Kinetic modeling for the biosorption of copper by pretreated *Aspergillus niger* biomass

Mausumi Mukhopadhyay [a,1], S.B. Noronha [a,*], G.K. Suraishkumar [b]

[a] *Department of Chemical Engineering, Indian Institute of Technology Bombay, Mumbai 400 076, India*
[b] *Department of Biotechnology, Indian Institute of Technology Madras, Chennai, India*

Abstract

In this present work, a kinetic model for biosorption of copper was developed considering the possibility of different forms of functional groups being present on the surface of the biomass prepared from *Aspergillus niger*. Results showed that metal uptake by *A. niger* was a mass transfer driven process, requiring only 30 min to achieve 70% adsorption efficiency. Copper sorption by *A. niger* was influenced by the biomass dose, initial metal ion concentration, and pH of the solution. The Langmuir and Freundlich adsorption isotherms were used to describe the behavior of the system at different pH. The retention capacity of the biomass was determined at pH 6.0 to be equal to 23.62 mg/g of biomass. The pretreatment with formalin improved the uptake of metal ion.

1. Introduction

Environmental contamination is a major problem being faced by the society today. Heavy metal removal from wastewater is important for the protection of the environment and human health. One of the more important toxic metals, copper, finds its way to the water stream from industries like electroplating, mining, electrical and electronics, iron and steel production, the non-ferrous metal industry, the printing and photographic industries and metalworking and finishing processes (Brauckmann, 1990). The effects of acute copper poisoning in humans and plants are very serious, in particular possible liver damage with prolonged exposure. Strict environmental regulations have enhanced the demand for new technologies for metal removal from wastewater to attain toxicity driven limits.

Previous studies have reported the use of biosorption methods for removal and recovery of heavy metals from contaminated industrial effluents. Biosorption has been investigated in recent years with a focus on different biomasses (Brierley, 1990). It has been reported that bacteria, fungi, yeast and algae can remove heavy metals in reasonably good amounts from aqueous solutions (Gadd, 1988). The biomass can be cheaply and easily procured as a byproduct from the established industrial fermentation processes, for the biosorption of heavy metals (Muraleedharan et al., 1991) that can also result in value addition for the waste biomass along with a reduction in biomass disposal costs.

Many reports exist on work to identify suitable and relatively cheap biosorbents, which are capable of removing copper ions (Schiewer and Wong, 1999; Esposito et al., 2001). Biosorption by *Aspergillus niger* has been identified for its potential to remove metals (Mukhopadhyay et al., 2006a,b) due to its availability from various industrial fermentation processes. Kapoor and Viraraghavan (1997, 1998) and Kapoor et al. (1999) performed experiments with raw and pretreated *A. niger* to determine the effectiveness of the biomass for removal of lead, cadmium, copper and nickel. They showed that the various functional groups in

the cell wall of *A. niger* are responsible for biosorption. In addition they showed that pretreatment increases adsorption capacity of the biomass for all metals but the magnitude of increment depends on the type and method of pretreatment.

There is no information in the literature on any mechanistic study of adsorption capacity as a function of the surface groups on biomass. These surface groups, which are responsible for biosorption of copper, are strongly affected by the pH of the solution. It is expected that different functional groups are active at different solution pH. The main objective of this study was to propose a kinetic model for the biosorption of copper by pretreated *A. niger* to support the experimental data at different operating conditions such as initial biomass concentration, initial metal ion concentration of the metal and pH of the solution.

2. Methods

2.1. Growth of culture

The fungus *A. niger* strain NCIM 618 (ATCC 10594), was obtained from NCIM, Pune, India. It was propagated on potato dextrose agar (PDA) 39 g/l and yeast extract 0.1 g/l for 5–7 days at 33 ± 2 °C. Fungal biomass was cultivated in liquid medium containing (g/l): dextrose, 30; peptone 10; $(NH_4)_2HPO_4$, 0.4; KH_2PO_4, 0.2; $MgSO_4$, $7H_2O$, 0.2. All reagents were from Himedia, or Merck (Mumbai, India). The pH of the growth medium was adjusted to 5.8–6.0 by the addition of 0.1 N HCl prior to autoclaving. After inooculation, flasks were incubated at 200 rpm for five days at 33 ± 2 °C. After harvesting the biomass, it was transferred to a 1% formalin solution for 24 h. The biomass was then dried at 60 °C for 20–24 h and powdered in a mortar. The powdered biomass residue was used for further studies.

2.2. Assays

The surface functional groups were characterized by FTIR (Magna 550, USA). Copper concentrations were measured by atomic absorption spectroscopy (AAS-SL 173, EIL).

2.3. Adsorption experiments

2.3.1. Particle sizing of adsorbents

The powdered biomass was passed through different British Standard Sieves (BSS) and fractions were collected. Maximum uptake of metal per g of biomass was observed corresponding to 0.75–1.0 mm of particles size, hence, for all experiment particle this size range was used.

2.3.2. Kinetic study

The effect of the time of exposure of the biomass powder to metals on the biosorption characteristics was investigated. Metal solutions at 100, 50, 25 and 10 mg/l (1.575, 0.787, 0.394 and 0.1575 mmol/l, respectively) were made by dissolving copper metal in conc. HNO_3 in double distilled water. The kinetic experiments were studied at initial pH of 5.0, 5.5 and 6.0, respectively. The final pH of the solution was measured. In each case, 0.002 g/ml of biomass was added with 50 ml of the metal solution at room temperature and continuous stirring at 200 rpm. At the indicated times, aliquots were withdrawn and used to determine the amount of metal remaining in solution. All experiments were performed in triplicate and the average value was taken for analysis.

2.3.3. Equilibrium experiments

The metal biosorption capacity was determined at different initial metal ion concentration of 100, 50, 25, 10 mg/l and a fixed concentration of biomass (100 mg, dry weight) and was used to calculate biosorption constants by using different isotherms. Fifty ml of each solution was tested at optimum pH. The solution was for 24 h at 200 rpm to allow the biomass to adsorb the metal ions until the solution reached equilibrium. The initial and the final concentration of the solutions were measured by AAS. These data were used to calculate the adsorption capacity of the adsorbent. Finally, a diagram of adsorption capacity against equilibrium concentration was plotted.

2.3.4. Influence of biomass dose

To find out the metal biosorption capacity of the treated biomass, the dissolved metal was taken at 50 mg l^{-1} while the concentration of biomass in the solution used in the range of 2–5 g l^{-1}.

2.3.5. Influence of initial metal ion concentration

Different initial metal concentrations in the range of 10–100 mg l^{-1} and a fixed concentration of biomass (2 g l^{-1}) were used to calculate biosorption capacity. Fifty ml of each solution was tested by varying pH. The initial and the final concentration of the solutions were measured by AAS. These data were used to calculate the adsorption capacity of the adsorbent.
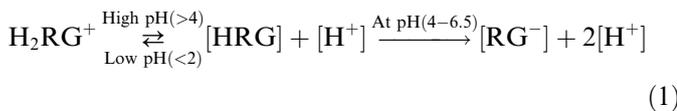
2.3.6. Influence of pH

The pH value of the wastewater has a large influence on the extent of biosorption. Fifty ml of metal solutions at 100, 50, 25 and 10 mg/l was tested with 0.002 g/ml of biomass by varying pH in between 2.0 and 8.0, respectively. The initial and the final concentration of the solutions were measured by AAS. The maximum sorption data was used to find out optimum pH and the remaining experiment was conducted at optimum pH.
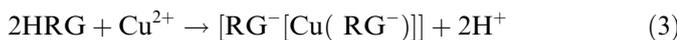
3. Modeling methods

3.1. Kinetic modeling

The biomass structure is complex in nature. From a biosorption perspective it may be assumed to contain combination of different active functional groups as determined by FTIR measurements (Mukhopadhyay et al., 2006a,b). These groups are involved in the reaction and responsible for the biosorption capacity. At different pH different groups are dominating and participating in the complexation process. pH dependence of surface reactive groups is presented in Eq. (1).

$$H_2RG^+ \underset{\text{Low pH}(<2)}{\overset{\text{High pH}(>4)}{\rightleftarrows}} [HRG] + [H^+] \xrightarrow{\text{At pH}(4-6.5)} [RG^-] + 2[H^+] \tag{1}$$

Considering the formation constant of Cu(II)-organic matter complexes (Coleman et al., 1956) and the proposed forms (Fig. 1) of surface reactive group sorption reactions of Cu(II) and biomass may be represented by the Eqs. (2)–(15).

$$2RG^- + Cu^{2+} \rightarrow [RG^-[Cu(RG^-)]] \tag{2}$$

$$2HRG + Cu^{2+} \rightarrow [RG^-[Cu(RG^-)]] + 2H^+ \tag{3}$$

$$2H_2RG^+ + Cu^{2+} \rightarrow [RG^-[Cu(RG^-)]] + 4H^+ \tag{4}$$
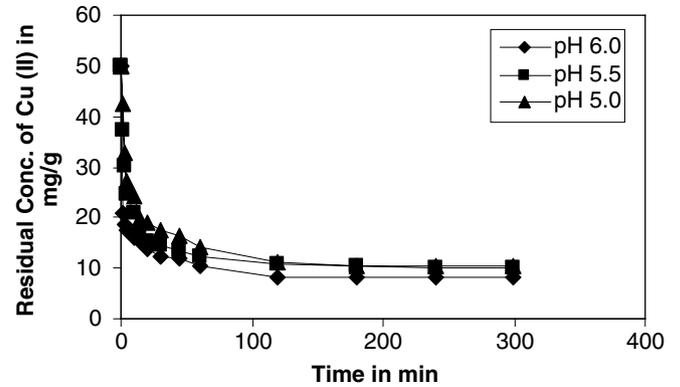
The rate equations for the biosorption described by the above equations is

Fig. 1. Kinetic plot for biosorption of Cu(II) in *A. niger* biomass.

$$\frac{d(RG^-)}{dt} = k[[RG^-]_e - [RG^-]_t]^2 \tag{5}$$

$$\frac{d(HRG)}{dt} = k[[HRG]_e - [HRG]_t]^2 \tag{6}$$

$$\frac{d(H_2RG^+)}{dt} = k[[H_2RG^+]_e - [H_2RG^+]_t]^2 \tag{7}$$

where $[RG^-]_t$, $[HRG]_t$ and $[H_2RG^+]_t$ are the number of active sites occupied on the biomass at time t and $[RG^-]_e$, $[HRG]_e$ and $[H_2RG^+]_e$ are the number of equilibrium sites available on the biomass.

The kinetic expression can be represented as the pseudo-second order rate expression as

$$\frac{Q_{RG_t^-}}{t} = k(Q_{RG_e^-} - Q_{RG_t^-})^2 \tag{8}$$

$$\frac{Q_{HRG_t}}{t} = k(Q_{HRG_e} - Q_{HRG_t})^2 \tag{9}$$

$$\frac{Q_{H_2RG_t^+}}{t} = k(Q_{H_2RG_e^+} - Q_{H_2RG_t^+})^2 \tag{10}$$

where k is the pseudo-second-order rate constant of biosorption, in g/mg min and $Q_{RG_e^-}, Q_{HRG_e}$ and $Q_{H_2RG_e^+}$ is the amount of copper ion sorbed at equilibrium (mg/g), $Q_{RG_t^-}, Q_{HRG_t}$ and $Q_{H_2RG_t^+}$ is amount of copper ion sorbed on the surface of the sorbent at any particular time t in mg/g. Integrating with the boundary conditions at $t = 0$, $Q_{RG_t^-}, Q_{HRG_t}$ and $Q_{H_2RG_t^+} = 0$ and at $t = t$, $Q_{RG_t^-} = Q_{RG_t^-}$, $Q_{HRG_t} = Q_{HRG_t}$, $Q_{H_2RG_t^+} = Q_{H_2RG_t^+}$ gives

$$\frac{t}{Q_{RG_t^-}} = \frac{1}{kQ_{RG_e^-}^2} + \frac{1}{Q_{RG_e^-}}t \tag{11}$$

$$\frac{t}{Q_{HRG_t}} = \frac{1}{kQ_{HRG_e}^2} + \frac{1}{Q_{HRG_e}}t \tag{12}$$

$$\frac{t}{Q_{H_2RG_t^+}} = \frac{1}{kQ_{H_2RG_e^+}^2} + \frac{1}{Q_{H_2RG_e^+}}t \tag{13}$$

Considering $t \rightarrow 0$, the initial biosorption rate r_i can be defined as

$$r_i = kQ_{RG_e^-}^2; \quad r_i = kQ_{HRG_e}^2; \quad r_i = kQ_{H_2RG_e^+}^2 \tag{14}$$

The rate constant for the intraparticle diffusion (k_{id}) is given by Weber and Morris (1962)

$$Q_{RG_t^-} = k_{id}t^{1/2}; \quad Q_{HRG_t} = k_{id}t^{1/2}; \quad Q_{H_2RG_t^+} = k_{id}t^{1/2} \quad (15)$$

where $Q_{RG_t^-}, Q_{HRG_t}$ and $Q_{H_2RG_t^+}$ is the amount adsorbed (mg/g) at time t min. In the operating pH the reactive group RG^- dominates (Eq. (1)), so $Q_{RG_t^-}$ is considered for surface reaction.

3.2. Equilibrium isotherms

Modeling the biosorption-binding equilibrium is a prerequisite for work involving batch studies that represent the most effective configuration of the sorption-based process. The Langmuir and Freundlich isotherm equations are used to predict the sorption of copper from aqueous solutions onto the *A. niger* biomass (Rakshit, 1986).

4. Results and discussion

Table 1 shows the biosorption characteristics of different biomasses for Cu(II) removal. Pretreatment of the biomass was performed following the work of (Kapoor and Viraraghavan, 1997, 1998; Kapoor et al., 1999). Formalin pretreatment significantly improved the surface active site that actually participates in Cu(II) sorption. Mukhopadhyay et al. (2006a,b) used infrared spectroscopy (IR) to characterize the raw biomass and reported the presence of –COOH, –NH$_2$, –OH groups. Volesky (1987) studied the chemical composition of the walls of the *A. niger* and reported (%) protein 8.3; chitin 8.3; chitosan 18.3; mannan 45.5; phosphate 11.5 and carbohydrate and lipids.

4.1. Kinetic study

Fig. 1 showed that biosorption of metal ion was rapid during the first 30 min with nearly 70% recovery being achieved in this time period and continued at slower rate for remaining time period. The measurements indicated active sorption sites of the biomass involved in Cu(II) complexation as soon as the biomass was introduced in to the system. Chen and Lin (2001) reported that Cu(II) adsorption with H-type granulated activated carbon occurred dramatically in the first 30 min and reached its equilibrium with complete removal in 3 h. Blanco et al. (1999) reported that Cu(II) biosorption by non-viable biomass of the *Phormidium laminosum* entrapped in polysulfone and epoxy resin beads was rapid during the first hour, 38% recovery achieved in this time period and continued at a slower rate for the several hours.

Fig. 2 showed that the pseudo-second-order fitted with experimental kinetic data at initial pH of 5.0, 5.5 and 6.0 of the solution, respectively. The initial biosorption rate, r_i, the equilibrium sorption capacity and the pseudo-second-order rate constant, k, were determined experimentally from the slope and intercept of the above plot of $t/Q_{RG_t^-}$ vs. t. The estimated regression coefficients of pseudo second order rate constant of biosorption are presented in Table 2.
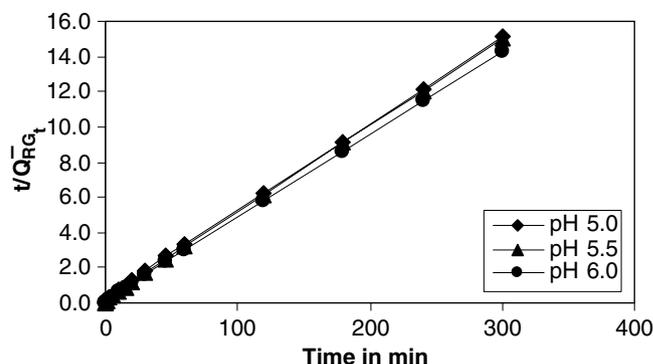

Fig. 2. Pseudo-second order plot of $t/Q_{RG_t}^-$ vs. t of biosorption of Cu(II) ions on the *A. niger* biomass.

Table 1
Biosorption characteristics of different biomasses for Cu(II) removal

Uptake in (mg/g)	Adsorbent	Source	Category	pH	Temp. (°C)	Conc. (mmol/l)	Reference
23.62	*Aspergillus niger*	Fungi	Biomass	6	33	0–1.575i	This work
15.6	*Aspergillus niger*	Fungi	Biomass	5	25	0–1.575i	Dursun et al. (2003)
28.7	*Aspergillus niger*	Fungi	Biomass	5	25	0–3.937i	Dursun (2006)
2.66	*Aspergillus niger*	Fungi	Biomass	4–6	22 ± 2	0–0.157i	Kapoor et al. (1999)
7.42	*Aspergillus niger*	Fungi	Biomass	5	22 ± 2	0–0.157i	Kapoor and Viraraghavan (1998)
8.89	*Aspergillus oryzae*	Fungi	Biomass	5	RT	0–2.23i	Huang and Huang (1996)
4.13	*Rhizopus oryzae*	Fungi	Biomass	5	RT	0–2.23i	Huang and Huang (1996)
9.5	*Rhizopus arrhizus*	Fungi	Biomass	5.5	25	0–0.394i	Fourest and Roux (1992)
19.5	*Cladosporium cladosporioides*	Fungi	Biomass	4	RT	1.575i	Petkar et al. (2001)
20.23	*Phanerochaete chrysosporium*	Fungi	Biomass	6	25	0.08–7.87i	Say et al. (2001)
1.25	*S. cerevisiae*	Yeast	Biomass	5	RT	0–2.23i	Huang and Huang (1996)
1.9	*S. quadricauda*	Algae	Biomass	5	RT	0–2.23i	Harris and Ramelow (1990)
26	*Ochrobactrum anthropi*	Bacteria	Biomass	3	30	1.442i	Ozdemir et al. (2003)
1.59	Activated carbon	Nuchar SA	Conventional	5	RT	0–2.23i	Corapcioglu (1984)
1.27	Activated carbon	Filtrasorb 200	Conventional	6	25	10–4 Mi	Chen and Wang (2004)
8.09	Petiolar felt-sheath of palm	Agriculture by-products	Other	5	25	0.08–1.575i	Iqbal et al. (2002)
11.7	Tree fern	Agriculture by-products	Other	n.a.	30	0.472–2.36i	Ho (2003)

Table 2
The pseudo-second-order kinetic constants for biosorption of Cu(II) ions on the *A. niger* biomass

pH	Second-order-kinetic			Intraparticle diffusion rate
	k (g/mg min)	r_i (mg/g min)	R^2	k_{id} (mg/g min$^{1/2}$)
6.0	0.021	9.23	0.9998	9.78
5.5	0.017	7.2	0.9999	6.1
5.0	0.01	3.94	0.9997	4.7

The impact of intraparticle diffusion was estimated from a plot of $Q_{RG_t^-}$ vs. $t^{1/2}$. Fig. 3 shows the effect of intraparticle diffusion on biosorption of Cu(II) ions at initial pH of 5.0, 5.5 and 6.0, respectively. The kinetics of adsorption may depend on the adsorbent porosity; the matrix must allow the adsorbate to diffuse through it until reaching the active sites. The plot indicated an initial curved portion followed by a linear portion and a plateau. The initial steep-sloped portion (0–1 h) was attributed to surface adsorption and gradual adsorption, where the intraparticle diffusion was rate controlled and the plateau at equilibrium. At this region, the intraparticle diffusion begins to slow due to extremely low solute concentration in the solution (Sun and Yang, 2003). The intraparticle diffusion rate was obtained from the slope of the steep-sloped portion. The intraparticle diffusion rate constant k_{id} in mg/g min$^{1/2}$ was calculated and tabulated in Table 2. The *t*-test data showed that the correlation at pH 6 was statistically significant at 95% confidence level. In the experimental conditions, the complexation of Cu(II) by the reactive groups did not depend only on the availability of surface active groups and the copper uptake might occurred on the sites that were reached also by diffusion effects.

4.2. Adsorption isotherm

The experimental data were fitted to Langmuir and Freundlich models. The Langmuir constants C_S^{max} and b were calculated from the experimental data and were 0.041 an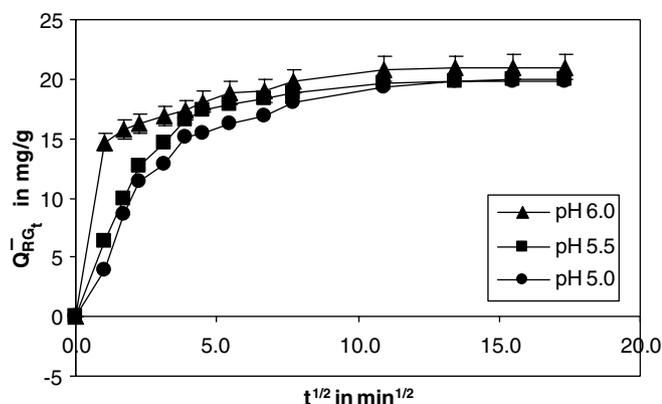d 12 l/mmol, respectively, with a regression coefficient of 0.99. The Freundlich constant K_F and n for Cu(II) adsorption by *A. niger* calculated from the equilibrium data were 5.35 g/l and 0.42 with a regression coefficient of 0.89. The magnitude of K_F and n value showed easy uptake of Cu(II) from aqueous medium with a high adsorption capacity of this biomass. Langmuir equation better represented the experimental isotherm data. Kapoor et al. (1999) reported both Langmuir and Freundlich isotherm data at pH 5 for Cu(II) biosorption by NaOH pretreated *A. niger* biomass were statistically significant at 95% confidence level.

4.3. Influence of biomass dose

Results on influence of biomass dose showed that the amount of metal bound per g of biomass in mg g^{-1} decreased as the biomass concentration increased (data not shown). This was due the interference between binding sites at higher concentrations or insufficiency of metal ions in solution with respect to available binding sites (de Rome and Gadd, 1987). Similar observations were made in studies on metal sorption by immobilized *P. laminosum* (Blanco et al., 1999), *Rhizopus arrhizus* (Fourest and Roux, 1992) and also in the case of copper and chromium uptake by *Aspergillus carbonarius* (Al-Asheh and Duvnjak, 1995). Higher uptake at lower biomass concentrations could be due to an increased metal to biosorbent ratio, which decreases upon an increase in biomass concentration. The highest uptake observed was at 23.62 mg of copper per g of biomass at metal to biomass ratio of 250:1000.

4.4. Influence of initial metal ion concentration

Fig. 4 indicated that the initial metal concentration had a strong effect on biosorption capacity. As the metal ion concentration increased, biosorption capacity also increased and reached a saturation value. This finding was similar to the reported data of biosorption of Cu(II) onto *P. chrysoorium* a fungal biomass (Say et al., 2001). It was observed that the pH of the solution was different

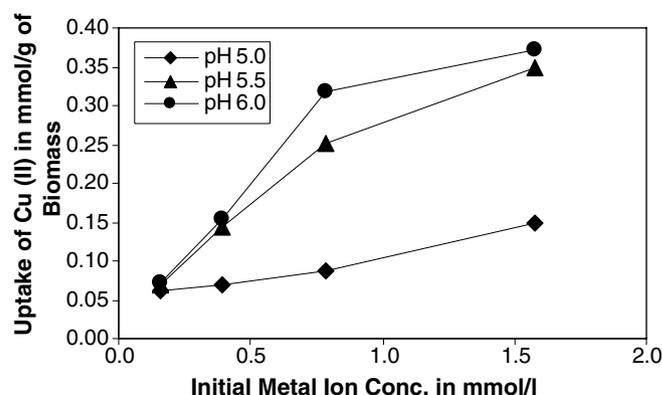Fig. 3. Plot of $Q_{RG_t}^-$ vs. $t^{1/2}$ of biosorption of Cu(II) ions in *A. niger* biomass.

Fig. 4. Initial metal ion concentration vs. uptake of biosorption of Cu(II) ions in *A. niger* biomass.

at the end of the experimentation. The final pH of the solution depends on the initial pH of the solution as well as the initial concentration of the metal ion used for sorption. The final pH of the solution for 50 mg/l initial copper ion solution and initial pH of 5.0, 5.5 and 6.0 were 4.55, 4.59 and 4.66, respectively, whereas for the same initial pH with 25 mg/l of initial metal solution, final pH were 5.49, 5.15 and 5.70, respectively. At high metal ion concentration, the number of metal ions sorbed more than at low metal concentration, where more binding sites were free for interaction. The maximum uptake in this condition as calculated from Langmuir isotherm was 0.41 mmol l^{-1}.

4.5. Influence of pH

Results on the effect of pH showed that the maximum Cu(II) uptake in mg of metal per g of biomass for 50 mg/l initial metal ion concentrations was at pH 6.0 (data not shown). The sorption of metal ions depends on solution pH, which influences electrostatic binding of ions to corresponding functional groups. *A. niger* contains abundant chitin–chitosan units and reasonable amount of protein and amino acids like hystidine, which serve as a matrix of –COOH and –NH$_2$ groups (Mukhopadhyay et al., 2006a,b), which in turn take part in binding of metal ion (Tsezos, 1983). The interaction of the matrix with the Cu(II) ion was determined by the extent of protonation of the cell wall functional groups, which in turn depended upon the solution pH. With increasing pH, these groups deprotonated and thus formed negatively charged sites. At pH values higher than 6.0, Cu(II) ions precipitated out because of the high concentrations of OH$^-$ ions in the biosorption medium (Baes and Mesmer, 1976).

5. Conclusions

The results obtained in this study on kinetic data could be useful for the design of a wastewater plant. A comparative data of adsorptive capacity indicated that the prepared biomass surface had more affinity for Cu(II).

References

Al-Asheh, S., Duvnjak, Z., 1995. Adsorption of copper and chromium by *Aspergillus carbonarius*. Biotechnol. Prog. 11, 638–642.

Baes, C.F.J., Mesmer, R.E., 1976. The hydrolysis of cations. Wiley, New York, 1–7.

Blanco, A., Sanz, B., Llama, M.J., Serra, J.L., 1999. Biosorption of heavy metals to immobilized *Phormidium laminosum* biomass. J. Biotech. 69, 227–240.

Brauckmann, B.M., 1990. Industrial solution amenable to biosorption. In: Volesky, B. (Ed.), Biosorption. CRC Press, Boca Raton, FL.

Brierley, C.L., 1990. Bioremediation of metal-contaminated surface and groundwater. Geomicrobiol. J. 8, 201–223.

Chen, J.P., Lin, M., 2001. Equilibrium and kinetics of metal ion adsorption onto a commercial H-type granular activated carbon: experimental and modeling studies. Water Res. 35, 2385–2394.

Chen, J.P., Wang, L., 2004. Characterization of metal adsorption kinetic properties in batch and fixed-bed reactors. Chemosphere 54, 397–404.

Coleman, N.T., McClung, A.C., Moore, D.P., 1956. Formation constants for Cu(II)-peat complexes. Science 1, 123–330.

Corapcioglu, M.O., 1984. Adsorption characteristics of Cu(II), Pb(II), Ni(II) and Zn(II) onto activated carbon surface in dilute aqueous solution: The effect of complex formation. Ph.D. thesis. University of Delaware.

de Rome, L., Gadd, G.M., 1987. Copper adsorption by *Rhizopus arrhizus*, *Cladosorium resinae* and *Penicillium italicum*. Appl. Microbiol. Biotechnol. 26, 84–90.

Dursun, A.Y., 2006. A comparative study on determination of the equilibrium kinetic and thermodynamic parameters of biosorption of copper (II) and lead (II) ions onto pretreated *Aspergillus niger*. Biochem. Eng. J. 28, 187–195.

Dursun, A.Y., Uslu, G., Cuci, Y., Aksu, Z., 2003. Bioaccumulation of copper (II), lead (II) and chromium (VI) by growing *Aspergillus niger*. Process Biochem. 38, 1647–1651.

Esposito, A., Pagnanelli, F., Lodi, A., Solisio, C., Vegliò, F., 2001. Biosorption of heavy metals by *Sphaerotilus natans*: an equilibrium study at different pH and biomass concentrations. Hydrometallurgy 60, 129–141.

Fourest, E., Roux, J.C., 1992. Heavy metal biosorption by fungal mycelial by- products: mechanisms and influence of pH. Appl. Microbiol. Biotechnol. 37, 399–403.

Gadd, G.M., 1988. Accumulation of metals by microorganisms and algae. In: Rehm, H., Reed, G. (Eds.), Biotechnology: A Complete Treatise, 6B, Special Microbial Processes. VCH, VerlagsgesellSchaft, Weinheim, Germany, pp. 401–433.

Harris, P.O., Ramelow, G.J., 1990. Binding of metal ions by particulate biomass derived from *Chlorella Vulgaris* and *Scenedesmus Quadricauda*. Environ. Sci. Technol. 24, 220.

Ho, Y.-S., 2003. Removal of copper ions from aqueous solution by tree fern. Water Res. 37, 2323–2330.

Huang, C., Huang, C.P., 1996. Application of *Aspergillus oryzae* and *Rhizopus oryzae* for Cu(II) removal. Water Res. 30, 1985–1990.

Iqbal, M., Saeed, A., Akhtar, N., 2002. Petiolar felt-sheath of palm: a new biosorbent for the removal of heavy metals from contaminated water. Biores. Technol. 81, 151–153.

Kapoor, A., Viraraghavan, T., 1997. Heavy metal biosorption sites in *Aspergillus niger*. Biores. Technol. 61, 221–227.

Kapoor, A., Viraraghavan, T., 1998. Biosorption of heavy metals on *Aspergillus niger*, effect of pretreatment. Biores. Technol. 63, 109–113.

Kapoor, A., Viraraghavan, T., Roy Cullimore, D., 1999. Removal of heavy metals using the fungus *Aspergillus niger*. Biores. Technol. 70, 95–104.

Mukhopadhyay, M., Noronha, S.B., Suraishkumar, G.K., 2006. Copper removal from industrial wastes. In: Pro. Int. Workshop on RD Frontiers in Water and Wastewater Manag., NEERI, Nagpur, India, 81.

Mukhopadhyay, M., Noronha, S.B., Suraishkumar, G.K., 2006. Copper removal from wastewater by biosorption. In: Pro. AIChE- 2006 Spring National Meeting and the World Congress on Particle Technology-5, Orlando, FL, USA.

Muraleedharan, T.R., Iyengar, L., Venkobachar, C., 1991. Biosorption: an attractive alternative for metal removal and recovery. Curr. Sci. 61, 379–385.

Ozdemir, G., Ozturk, T., Ceyhan, N., Isler, R., Cosar, T., 2003. Heavy metal biosorption by biomass of *Ochrobactrum anthropi* producing exopolysaccharide in activated sludge. Biores. Technol. 90, 71–74.

Petkar, A.V., Kulkarni, S.K., Paknikar, K.M., 2001. Comparative studies on metal biosorption by two strains of *Cladosporium cladosporioides*. Biores. Technol. 80, 211–215.

Rakshit, P.C., 1986. Physical Chemistry, fourth ed. Sarat Book House, Kolkata, 608.

Say, R., Denizil, A., Arica, M.Y., 2001. Biosorption of cadmium (II), lead (II) and copper (II) with the filamentous fungus *Phanerochaete chrysosporium*. Biores. Technol. 76, 67–70.

Schiewer, S., Wong, M.H., 1999. Metal binding stoichiometry and isotherm choice in biosorption. Environ. Sci. Technol. 33, 3821–3828.

Sun, Q.Y., Yang, L.Z., 2003. The adsorption of basic dyes from equilibrium solution on modified peat-resin particle. Water Res. 37, 1535–1544.

Tsezos, M., 1983. The role of chitin in uranium adsorption by *Rhizopus arrhizus*. Biotechnol. Bioeng. 25, 2025–2040.

Volesky, B., 1987. Biosorption for metal recovery. Trends in Biotechnol. 5, 96–101.

Weber, W.J., Morris, C.J., 1962. Advances in water pollution research. In: Proc. First Int. Conf. on Water Pollut. Res. 2, pp. 231.