

Removal of Copper (II) from Aqueous Solutions Using Teak (*Tectona grandis* L.f) Leaves

S. Rathnakumar, R. Y. Sheeja, and T. Murugesan

Abstract—The experiments were performed in a batch set up under different concentrations of Cu (II) (0.2 g.l^{-1} to 0.9 g.l^{-1}), pH (4-6), temperatures (20°C – 40°C) with varying teak leaves powder (as biosorbent) dosage of 0.3 g.l^{-1} to 0.5 g.l^{-1} . The kinetics of interactions were tested with pseudo first order Lagergran equation and the value for k_1 was found to be $6.909 \times 10^{-3} \text{ min}^{-1}$. The biosorption data gave a good fit with Langmuir and Freundlich isotherms and the Langmuir monolayer capacity (q_m) was found to be $166.78 \text{ mg. g}^{-1}$. Similarly the Freundlich adsorption capacity (K_f) was estimated as 2.49 l g^{-1} . The mean values of the thermodynamic parameters ΔH , ΔS , and ΔG were $-62.42 \text{ KJ. mol}^{-1}$, $-0.219 \text{ KJ.mol}^{-1} \text{ K}^{-1}$ and $-1.747 \text{ KJ.mol}^{-1}$ at 293 K from a solution containing 0.4 g l^{-1} of Cu(II) showing the biosorption to be thermodynamically favourable. These results show good potentiality of using teak leaves as a biosorbent for the removal of Cu(II) from aqueous solutions.

Keywords—Teak leaves, Cu(II) removal, biosorption, Lagergran, Langmuir, Freundlich isotherm.

I. INTRODUCTION

HEAVY metals are stable and are persistent environmental contaminants. They have a tendency to accumulate in the soil, sea water, fresh water and sediments due to their high dispersion from where they enter into the food chain. Being toxic, they have adverse effects on the environment and human health [1]. These metals are directly or indirectly discharged into the environment and resulting in serious environmental pollution [2]. Copper is a toxic heavy metal discharged into the environment due to industrial operations carried out by brass industries, electrical goods production, electrodeposition of metals, metallurgical processes, copper-ammonium rayon industries, mining and battery manufacturing[3] and agricultural activities[4]. Natural source of copper exposure include windblown dust, volcanic emissions, decaying vegetation, forest fire and sea spray. Anthropogenic emissions include smelters, iron foundries, power plant stations and incinerators [5]. Copper present in industrial waste is primarily in the form of bivalent Cu (II) as a hydrolysis product or as CuCO_3 or in the form of organic complexes. In copper cleaning, copper plating and metal processing industries Cu (II) concentrations may approach 0.1 - 0.12 g.l^{-1} , which has to be reduced to 0.0010 - 0.0015 g.l^{-1}

according to water quality standards to render the waste water to be free from the toxicity[6]. Beyond the threshold concentration of $>0.002 \text{ g.l}^{-1}$ they become toxic to plants and animals[7]. The excessive intake of copper (II) results in its accumulation in the liver causing gastrointestinal problems, kidney damage and anaemia [8]. The search for new technologies involving the removal of toxic metals from waste water has directed attention to biosorption, based on metal binding capacities of various biological materials.

Biosorption can also be defined as the ability of biological materials to accumulate heavy metals from wastewater through metabolically mediated or physico-chemical pathways of uptake [9]-[11]. The various biological materials that has been investigated includes bacteria [12], fungi [13], yeast [14], microalgae and macroalgae[15] seaweeds, shells of aquatic and terrestrial organisms[16]. All these materials have shown adequate capacity for the sorption of heavy metals. Biosorption of heavy metals by these biological materials involves several mechanisms that differ qualitatively and quantitatively depending upon the species used, the origin of biomass and its processing procedure [17].

In the present work, biosorption of Cu (II) was studied using dried teak leaves as biosorbent at various initial Cu(II) concentration, pH, temperature and biosorbent dosage. Sorption isotherms were studied and the isotherms were tested for Lagergran, Langmuir and Freundlich equations.

II. MATERIALS AND METHODS

Mature teak leaves were collected from trees in Chennai, southern part of India and were washed repeatedly with water to remove dust and other soluble impurities and dried at room temperature in shade and then in an air oven at 343 K for 30 hours till the leaves became crisp[18]. These were crushed into fine powder in a mechanical grinder and sieved to a particle size of approximately $70.0 \mu\text{m}$. It was then washed further with double distilled water till the washings were free from colour and turbidity. It was then dried and preserved for further use.

Analytical grades of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ were purchased from Merck, India. Aqueous copper solution were prepared by dissolving its corresponding sulphate salt in distilled water. The pH of the solutions was adjusted using 0.1 M HCl and 0.1 M NaOH . All the experiments were carried out in duplicate and the average values are reported. For biosorption studies, desired quantities of the chosen biosorbents (teak leaves powder) were mixed with 100 ml of Cu(II) solution in a

S. Rathnakumar and R. Y. Sheeja are with Department of Chemistry, Anna University, Chennai 60 025, India.

T. Murugesan is with Chemical Engineering Department, Universiti Teknologi PETRONAS, Bandar Seri Iskandar, 31750, Tronoh, Malaysia (e-mail: murugesan@petronas.com.my).

250 ml Erlenmeyer flasks. The flasks were placed on a rotary shaker at 150 rpm and the samples were taken at regular time intervals. The experiments were carried out at different initial Cu(II) concentrations (0.2 - 0.9 g.l⁻¹), pH (4-6), temperature (20 - 40°C) and also by varying the biosorbent dosage (0.3 - 0.5 g.l⁻¹). The samples were then centrifuged at 3000 rpm for 10 minutes. The Cu (II) content in the supernatant was determined according to the standard methods of analysis using UV-Visible spectrophotometer at $\lambda_{\text{max}} = 457 \text{ nm}$.

III. RESULTS AND DISCUSSION

A. Effect of Initial Metal Concentration

Biosorption of copper using teak leaves powder was carried out at various initial copper (II) concentration namely (0.2g.l⁻¹, 0.4 g.l⁻¹, 0.6 g.l⁻¹ and 0.9 g.l⁻¹) at a pH of 6, with a biosorbent dosage of 0.5 g.l⁻¹ at a temperature of 20°C.

Biosorption rate was found to be fast and was completed within 5 hours. Increase in the initial metal concentration resulted in the decrease in the percentage sorption (as shown in Table I) and increasing the initial metal concentration from 0.2 g.l⁻¹ to 0.9 g.l⁻¹, the metal uptake (q) increased from 29.71 mg g⁻¹ to 100.28 mg.g⁻¹. At lower concentration of the Cu(II) ion (i.e. 0.2 g.l⁻¹), the ratio of the initial moles of metal ions to the available surface area was low and subsequently, the fractional sorption became independent of initial metal concentration. However, at higher concentration of Cu(II) ion, the available sites for sorption became fewer compared to the moles of metal ions present and hence the percentage sorption of metal would be dependent upon the initial metal concentration[19]-[21]

B. Effect of pH

The pH of the metal solution played an important role in the biosorption of copper (II). Optimization of pH was done at pH 4, 5 and 6 and it was observed that biosorption was insignificant at acidic pH (pH = 4), but increased continuously from moderately acidic pH to nearly neutral condition as pH affects the solubility of the metal ions.

With an increase in pH, percentage sorption and metal uptake (q) also increased. At lower pH values (pH ≤ 5.0), the surface charge on the biomass is positive and biosorption was not favourable and also the H⁺ ions competes strongly with metal ions for active sites in the biosorbent[22]. Increase in pH results in the electrostatic repulsion between the cations and surface sites thereby the competing effect of the H⁺ ions decreases and the positively charged Cu (II) ions gets

adsorbed on the free binding sites, resulting an increase in the total metal uptake.

C. Effect of Biosorbent Dosage

Biosorption experiments were performed at different biosorbent dosages namely 0.3 g.l⁻¹, 0.4 g.l⁻¹ and 0.5 g.l⁻¹ of teak leaves powder. The sorption efficiency increased with an increase in biosorbent dosage and the results are given in Table I. This is due to an increase in the surface area of the biosorbent which in turn increases the number of binding sites [25]. However, at high sorbent dosages (D = 0.5 g.l⁻¹), the available metal ions are insufficient to cover all the exchangeable sites on the biosorbent, resulting in low metal uptake.

D. Effect of Temperature

The biosorption of Cu(II) at different temperatures namely 20°C, 30°C and 40°C were studied. The biosorption was found to decrease with increase in temperature (Table I) and the sorption capacity (q) was also found to decrease, there by biosorption affinity also decreases at higher temperature (i.e.) 40°C. The interactions are found to be exothermic in nature [18],[23] for which the evaluation of thermodynamic parameters were carried out.

E. Evaluation of Thermodynamic Parameters

Thermodynamic parameters namely ΔG , ΔH and ΔS were calculated at constant temperature using the following relation.

$$\Delta G = -RT \log K \quad (1)$$

$$\Delta G = \Delta H - T\Delta S \quad (2)$$

Where $K = q_e / c_e$

q_e - Metal uptake (or) sorption capacity at equilibrium (mg.g⁻¹)

c_e - Concentration of metal ion at equilibrium (g.l⁻¹).

R - Gas constant

T - Absolute temperature in K

Fig. 1 shows the plot of log K versus 1/T at different initial Cu (II) concentrations and the values of the estimated thermodynamic parameters are given in Table II. The negative value of ΔG confirms the feasibility of the reaction and the spontaneous nature of sorption and the negative value of ΔH indicates the sorption reaction to be in agreement with the exothermic nature of interactions [24].

TABLE I
EXTENT OF BIOSORPTION OF CU(II) USING TEAK LEAVES POWDER

C ₀ g.l ⁻¹	% sorption	q mg g ⁻¹	pH	% sorption	Q mg.g ⁻¹	T (°C)	% sorption	Q mg g ⁻¹	D (g.l ⁻¹)	% sorption	q mg g ⁻¹
0.2	73.76	29.71	4	26.52	21.14	20	68.97	54	0.3	53.33	68.57
0.4	68.97	54	5	41.69	33.72	30	55.35	42.86	0.4	61.54	60
0.6	66.1	66.86	6	68.97	54	40	51.26	40.57	0.5	68.97	54
0.9	57.56	100.28									

TABLE II
THERMODYNAMIC PROPERTIES FOR THE BIOSORPTION OF Cu(II) AT
DIFFERENT CONCENTRATIONS (BIOADSORBANT DOSAGE(D) = 0.5 g.l⁻¹)

Co g.l ⁻¹	ΔH KJ mol ⁻¹	ΔS KJ mol ⁻¹ K ⁻¹	ΔG (KJ mol ⁻¹)		
			293 K	303 K	313 K
0.2	-62.42	-0.219	-1.747	-3.937	-6.127
0.4	-31.22	-0.119	-1.889	-3.019	-4.149
0.6	-22.34	-0.083	-1.979	-2.809	-3.639
0.9	-2.07	-0.018	-3.204	-3.384	-3.564
mean	-29.51	-0.108	-2.204	-3.287	-4.369

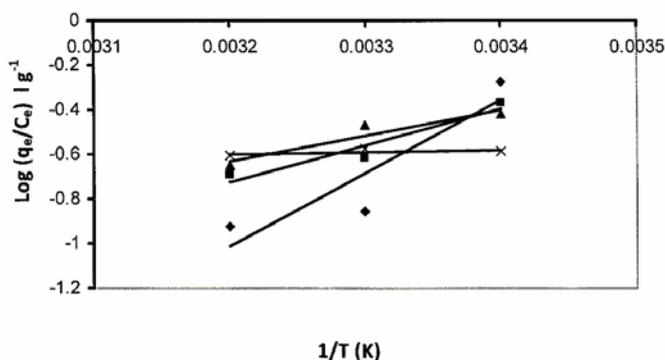


Fig. 1 Plot of log K versus 1/T for the adsorption of copper(II) at different concentrations (♦) 0.2 g l⁻¹, (■) 0.4 g l⁻¹, (▲) 0.6 g l⁻¹, (×) 0.9 g l⁻¹ biosorbent (teak leaves) dosage (D) - 0.5 g l⁻¹

F. Kinetics of Biosorption

The kinetics of interactions were studied by determining the amount of Cu(II) adsorbed at different agitation times for various dosages of teak leaves powder viz., 0.3 g.l⁻¹, 0.4 g.l⁻¹ and 0.5 g.l⁻¹ for an optimum copper (II) concentration of 0.4 g.l⁻¹. The kinetics was tested with respect to the pseudo first order model of Lagergren given by the equation:

$$\log(q_e - q_t) = \log q_e - (k_1 / 2.303) * t \quad (3)$$

where

- q_t - amount of Cu(II) biosorbed at time t (mg g⁻¹)
- q_e - amount of Cu(II) biosorbed at equilibrium (mg g⁻¹)
- k_1 - pseudo first order rate constant (min⁻¹)

Plots of $\log(q_e - q_t)$ versus time (t) (Fig. 2) were found to be linear and the pseudo first order rate constant was obtained from the slopes of the best fit lines (correlation coefficient, R² = 0.97 to 0.99) and it was found that the biosorption of Cu(II) using follows first order kinetics and the pseudo first order rate constant values are given in Table III.

At constant temperature the extent of biosorption depends on the amount of biosorbent added as well as on Cu (II) concentration. The percentage sorption increased when more amount of biosorbent namely teak leaves powder was added, but decreased when Cu (II) concentration was increased.

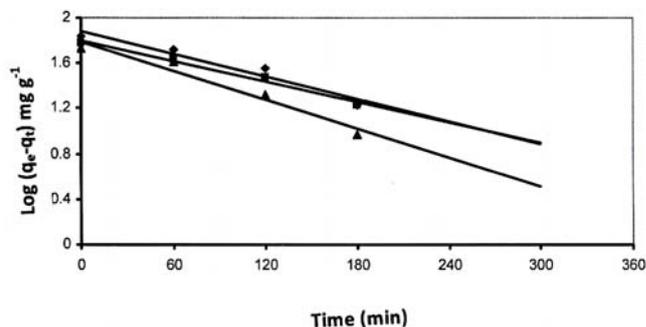


Fig. 2 Plots of pseudo first order kinetics of the interaction between Copper(II) and teak leaves powder dosage at 293 K (♦) D = 0.3 g.l⁻¹, D = (■) 0.4 g.l⁻¹, D = (▲) 0.5 g.l⁻¹

Two types of adsorption isotherm models namely Langmuir isotherm and Freundlich isotherm were tested. The Langmuir isotherm model is given as follows:

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m} \quad (4)$$

where,

- C_e - concentration of copper (II) at equilibrium (g l⁻¹)
- q_e - amount of Cu(II) biosorbed at equilibrium (mg g⁻¹)
- q_m - amount of copper (II) sorbed per unit mass of the biosorbent (mg g⁻¹)
- $b = K_a / K_b$

K_a - adsorption rate constant

K_b - desorption rate constant

A plot of (C_e/q_e) versus C_e (Fig. 3) was found to yield a straight line and the slopes and intercepts of the plots gives the values of q_m and b respectively. The values of ' q_m ' and ' b ' obtained from the plots are given in Table III.

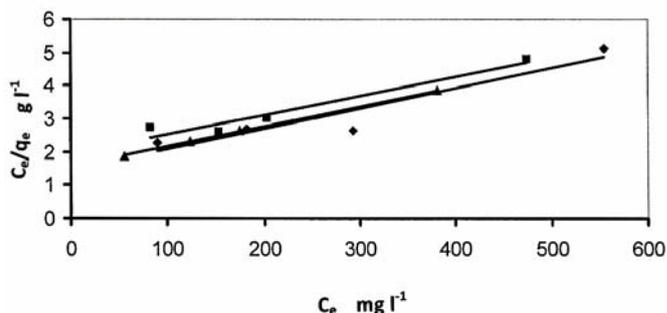


Fig. 3 Langmuir isotherm for biosorption of copper(II) at different concentrations at 293 K (♦) D = 0.3 g l⁻¹, D = (■) 0.4 g l⁻¹, D = (▲) 0.5 g l⁻¹

The monolayer capacity of the biosorbent ($q_m = 166.71$ mg.g⁻¹) was found to be quite large when compared to other adsorbents¹⁸ such as Crab shell 0.012 mg g⁻¹, Chitin 14.71 mg.g⁻¹, Coffee residue 39.52 mg.g⁻¹ and activated carbon 95.24 mg.g⁻¹.

TABLE III
BIOADSORPTION COEFFICIENTS FOR CU (II); AGITATION TIME % HRS; CU (II)
CONCENTRATION

D g.l ⁻¹	k ₁ x 10 ⁻³ min ⁻¹	R ²	q _m mg.g ⁻¹	B l.mg ⁻¹	R ²	k _f l.g ⁻¹	n
0.3	7.5999	0.99	172.41	0.0029	0.97	3.065	0.59
0.4	6.909	0.97	166.66	0.0038	0.97	1.951	0.65
0.5	9.6726	0.99	161.29	0.0042	0.99	2.468	0.63
mean	8.0605	0.98	166.78	0.0036	0.98	2.495	0.62

The logarithmic form of Freundlich isotherm model is given as follows:

$$\log q_e = \log k_f + nC_e \quad (5)$$

where,

q_e - amount of copper (II) sorbed at equilibrium (mg.g⁻¹)

C_e - concentration of the copper (II) at equilibrium (g.l⁻¹) and

k_f - Adsorption capacity (l.g⁻¹)

n - (1/n_f) = Adsorption affinity (dimensionless)

Plots of log q_e versus log C_e (Fig. 4) were found to yield a straight line whose slopes and intercepts corresponds to values of adsorption affinity 'n' and adsorption capacity 'k_f' respectively.

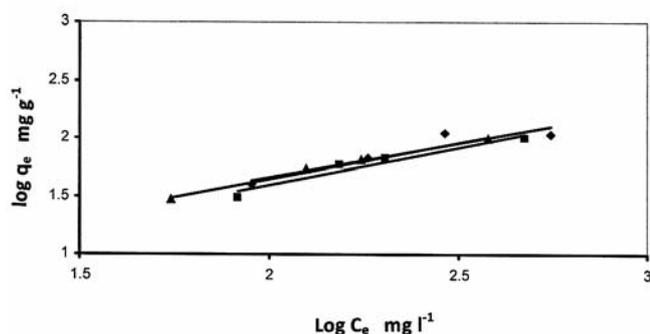


Fig. 4 Freundlich isotherm for adsorption of copper (II) of different concentrations of Biosorbent at 293 K. (♦) D = 0.3 g.l⁻¹, D = (■) 0.4 g.l⁻¹, D = (▲) 0.5 g.l⁻¹

The results obtained are tabulated in Table III. The adsorption affinity 'n' had values ranging within 0 < n < 1. The value of 'n' was found to be 0.62 respectively which is comparable with the reported values of chitin (n=0.45) and coconut husk (n = 0.48)¹⁸

IV. CONCLUSION

Biosorption is a potentially attractive technology for the treatment of heavy metals such as copper (II) from industrial effluents. The present work was carried out using teak leaves powder as biosorbent. The experiments were carried out at various initial concentrations of Cu (II) (i.e. 0.2 g l⁻¹, 0.4 g l⁻¹, 0.6 g l⁻¹, and 0.9 g l⁻¹), biosorbent dosages (0.3 g l⁻¹, 0.4 g l⁻¹, and 0.5 g l⁻¹), pH (4, 5 and 6) and temperature (20^o C, 30^o C, and 40^o C). It was observed that the percentage sorption of Cu (II) increased at lower concentrations of Cu (II) (0.2 g l⁻¹),

since the available sites for sorption became fewer at lower concentrations compared to the moles of metal ions present. The other factors which influenced the biosorption are pH and temperature. The maximum percentage sorption occurred at a pH of 6 and at a temperature of 20^oC respectively. The kinetics of biosorption of copper (II) were tested with pseudo first order Lagergran model. The experimental data gave good fit to both Langmuir and Freundlich isotherms.

REFERENCES

- [1] Ahluwalia SS and Goyal D, Microbial and plant derived biomass for the removal of heavy metals from wastewater. *Bioresour. Technol.* 98: 2243-2257 (2007).
- [2] Mallick N, Biotechnological potential of immobilized algae for wastewater N,P and metal removal: a review. *Biomaterials*. 15: 337-390 (2002).
- [3] Klimmek S, Stan HJ, Wilke A, Bunke G and Buchholz R, Comparative analysis of the biosorption of cadmium, lead, nickel and zinc by algae. *Environ. Sci. Technol.* 35: 4283-4288 (2001).
- [4] Hawari AH and Mulligan CN, Biosorption of lead (II), cadmium (II), copper (II) and nickel (II) by anaerobic granular biomass. *Bioresour. Technol.* 97: 692 – 700 (2006).
- [5] Vilar VJP, Botelho CMS and Boaventura AAR, Copper removal by algae Gelidium, agar extraction algal waste and granulated algal waste: Kinetics and equilibrium. *Bioresour. Technol.* 99: 750-762 (2008).
- [6] Ekmekyapar F, Aslan A, Bayhan YK and Cakici A, Biosorption of copper (II) by nonliving lichen biomass of *Caldonia rangiformis* hoffm. *J. Hazard.Mater. B* 137: 293-298 (2006).
- [7] Kiran B, Kaushik A and Kaushik CP, Response surface methodological approach for optimizing removal of Cr(VI) from aqueous solution using immobilized cyanobacterium. *Chem. Engg. J.* 126: 147-153 (2007).
- [8] Yazici H, Kilic M and Solak M, Biosorption of copper (II) by *Marrubium globosum* subsp. *Globosum* leaves powder: Effect of chemical pretreatment. *J. Hazard. Mater.* 151: 669 – 675 (2008).
- [9] Naddafi K, Nabizadeh R, Saeedi R, Mahvi AH, Vaezi F, Yaghmaei K, Ghasri A and Nazmara S, Biosorption of lead(II) and cadmium (II) by protonated *Sargassum glaucescens* biomass in a continuous packed bed column. *J. Hazard. Mater.* 147: 785 – 791 (2007).
- [10] Fourest E, Roux JC, Heavy metal biosorption by fungal mycelial by-products: mechanism and influence of pH. *Appl. Microbiol.Biotechnol.* 37: 399- 403 (1992) 399-403.
- [11] Fourest E, Canal C and Roux J, Improvement of heavy metal biosorption by mycelial dead biomasses (*Rhizopus arrhizus*, *Mucor miehei* and *Penicillium chrysogenum*): pH control and cationic activation. *FEMS Microbiol. Rev.* 141: 325 – 332 (1994).
- [12] Dursun AY, Uslu G, Cuci Y and Aksu Z, Bioaccumulation of copper(II), lead(II) and chromium(II) by growing *Aspergillus niger*. *Process. Biochem.* 38: 1647-1651 (2003).
- [13] Tsezos M and Volesky B, The mechanism of Thorium biosorption by *Rhizopus arrhizus*. *Biotechnol. Bioengg.* 24: 955 - 969 (1982).
- [14] Volesky B, May H and Holan ZR, Cadmium biosorption by *Saccharomyces cerevisiae*. *Biotechnol. Bioengg.* 41: 826 – 829 (1993).
- [15] Kuyucak N and Volesky B, Biosorbent for recovery of metals from industrial solutions. *Biotechnol. Lett.* 10: 137-142 (1988).
- [16] Lee MY, Park JM and Yang JW, Microprecipitation of lead on the surface of crab shell particles. *Proc. Biochem.* 22: 671 – 677 (1997).
- [17] Volesky B and Holan ZR, Biosorption of heavy metals. *Biotechnol. Prog.* 11: 235 - 250 (1995).
- [18] Sharma A and Bhattacharyya KG, *Azadirachta indica* (Neem) leaf powder as a biosorbent for removal of Cd(II) from aqueous medium. *J. Hazard.Mater. B*125: 102 – 112 (2005).
- [19] Vijayaraghavan K, Palanivelu K and Velan M, Biosorption of copper (II) and cobalt(II) from aqueous solutions by crab shell particles. *Bioresour. Technol.* 97: 1411 – 1419 (2006).
- [20] Nasir MH, Nadeem R, Akhtar K, Hanif MA and Khalid AM, Efficacy of modified distillation sludge of rose(*Rosa centifolia*) petals for lead(II) and zinc(II) removal from aqueous solutions. *J. Hazard.Mater.* 147: 1006 – 1014 (2007).
- [21] Dahiya S, Tripathi RM and Hegde AG, Biosorption of lead and copper from aqueous solutions by pretreated crab and arca shell biomass. *Bioresour.Technol.* 99: 179- 187 (2008).

- [22] Matheickal JT, Yu Q and Woodburn GM, Biosorption of cadmium (II) from aqueous solutions by pretreated biomass of marine alga *Durvillaea potatorum*. *Wat. Res.* 33: 335 - 342 (1999).
- [23] Khormaei M, Nasernejad B, Edrisi M and Eslamzadeh T, Copper biosorption from aqueous solution by sour orange residue. *J. Hazard. Mater.* 149: 269 – 274 (2007).
- [24] Prasanna Kumar Y, King P, Prasad VSRK, Equilibrium and kinetic studies for the biosorption of copper (II) ion from aqueous solution using *Tectona grandis* L.f leaves powder. *J. Hazard. Mater.* B137: 1211 – 1217 (2006).
- [25] Esposito A, Pagnanelli F, Lodi A, Solisio C and Veglio F, Biosorption of heavy metals by *Sphaerotilus natans*: an equilibrium study at different pH and biomass concentrations. *Hydrometallurgy.* 60: 129 -141 (2001).