Penicillium citrinum as a potential biosorbent for Ni (II) sequestration from simulated wastewater

Anamika Verma, Shalu, Asha Gupta and Narsi R. Bishnoi
Department of Environmental Science & Engineering,
Guru Jambheshwar University of Science and Technology
Hisar, 125001, Haryana, India

Abstract:
The ability of non-living biomass of *Penicillium citrinum* has been explored for removal and recovery of Ni (II) from aqueous solutions. Biosorption potential of immobilized and free biomass of fungus *P. citrinum* was studied in batch system for metal removal. The influence of different experimental parameters such as pH, contact time, metal ion concentration and biosorbent dose were investigated. *P. citrinum* exhibited highest Ni (II) sorption i.e. 97.5 % at pH 6.0, contact time of 30 minutes and biosorbent dose of 0.1 g/100 mL using immobilized biomass whereas maximum removal of 90.2 % was observed with free biomass at 6.0, pH, 40 minutes, contact time and 0.2 g/100mL, biosorbent dose. The biosorption potential of immobilized biomass was higher than that of free biomass of *P. citrinum.* The adsorption process complied with Langmuir and Freundlich isotherms exhibited very high correlation coefficients which confirmed suitability of model and biosorption process.

Key words: Ni (II); Isotherm; Immobilized Biomass; *Penicillium citrinum*; pH

1. Introduction

Environmental pollution by heavy metal ions is one of the major issues. Rapid industrialization has created a major global concern as it emanates aqueous effluents from many industries containing dissolved heavy metals (Keng et al., 2014; Yadav et al., 2013). If these discharges are emitted without treatment, they pose adverse impacts on the environment. As "heavy metals" have highly toxic or ecotoxic properties (Colin et al. 2012) these should be strictly regulated and must be treated before being discharged into environment. Ni (II) is one such metal mainly discharged from various industries such as mining and metallurgy, electroplating and sintered metal coatings, steel foundries, aircraft and motor vehicle industries, printing, storage batteries, chemical industries, leather tanning, pigments for paints or ceramics, electronic or computer equipments, preparation of alloys, etc. (Kumar et al. 2011; Mishra and Malik, 2012). It is of major concern because of its higher toxic effects on living systems. It causes diverse toxic and carcinogenic effects such as allergy, lung fibrosis, cardiovascular and kidney diseases, gastrointestinal irritation (Kasprzak et al. 2003; Fu and Wang, 2011; Sekhon and Singh, 2013). Ni (II) is more deleterious and carcinogenic metal than Ni (IV). So stringent limit has been imposed for discharge of nickel into environment. According to ISI: Bureau of Indian Standard (BIS) the industrial effluent permissible discharge level of Ni (II) into inland water is 3.0 mg/L and levels permitted in water for human consumption are < 0.01 mg/L by World Health

Organization (WHO) (Shroff and Vaidya, 2011; Sharma and Singh, 2013). Multifarious technologies have been developed in recent years to sequester heavy metals from wastewater. The conventional techniques such as ion-exchange, membrane filtration, solvent extraction, dialysis, oxidation-reduction, chemical precipitation, adsorption, reverse osmosis and evaporative recovery are cost-intensive, involves high consumption of reagent and generate huge amount of toxic secondary pollutants (Fenglian and Wang, 2011; Yadav et al. 2013).

Biosorption has emerged as a substitute and feasible approach for treatment of wastewater contaminated with heavy metals by anthropogenic activities and by natural processes, as it is cost-effective and environment friendly (Suazo-Madrid et al. 2011). In this exertion, microbial biomass has emerged as an equivalent, economic and eco-friendly device for controlling the mobility and bioavailability of metal ions. The use of living and nonliving microorganisms such as fungi, yeast, bacteria and algae has gained important credibility during past years in the removal of toxic or precious metals from industrial wastes (Anjana et al. 2007). One of the most extensively investigated biopolymers is Ca- alginate for binding heavy metals from dilute aqueous solutions (Bishnoi et al. 2007; Kumar et al. 2011). Dead fungal biomass has been preferred in numerous studies for biosorption of toxic metal ions from aqueous solution. It represents the sum of all passive interactions of the cell wall with metal ions. These include adsorption reactions, ion exchange reactions with functional groups at the cell surface, and surface complexation reactions. Binding sites for metal ions localized at cell surface include carboxylic, hydroxylic, and phosphate groups of lipids, proteins, and polysaccharides localized at the cell surface (Selatnia et al. 2004). The use of dead biomass is more advantageous than the use of live biomass as there are no requirements of growth media or nutrients, no toxicity concerns and also various techniques are used to desorb contaminants from the biomass to reuse them (Mathialagan et al. 2009). However, reports on fungal biomass of *P. citrinum* as a potential biosorbent of heavy metals are limited.

The purpose of this study was to investigate the requisition of Ni (II) from aqueous solution on to free and immbolized fungal biomass of *P. citrinum.* Experiments were conducted in a batch system and sorption of Ni (II) was investigated with respect to initial pH, amount of biomass, contact time and Ni (II) ion concentration. The adsorption equilibrium was modeled using the Langmuir and Freundlich isotherm.

Materials and methods

2.1 Preparation of synthetic solutions

All the chemicals used in this study were of analytical reagent grade. The solution (1000 mg/L) of Ni (II) was prepared by dissolving the Nickel sulfate ($NiSO_4$; 4.46 g) in 1L of double distilled water. It was used as stock solution. All solutions used in experiments were prepared through dilution of the initial solution with distilled water. pH was adjusted by addition of 0.1 M HCl or 0.1 M NaOH.

2.2 Isolation of fungal strain

Metal resistant fungal strain was isolated from the soil sample of electroplating industry, Lakshmi Precision Screws Ltd. (LPS) Rohtak, Haryana, India. The strains were maintained on solid Rose Bengal agar medium comprising D-glucose (10 g/L), bacteriological peptone (5 g/L), potassium dihydrogen phosphate (1 g/L), magnesium sulphate (0.5 g/L), streptomycin (0.03 g/L) Rose Bengal (0.03 g/L), agar (15.0 g/L) (Martin, 1950). All glasswares were cleaned thoroughly with water, dried and sterilized in hot air oven at 180^{o}C for 4-6 hours before use.

2.3 Preparation of biosorbent

P. citrinum was cultivated in liquid medium using a rotating incubator for the production of biomass. The culture of *P. citrinum* was prepared in 250 ml conical flasks filled with 100 ml of Rose Bengal growth medium. The flasks were shaken on a rotary shaker at 120 rpm for 5 days (end of exponential phase) at 30+2^{o}C. The composition of liquid growth medium was sucrose (50 g/L), NH_4NO_3 (2 g/L), KH_2PO_4 (0.15 g/L), $MgSO_4$ (0.15 g/L). The medium was sterilized by autoclaving at pressure of 15 psi and temperature of 121^{o}C for 20 min. The pH of growth medium was adjusted to 5.5 by using 0.1 M HCl. Fungus biomass was deactivated by heating it in an autoclave at 121^{o}C for 15 min (Schiewer and Volesky, 1995). The biomass was then harvested by filtering the cultured medium through muslin cloth. To remove the growth medium sticked on biomass, surface was washed thoroughly with double distilled water and dried in oven at 50^{o}C for 24 h and powdered in an electrical grinder. The powdered biomass was sieved through standard sieve to obtain particle size upto 0.3 mm and used for immobilisation.

2.4 Immobilization of *P. citrinum*

The powered biomass was immobilized by entrapment in polymer matrix of sodium alginate. 2% (w/v) slurry of sodium alginate was prepared in hot distilled water (60^{o}C). After cooling, 1% (w/v) biomass was added and stirred on magnetic stirrer. The alginate biomass slurry was injected drop-wise into a $CaCl_2$ solution (4%) using an injector to form beads. The resultant beads were of 4 mm diameter. To enhance the mechanical stability of immobilized beads they were cured in the $CaCl_2$ solution for 4 h. The beads were washed twice with sterile distilled water and transferred into culture medium in conical flasks. Blank beads without *P. citrinum* were served as control.

2.5 Biosorption studies

The biosorption experiments were conducted on Ni (II) removal from synthetic solution concentration of 20 mg/L Ni (II) ions, 0.1 g of biosorbent dose in 100mL metal solution for 60 min with varying pH from 2.0 to 9.0 using free and immobilized biomass of *P. citrinum* The pH value of the solution was adjusted using 1N HCl or 1N NaOH. Effect of biosorbent dose were studied ranging from 0.05 to 0.3 g/100mL of Cu (II) solution in 250mL of conical flask while keeping the optimum pH from above experiments and concentration of the Ni (II) ions 20 mg/L. Effect of initial metal ions concentration on biosorption of Ni (II) ions from 10 to 90 mg/L at optimum conditions of pH and biosorbent dose from above experiments was studied. Effect of contact time was studied from 10 to 90 min at optimum conditions and samples were taken after an interval of 10 min. All biosorption experiments were conducted in triplicates in an incubator cum shaker (120 rpm) at 30±2 ^{o}C. Solutions were filtered and then the filtrate was analysed for residual Ni (II) concentration using a atomic absorption spectrophotometer. Uptake capacity and % removal of metal ions were calculated according to equations given in Kumar et al. (2008).

$$q = [(C_0 - C)\, V] / M \qquad \ldots\ldots \text{(II)}$$

Where q (mg/g) is the amount of Ni (II) adsorbed onto unit amount of adsorbent, C_0 and C (mg/L) are the concentrations of Ni (II) in solution before and after biosorption, respectively. V (L) is the volume of aqueous solution and M (g) is the mass of the biosorbent.

2.6 Adsorption isotherm studies

Experiments were conducted in the sequential order used for the determination of optimum value of parameters and the optimized values were applied for the subsequent experiments followed in the sequence. After determination of optimum values that supported maximum sorption of Ni (II), the biosorption data obtained for Ni (II) was analyzed using Langmuir and Freundlich

isotherms. Langmuir's isotherm model is valid for monolayer adsorption onto a surface containing a finite number of identical sites, which is represented as equation (Langmuir, 1918):

$$1/qe = 1/qmax + (1/qmaxK_L)\ 1/Ce \quad ...(III)$$

Where qe is the amount adsorbed at equilibrium (mg/g); Ce is the equilibrium concentration (mg/L); qmax is the maximum amount of the amount adsorbed per unit weight of biosorbent to form a complete monolayer on the surface and K_L is a constant related to the energy of biosorption (L/ mol).

The Freundlich equation (Freundlich, 1906) proposes an empirical model that is based on the sorption on heterogenous surface and has the form:

$$\ln qe = \ln K + 1/n \ln Ce \quad ... (IV)$$

Where K (mg/g) and n are Freundlich isotherms constants and indicators of the biosorption capacity and biosorption intensity, respectively; Ce is the equilibrium concentration (mg/L); qe is the amount adsorbed (mg/g).

3.Results and discussion

3.1 Effect of pH

pH plays a critical role in the biosorption of Ni (II) from aqueous solutions. It influences both speciation of Ni (II) in aqueous solution and the binding sites present on the surface of biomass (Uslu and Tanyol, 2006). The biosorption of Ni (II) increased with rise in pH but had marginal effect beyond pH 6.0 by both immobilized and free biomass (Fig.1).

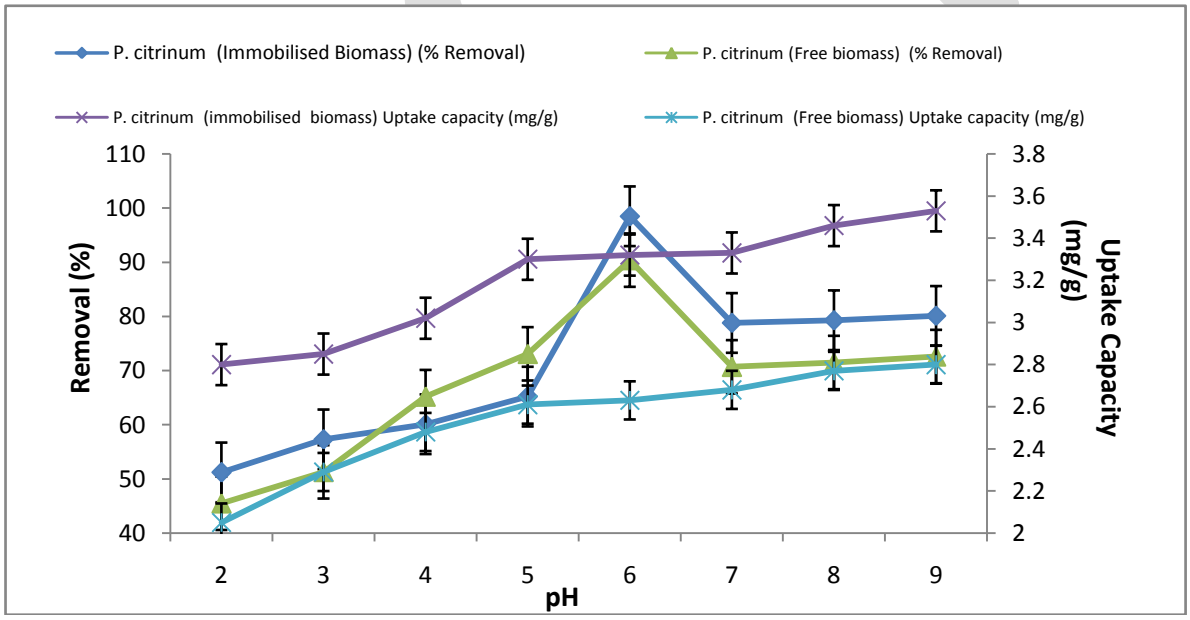

Fig. 1 Effect of pH on Ni (II) removal, (initial Ni (II) concentration=20 mg/L, biosorbent dose = 0.1 g/100 mL, contact time=60 min, shaking speed = 120 rpm and temp. = 32°C)

The percentage removal of Ni (II) at pH 6.0 was 98.5% and 90.4%, and uptake capacity was found to be 3.32 mg/g and 2.63 mg/g for immobilized and free biomass, respectively. So optimum pH was found to be 6.0 and all the subsequent experiments were conducted at this pH value. At pH below 6.0, the low uptake of Ni (II) can be attributed to the competition of Ni (II)

with H_3O^+ ions that restrict the access of Ni (II) ions to cell walls as a result of repulsive forces to surface functional groups (Xu et al. 2006; Zafar et al. 2007). As pH increases (2.0 < pH < 6.0), the competing effect of H_3O^+ ions decreases. More functional groups such as carboxylic, phosphate and amino groups carrying negative charges are exposed (Kumar et al. 2009).
The degree of ionization of these negative groups also increases; leading to electrostatic attractions between positively charged cations such as Ni (II) and negatively charged binding sites, thereby promoting binding of Ni (II) (Zafar et al. 2007). Our results corroborate with that of Mishra and Malik (2012) with respect to the optimum pH for Ni (II) ion removal as 6.0 by *Aspergillus lentulus.*

3.2 Effect of biosorbent dose

The percentage removal and adsorption capacity of Ni (II) at different biosorbent concentrations are presented in Fig. 2. Ni (II) removal increased with increasing biosorbent dose up to 0.1 g/100 mL and 0.2 g/100 mL for immobilised and free biomass of *P. citrinum.* Ni (II) removal was found to be increased from 61.3% to 70.1% for immobilized biomass and 55.3% to 67.6% for free biomass (Fig. 2). The percentage removal increased with the increase of biosorbent dose, this is due to enhanced number of binding sites which in turn resulted in increased surface area of the biosorbent, (Esposito et al., 2001). Uptake capacity was reduced from 24.5 to 4.8 mg/g and 22.1 to 4.4 mg/g for immobilized and free biomass, respectively. At high sorbent doses beyond 0.15 and 0.25 g/100 mL for immobilized and free *P. citrinum* respectively, a significant improvement in adsorption was not observed. The reason behind, reduced uptake capacity at higher biomass concentration includes competition of solute ions for limited available sites, overlapping or aggregation of adsorption sites resulting in a decrease in total adsorbent surface area, electrostatic interactions, interference between binding sites and reduced mixing at higher biomass densities (Saifuddin et al. 2007; Kumar et al. 2012). Optimum dose for Ni (II) removal was found to be 0.1 g/100 mL for immobilized biomass and 0.2 g/100 mL for free biomass of *P. citrinum.*

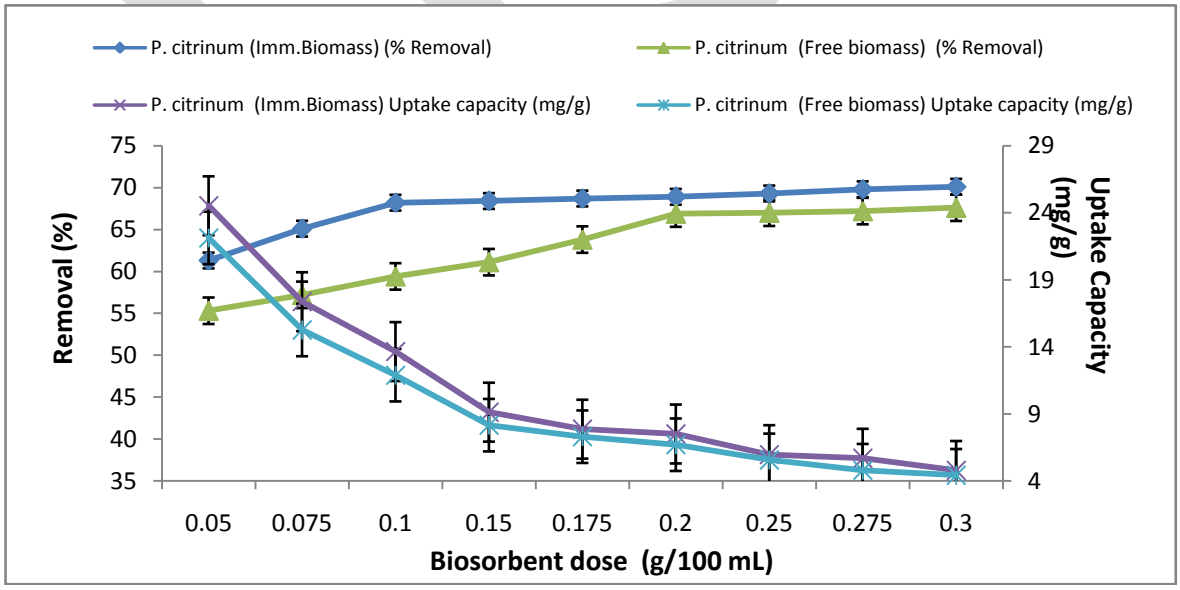

Fig. 2 Effect of biosorbent dose on Ni (II) removal, (initial Ni (II) concentration = 20 mg/L, pH 6.0, contact time = 60 min, shaking speed = 120 rpm & temp. = 32°C)

3.3 Effect of contact time

The rate of biosorption is an important parameter for designing batch biosorption experiments. Therefore, the effect of contact time on biosorption of Ni (II) was investigated. As seen in Fig. 3, the Ni (II) uptake as a function of time indicated a biphasic pattern (El-Ashtoukhy et al. 2008) as it occured in two main stages: an initial rapid stage which is related to external surface biosorption, and a second slow stage which referred to gradual biosorption stage and occurs due to quick exhaustion of the adsorption sites before Ni (II) uptake reached equilibrium. The first step would involves sorption of metal ions onto external sites and second included metal ion diffusion into biomass, surface precipitates, formation of the multinuclear surface complexes, and other slow chemical reactions. The results indicated that Ni (II) removal was found to be increased from 52.1% to 70.0% for immobilized biomass and 50.2% to 65.2% for free biomass (Fig.3). The biosorption of Ni (II) ions is rapid in the first 30 and 40 min for immobilized and free biomass respectively as a result of free binding sites on the biomass. Shroff and Vaidya, (2011) reported similar findings on biosorption of Ni (II) from aqueous solution by dead fungal biomass of *Mucor hiemalis*. The same findings were published by (Gorgievski et al. 2013) as kinetics of adsorption was relatively fast and reached equilibrium after 30 min of the adsorption process in the case of Ni (II) using wheat straw.

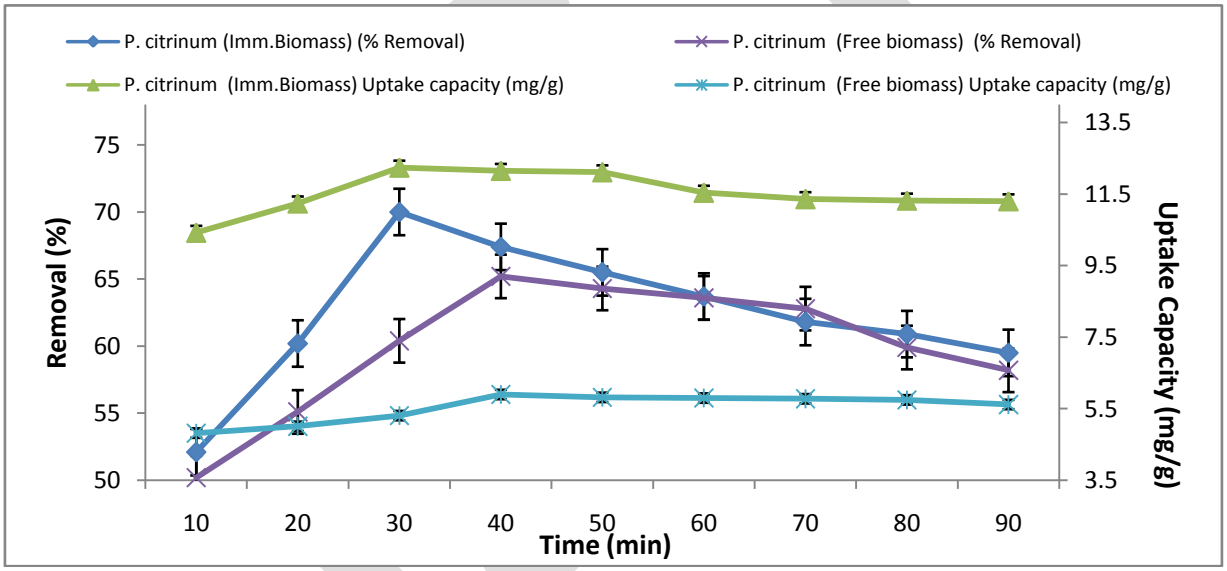

Fig. 3 Effect of contact time on Ni (II) removal, (initial Ni (II) concentration = 20 mg/L, dose= 0.1g (imm. biomass) and 0.2 g (free biomass) and pH 6.0, shaking speed = 120 rpm and temp. = 32^{o}C)

3.4 Effect of initial metal ion concentration

The removal percentage for adsorption of metal ions was studied at different Ni (II) concentrations keeping adsorbent dose (0.1 and 0.2g/100mL of free and immobilized biomass respectively), pH (6.0) and contact time (30 and 40 min for immobilized and free biomass respectively) constant. As presented in Fig. 4 maximum biosorption was investigated at 40 mg/L and 30 mg/L i.e. 97.5% and 90.2% for Ni (II) ions by immobilized and free biomass, respectively. From the experiments it is found that the percentage metal ion adsorption was decreased with increase in initial metal ion concentration. Tay et al. (2010) also reported similar trend on Ni (II) biosorption by *Pleurotus* spent mushroom compost. The immobilized beads of *P.*

citrinum had a higher biosorption capacity for the Ni (II) concentration than free biomass because of surface sorption capacity of alginate beads. At initial Ni (II) concentration, adsorption sites on the biosorbent remain unsaturated during the adsorption reaction and hence biosorption of metal ions was very effective, while at higher concentrations of Ni (II), the number of ions competing for the available binding sites on the biomass increase and results in lack of binding sites for complexation of Ni (II) ions which resulted in decreased biosorption efficiency of Ni (II).

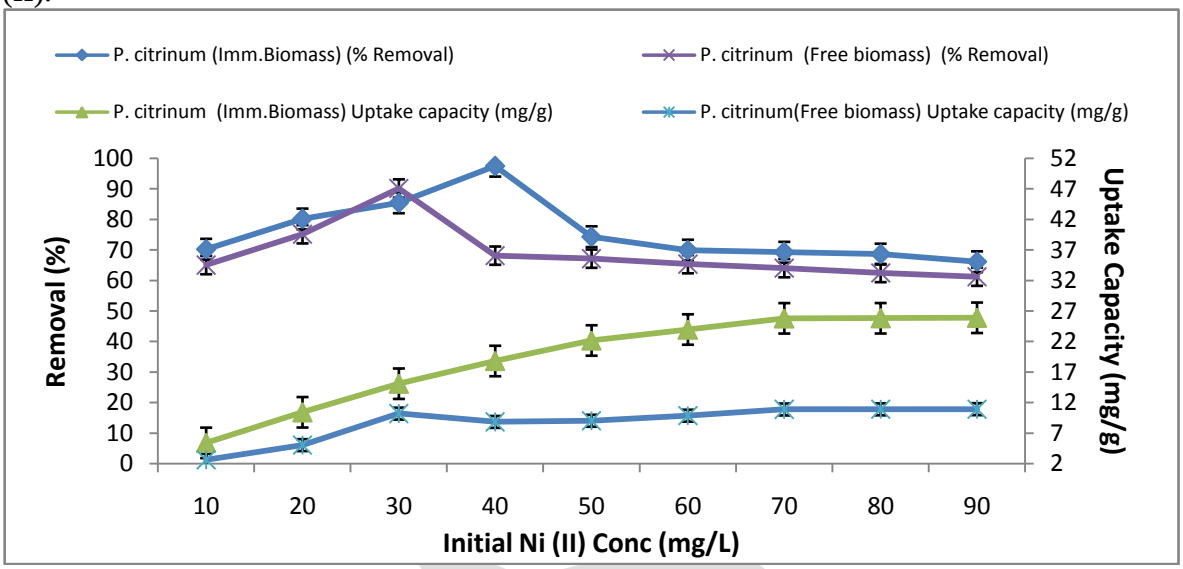

Fig. 4 Effect of initial concentration of metal Ni (II) for removal by free and immobilized biomass of *P. citrinum* (dose= 0.1g (imm. biomass) & 0.2 g (free biomass), pH 6.0, contact time = 30 min. (imm. biomass), contact time = 40 min. (free biomass), shaking speed = 120 rpm and temp. = 32^{o}C)

3.5 Biosorption study:

The equilibrium models are extensively used to investigate the amounts of metal ions sorbed by a certain biomass. The distribution of metal ions between solution and biomass is a measure of the position of equilibrium and can be expressed by one or more isotherms. In present study, the Freundlich and Langmuir adsorption models were used for mathematical description of adsorption of Ni (II) ions. Isotherms constants were determined to find out the adsorption capacity of biosorbent, *P. citrinum* for Ni (II). Higher value of correlation coefficients $R^2 \geq 0.99$ indicated that the biosorption data are best fitted in both Freundlich and Langmuir models. Langmuir equation:

$Ce/ qe = 1 / Qob + Ce / Qo$ ... (V)

Ce is the equilibrium concentration (mg/L), qe is the amount adsorbed at equlibrium (mg/g), Qo and b are Langmuir constants indicating the sorption capacity and energy, respectively, and are determined from slope and intercept of the plot. The results indicated that the sorption capacity of immobilized biomass is higher than that of free biomass. The Langmuir constant values for P. citrinum(Immobilized biomass) were as Qo 25 mg/g, b 0.02 and R^2 0.99. The Langmuir constant values for P. citrinum(free biomass) were as Qo 22.7 mg/g, b 0.02 and R^2 0.99. The essential features of Langmuir isotherm can be expressed in terms of dimensionless "separation factor or equilibrium constant RL".

$R_L = 1 / (1+QoCi)$ ... (VI)

Where Ci is the initial concentration and Qo is the Langmuir constant indicating the nature of adsorption.

Freundlich equation:

$Qe = x/m = K\ Ce\ 1/n$ ... (VII)

Logarithmically, $Log\ (x / m) = log\ K + 1/n\ log\ Ce$ ... (VIII)

The present data fitted well in Freundlich isotherm model (Tables 1). K and 1/n are Freundlich biosorption isotherm constants denoting the adsorption capacity and the intensity of adsorption, respectively. The values of K for Ni (II) are 1.27 and 1.15 with immobilized and free biomass, respectively. The higher magnitude of K for Ni (II) i.e 1.27 illustrated high adsorption capacity of immobilized biomass over free biomass (1.15). Similarly higher value of 1/n i.e 0.59 indicated high intensity of adsorption for immobilized biomass as compared to free biomass (0.52) for Ni (II). The values of n for P. citrinum (immobilized biomass) was 1.92 and for P. citrinum (free biomass) was 1.70. The data showed a high value of correlation coefficient (R^2) 0.99 in both the cases (free as well as immobilized biomass).

4.0 Conclusion

In this study, immobilized biomass was found to be an efficient biosorbent for sorption of Ni (II) ions from aqueous solutions in batch biosorption study. Maximum removal of Ni (II) was found to be 97.5% and 90.2% with immobilized and free biomass, respectively. The immobilized biomass showed higher affinity towards Ni (II). The maximum adsorbed amounts of Ni (II) were obtained at pH values of 6.0 and contact time of 30 and 40 minutes for immobilized and free biomass, respectively. Optimum dose for Ni (II) removal was found to be 0.1 g/100 mL for immobilized biomass and 0.2 g/100 mL for free biomass of *P. citrinum*. The experimental data were well analyzed using isotherm models to evaluate the performance of the fungal biosorbent. The low-cost and the possibility of using dead cells as well as high adsorption amount for Ni (II) make the *P. citrinum a* promising biosorbent for the removal of Ni (II) from simulated wastewater.

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