Original Research Article

Biological Uptake of Chromium and Copper from Aqueous Systems by *Penicillium notatum* Biomass

ABSTRACT

The biosorption potential of *Penicillium notatum* for Cr(VI) and Cu(II) ions in aqueous was investigated in this study. The effects of biosorbent dose, solution pH, contact time and initial metal ion concentration were evaluated. The results showed that the maximum removal efficiency for Cr(VI) ions was recorded at pH 5 while that for Cu(II) was attained at pH 9. There was also an increase in biosorptive amount with increase in initial metal ion concentration for both ions. The equilibrium data for Cu (II) fitted better to the Langmuir isotherm compared to the Freundlich isotherm while that of Cr(VI) had a better fit for Freundlich isotherm compared to the Langmuir model. The maximum biosorption capacity, Q^o, for Cr(VI) and Cu(II) obtained from the Langmuir plots are 23.15 and 4.02 (mg/g) respectively. This shows that *Penicillium notatum* biomass has the ability to remove these metal ions from contaminated waters under suitable conditions.

Keywords: Biosorption, Freundlich, Isotherm, Langmuir, *Penicillium notatum*

1. INTRODUCTION

The prevalence of heavy metals in the environment is an issue of current global concern. This is due to their persistence and toxicity. They are non-biodegradable and possess the ability to bio-magnify. They are released into the soil and wastewaters as effluents from various industries. Some of these industries include fertilizer and pesticide manufacturing, mining, electroplating, pulp and paper manufacturing and so on [1].The presence of these heavy metals in the environment causes harmful effects on humans and other organisms. Copper and chromium are among the metals of concern according to the World Health Organization, (WHO), [2]. Chromium does not occur naturally in elemental form but only in compounds. It is only as a result of human activities that substantial amounts of Cr(VI) become present in the environment. The main sources of copper contamination to the aquatic environment are mining, metal plating industry, fertilizers, fungicidal sprays, and animal wastes. Other sources include discharges from basic steel works and non-ferrous metals, motor vehicles and aircraft plating industries [3]. Copper is an essential micronutrient required in the growth of both plants and animals. High intakes of copper may cause liver and kidney damage and even death [4]. The methods that are currently being used y for the treatment of metal-polluted wastewaters have many drawbacks. These include high cost, low efficiency especially at low metal concentration and production of toxic sludge among others [5]. Biosorption which involves the use of materials of biological origin, such as fungi, yeasts, bacteria, algae and agricultural wastes, is now being employed because of its advantages over the conventional methods. This study was embarked upon to investigate the potential of the microfungi *Penicillium notatum* to remove copper and chromium ions from aqueous solutions of their salts.

2. MATERIALS AND METHODS

2.1 Preparation of the Biosorbent

The mycelium of *Penicillium notatum* was cultured over Potato Dextrose Agar (PDA) plates. The fungal biomass was cultivated in conical flasks containing the culture medium having the following composition (g/L): K_2HPO_4, 0.5; NaCl, 0.5; $MgSO_4$, 0.5; NH_4NO_3, 0,5; yeast extract, 0.5, peptone, 10.0, glucose, 20. The pH of the media was adjusted to 5.0. The flask was autoclaved at 121 $^{\circ}$C for 15 minutes and then incubated in a rotary orbital shaker at 180 rpm and 30 ^{o}C. The cells were dried at 80 ^{o}C overnight [6]. To immobilize the cells 100 mL of 4 % (w/v) sodium alginate was prepared in a volumetric flask and was shaken to make it homogenous. The sodium alginate slurry was dropped through a 10 mL syringe into 2% (w/v) $CaCl_2$ solution. Durable spherical beads of the alginates were formed immediately. The beads were washed with distilled water and stored for use in the experiments.

2.2 Batch Adsorption Experiments

The contact experiments were done in replicates in 100 mL conical flasks containing 50 mL of solution. The flask contents were mechanically agitated on a conical flask shaker at 150 rpm and a temperature of 29 ^{o}C. To determine the optimum conditions for biosorption, the pH of the solutions were varied from 3.0 – 9.0, contact time from 10 – 150 minutes and initial metal ion concentrations were varied from 10 – 100 mg/L. At the end of the reaction, the contents of the flask were separately filtered into polypropylene bottles using Whatman No 1 filter paper. Atomic Absorption Spectrometer (AAS) was used to determine Cu(II) and Cr(VI) ion concentrations in the solution before and after contact with the adsorbent. The percentage metal removal (%) was calculated using the following equation:

3. RESULTS AND DISCUSSION

The removal efficiency (%) (or percentage metal removal) was calculated using the following equation:

$$\text{Removal } \% = \frac{(C_o - C_e)}{C_o} x\ 100 \quad \text{...} \quad (1)$$

The amount of each ion adsorbed was calculated from the difference between the added and equilibrium concentration by using the equation below:

$$q_e = \frac{V(C_o - C_e)}{M} \quad \text{...} \quad (2)$$

Where q_e is the amount adsorbed in mg/g of the absorbent at equilibrium, C_o and C_e are the initial and the equilibrium concentrations in mg/L, respectively, V is the volume in litres of the solution used during the experiment and M is the mass of the adsorbent in grams.

3.1 Influence of biosorbent weight

The effect of biosorbent weight on the removal efficiency of Cr(VI) and Cu(II) ions by the biomass of *Penicillium notatum* is presented in Figure 1. The dependence of removal efficiency on biosorbent weight was studied by varying the biosorbent weights while keeping other parameters constant. The figure shows that there was an increase in removal efficiency of Cr(VI) from 10.98% at 10 mg to 38.74% at 200 mg biosorbent weight while that for Cu(II) showed an increase from 36.93% at 10 mg to 92.27% at 200 mg biomass weight. The increase in percentage removal with increase in biosorbent weight is due to the greater availability of the exchangeable sites at higher concentration of the biosorbent [7].

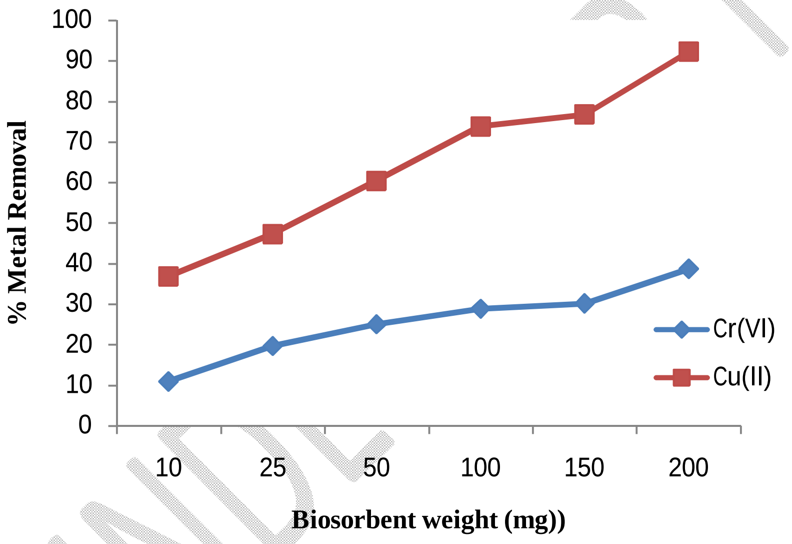

Fig 1: Effect of Biosorbent weight on the removal of Cr(VI) and Cu(II) from solution by *P. notatum* biomass

3.2 Influence of solution pH

The effect of the pH on the removal of Cr(VI) and Cu(II) ions from solution is presented in Figure 2. The effect of the pH was investigated by varying the pH of the solution of the ions from 3.0 to 9.0 while keeping the other parameters constant. For Cr(VI), the highest percentage removal (34.46%) was recorded at pH 5.0 while the lowest (19.12%) was observed at pH 3.0. For Cu(II) the removal percentage increased from 2.39% at pH 3.0 to 94.68% at pH 9.0. There was a decrease in percentage removal at pH above the optimum. Chromium(VI) displays a pH dependence that is different from that of other metal ions. At pH range 2 to 4 the dominant species of Cr(VI) ions present in solution are $Cr_2O_7^{-2}$, $HCrO_4^-$, CrO_4^{-2}, and $HCr_2O_7^-$. The cell walls of the microorganisms are rich in protein, amino-acids and other functional groups [8]. Some of these functional groups, such as amines, are positively charged when protonated and may electrostatically bind with negatively charged metal complexes [9]. At lower pH the biosorbent is positively charged due to protonation and the dichromate ion exists as an anion leading to an electrostatic attraction between them [10]. These accounted for the high percentage removal at lower pH. The decrease in adsorption at higher pH may be due to the occupation of the adsorption sites by anionic species like $HCrO_4^-$, $Cr_2O_7^{-2}$, CrO_4^{-2}, etc., which retards the approach of such ions further towards the adsorbent surface. The decrease in adsorption at high pH may also be due to the competitiveness of the oxyanion of chromium and OH^- ions in the bulk [9].

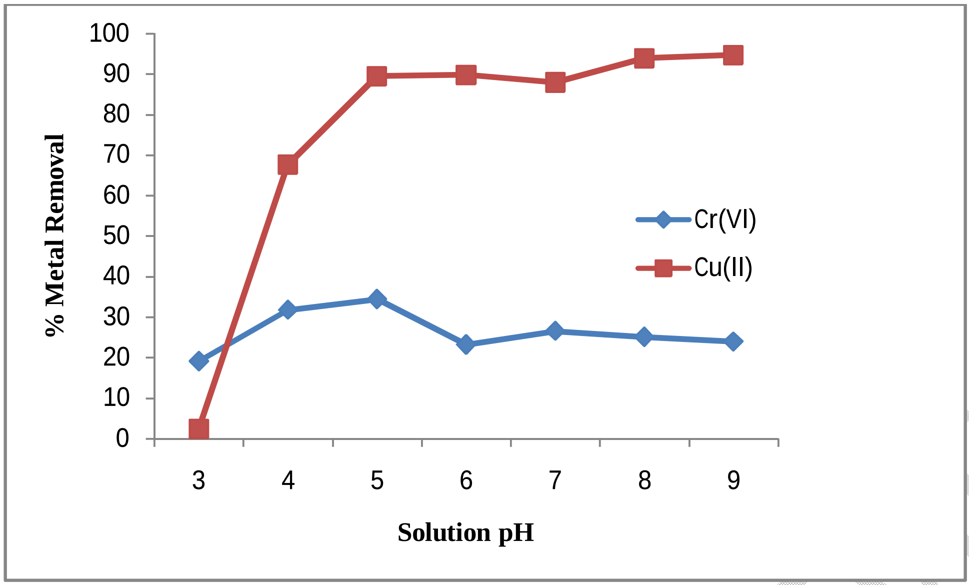

Fig 2: Effect of solution pH on the removal of Cr(VI) and Cu(II) from solution by *P. notatum* biomass

3.3 Influence of contact time

The effect of the contact time on the removal of Cr(VI) and Cu(II) ions from solution is presented in Figure 3. The effect of contact time was investigated by analyzing the contents of the reaction flasks withdrawn at intervals from 10 minutes to 150 minutes while maintaining a constant pH of 5.0, adsorbent weight of 100 mg and initial metal ion concentration of 10 mg/L. For Cr(VI) , the removal percentage increased from 19.92% at 10 minutes contact time to 68.09% at 80 minutes which was the maximum removal percentage. It became fairly constant after that and decreased to 23.32% at 150 minutes. For Cu(II), the removal percentage increased from 26.24% at 10 minutes contact time to 75.77% at 100 minutes after which there was a decrease to 59.61% and 62.35% at 120 minutes and 150 minutes contact time respectively.

Before attainment of equilibrium the increase in metal sorption could be due to a high electrostatic attraction between the two which gradually reduces as more binding sites become occupied [11].

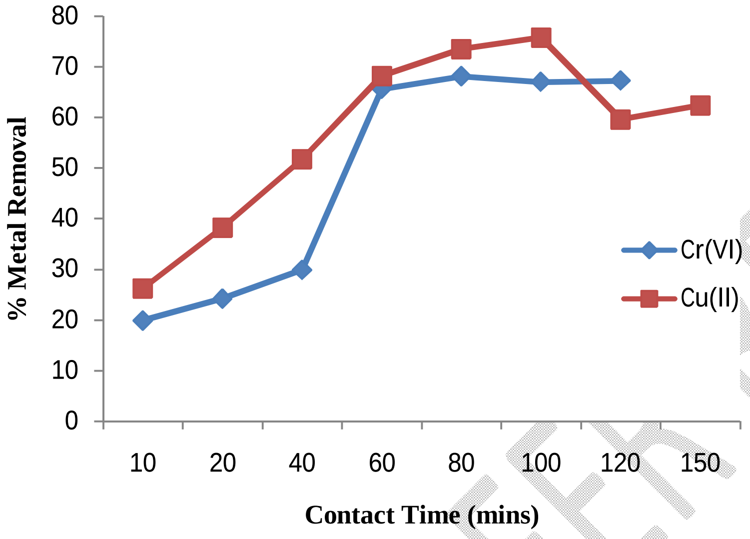

Fig 3: Effect of contact time on the removal of Cr(VI) and Cu(II) from solution by *P. notatum* biomass

3.4 Influence of initial metal ion concentration

The effect of initial metal ion concentration on the removal of Cr(VI) and Cu(II) ions from solution is shown in the Figure 4. The effect of initial metal ion concentration was investigated by varying the concentration of the Cr(VI) ions from 10 mg/L to 100 mg/L while keeping the other parameters constant. The removal percentage of Cr(VI) ions increased from 5.33% at 10 mg/L to 40.96% at 40 mg/L after which there was a decrease to 38.70%, 30.79% and 27.08% at 60 mg/L, 80 mg/L and 100 mg/L respectively. For Cu(II), the removal percentage decreased from 83.42% at 10 mg/L to 12.56% at 100 mg/L. These results show that the removal of the metal ions was dependent on the initial concentration. At lower concentrations, the ratio of available surface to the initial concentration of the ions was larger, so the removal efficiency was higher. However, in the case of higher concentrations this ratio became lower hence the removal percentage decreased with an increase in ion concentration [12].

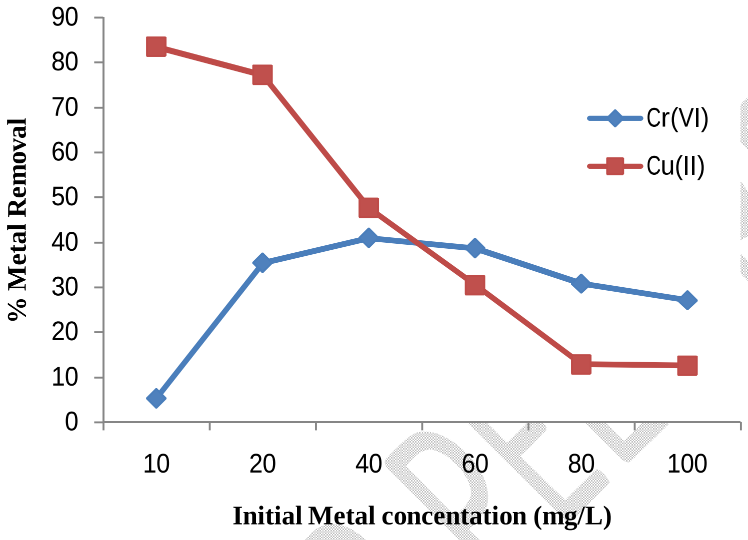

Fig 4: Effect of initial metal concentration on the removal of Cr(VI) and Cu(II) from solution by *P. notatum* biomass

3.5 Biosorption Isotherms

Adsorption isotherms are important in describing the mutual relationship between adsorbate and adsorbent and identifying critical conditions to be optimized [12]. It represents the equilibrium relationship between the adsorbate concentration in the fluid phase and the adsorbate concentration in the adsorbent particles at a given temperature [13]. By knowing the adsorption isotherm, the affinity of the adsorbate for an adsorbent is quantified.

3.5.1 Langmuir isotherm

Langmuir adsorption isotherm describes quantitatively the formation of a monolayer of adsorbate on the outer surface of the adsorbent. It is based on the assumptions that the surface of the adsorbent is uniform, that is, all the adsorption sites are equivalent and that there is no interaction between molecules adsorbed on neighbouring sites. It also assumes that molecules are adsorbed at definite sites on the surface.

Where q_e is milligrams of metal accumulated by per gram of the biosorbent materials; C_e is the metal residual concentration in solution; Q^o is the maximum specific uptake corresponding to the site saturation and K_L is the ratio of adsorption and desorption rates. The linearized form of the equation given as

$$\frac{C_e}{q_e} = \frac{1}{K_L Q^o} + \frac{C_e}{Q^o}$$

Where q_e is milligrams of metal accumulated by per gram of the biosorbent materials; C_e is the metal residual concentration in solution; Q^o (mg/g) is the maximum specific uptake corresponding to the site saturation and K_L (L/g) is the ratio of adsorption and desorption rates.

A graph of C_e/q_e against C_e will have K_L (L/g) as the slope and Q^o (mg/g) as the intercept.

The Langmuir isotherm plots for the biosorption of Cr(VI) and Cu(II) by immobilized *Penicillium notatum* are shown in Figure 5. The values of the coefficient of determination, R^2, for Langmuir equations for the two metals are 0.6921 and 0.9049 for Cr(VI) and Cu(II) respectively. Maximum biosorption capacity Q^o (mg g^{-1}) for Cr(VI) and Cu(II) are 23.15 and 4.02 mg g^{-1} respectively (Table 1). The value of R^2 for Cu(II) was higher than the value for Cr(VI) indicating a monolayer adsorption process onto the biosorbent.

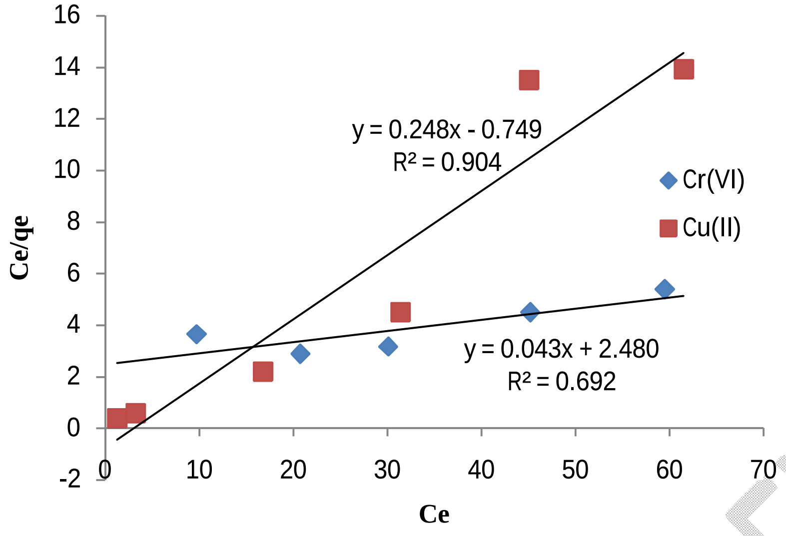

Fig 5: Langmuir isotherm plots for the removal of Cr(VI) and Cu(II) from solution by *P. notatum* biomass

3.5.2 Freundlich isotherm

The Freundlich Isotherm is commonly used to describe the adsorption characteristics for the heterogeneous surface. It represents an initial surface adsorption followed by a condensation effect resulting from strong adsorbate-adsorbate interaction.

The linearized form of the Freundlich equation is

$$log q_e = log K_f + \frac{1}{n} log C_e ..$$

where q_e (mg/g) is the adsorption density, C_e is the concentration of metal ion in solution at equilibrium (mg/L), K_f and n are the Freundlich constants which determine the curvature and steepness of the isotherm. Also the value of $\frac{1}{n}$ indicates the affinity of the adsorbate towards the biomass. A plot of $1og\ C_e$ against $1og\ q_e$ will give the value of $\frac{1}{n}$ and $1og\ K_f$ from the slope and the intercept respectively.

The Freundlich isotherm plots for the biosorption of Cr(VI) and Cu(II) ions by *P. notatum* are presented in Figure 6. The values of the determination coefficient, R^2, are 0.8253 and 0.8197 for Cr(VI) and Cu(II) respectively. The values of K_f and n were calculated from slope and intercept of the Freundlich plots as presented in Table 1. An n value of 0.57 (i.e. < 1) for the Cr(VI) ion indicates an unfavourable adsorption [14].

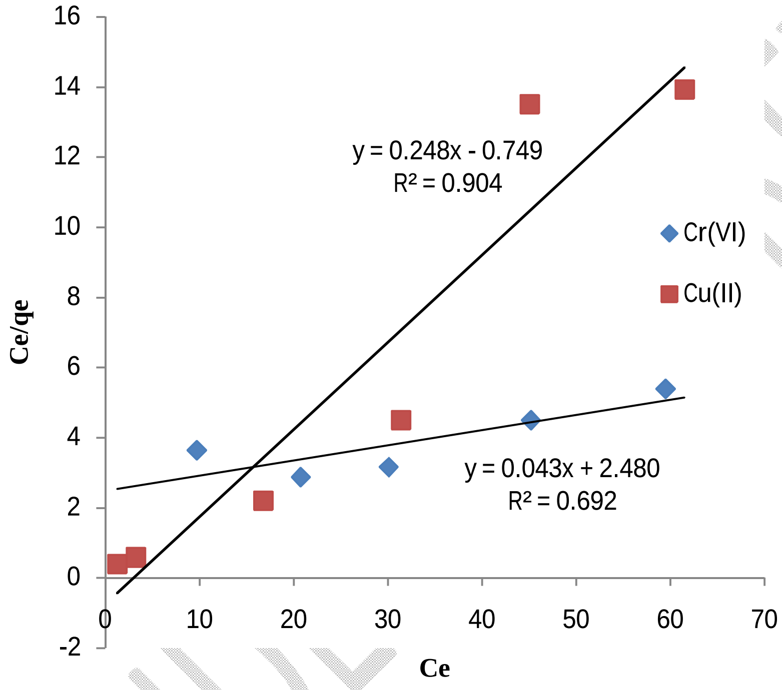

Fig 6: Freundlich isotherm plots for the removal of Cr(VI) and Cu(II) from solution by *P. notatum* biomass

Table 1: Isotherm parameters for the removal of Cr(VI) and Cu(II) from solution by *P. notatum* biomass

	Langmuir isotherm constants			**Freundlich isotherm constants**		
Metal Ion	R^2	K_L(L mg^{-1})	Q^o(mg g^{-1})	R^2	K_f(mg g^{-1})	n (L mg^{-1})
Cr(VI)	0.6921	0.02	23.15	0.8253	0.02	0.57
Cu(II)	0.9049	0.33	4.02	0.8197	3.47	4.17

4. CONCLUSION

This study has shown that *Penicillium notatum* possesses the ability to remove chromium and copper ions from aqueous solution of their salts. The biosorption process is influenced mainly by solution initial pH and initial metal ion concentration. The isotherm studies indicate that the reaction fits the Langmuir model better than the Freundlich model indicating a monolayer adsorption. *Penicillium notatum* can therefore be used as a low cost adsorbent for the removal of heavy metals from wastewaters.

RFERRENCES

1. Kanamarlapudi SLRK, Chinalpudi VK, Mudadda S. Application of biosorption for heavy metals removal from wastewaters. Biosorption. 2018; 18: 69 – 97
2. WHO (2006). Guidelines for Drinking-Water Quality, Incorporating First Addendum to the Third Edition. World Health Organization, Geneva. vol. 1

3. Yahaya YA, Don MM. *Pycnoporus sanguineus* as potential biosorbent for heavy metal removal from aqueous solution: a review. *J. Phys. Sci.* 2014; 25(1): 1 – 32
4. Gadd GM.. Biosorption: critical review of scientific rationale, environmental importance and significance for pollution treatment. J. Chem. Technol. Biotech.

2009; 84(1): 13 – 28

5. Ahalya N, Ramchanra TV, Kanamodi RD. Biosorption of heavy metals. Res. J. Chem. Environ. 2003; 7: 71- 78
6. Pundir R, Dastidar MG. Recovery of Cu and Ni ions from metal – loaded fungal biomass using acidic eluent. Int. J. Chem. Environ. Eng. 2010; 1(1): 63-66
7. Jayaraman M, Arumugam R. Biosorption of copper (II) by *Aspergillus flavus*. Int. J. Sci. Res. 2014; 3: 335 – 340
8. Wang J, Chen C. (2009). Biosorbents for heavy metals removal and their future. Biotech. Adv. 2009; 27: 195 - 226
9. Popuri SR, Jammala A, Reddy KVNS, Abburi K. Biosorption of hexavalent chromium using tamarind (*Tammarindus indica*) fruit shell. A comparative study. Electronic J. Biotech. 2007; 10: 358 - 357
10. Boddu VM, Abburi K, Talbott JL, Smith ED. Removal of hexavalent chromium from wastewater using a new composite chitosan biosorbent. Environ. Sci. Technol. 2003; 37(19): 4449 - 4456
11. Abdel-Ghani N, Hegazy A, El-Chaghaby G. *Typha domingensis* leaf powder for decontamination of aluminum, iron, zinc and lead: Biosorption kinetics and equilibrium modelling. Int. J. Environ. Sci. Technol. 2009; 6:243 - 248
12. Galedar M, Younesi H. Biosorption of ternary cadmium, nickel and cobalt ions from aqueous solution onto *Saccharomyces cerevisiae* cells: Batch and column studies. Amer. J. Biochem. Biotech. 2013; 9(1): 47 - 60
13. Hlihor RM, Bulgariu L, Sobariu DL, Diaconu M, Tavares T, Gavilescu M. Recent advances in biosorption of heavy metals: Support tools for biosorption equilibrium, kinetics and mechanism. 2014; 59: 527 – 539

14. Kadirvelu K, Namasivayam C. Activated carbon from coconut coir pitch as metal adsorbent: adsorption of Cd (II) from aqueous solution. Adv. Environ. Res. 2003; 7: 471 – 478