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

ABSTRACT

Fungi have been shown to play an important role in the bioremediation of contaminated water and soils. The biosorption potential of a fungus, *Penicillium notatum* for chromium and copper ions in aqueous solution of their salts was investigated **in this study**. **The effects of various parameters on the biosorption process were evaluated. These parameters include** biosorbent dose, solution pH, contact time and initial metal ion concentration were evaluated. The study showed that the maximum removal efficiency for chromium ions was recorded at pH 5 while that for copper 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 copper fitted better to the Langmuir isotherm compared to the Freundlich isotherm while that of chromium had a better fit for Freundlich isotherm compared to the Langmuir model. The maximum biosorption capacity, Q^o, for chromium and copper 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 presence of heavy metals has a considerable negative impact on the environment. There are persistent and toxic even when present in low concentrations. They are non-biodegradable and possess the ability to bio-magnify" [1]. They are released into the soil and wastewater as effluents from various industries. Some of these industries include fertilizer and pesticide manufacturing, mining, electroplating, pulp and paper manufacturing and so on [2]. Copper and chromium are among the metals of concern according to the World Health Organization, (WHO), [3]. "Chromium does not occur naturally in elemental form but only in compounds. Copper is an essential micronutrient required in the growth of both plants and animals. Because of the high toxicity of these metals and their impact on human health, the World Health Organization has set the maximum permissible levels of chromium and copper in drinking water at 0.5 mg/L and 1.5 mg/L respectively" [4]. The methods that are currently being used 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 biological materials like 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 ability of the microfungus *Penicillium notatum* to remove copper and chromium ions from aqueous solutions and to optimize the conditions for the biosorption process.

2. MATERIALS AND METHODS

2.1 Preparation of the Biosorbent

The biomass of *Penicillium notatum* was cultivated in 250 mL conical flasks according to the procedure reported by Pundir and Dastidar [6]. The culture medium prepared for the growth of the fungus had the following composition in 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. 0.1M HCl and 0.1M NaOH were used to adjust the pH of the medium to 5.0. The flask was autoclaved at 121 ^{o}C for 15 minutes and then incubated in a rotary orbital shaker at 180 rpm and 30 ^{o}C. The cells were kept dried in an oven at 80 ^{o}C overnight. The immobilization of the cells was carried out as follows: 100 mL of 4 % (w/v) sodium alginate was mixed with 100 mL of the fungal biomass and the mixture was shaken on a flask shaker to ensure proper mixing. The slurry obtained was extruded 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 many times with distilled water.

2.2 Batch Adsorption Experiments

The experiments were done in the batch mode. The batch reactor was 100 mL conical flasks which contained 50 mL of reaction solution. The equilibration process was carried out by mechanically agitating the flask contents 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. After each contact session, the contents of the flask were separately filtered and the concentrations of the metal ions before and after contact with the biosorbent were analyzed using Atomic Absorption Spectrophotometer (AA280AFS, Agilent Technologies, California, USA).

3. RESULTS AND DISCUSSION

The removal efficiency (%) and the amount of chromium and copper adsorbed were calculated by using equation (1) and (2) below respectively:

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

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

Where q_e is the amount of chromium/copper adsorbed per gram of the biosorbent at equilibrium, C_o and C_e are the initial and final concentrations of the metal ions in mg/L, respectively, V is the volume in litres of the reaction solution and M is the mass of the adsorbent in grams.

3.1 Influence of biosorbent weight

The biosorbent provides the active sites for metal biosorption hence the amount of the biosorbent is an important factor in the biosorption process. The Figure1 below shows the influence of the biosorbent weight on the removal efficiency of Cr(VI) and Cu(II) ions by the biomass of

Penicillium notatum. To investigate this effect, the mass of the biosorbent was varied from 10 mg to 200 mg while the other parameters were kept constant. As the figure shows, there was an increase in removal efficiency of Cr(VI) from 10.98% at 10 mg to 38.74% at 200 mg biosorbent mass 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 removal efficiency with increase in biosorbent weight at a given metal ion concentration is due to the increase in the number of available binding sites which is in itself results from greater surface area and hence greater biosorption [7].

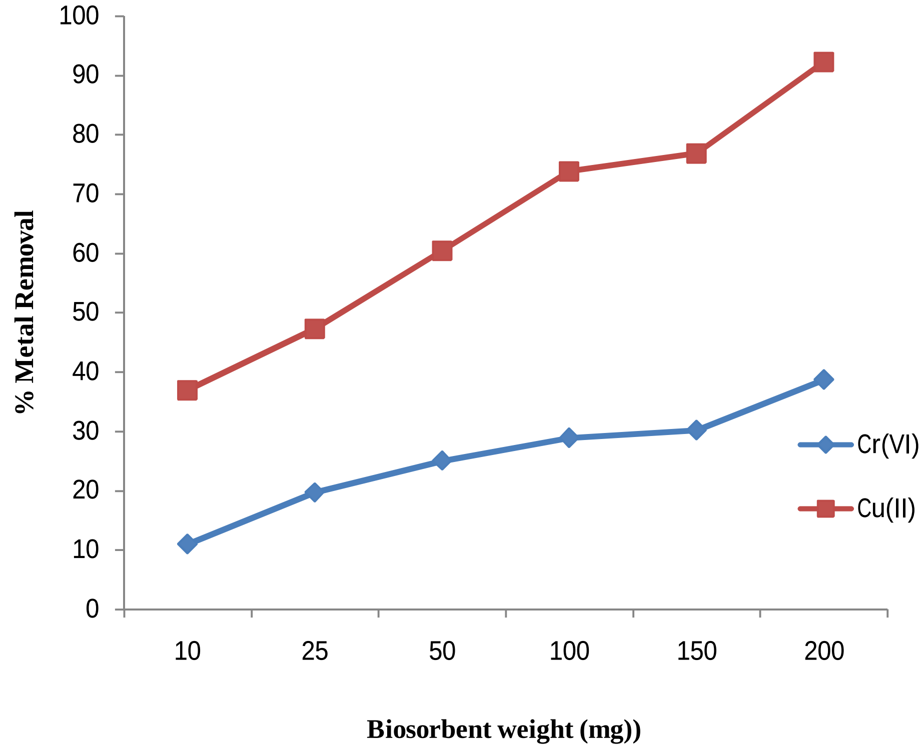

Fig 1: Effect of Biosorbent weight on the removal of Cr(VI) and Cu(II) from solution by *P. notatum* biomass

3.2 Influence of solution pH

The pH of the reaction solution is an important factor that affects the biosorption reaction. This was studied by keeping the other parameters constant while the pH was varied from 3.0 -9.0. The results are presented in Figure 2. Optimum pH for Cr(VI) removal was 5.0 while for Cu(II) it was 9.0. At low pH there was some competition between the H_3O^{-+} ions in the solution and the Cr(VI) and Cu(II) ions. As the pH increased more the number of negatively charged groups present on the ligands are displayed leading thereby to an increase in the adsorption of the cationic species [8].

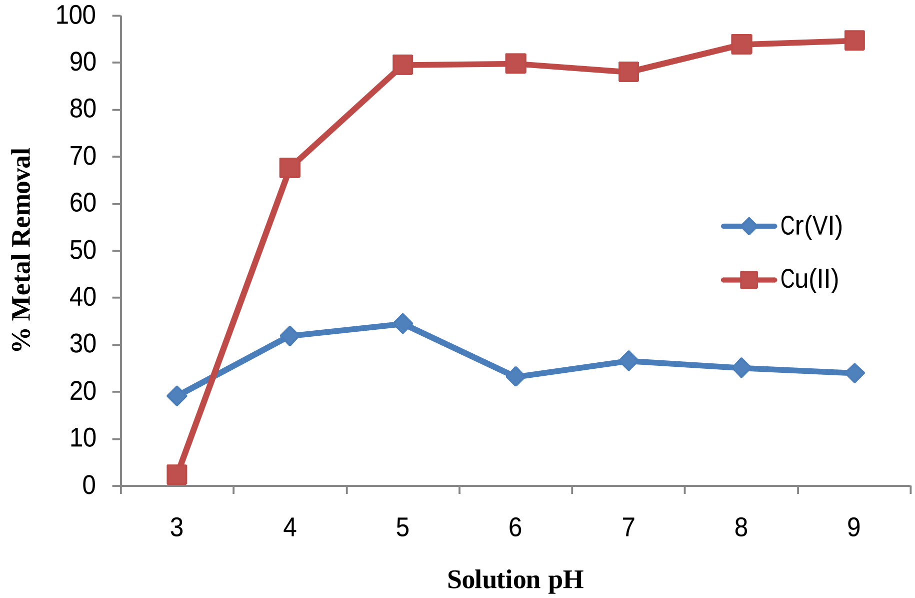

Fig 2: Effect of solution pH on the removal of Cr(VI) and Cu(II) from solution by *P. notatum* biomass

3.3 Influence of contact time

The Figure 3 below shows the influence of the equilibration time on the removal of the metal ions from solution. This was investigated by withdrawing the reaction flasks at intervals from 10 minutes to 150 minutes while the other parameters were kept constant. For Cr(VI), the maximum removal efficiency (68.09%) was recorded at 80 minutes contact time while the optimum removal efficiency for Cu(II) which was 75.77% at 100 minutes contact time. The reaction was fast at the beginning because all the binding sites were vacant but as time went on the rate of adsorption of the metals decreased due to increase in the saturation by the metal ions still remaining in the reaction solution [9].

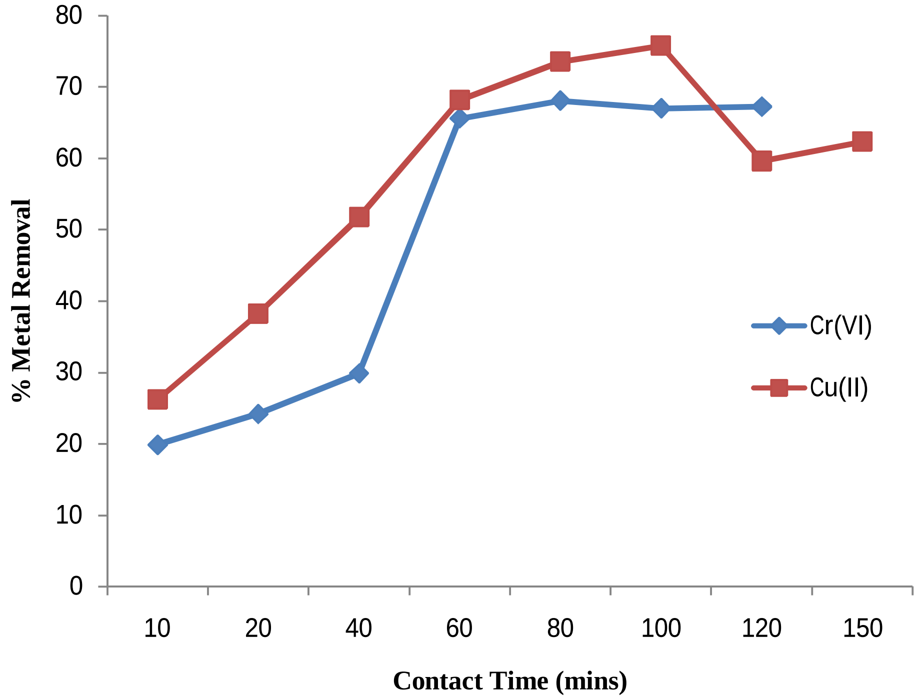

Fig 3: Effect of contact time on the removal of Cr(VI) and Cu(II) from solution by *P. notatum* biomass

3.4 Influence of initial metal ion concentration

The Figure 4 below shows the influence of initial metal ion concentration on the removal of Cr(VI) and Cu(II) ions from solution. To evaluate this effect, the concentration of the metals were varied from 10 mg/L – 100 mg/L while the other parameters were kept constant. The results showed a decrease in removal efficiency with increase in initial metal concentration. For Cr(VI), the highest removal efficiency (40.96%) was at 40 mg/L concentration while for Cu(II) the highest was 83.42% at 10 mg/L concentration. At low concentration, many binding sites on the adsorbent remain unoccupied hence the high efficiency, but as the concentration of the metal ion increases, competition between the ions for the binding sites leads to a reduction in the removal efficiency as the graph shows [10].

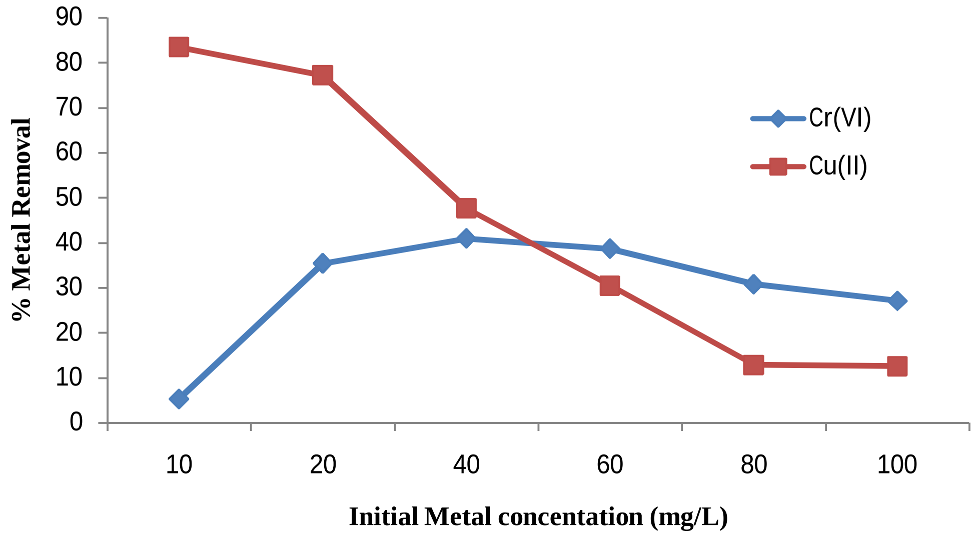

Fig 4: Effect of initial metal concentration on the removal of Cr(VI) and Cu(II) from solution by *P. notatum* biomass

3.5 Biosorption Isotherms

Adsorption isotherms are used to describe the equilibrium relationship between the amount of adsorbate adsorbed on a given amount of the adsorbent at a constant temperature. It is useful in quantifying the affinity of the adsorbate for a given adsorbent [11].

3.5.1 Langmuir isotherm

The Langmuir isotherm is based on the assumptions that the layer of adsorbent is a monolayer and that the adsorbed layer is uniform all over the adsorbent.

In its linear form the equation is 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.

If a graph of C_e/q_e is plotted against C_e, K_L (L/g) will be the slope and Q^o (mg/g) will be the intercept.

The Figure 5 below shows the Langmuir isotherm plots for the biosorption of Cr(VI) and Cu(II) by immobilized *Penicillium notatum*. The values of the coefficient of determination, R^2 values for the Langmuir equations are, respectively, 0.6921 and 0.9049 for Cr(VI) and Cu(II). Maximum adsorption capacity Q^o for Cr(VI) and Cu(II) are 23.15 and 4.02 mg g^{-1} respectively (Table 1).

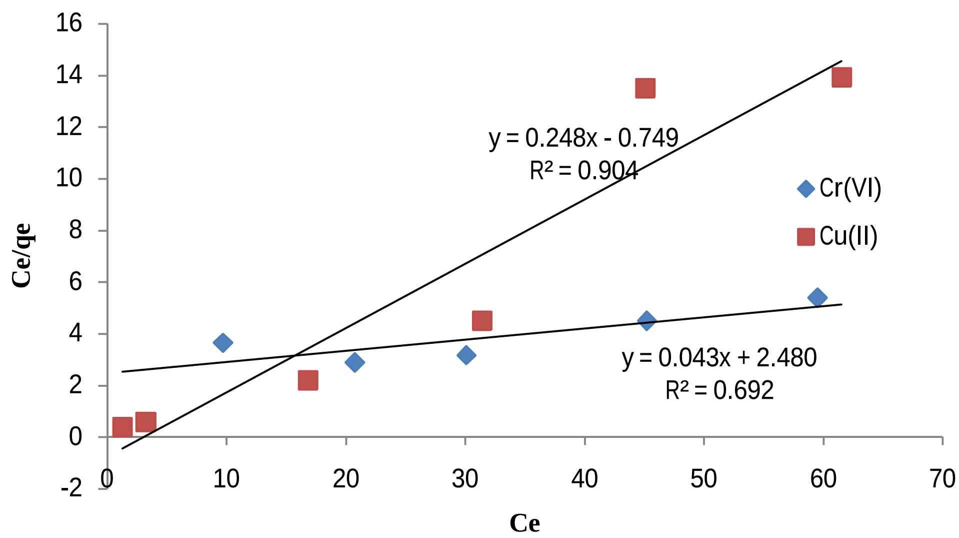

Fig 5: Langmuir isotherm plots for the removal of Cr(VI) and Cu(II) from solution by *P. notatum* biomass

3.5.2 Freundlich isotherm

The Freundlich isotherm is commonly used to describe the adsorption reaction that takes place at heterogeneous surfaces.

The linear form of the Freundlich equation is

$$logq_e = \quad logK_f \ + \frac{1}{n} logC_e ..$$

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 describes the curvature and steepness of the isotherm. The value of the constant $\frac{1}{n}$ indicates the affinity of the adsorbate for adsorbent. If *1og* C_e is plotted against *1og* q_e $\frac{1}{n}$ will be the slope and *1og* K_f will be the intercept respectively.

The Figure 6 below shows the Freundlich isotherm plots for the biosorption of Cr(VI) and Cu(II) ions by *P. notatum.* are presented in Figure 6. The R^2 values are 0.8253 and 0.8197 for Cr(VI) and Cu(II) respectively. The values of K_f and n are presented in Table 1. An n value of 0.57 (i.e. < 1) for the Cr(VI) ion indicates an unfavourable adsorption [12].

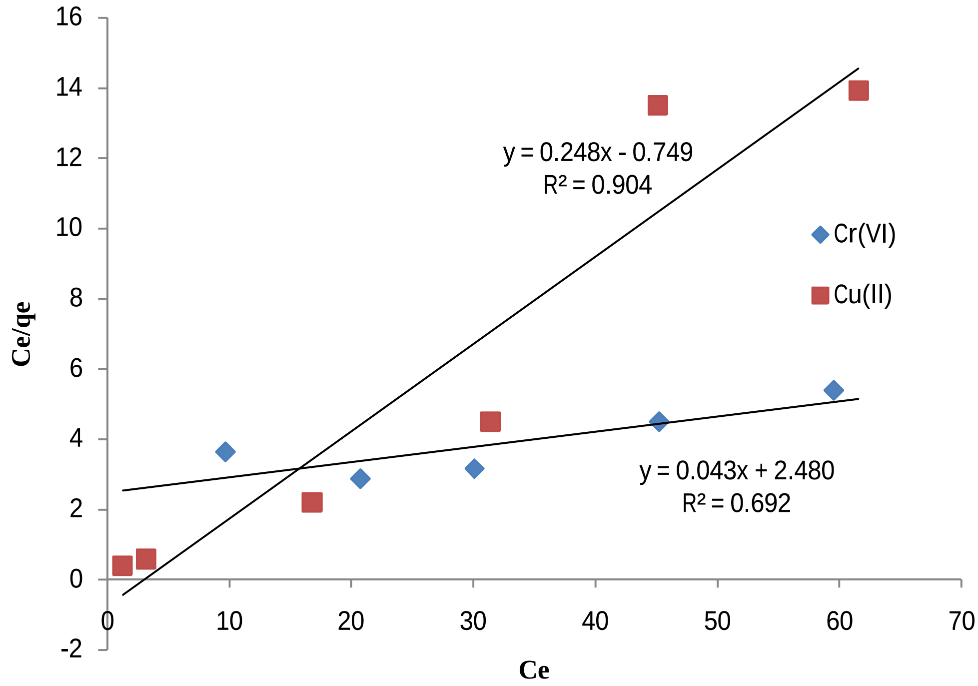

Fig 6: Freundlich isotherm plots for the removal of Cr(VI) and Cu(II) from solution by *P. notatum* biomass

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

	Langmuir			**Freundlich**		
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 concentration of the metal ion. The isotherm studies indicate that the reaction fits the Langmuir model better than the Freundlich model. This shows that monolayer adsorption is the likely mode of the adsorption process. *Penicillium notatum* may therefore be used as a cheap and relatively available adsorbent for the removal of heavy metals from contaminated waters.

COMPETING INTERESTS

The authors declare that no competing interests exist.

AUTHORS' CONTRIBUTIONS

This work was carried out in collaboration between all the authors. All the authors read and approved the final manuscript.

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