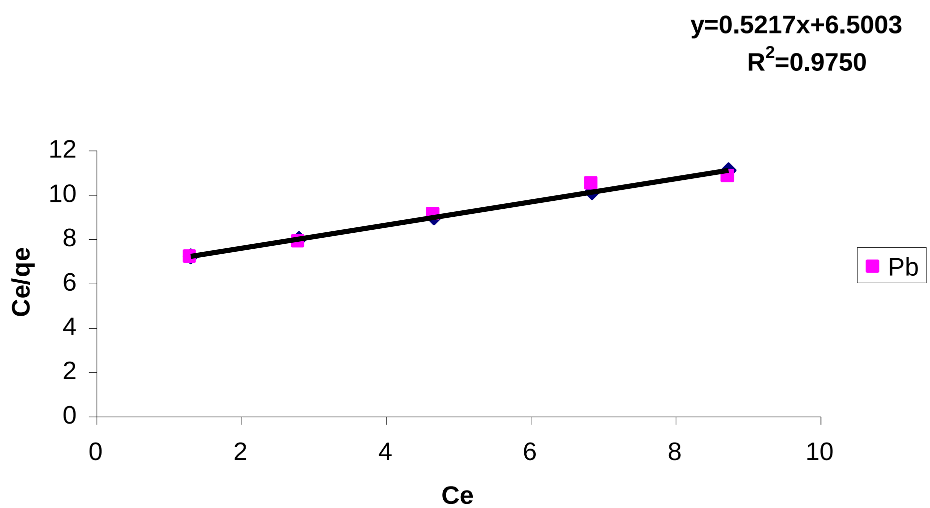

Fig 6 Langmuir Adsorption Isotherm of Pb

ISSN: 0975-8585

Freundlich Isotherm

The Freundlich isotherm [27] may be written a

$$\log q_e = \log K_f + 1/n \log C_e \qquad (3)$$

Where

C_e = equilibrium concentration of solute (mg/L)
q_e = the amount of solute adsorbed at equilibrium time (mg/g)
K_f = indicator of sorption capacity (mg/g)
$1/n$ = intensity of the sorption

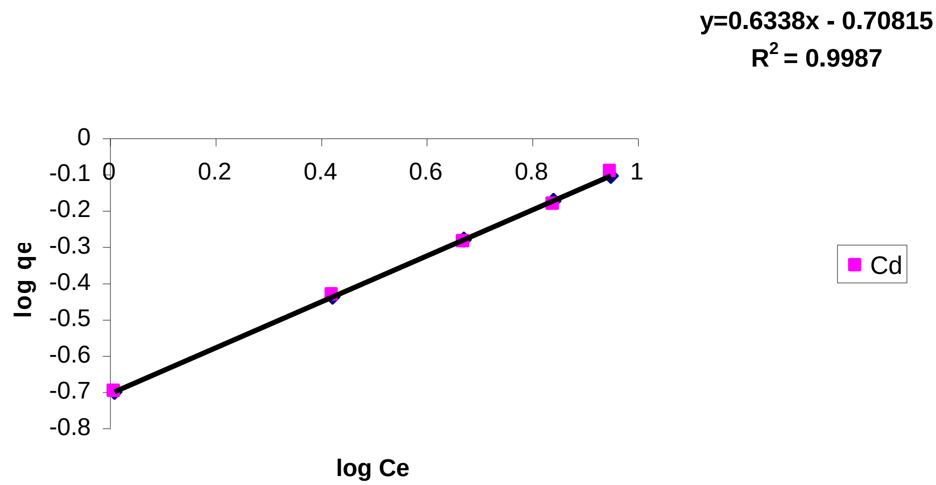

Fig. 7 Freundlich Adsorption Isotherm of Cd

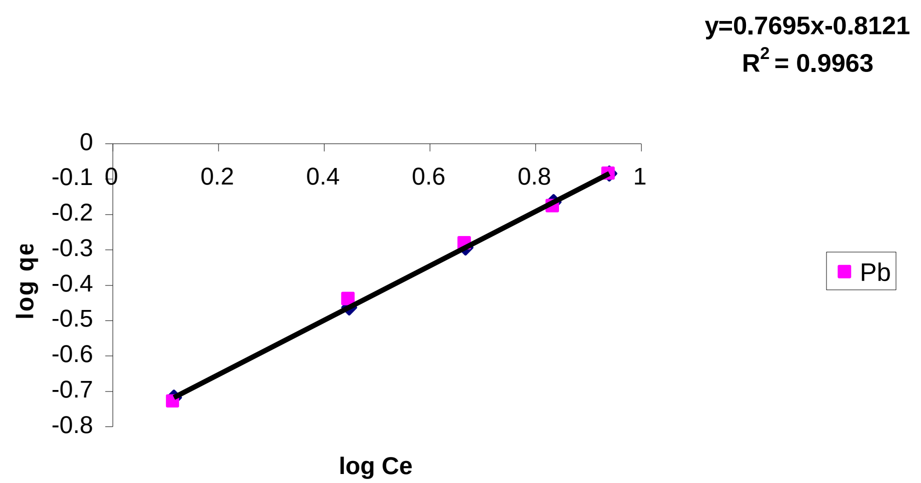

Fig. 8 Freundlich Adsorption Isotherm of Pb

The isotherm adsorption data shown in Fig. 5,6 and in Fig. 7,8 are fitted to obtain the Langmuir and Freundlich isotherm model parameters. The parameters are represented in Table 1.

Results show that the adsorption of Cd(II) and Pb(II) are best explained by Freundlich model as the value of correlation regression (R^2)for both metals are 0.9987 and 0.9963 respectively.

Table 1: Langmuir and Freundlich constants

Elements	Langmuir			Freundlich		
	Q_m	b	R^2	K	n	R^2
Cd	32.84	0.1516	0.9452	0.493	1.5777	0.9987
Pb	80.99	0.0802	0.9750	0.444	1.2995	0.9963

Table 2: Adsorption capacities of Cd(II) on various adsorbents

Biosorbents	Adsorption Capacity (mg/g)	References
Coconut copra meal	1.7	28
Bengal gram husk	39.99	29
Jack fruit peel	52.08	30
Rice husk (NaOH treated)	20.2	24
Sugar beet pulp	17.2	31
CcSB	32.84	Present study

Table 3: Adsorption capacities of Pb(II) on various adsorbents

Biosorbents	Adsorption Capacity (m g/g)	References
Bengal gram husk	49.97	29
Coir fibers	18.9	32
Hop leaf &stem biomass	74.2	33
Maize bran	142.86	34
Rice husk	8.6	35
CcSB	80.99	Present study

CONCLUSIONS

The current investigation shows that *Carissa carandus* stem bark is very effective biosorbent in removal of Cd(II) and Pb(II) ions. The adsorption of Cd(II) and Pb(II) ions are dependent on initial concentration of the metal ion, adsorbent dosages, pH and the contact time. In adsorption isotherm analysis, the Freundlich isotherm model well described the adsorption of both the metals. Hence, this biosorbent can be used as a low cost adsorbent in the treatment of wastewater containing Cd(II) and Pb(II) ions.

ACKNOWLEDGEMENTS

The author and investigator, Amrita Tanwar, of this project is thankful to the Principal, Head of Department of Chemistry, Government College Ajmer, for providing laboratory facilities and to Scientist Emeritus Guide Dr. S.P. Mathur for guiding in excellent way, for scientific sources.

REFERENCES

[1] Budinova TK, Gergova KM, Petrov NV, Minkova VN. J Chem Technol Biotechnol 1994; 60: 177-182.
[2] Ahluwalia SS, Goyal D. Bioresour Technol 2007; 98 (12): 2243-2257.
[3] Wu X, Jin T, Wang Z, Ye T, Kong Q, Nordberg G. J Occup Environ Med 2001; 43: 898-904.
[4] Jarup L. Br Med Bull 2003; 68: 167-182.
[5] Awofolu OR, Mbolekwa Z, Mtshemla V, Fatoki OS. Water SA 2005; 31: 87-94.
[6] Swarup D, Patra RC, Naresh R, Kumar P, Shekhar P. Science of the total environment 2005; 115 (1-3): 67-71.
[7] Kaewsarn P, Yu Q. Sep Sci Technol 1999; 34 (8): 1595-1605.
[8] Benjamin MM, Hayes KF, Leckic JO. J Water Pollut Contr Fed 1982; 54: 1472-1481.
[9] Bhatti HN, Mumtaz B, Hanif MN, Nadeem R. Process Biochem 2007; 42: 547-553.
[10] Monser L, Adhoum N. Sep Purif Technol 2002; 26: 137-146.
[11] Shim JW, Park SJ, Ryu SK. Carbon 2001; 39: 1635-1642.
[12] Jha IN, Iyengar L, Rao AVSP. J Environ Eng 1988; 114: 962-974.
[13] Kesraoui SO, Cheeseman CR, Perry R. J Chem Technol Biotechnol 1994; 59: 6-121.
[14] Panday KK, Prasad G, Singh VN. Water Res 1985; 19 (7): 869-873.
[15] Tasi T, Vesilind PA. J Environ Sci Health 1999; 34 (1): 24-103.
[16] Cheung CW, Porter JF, Mckay G. J Chem Technol Biotechnol 2000; 75: 70-963.
[17] Gosset T, Trancart JL, Thevenot DR. Water Res 1986; 20: 21-26.
[18] Ghani NT, Elchaghaby GA. Int J Environ Sci Tech 2007; 4 (4): 451-456.
[19] Dursan AY, Usla G, Cuci Y, Aksu Z. Process Biochem 2003; 38: 1647-1651.
[20] Tsezos M, Volesky B. Biotechnol Bioengg 1982; 24: 955-969.
[21] Sheng PS, Ting YP, Chen JP, HongL. J Colloid Interface Sci 2004; 275: 131-141.
[22] Saeed A, Akhtar MW, Iqbal M. Separat Purific Technol 2005; 45: 25-31.
[23] Malik UR, Hasany SM, Sabhani MS. Talanta 2005; 66: 166-173.
[24] Kumar U, Bandyopadhyay M. Biores Technol 2006; 97: 104-109.
[25] Kumita M, Hossain MA, Michigami Y, Mori S. Adsorption 2005; 1: 561-568.
[26] Mohan D, Singh KP. Water Res 2002; 36: 2304-2318.
[27] Rao MM, Reddy DHKK, Venkateswarlu P, Scshaiah K. J Environ Manage 2009; 90 (1): 634-643.
[28] Ofomaja AE, Ho YS. J Hazard Mater 2006; 139 (2): 356-362.
[29] Sadeed A, Iqubal M, Akhtar MW. J Hazard Mater 2005; 117: 65-73.
[30] Inbaraj BS, Sulochana N. Biores Technol 2004; 94: 49-52.
[31] Zacaria R, Gerente C, Andres Y, Cloirec PL. Environ Sci Technol 2002; 36: 2067-2073.

[32] Conrad K, Hansen HCB. Biores technol 2007; 98: 89-97.
[33] Gardea-Torresdey J, Hejazi M, Tiemann K, Parsons JG, Duarte-Gardea M, Henning J. J Hazard Mater 2002; 91: 95-112.
[34] Singh KK, Talat M, Hasan SH. Biores Technol 2006; 97: 2124-2130.
[35] Zulkali MMD, Ahmed AL, Norulakmal NH. Biores Technol 2006; 97: 21-25.