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Nickel Biosorption from Aqueous Systems: Studies on Single and Multimetal Equilibria, Kinetics, and Recovery

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ABSTRACT

This paper reports studies on the removal of toxic trace metals (nickel separately, and simultaneously with cobalt) from aqueous solutions by employing fungal biosorbents, PFB1 and PFB2, which were developed in our laboratory. The observed maximum equilibrium uptake of nickel on the biosorbent was 214 $mg \cdot g^{-1}$ (PFB1) and 110 $mg \cdot g^{-1}$ (PFB2). The average efficiency for nickel removal was 84.5% (PFB1) and 60.8% (PFB2). The equilibrium uptake of nickel followed first-order Langmuir kinetics in the case of PFB1 and second-order Langmuir kinetics in the case of PFB2. Studies on simultaneous removal of cobalt and nickel indicated that the extent of secondary interactions between cobalt and nickel can be quantified by the change in Langmuir equilibrium constants for both metals. A mathematical model based on Fick's law of diffusion and Langmuir adsorption was developed to simulate the kinetics of nickel removal. The model was able to predict the experimentally observed kinetics well. From the simulations, the diffusivity of nickel in PFB1 was found to be 1.6×10^{-8} $m^2 \cdot s^{-1}$. Desorption studies indicated that it was possible to reuse the biosorbent over three

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sorption–desorption cycles, and that acidic solutions desorbed better than basic or salt solutions. Among the desorbents studied, HCl and $CaCl_2$, with desorption efficiencies equal to 73.2 and 74.1%, respectively, for PFB1 and 70.0 and 63.1%, respectively, for PFB2 at the end of three cycles, were found to be the best desorbents.

Key Words. Biosorption; Nickel; Kinetics; Multimetal Equilibria; Desorption

INTRODUCTION

Biosorption is an attractive alternative (1, 2) to physicochemical methods such as reduction and precipitation for the removal of toxic trace metals such as nickel, cobalt, mercury, chromium, lead, and others. The toxic trace metals enter the environment through industrial effluents, and their compounds and complexes circulate through and eventually accumulate in the food chain, leading to large imbalances in ecological systems (1). Nickel is found in the effluents of electroplating, inorganic, and dye industries; exposure to nickel can cause dermatitis and allergic sensitization, and regulations do not permit greater than 2 ppm nickel in effluents (3).

Holan and Volesky (4) reported the use of marine alga, *Sargassum fluitans*, for nickel biosorption, and they obtained a maximum uptake of 135 $mg \cdot g^{-1}$ for a relatively high equilibrium solution concentration of about 1900 $mg \cdot L^{-1}$. Studies on continuous nickel removal using columns of immobilized, nonfilamentous fungus, *Saccharomyces cerevisiae* (5, 6), are also found in the literature with a saturation uptake of about 3 $mg \cdot g^{-1}$. The use of the biomass of the filamentous fungus *Penicillium digitatum* has also been reported for nickel biosorption where variation of the initial sorption rates with temperature and chemical treatments are given, but not the equilibrium uptakes (7). A report on another filamentous fungus, *Rhizopus arrhizus*, for nickel removal (8) is also found in the literature with a maximum uptake capacity of 18.7 $mg \cdot g^{-1}$, which was 13.9% of that reported by Holan and Volesky (4) with *Sargassum fluitans*.

However, nickel biosorption seems not to have received as much attention in the literature as biosorptive removal of other trace metals, probably because of the relatively low uptake capacities achieved. Even for a marine alga, uptakes above 70 $mg \cdot g^{-1}$ occur at reasonably high equilibrium solution concentrations (above 400 $mg \cdot L^{-1}$). In this paper we report higher uptake capacities for nickel at comparatively low equilibrium solution concentrations using PFB1 and PFB2 (biosorbents developed in our laboratory) than those found in the literature, along with sorption equilibrium information. Also, Langmuir or Freundlich isotherms are normally used to describe biosorption equilibrium data. However, we developed a second-order Langmuir isotherm to better de-

scribe equilibrium data for nickel biosorption by PFB2. Further, a model for simultaneous biosorption of two metals has been developed to describe the simultaneous sorption of nickel and cobalt, and secondary interactions between nickel and cobalt could be quantified using that model. In addition, a kinetic model has been developed for nickel biosorption which incorporates the more general, polymolecular Langmuir isotherm to describe the relationship between sorbed species and that in the liquid. Desorption studies to recover nickel from the biosorbents using six different desorbents (acidic, basic, or salt in nature) are also reported.

MATERIALS AND METHODS

Biosorbents, Equipment, Reagents, and Analyses

The biosorbents PFB1 (patent pending) and PFB2 were prepared in our laboratory. First the fungus, *Rhizopus* sp., was grown in 250 mL shake flasks placed in an orbital shaker cum incubator (Neolab Instruments, Mumbai) maintained at 30°C and 80 rpm. The growth medium contained 2% w/v dextrose, 0.5% w/v yeast extract, and 0.1% w/v diammonium phosphate in sterilized tap water (to provide micronutrients). The medium was autoclaved without dextrose, and later sterilized dextrose was added. The cells were harvested after 24 hours, rendered nonviable by immersion in 1% formalin solution, dried, and reduced in size using a pestle and mortar, followed by sieving to obtain sizes in the range of 0.35 to 0.42 mm to yield PFB1. The PFB2 was prepared in a similar fashion, except that before being dried it was contacted with 2 N NaOH solution for 1 hour. The biomass to NaOH solution ratio used was 10 g/50 mL. The biomass was also rinsed with deionized water before drying. All biosorbent masses reported in this paper are on a dry basis.

Biosorption experiments were performed using appropriately diluted 1000 ppm stock solutions (in deionized water) of cobalt sulfate, $CoSO_4$, and nickel chloride, $NiCl_2$ (Loba Chemie, Mumbai). An analysis of the deionized water showed neither nickel nor cobalt present in it. Desorbent solutions of the following chemicals (S. D. Fine-Chem Ltd., Boisar) were also prepared in deionized water at 0.1 N concentration: sulfuric acid, H_2SO_4; hydrochloric acid, HCl; calcium chloride, $CaCl_2$; ammonium chloride, NH_4Cl; sodium hydroxide, NaOH; and potassium hydroxide, KOH.

Equilibrium studies were carried out in 250 mL shake flasks containing 0.1 g of the biosorbent suspended in 50 mL solutions of Co^{2+} and Ni^{2+} at various concentrations in the 20–500 ppm range. For the two-metal experiments, the solutions were prepared by mixing 25 mL each of pure cobalt and nickel solutions to obtain various concentrations in the 20–500 ppm range. The biosorbent was removed from the solutions by centrifugation after 24 hours, and the solutions were analyzed for residual metal concentration. The metal content in

the biomass was found through material balance, and the loss of metal to the container was found to be negligible. In the kinetics experiments the same amount (0.1 g) of biosorbent was contacted with 500 ppm $NiCl_2$ solution in different shake flasks. Samples were drawn at predetermined intervals, the biosorbent particles were separated from the solution by centrifugation, and the supernatants were analyzed for Ni^{2+} concentration. In the desorption experiments the desorbent was contacted with the metal for 24 hours and then analyzed for nickel concentration. The biosorbent was rinsed with deionized water after one sorption–desorption cycle, reused, and desorbed again. These cycles were repeated three times.

All experiments were performed in a shaker-incubator (NeoLab Instruments, Mumbai, India), at 80 rpm. The temperature was maintained at 30°C, and the initial pH was adjusted to 7.0. No precipitation was observed at pH 7.0. Metal ion concentrations were analyzed using an Inductively Coupled Plasma Atomic Absorption Spectrophotometer (ICPAES 8440 PlasmaLab, G. B. C. Scientific Pvt. Ltd., Australia). The instrument was calibrated using a monochromator arrangement at wavelengths 224.654 nm (for Ni^{2+}) and 238.982 nm (for Co^{2+}) for metal ion concentrations up to 500 ppm.

All experiments were done in duplicate or triplicate and were also reproduced on different days. The maximum variation in single metal sorption data between duplicate/triplicate experiments done on the same day was 4.6%. The same between experiments done on two different days was 6.3%. The maximum variation in single metal desorption data between duplicate/triplicate experiments done on the same day was 5.7%, and the same between experiments done on two different days was 6.8%. The errors associated with multimetal sorption data as well as the other errors are discussed at appropriate places in the text.

MATHEMATICAL MODEL FOR SINGLE METAL BIOSORPTION

We have analyzed the kinetics of nickel biosorption using a mathematical model wherein it was assumed that the sorption of the metal ion on or inside the biomass particles can be described by a polymolecular Langmuir isotherm, and that diffusion through the biosorbent (assumed to follow Fick's first law) is the rate-controlling step in the sorption process.

The biosorbent was assumed to consist of porous spherical particles of uniform radius R and porosity ε. This is a reasonable assumption since the difference between the minimum and maximum particle sizes, as obtained from scanning electron microscope characterization studies, is not greater than 20% of the average size.

A balance can then be written as follows for the accumulation of Ni^{2+} ion (A) in a shell of thickness Δr at a distance r from the center of the spherical

particle. The accumulation of A in the aqueous phase and in the biomass within the shell is equal to the difference between the radial fluxes of A into and out of the shell:

$$4\pi r^2\,\varepsilon\Delta r\,\frac{\partial C_A}{\partial t} + 4\pi r^2(1-\varepsilon)\Delta r\rho_i\,\frac{\partial q_A}{\partial t} = 4\pi r^2\varepsilon N_{Ar}|_{in} - 4\pi r^2\varepsilon N_{Ar}|_{out} = \Delta(4\pi r^2\varepsilon N_{Ar})$$

where N_{Ar} is the radial flux of the A, C_A is the concentration of the metal in the aqueous phase, q_A is the concentration of the metal on the biosorbent, and ρ_i is the intrinsic density of the biosorbent. Assuming Fick's first law for the diffusion of A, N_{Ar} can be written as

$$N_{Ar} = D\,\frac{\partial C_A}{\partial r}$$

where D is the diffusivity of A in the aqueous phase. Thus the above material balance becomes

$$4\pi r^2\varepsilon\Delta r\,\frac{\partial C_A}{\partial t} + 4\pi r^2(1-\varepsilon)\Delta r\rho_i\,\frac{\partial q_A}{\partial t} = \Delta\left(4\pi r^2\,\varepsilon D\,\frac{\partial C_A}{\partial r}\right)$$

Dividing throughout by $4\pi r^2\Delta r$ and letting $\Delta r\to 0$ in the limit gives the relationship

$$\frac{\partial C_A}{\partial t} + \left(\frac{1-\varepsilon}{\varepsilon}\right)\rho_i\,\frac{\partial q_A}{\partial t} = \frac{1}{r^2}\,\frac{\partial}{\partial r}\left\{Dr^2\,\frac{\partial C_A}{\partial r}\right\} \tag{1}$$

Also, it has been assumed that the sorption of A on the biomass is instantaneous and can be adequately represented, in general, by a polymolecular Langmuir isotherm, so that

$$q_A = q_M\,\frac{K_A C_A^n}{K_A C_A^n + 1} \tag{2}$$

where K is the equilibrium constant for the sorption, q_M is the maximum sorbate which can accumulate on the sorbent, and n is the molecularity of the sorption. Since the sorption is assumed to be instantaneous as compared to the diffusion, Eq. (2) can be differentiated to give

$$\frac{\partial q_A}{\partial t} = \frac{\partial C_A}{\partial t}\left\{\frac{nC_A^{n-1}q_M K_A}{(K_A C_A^n + 1)^2}\right\} \tag{3}$$

From Eqs. (1) and (3) we obtain

$$\frac{\partial C_A}{\partial t}\left\{1 + \left(\frac{1-\varepsilon}{\varepsilon}\right)\rho_i\,\frac{nC_A^{n-1}\,q_M K_A}{(K_A C_A^n + 1)^2}\right\} = D\left\{\frac{\partial^2 C_A}{\partial r^2} + \frac{2}{r}\,\frac{\partial C_A}{\partial r}\right\} \tag{4}$$

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Equation (4) is a partial differential equation for C_A, second order in r, and first order in t. The initial condition is

$$C_A(r, 0) = \begin{cases} C_{A0}, & r = R \\ 0, & r < R \end{cases}$$

Of the two boundary conditions needed for a solution, the first boundary condition is due to symmetry of the distribution $C_A(r, t)$ at $r = 0$:

$$\left.\frac{\partial C_A}{\partial r}\right|_{r=0} = 0 \tag{5}$$

Since the concentration of A at the periphery ($r = R$) of the particle (which is also the bulk concentration of A) decreases with time due to biosorption, we have, as the second boundary condition, a material balance for A: the amount of A lost from the bulk solution is the sum of the amounts of A accumulated (in the pores and the biomass) within the biosorbent. Thus,

$$V\left.\frac{dC_A}{dt}\right|_{r=R} = N_p \int_0^R 4\pi r^2 dr \left\{\varepsilon\left(\frac{\partial C_A}{\partial t}\right)_r + (1-\epsilon)\rho_i\left(\frac{\partial q_A}{\partial t}\right)_r\right\} \tag{6}$$

where $\partial q_A/\partial t$ can be evaluated from Eq. (3). N_p is the total number of biosorbent particles present in the vessel.

Equation (4) was solved with the boundary conditions (5) and (6) by using a finite difference method with appropriately small step sizes along the t and r dimensions. The values of the parameters which were used for the simulation, and the methods used to evaluate them, are given in Table 1. The diffusivity D of A in the biosorbent is the only fitted parameter, and the value which fitted the experimental data best, as determined from a least-squares fit, was chosen.

TABLE 1
Values of Parameters in the Unsteady-State Model for Nickel Biosorption

Parameter	Value	Basis
D	1.6×10^{-9} m^2·s^{-1}	Fitted parameter
K_A	8.44×10^{-3} L·mg^{-1}	Equilibrium data
N_p	1613	SEM studies
q_M	536.1 mg·g^{-1}	Equilibrium data
R	0.0002 m	SEM studies
V	0.05 L	Experimental conditions
ϵ	0.57	Estimated from SEM studies
ρ_i	4310 kg·m^{-3}	Estimated from SEM studies

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RESULTS AND DISCUSSION

Extent of Removal with PFB1 and PFB2

The maximum observed equilibrium uptake of nickel obtained in this work with PFB1 was 214.7 $mg \cdot g^{-1}$ at an equilibrium solution concentration 75 $mg \cdot L^{-1}$. This uptake was 690% of the highest among the equilibrium uptakes reported in the literature (4) for nickel biosorption at the corresponding equilibrium solution concentration. It was also 172% of the highest maximum uptake reported in the literature (4) for nickel biosorption at much higher equilibrium solution concentrations (1900 $mg \cdot L^{-1}$). The maximum uptakes reported by others are given in the Introduction. With PFB2, the maximum observed equilibrium uptake was 110 $mg \cdot g^{-1}$ at an equilibrium solution concentration 200 $mg \cdot L^{-1}$. The metal removing efficiency for the sorption of nickel, defined as the ratio of the amount of metal sorbed to the initial amount of metal present in solution, was 84.5% for PFB1 and 60.8% for PFB2.

The estimated material preparation cost for nickel removal using PFB1, the better of the two developed biosorbents, when it is employed once in stirred tank geometry is Re. 0.5 (US$ 0.01) per 100 mg of nickel removed.

Biosorption Isotherm for Nickel

The biosorption isotherm for nickel, representing the equilibrium uptake versus equilibrium concentration, is shown in Fig. 1a (PFB1) and Fig. 1b (PFB2). Typically, metal sorption by biomass has been modeled using first-order Langmuir $\{q = q_M[KC/(KC + 1)]\}$ isotherms (9–11) or Freundlich ($q = q_0 C^{1/n}$) isotherms (12). The Langmuir isotherms fitted to the data obtained in this study are also shown in Figs. 1a and 1b. The equations for these isotherms are

$$\text{PFB1:} \qquad q_A = 536.1 \frac{8.4 \times 10^{-3} C_A}{1 + 8.4 \times 10^{-3} C_A}$$

$$\text{PFB2:} \qquad q_A = 670.0 \frac{9.8 \times 10^{-4} C_A}{1 + 9.8 \times 10^{-4} C_A}$$

These equations were obtained by linearizing the Langmuir isotherm equation and determining the parameters therein by linear regression. The root-mean-square errors when the first-order Langmuir isotherm was used to fit were 7.38 $mg \cdot g^{-1}$ for PFB1 and 66.91 $mg \cdot g^{-1}$ for PFB2. The corresponding average percentage errors were 2.27 for PFB1 and 430.84 for PFB2. Thus, it can be seen that the first order Langmuir isotherm is a good fit for the PFB1 data but does not fit the PFB2 data well, particularly in the initial region of low slope. Also, the Freundlich isotherm did not fit the data well (isotherm not shown). For PFB1, the standard deviation in q_M was 8.32 $mg \cdot g^{-1}$ and that in K_A was 0.42×10^{-3}.

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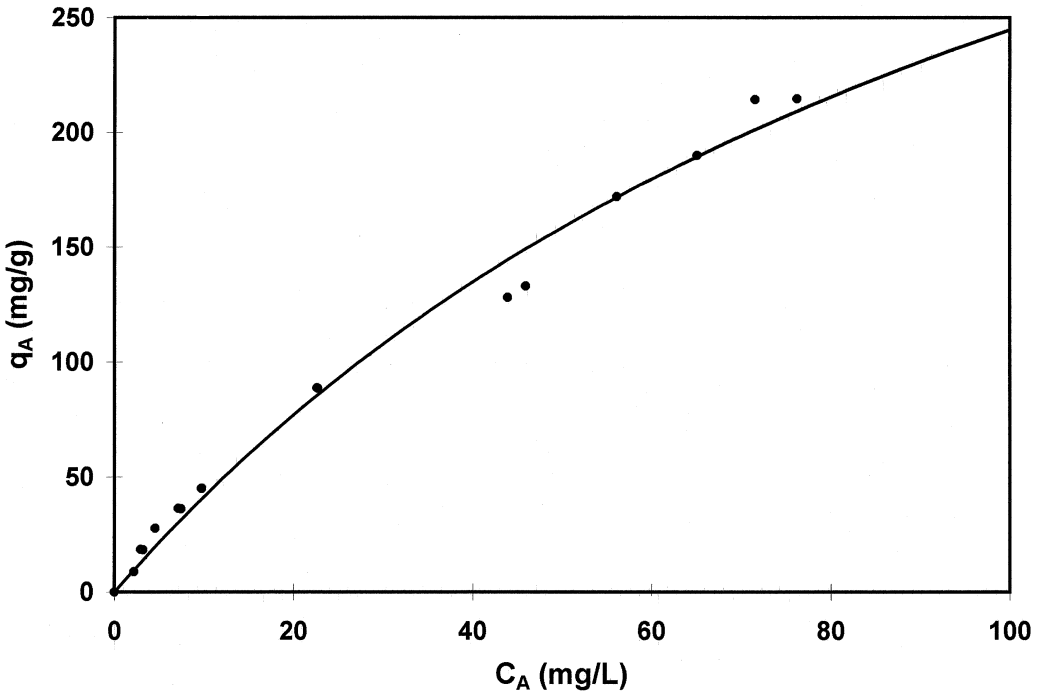

FIG. 1a Equilibrium uptake by PFB1 for nickel and prediction by first-order Langmuir isotherm.

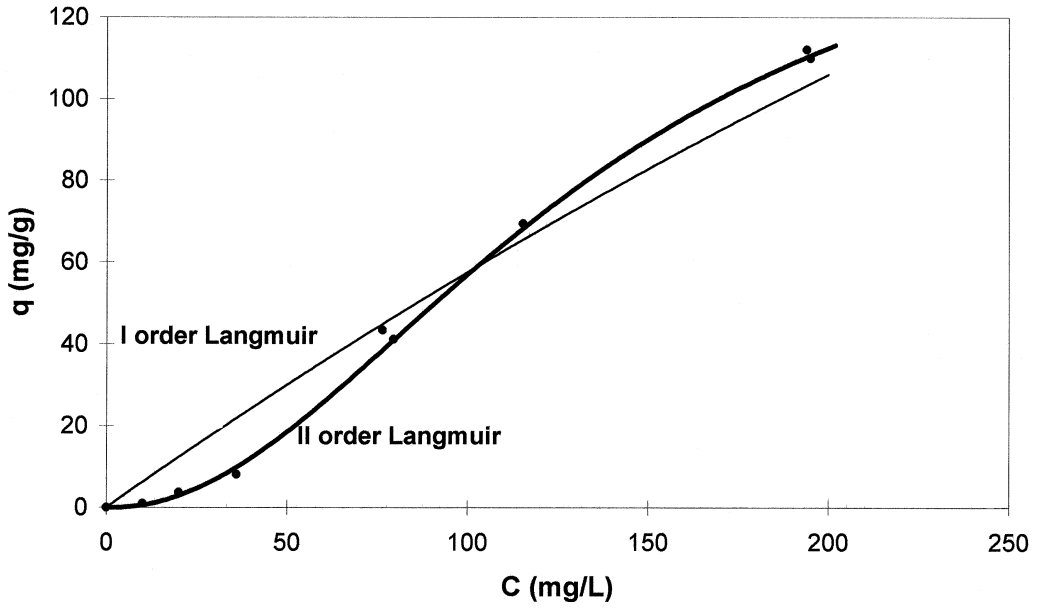

FIG. 1b Equilibrium uptake by PFB2 for nickel, prediction by first-order and second-order Langmuir isotherms. The second-order isotherm fits the data better, especially in the initial region of low slope.

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When it is assumed that the sorption is *second order* in nickel, the following relationship can be obtained:

$$q_A = q_M \frac{KC_A^2}{KC_A^2 + 1} \tag{7}$$

where subscript A stands for nickel. This isotherm predicted the sorption equilibrium for nickel better than the corresponding first-order isotherm, as is evident in Fig. 1b. Also, the root-mean-square error with the second-order Langmuir isotherm was 1.67 $mg \cdot g^{-1}$ compared to 66.91 $mg \cdot g^{-1}$ with the first-order Langmuir isotherm, and the average percentage errors were 1.69 for the second-order Langmuir isotherm compared to 430.84 for the first-order Langmuir isotherm.

The relationship in Eq. (7) is obtained as follows: Assuming that the sorption of A on site S is described by the equilibrium $2A + S \rightleftharpoons (A_2{*}S)$, with equilibrium constant K_A (assuming that the forward reaction is bimolecular in A), a balance can be written for the total number of sites, which is equal to the number of sites occupied by A, $(A_2{*}S)$, plus the number of empty sites, S, so that

$$(A_2{*}S) + S = q_M \tag{8}$$

where q_M is the total number (or concentration) of initially available sites. Then, Eq. (7) follows from Eq. (8) and the equilibrium relationship

$$K = \frac{(A_2{*}S)}{A^2 S} \tag{9}$$

The values of q_M and K in the case of the second-order isotherm for PFB2 are 164.4 $mg \cdot g^{-1}$ and 5.5×10^{-5} $L^2 \cdot mg^{-2}$, respectively. Previous work conducted on cobalt in our laboratory (13) showed that the sorption equilibrium for cobalt could be well represented by a first-order Langmuir relationship in both the PFB1 and PFB2 cases. This leads to the interesting conclusion that two similar metals, occupying the same group in the periodic table, and whose ions have the same valency, are sorbed by the same biomass (PFB2) in different molecularities: two ions occupy a single site in the case of nickel, whereas in the case of cobalt, one ion occupies a single site on the biosorbent.

Additionally, since the uptake by PFB1 was represented by a first-order Langmuir isotherm, it can be concluded that each site on PFB1 has a valency of -2. This is because, the first-order Langmuir isotherm is based on the equilibrium

$$A + S \rightleftharpoons (A{*}S)$$

Since the site S binds to a single (divalent) Ni^{2+} ion, it must have a valency of -2. If S had a valency of -1, each nickel ion would bind to 2 sites, result-

ing in a one-half-order isotherm:

$$q_A = q_M \frac{KC_A^{1/2}}{KC_A^{1/2} + 1}$$

which, in this study, was found to be a very poor fit to the data (results not shown). Also, the sites in PFB2 must have a valency of -4, since each site in PFB2 binds to two nickel ions. PFB2 was obtained with NaOH treatment of PFB1. This indicates that OH^- ions may have occupied certain sites, thus increasing the molecularity of those sites, whereas Na^+ ions may have bound other sites, thus blocking those sites and making them unavailable. Since the uptake of PFB2 was considerably less than of PFB1, the effect of Na^+ in reducing the uptake was evidently higher than the effect of OH^- in increasing the molecularity of the sites.

Studies on Multimetal Biosorption

Since industrial effluents contain a number of metals, it is necessary to study the simultaneous sorption of two or more metals (14) and also to quantify the interference of one metal over the sorption of the other. Further, in many common effluent treatment facilities (CETFs) in India, wastewaters containing nickel (from say, the fat hydrogenation or electroplating or the dye industries) are mixed with wastewaters containing cobalt (from say, the petrochemical industries) and hence the toxic metals need to be removed simultaneously at the tertiary stage. Therefore, nickel and cobalt were chosen for simultaneous sorption studies. The studies were also done on the biosorbent with the higher uptake capacity, PFB1.

The following two equilibria are assumed to exist simultaneously for deriving a relationship to predict the equilibrium uptake in multimetal sorption:

$$A + S \rightleftharpoons (A*S)$$

$$B + S \rightleftharpoons (B*S)$$

where A denotes nickel and B denotes cobalt. We assume that the equilibrium constants for the above equilibria, K_A and K_B are, in general, different from the equilibrium constants for single metal biosorption. This could be attributed to secondary interactions between the metals. However, it is reasonable to expect that the total number of sites available for biosorption, q_M, remains unchanged irrespective of the species being sorbed. The equilibrium relationships can be written as

$$K_A = \frac{(A*S)}{AS} \tag{10}$$

$$K_B = \frac{(B*S)}{BS} \tag{11}$$

A balance made for the total number of sites, taking into account the sorption of both *A* and *B*, can then be written as

$$(A*S) + (B*S) + S = q_{\mathrm{M}} \tag{12}$$

The following relationships can be obtained from Eqs. (10), (11), and (12):

$$q_A = q_{\mathrm{M}} \frac{K_A A}{1 + K_A A + K_B B} \tag{13}$$

$$q_B = q_{\mathrm{M}} \frac{K_B B}{1 + K_A A + K_B B} \tag{14}$$

Two-metal sorption experiments were performed as described in the Materials and Methods section. The constants q_{M}, K_A, and K_B were obtained through least-squares fitting. It was found that the difference between the q_{M} values found by least-squares fitting and that found experimentally (536.1 $\mathrm{mg \cdot g^{-1}}$) was less than 1%, and this supports the expectation that the total number of sites available for biosorption remains the same. The prediction of total uptake by this relationship is shown as a three-dimensional isotherm in Figs. 2(a) (uptake of nickel versus nickel and cobalt concentrations) and 2(b) (uptake of cobalt versus cobalt and nickel concentrations). The root-mean-square errors were 4.31 and 3.32 $\mathrm{mg \cdot g^{-1}}$, respectively, and the average percentage errors were 2.83 and 7.32, respectively, for the above data between experimental and predicted values. Thus, the relationship above is a good fit to the experimental data.

The mathematical form of the derived equation is similar to the modified competitive Langmuir isotherm, i.e.,

$$q_i = \frac{q_{\mathrm{M}}(C_i/\eta_i)}{1 + \sum_{j=1}^{N} K_j(C_j/\eta_j)}$$

which uses correction factors η_i and η_j to fit the data during simultaneous sorption. In contrast, the model in this paper was developed from first principles and hence it provides a mechanistic viewpoint.

The variation in equilibrium constants for nickel or cobalt sorption (K_A or K_B) in the presence of the other metal is shown in Table 2. The K_A value (for nickel) decreased from 8.44×10^{-3} $\mathrm{L \cdot mg^{-1}}$ when no cobalt was present to 5.57×10^{-3} $\mathrm{L \cdot mg^{-1}}$ when cobalt was present. This 34% decrease in the nickel biosorption equilibrium constant resulted from secondary interactions between nickel and cobalt. The phrase "secondary interactions" is used to denote the interactions other than competition between the metals for the same binding sites as used by Schiewer and Volesky (15). Similarly, the biosorption equilibrium constant for cobalt decreased from 3.91×10^{-3} in the absence of nickel (13) to 1.99×10^{-3} in the presence of nickel, a decrease of about 49%.

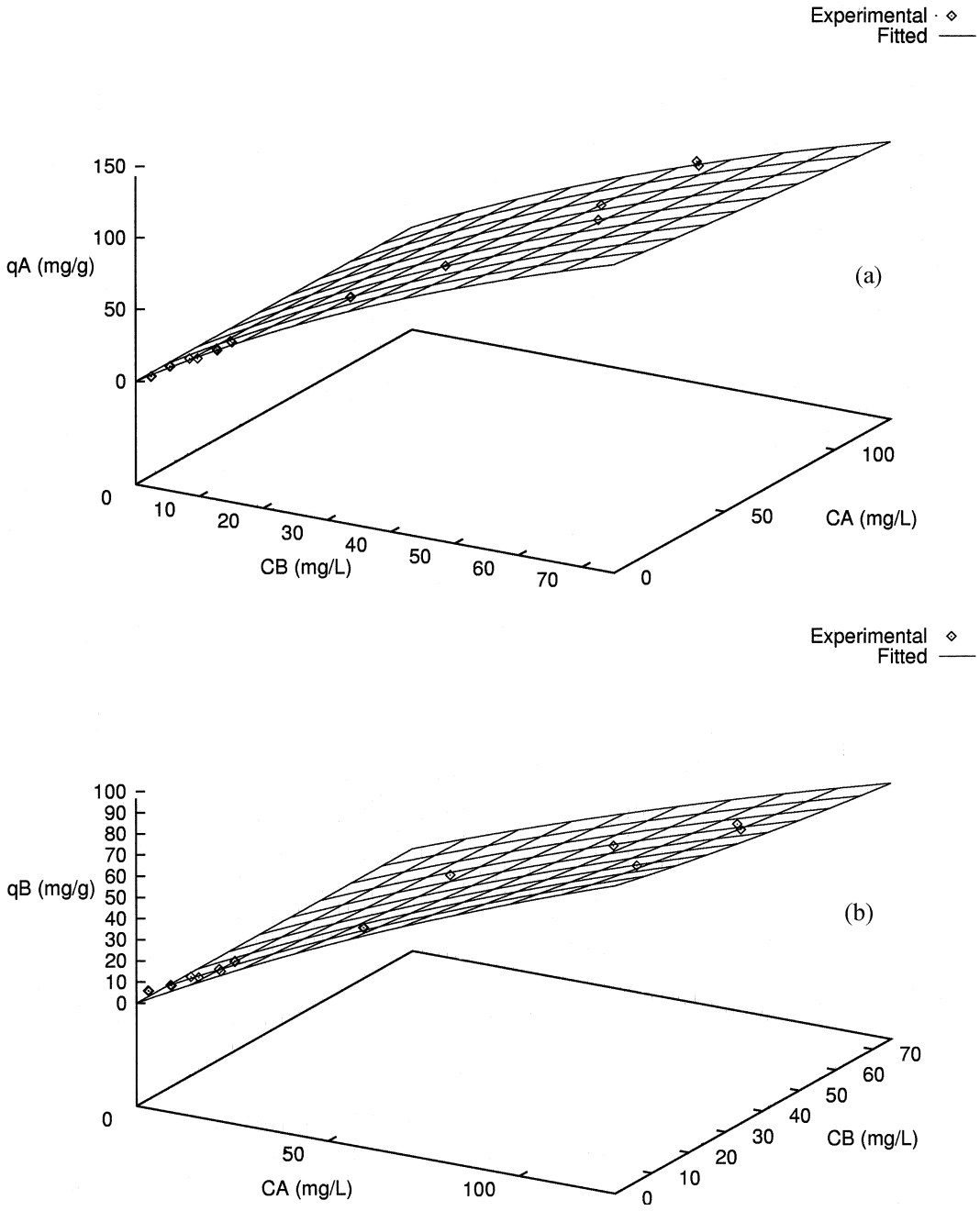

FIG. 2 Simultaneous sorption of nickel and cobalt by PFB1. (a) Uptake of nickel versus solution concentrations of nickel and cobalt at equilibrium. (b) Uptake of cobalt versus solution concentrations of nickel and cobalt at equilibrium. The points denote experimentally obtained values and the surface corresponds to the model predictions. The label q_A represents nickel uptake in $mg \cdot g^{-1}$; q_B, the cobalt uptake m $mg \cdot g^{-1}$; C_A, the nickel concentration in solution in $mg \cdot L^{-1}$; and C_B, the cobalt concentration in solution in $mg \cdot L^{-1}$.

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TABLE 2
Sorption Equilibrium Constants for Nickel and Cobalt Sorption on PFB1 When Present Alone and with the Second Metal

	K_A (nickel), ($L \cdot mg^{-1}$)	K_B (cobalt), ($L \cdot mg^{-1}$)
Alone	8.44×10^{-3}	3.91×10^{-3}
With a second metal	5.57×10^{-3} (with cobalt)	1.99×10^{-3} (with nickel)

If the interactions between metals had been only in the liquid phase, then the same percentage decrease in equilibrium constants would have been obtained for both metals. That not being the case, it can be suspected that the interactions took place after sorption of the metals (secondary interactions) and the extent to which cobalt affects nickel sorption is 15% less than the extent to which nickel affects cobalt sorption. Thus, it is suggested that the change in biosorption equilibrium constants can be used as a measure of secondary interactions between the sorbed metals.

Kinetics of Nickel Uptake

The kinetics of nickel uptake were studied as described in the Materials and Methods section. The experimental data for PFB1, as well as the prediction by the model described earlier, are presented in Fig. 3. The model fits the data reasonably well.

As can be observed from Fig. 3, the rate of decrease of the bulk metal ion concentration is very large initially, and slow toward the end of the process. It can be observed that about 90% of the uptake is complete in the first 5 minutes since the bulk concentration decreases from 500 to 100 ppm within minutes whereas to decrease from 100 ppm to the equilibrium concentration of approximately 90 ppm, more than 6.5 hours are required. This was verified experimentally as well as by the model (simulation results are not shown beyond $t = 30$ minutes).

The retardation in the rate of biosorption can be explained by the argument that the rate-determining step in the decrease of the bulk concentration is diffusion, and that sorption is substantially fast in comparison to diffusion through the particle. The instantaneous attainment of sorption equilibrium was assumed earlier in the formulation of the model, and the fit of the model to the data is a verification for this assumption.

The diffusivity of nickel in the biosorbent was found to be 1.6×10^{-8} $m^2 \cdot s^{-1}$ for PFB1 from the simulations. Figure 4 shows the variation of the concentration profiles inside the biosorbent particle for PFB1. From this figure it can be noted that the change in the concentration profiles is extremely

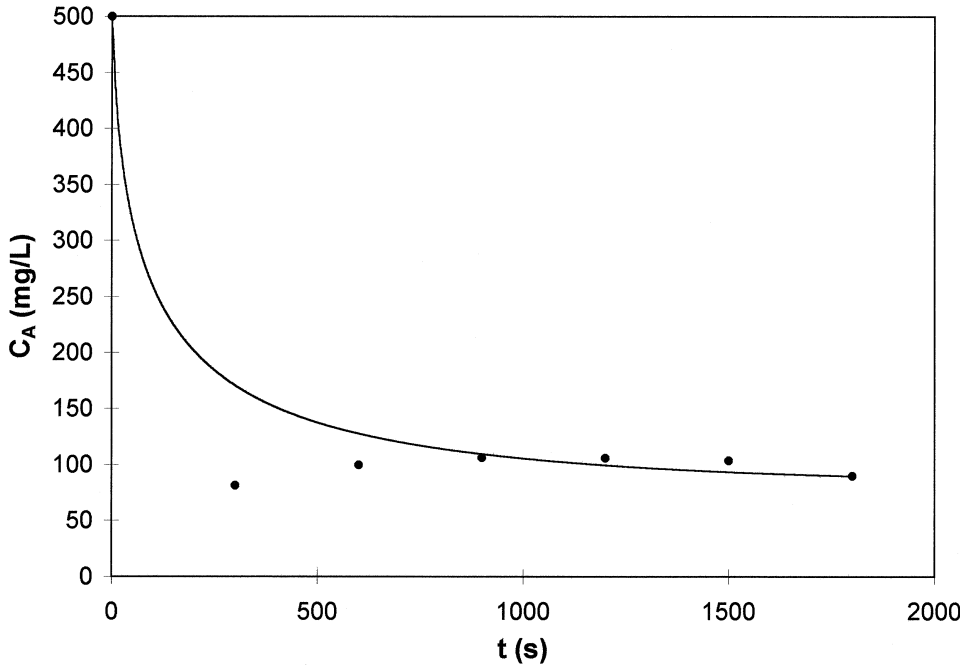

FIG. 3 Kinetics of nickel uptake by PFB1. The points represent experimental data and the line shows simulated results.

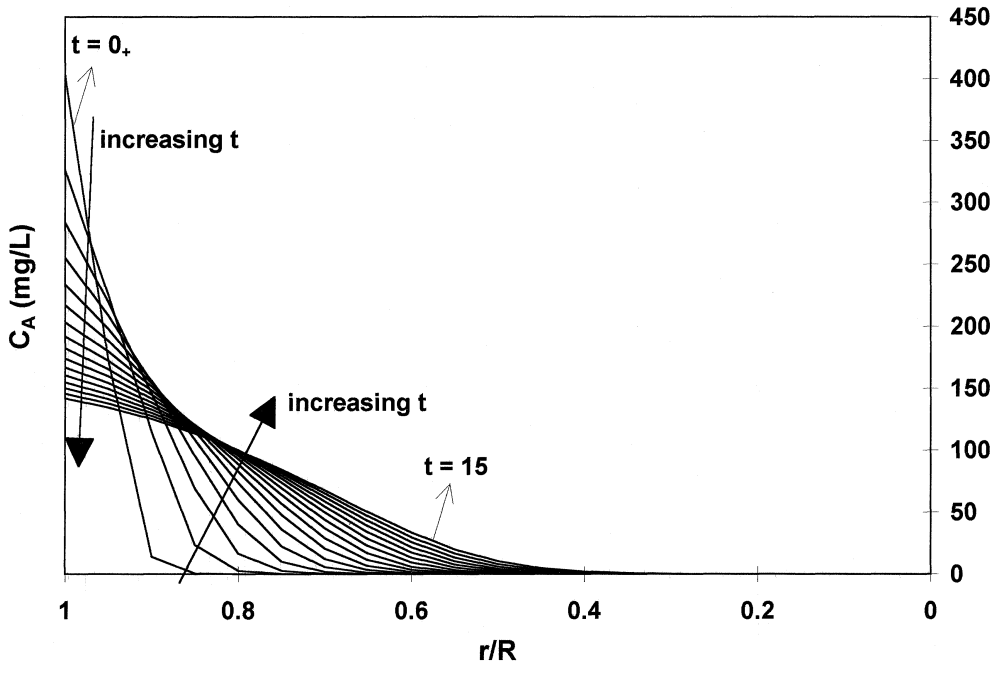

FIG. 4 Simulated concentration profiles inside the biosorbent, PFB1. The topmost profile is at $t = 0_+$, and subsequent profiles are at 1 minute intervals of time up to $t = 15$ minutes. The heavy arrows indicate the direction of increasing time.

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slow after about 10 minutes. The final ($t = \infty$) concentration profile is flat, with the concentration everywhere equal to the equilibrium concentration, and this is achieved very slowly in the latter part of the sorption process as diffusion becomes increasingly difficult with increasing depth.

While the concentration at the periphery ($r/R = 1$) of the particle, which is also the bulk concentration, decreases with time on account of diffusion and sorption inside the particle, the concentrations in a region near the periphery ($r = 0.6$ to $r < 1$) initially increase with time, and then decrease. This is because, due to slow diffusion, the sorbate accumulates (in the liquid contained in the pores) in this region. The concentration in this region begins to decrease only after the accumulated sorbate has diffused to the interior of the particle.

Also, it is interesting to note that within $t = 15$ minutes, when more than 95% of the uptake is complete, the sorbate concentration within the $r = 0.3$ shell is still zero. This means that the metal ions have not "penetrated" beyond $r = 0.3$. However, the volume corresponding to 30% of the radius is only 2.7% of the total volume, so that the mass of biosorbent which has not been penetrated by the biosorbent is also about 3% of the total mass, which explains the fact that more than 95% of the uptake is complete.

Desorption Studies

The attractiveness of biosorption increases when there exists a possibility of desorbing the metal from the biomass (16) so the metal can be recovered and the biosorbent can be reused. However, different desorbents interact differently with metal-laden biomasses, resulting in different extents of recovery. Therefore, we conducted desorption studies with six different desorbents (acidic, basic, and salt solutions): 0.1 N H_2SO_4, 0.1 N HCl, 0.1 N NH_4Cl, 0.1 N $CaCl_2$, 0.1 N NaOH, and 0.1 N KOH.

Desorption experiments were carried out as described in the Materials and Methods section. As the amount of metal recovered at the end of the third cycle (a cycle consists of one sorption and one desorption) was less than 50% in some cases, a maximum of three cycles was studied. The desorption efficiency (ratio of the mass of nickel desorbed to that present on the biomass before contact with the desorbent) with each of the desorbents is given in Table 3a (PFB1) and Table 3b (PFB2). It can be seen from the data that the desorption efficiencies of PFB2 are approximately 10% lower than those of PFB1 in all cases. It can also be observed that the desorption efficiency decreased with the number of cycles. However, it was possible to use the biosorbent successfully over at least three cycles.

The acidic desorbents were used because of their potential to dissolve nickel and nickel compounds: hydrogen ions can replace nickel ions in the biosorbent, thus functioning as an ion exchanger. It can be seen from Tables 3a and 3b that the desorption efficiencies with 0.1 N HCl were 90.2% (PFB1)

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TABLE 3a
Desorption Efficiencies for PFB1

Desorbent	Cycle	Desorption efficiency (%)
0.1 N HCl	1	90.2
	2	82.1
	3	73.2
0.1 N H_2SO_4	1	64.3
	2	58.9
	3	44.6
0.1 N NaOH	1	60.7
	2	62.5
	3	38.4
0.1 N KOH	1	75.9
	2	64.3
	3	42.9
0.1 N NH_4Cl	1	48.2
	2	44.6
	3	38.4
0.1 N $CaCl_2$	1	85.7
	2	79.5
	3	74.1

TABLE 3b
Desorption Efficiencies for PFB2

Desorbent	Cycle	Desorption efficiency (%)
0.1 N HCl	1	84.4
	2	79.9
	3	70.0
0.1 N H_2SO_4	1	58.8
	2	46.8
	3	32.2
0.1 N NaOH	1	59.8
	2	60.5
	3	35.6
0.1 N KOH	1	62.9
	2	60.7
	3	58.6
0.1 N NH_4Cl	1	32.4
	2	41.4
	3	25.3
0.1 N $CaCl_2$	1	80.9
	2	73.4
	3	63.1

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and 84.4% (PFB2) after the first cycle, which reduced to 73.2% (PFB1) and 70.0% (PFB2) after the third cycle. The other acid used (0.1 N H_2SO_4) as a desorbent gave comparatively lower desorption efficiencies, 64.3% (PFB1) and 58.8% (PFB2) after the first cycle, and 44.6% (PFB1) and 32.2% (PFB2) after the third cycle. The high desorption efficiency of HCl also indicates the possibility that nickel could have been sorbed as a cationic species, just as cobalt is (16).

The basic solutions were used as desorbents because ion exchange was suspected of playing an important role in the biosorption process, although the use of basic desorbents is not reported in the literature. With the basic desorbents (0.1 N NaOH and 0.1 N KOH) also, the desorption efficiency decreased with the number of cycles but was substantially lower when compared with 0.1 N HCl. For example, the efficiencies for 0.1 N NaOH were 60.7% (PFB1) and 59.8% (PFB2) after the first cycle, and 38.4% (PFB1) and 35.6% (PFB2) after the third cycle. The corresponding values for 0.1 N KOH were 75.9% (PFB1) and 62.9% (PFB2) (after the first cycle), and 42.9% (PFB1) and 58.6% (PFB2) (after the third cycle).

Among the salt solutions which were employed for desorption, 0.1 N NH_4Cl exhibited lower desorption efficiencies than all the other desorbents: the efficiencies at the end of the first and third cycles were 48.2 and 38.4%, respectively, for PFB1, and 32.4 and 25.3%, respectively, for PFB2. However, 0.1 N $CaCl_2$ showed desorption efficiencies comparable with HCl, the better of the two acidic desorbents: the efficiencies after the first cycle were 85.7% (PFB1) and 80.9% (PFB2) whereas the efficiencies after the third cycles were 74.1% (PFB1) and 63.1% (PFB2). It can also be seen that the efficiency at the end of the third cycle is slightly higher than the corresponding efficiency for HCl. The high desorption efficiencies for $CaCl_2$ can be explained by the fact that a high possibility of exchange exists between the Ca^{2+} and Ni^{2+} ions. In our earlier work on cobalt biosorption (13), it was observed from EDAX investigations that there is a possibility of cobalt replacing calcium from the cellular interstices during biosorption. The reverse process, i.e., calcium replacing the sorbed metal ion (nickel in this case), could be taking place, thus accounting for the high desorption efficiencies of $CaCl_2$.

CONCLUSIONS

Two biosorbents, PFB1 and PFB2, have been developed. They gave high uptakes for nickel in comparison with existing information in the literature. The kinetics of nickel uptake could be predicted reasonably well by a model which assumed that diffusion controls the process of uptake. The diffusivity of nickel in the biosorbent was also estimated.

The equilibrium uptake and concentration of nickel could be represented well by first- and second-order Langmuir isotherms, respectively, for PFB1

and PFB2. The simultaneous removal of nickel with cobalt indicated secondary interactions between the metals, which modified the single metal equilibrium constants for both metals.

Desorption studies demonstrated that the biosorbent is reusable over at least three sorption–desorption cycles, and that HCl and $CaCl_2$ are efficient desorbents for nickel from PFB1 and PFB2.

NOMENCLATURE

A	Ni^{2+} ion or its concentration ($mg \cdot L^{-1}$)
B	Co^{2+} ion or its concentration ($mg \cdot L^{-1}$)
C	concentration ($mg \cdot L^{-1}$)
D	diffusivity of A in the biosorbent ($m^2 \cdot s^{-1}$)
K	(with subscript) equilibrium constant ($L^n \cdot mg^{-n}$)
N_{Ar}	radial flux of A ($mg \cdot m^{-2} \cdot s^{-1}$)
N_p	total number of biosorbent particles in vessel
n	molecularity of sorption
q	metal uptake ($mg \cdot g^{-1}$)
q_M	concentration of total sites available ($mg \cdot g^{-1}$)
r	radial distance (m)
R	radius of the biosorbent particle (m)
t	time (s)
V	vessel volume (L)
ρ_i	intrinsic density of biosorbent ($kg \cdot m^{-3}$)
ε	biosorbent porosity

Subscripts

A	Ni^{2+} ion or its concentration
B	Co^{2+} ion or its concentration
0	at $t = 0$

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