Separation & Purification Reviews
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597294

BIOSORPTION OF HEAVY METALS BY FUNGAL BIOMASS AND MODELING OF FUNGAL BIOSORPTION: A REVIEW

Y. Sağ[a]
[a] Department of Chemical Engineering, Hacettepe University, Ankara, Turkey

Online publication date: 28 February 2001

To cite this Article Sağ, Y.(2001) 'BIOSORPTION OF HEAVY METALS BY FUNGAL BIOMASS AND MODELING OF FUNGAL BIOSORPTION: A REVIEW', Separation & Purification Reviews, 30: 1, 1 — 48
To link to this Article: DOI: 10.1081/SPM-100102984
URL: http://dx.doi.org/10.1081/SPM-100102984

SEPARATION AND PURIFICATION METHODS, 30(1), 1–48 (2001)

BIOSORPTION OF HEAVY METALS BY FUNGAL BIOMASS AND MODELING OF FUNGAL BIOSORPTION: A REVIEW

Y. Sağ

Department of Chemical Engineering, Hacettepe University, 06532, Beytepe, Ankara, Turkey

CONTENTS

E-mail: yesims@hacettepe.edu.tr

ABSTRACT

The wastewaters discharged from chemical industries which may contain heavy metal ions have toxic effect on all the living organisms. Because of this, disposal of them to the environment is a major threat to both human health and ecosystem. So the development of new technologies is required to treat wastewaters as an alternative to traditional physicochemical processes. Biosorption, the process of passive cation binding by dead or living biomass, represents a potentially cost-effective way of eliminating toxic heavy metals from industrial waste waters. While the abilities of microorganisms to remove metal ions in solution have been extensively studied, fungi have been recognized as a promising class of low-cost adsorbents for removal of heavy-metal ions from aqueous waste streams. Algae, fungi and bacteria differ from each other in their constitution, giving rise to different mechanisms of metal biosorption. The paper reviews the biosorption capacities of various fungi (free or immobilized or subjected to physical and chemical treatments) and, chitin and chitosan, important fungal cell wall components, in different reactor systems for heavy metal ions and discusses the fungal biosorption mechanisms. To explore the biosorption mechanisms, it is necessary to identify the functional groups involved in the biosorption process. As single toxic metallic species rarely exist in natural and waste waters, any approach that attempts to removal heavy metals from multi-component systems using fungi would be more realistic. The effects of various combinations of the metal ions on the biosorption capacity of various fungi are discussed and the actions of the metal ion combina-

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

tions synergistic or antagonistic are identified. Equilibria and capacity relationships for mono-component systems are well established and quantitatively expressed by various types of adsorption isotherms. In the case of multi-metal systems, models should be modified in order to take into account all metals and cover experimental data over a wide range of solution concentrations. The researcher is often puzzled as to what are the basic differences or similarities between the isotherms and what isotherm to select for practical use to predict adsorption capacities or to incorporate it in predicting breakthrough of columnar operations. The paper reviews the range of equilibrium sorption models, and diffusion and sorption models in different reactor systems used by different researchers to correlate experimental data for fungal biosorption.

Key Words: Wastewater; Fungi; Heavy metal ions; Biosorption

INTRODUCTION

Although many biological materials bind heavy metals, only those with sufficiently high metal-binding capacity and selectivity for heavy metals are suitable for use in a full-scale biosorption process. The first major challenge for the biosorption field was to select the most promising types of biomass from an extremely large pool of readily available and inexpensive biomaterials. Although this task is not complete, a large number of biomass types have been tested for their metal binding capability under various conditions. Some types of seaweed biomass offer excellent metal-sorbing properties while activated sludge from waste water treatment plants has not demonstrated high enough metal-sorbing capacities[1-3]. High metal-sorbing biomass could be specifically propagated relatively cheaply in fermentors using low-cost or waste carbohydrate-containing growth media based on e.g. molasses or cheese whey. On the other hand, using waste biomass for preparing new biosorbents is particularly advantageous. Fungi can be of interest for biosorption because

1. Fungi are able to remove heavy metals from aqueous solutions in rather substantial quantities. In certain instances the removal of heavy metal ions by fungal biomass has been observed to be more than that by conventional adsorbents such as activated carbon, ion-exchange resins, even green algae, brown marine algae and seaweeds[4-7],
2. Fungal biosorption has been studied more extensively because of the availability of large amounts of waste fungal biomass from fermenta-

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

tion industries and the amenability of the microorganisms to genetic and morphological manipulation[8],
3. Many species have low nutritional requirements and are versatile in physical growth conditions,
4. Biomass separation from the growth liquid medium constitutes a simple operation,
5. Dead biomass can be subjected to physical and chemical treatments to enhance its performance,
6. Particle size can be optimized[9-11].

DISCUSSION

General

Fungi are a truly nucleate (eukaryotic), nonphotosynthetic group of microorganisms relying on organic substrates as their sole source of carbon and energy for growth and metabolic activities. Yeasts form one of the important subclasses of fungi. Yeasts are single small cells of 5 to 10 μm size. Molds are filamentous fungi and have a mycelial structure. The mycelium is a highly branched system of tubes that contains mobil cytoplasm with many nuclei. Some molds reproduce by sexual means and form sexual spores. These spores provide resistance against heat, freezing, drying, and some chemical agents. The typical size of a filamentous form of mold is 5 to 20 μm. When grown in submerged culture, molds often form cell aggregates and pellets. The typical size of a mold pellet varies between 50 μm and 1 mm, depending on the type of mold and growth conditions[9,12,13]. On the basis of their mode of sexual reproduction, the classification of fungi start with four large groups:

1. The phycomycetes are algalike fungi; however, they do not possess chlorophyll and can not photosynthesize. Aquatic and terrestrial molds belong to this category. *Rhizopus arrhizus* which belongs to a large class of phycomycetes is known for its strong metal-sorbent properties which are common to the whole genus. Its name will be seen throughout this review because it has become very prominent in the area of biosorption.
2. The ascomycetes form sexual spores called ascospores, which are contained within a sac. Some molds of the genera *Neurospora* and *Aspergillus* and yeasts belong to this category.
3. The basidiomycetes reproduce by basidiospores, which are extended from the stalks of specialized cells called the basidia. Mushrooms are basidiomycetes.

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

4. The deuteromycetes (Fungi imperfecti) lack a sexual reproduction mode. Some pathogenic fungi, such as *Trichophyton*, belong to deuteromycetes[9,12,13].

The paper reviews the biosorption capacities of phycomycetes, ascomycetes except yeasts and deuteromycetes for heavy metal ions and discusses the biosorption mechanisms. The suitability of the various kinetic and equilibrium models for the biosorption of heavy metal ions from waste waters on different fungal cells in different reactor systems is discussed.

Fungal Cell Wall Structure

The eukaryotic microorganisms are always of unicellular nature; however, the vegetative phases of fungi and algae are frequently multicellular. The fungal cells are protected by a true cell wall which is rigid as in bacterial cells. The sequestering of metallic species by fungal biomass has mainly been traced to the cell wall. The cell wall is not necessarily the only site where the sequestered metals are located. Various polysaccharides are the main (up to 90%) constituents of the fungal cell wall. They are often complexed with proteins, lipids, and other substances (e.g., pigments). The fungal cell wall presents a multilaminate, microfibrillar structure. Ultrastructural studies revealed two phases: i.) an outer layer consisting of glucans, mannans, or galactans and ii.) an inner microfibrillar layer, the crystalline properties of which are conferred by the parallel arrangement of chitin chains, sometimes of cellulose (a polymer of D-glucopyranose) chains, or, in certain yeasts, of noncellulosic glucan. There is a continuous transition between both layers. Pigments, polyphosphates, and inorganic ions are also found in the fungal cell wall. However, its chemical and structural characteristics are different. The isolated cell wall of *Aspergillus niger*, for instance, consists of neutral carbohydrate (73 to 83%) and hexomine (9 to 13%), with smaller amounts of lipid (2 to 7%) and phosphorus (less than 0.1 % of wall weight). The acetyl content was 3 to 3.4%, which corresponded to 1 mol/mol of hexosamine. An interesting observation is the lack of chitosan in the *Aspergillus* cell wall. This may be one of the reasons why the metal biosorbent performance of this fungus was inferior to that of *R. arrhizus* which belongs to the Mucorales family possessing usually higher chitin content in the cell wall. On the other hand, the best-known yeast *Saccharomyces cerevisiae* possesses a mannan-glucan cell wall which contains only 1% chitin. This may suggest the involvement of other components beside chitin in the metal sequestering. The structure of Mucorales cell walls containing positively charged chitosan and negatively charged phosphate and glucuronic acid residues is maintained at least in part by electrostatic interactions between ionizable groups. Large quantities of phosphate and glucuronic acid and chitin-chitosan

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

complex existing in these cell walls offer extensive possibilities for binding metals through ion exchange and coordination. In the fungal cell wall, several types of ionizable sites affect the metal uptake capacity: phosphate groups, carboxyl groups on uranic acids and proteins, and nitrogen-containing ligands on protein as well as on chitin or chitosan[9,12-15].

Industrial Fungal Biomass

Fungi are used in fermentation industries to produce varied metabolites such as antibiotics (penicillin, gentamicin, cyclosporin, alamethicin, beauvericin, ergot peptides, ferrichrome, enniantins, cephalosporin), steroids (progesterone to 11α-hydroxyprogesterone, compound S to 11β-hydroxyprogesterone), industrial chemicals (fumaric acid, kojic acid, gallic acid, gibberellins, carotenoids, citric and gluconic acids, itaconic acid), enzymes (amylases, proteolytic, rennet preparation, proteases, glucose isomerase, pectinase, cellulases, lipases, esterases, glucanases, lactase), microbial insecticides, flavors and fragrances (methyl ketones, lactones, mushroom flavors). Thousands of tons of residual biomass that are produced each year contain poorly biodegradable biopolymers (cellulose, chitin, glucans, etc.) and make bad fertilizers for agricultural use. To date, incineration is the main way of destroying this by-product[9,12,13,16,17]. On the other hand, some types of industrial fermentation waste biomass are excellent metal biosorbents. It is necessary to realize that some "waste" biomass is actually a commodity, not a waste.

Use of Immobilized Fungi for Heavy Metal Biosorption

For industrial application, a freely suspended fungal biomass has several disadvantages which include low density and mechanical strength, which may make biomass/effluent separation difficult. The principle reasons of employing immobilization techniques are summarized as follows[18]:

1. To permit recovery of a metal-laden adsorbent,
2. To permit biosorbent usage in fixed columns or fluidized bed reactors,
3. To enhance chemical and physical stabilities of biosorbents,
4. To improve metal adsorption and desorption characteristics of an biosorbent,
5. To alter or extend the range of metal selectivity of an biosorbent.

Fungal biomass has been immobilized using gelatin, casein, and other polypeptidic materials or mixing the mycelium with a nonpolar medium such as xylene and then cross-linking using reagents such as formaldehyde, formaldehyde-resor-

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

cinol solutions, formaldehyde-urea solutions, or polyvinyl acetate[6,18,19]. A proprietary technical biological origin adsorbent (MSR) has been developed by M. Tsezos *et al*[20,21]. Inactive cells of *R. arrhizus* have been immobilized into the form of particles of particle size 0.5-1.2 mm. The immobilized biomass particles have been reported to have high porosity and good wetting ability. In recent studies, the long term uranium biosorptive uptake capacity of the immobilized *R. arrhizus* (MSR) has been studied in a continuous packed-bed laboratory pilot scale pilot plant reactor. The immobilized *R. arrhizus* recovered all of the uranium from the dilute (less than 500 mg U dm^{-3}) solutions and maintained its uranium biosorptive uptake capacity over 12 successive sorption-elution cycles when synthetic uranyl nitrate solutions were used (Tsezos et. al., 1997)[22]. Adsorption on inert supports has been used as immobilization technique. In this technique, support materials are introduced into the batch-stirred tank reactor or tower fermenter prior to sterilization and inoculation with starter culture and are left inside the batch or continuous culture for a period of time, after which a film of microorganisms is apparent on the support surfaces. This technique has been used by Ileri *et al*[23] and Zhou and Kiff[8] for the immobilization of *R. arrhizus* in reticulated (polyurethane or polyester) foam biomass support particles (BSPs). Polyvinyl formal (PVF) immobilized *R. arrhizus* (laboratory cultured) has been tested for capacity to adsorb copper from solution in batch and continuous-flow column systems. The PVF was polymerized by dichloromethane. After solidification the resultant discs with biomass loadings of 60% (w/w) were reduced to particle sizes of 0.5-1.0 mm in diameter. Immobilization of *R. arrhizus* in PVF did not diminish metal uptake levels[24].

Despite the advantages listed, biosorbent immobilization may constitute an additional and significant economic cost which may prevent its use under certain conditions. Treatment of the highly acidic effluent may lead to complications with organic and polymeric matrices. The major limitation of immobilization is that immobilization of cells may cause extra diffusional limitations as compared to free cultures. Diffusional limitations lead to a more dispersed breakthrough curve, with a decrease in column utilization for a given breakthrough concentration[13,25,26]. Cultivating *Aspergillus oryzae* in pellet form is an effective means of mycelium immobilization. The method established by Huang and Huang[27] provides the high yield, uniformly-sized particles (2-3 mm in diameter), which are effective in solid-liquid separation. To investigate simultaneous biosorption of Cr(VI) and Cu(II) on *R. arrhizus* in a packed column reactor, a surface-attached *R. arrhizus* (NRRL 2286) was grown at a very low stirring rate, and free-dead cells were used in the packed column. To use surface- attached *R. arrhizus* in a column-type reactor without immobilization, it can be obtained in an appropriate diameter based on the method used to grow, kill, and homogenize the cells. The diameter of thermally killed *R. arrhizus* in the biosorption medium was determined to be in the 150-200 μm size range as the result of wet measurement[28]. Obtained as

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

a waste of the enzyme fermentation industry, biocide-treated *Mucor miehei* biomass was prepared to biosorbent particles 0.1-0.6 mm in diameter[29]. This powdered biomass has been used for the biosorption of Cu(II) ions in continuous-flow column systems[24].

Comparison of Metal Biosorption Capacities of Various Fungal Cells

Biosorption of heavy metal ions on various free and immobilized fungal cells in different reactor systems are compared in Table I. The uptake is usually measured by the parameter q (mmol or mg of metal accumulated per g of biosorbent). Within the table the highest experimentally observed value of the specific uptake, q_{max}, is reported as a function of metal accumulated, fungal cell species used, and operating conditions (pH, T, C_i, X). It is seen that some values of q_{max} are not comparable with other values found for the same metal. It may depend not only on different biosorption abilities of fungi, but also on not exactly equal operating conditions. In fact, works of different authors cannot be compared directly: operating conditions are often different even if they are nominally equal. The relationship between the amount of metal adsorbed per unit weight of dried biomass and the metal ion concentration remaining in solution is described by an isotherm equation. The two most common types for describing this type of system are the Langmuir (L) and Freundlich (F). The isotherms and mathematical models used to describe fungal biosorption in different reactor systems in the literature have been incorporated into Table I using the designated letters L, F, BET, LPSKM, TPFBAM, etc.

Comparing maximum biosorption capacities obtained by various fungi in batch stirred tank reactors (BSTR) listed in Table I, biosorption preference for metals decreases in the following order: Cd>Co>Cr>Au=Cu>Fe>Ni>Th >U>Pb>Hg>Zn. Good evidence exists by now that the biomass of filamentous fungi of the order Mucorales represents a good biosorbent material for a wide range of heavy metals[4,17,23,30,34,37,42,46]. It is known that the cell walls of Mucorales, of which *Rhizopus* is a genus, are very sensitive to the medium composition and conditions of growth. Different media as well as growth conditions produce different metal sequestering abilities[4,17,23,24,27,37,40,42,44,47]. Despite earlier pessimistic reports on *Aspergillus* biosorption, the mycelium seems to sorbing well Au, Co, Th, Zn[5,30,44]. The common fungus *Penicillium* is also excellent biosorbent for Cd, Fe, Pb, Th, U, Zn[4,5,31,32]. It has been interestingly found that *Fusarium flocciferum*, dried powdered mycelium of Deuteromycetes, exhibits higher affinities for Cd, Cu, Ni[11] than most of the biosorbents reported in the literature. As seen from Table I, Cu(II) is one of the most studied metal ions due to its biological functions: it is an essential micronutrient for most living organisms but is toxic

Marcel Dekker, Inc.
270 Madison Avenue, New York, New York 10016

Table I. Comparison of Biosorption Capacities of Various Fungi in Terms of the Highest Observed Value of the Specific Uptake, q_{max}, as a Function of Metal Accumulated, Operating Conditions and Reactor Type, and the Adsorption Models Applied to Fungal Biosorption

Fungal Biomass		Metal	pH	T (°C)	C_i (mg l^{-1})	X (g l^{-1})	q_{max} (mmol g^{-1})	Reactor Type	Isotherm or model	Reference
Aspergillus niger		Au(II)	2.5	23	8.5-1000		1.015	BSTR		30
Rhizopus arrhizus		Au(II)	2.5	23	8.5-1000		0.812	BSTR		30
Fusarium flocciferum		Cd(II)	7.5-8.0	Room T	19-96	0.5	1.708	BSTR	L	11
Penicillium chrysogenum		Cd(II)			0-100		0.347	BSTR	L	5
Rhizopus arrhizus		Cd(II)	6.0-7.0		10-600	3.0	0.240	BSTR	L	17
Rhizopus arrhizus		Cd(II)	3.5	26	10-400		0.231	BSTR	L	5
Penicillium chrysogenum	formaldehyde-urea crosslinked	Cd(II)			0-100		0.196	BSTR	L	5
Penicillium digitatum		Cd(II)	5.5	25	39.3-393.4	6.5	0.100	BSTR		31
Penicillium chrysogenum		Cd(II)	4.5	23	0-100		0.098	BSTR		32
Aspergillus oryzae	immobilized in BSPs	Cd(II)	8	25			0.089	PCR		33

(continued)

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

Table I. Continued.

Fungal Biomass		Metal	pH	T (°C)	C_i (mg l^{-1})	X (g l^{-1})	q_{max} (mmol g^{-1})	Reactor Type	Isotherm or model	Reference
Rhizopus arrhizus	free-biomass	Cr(VI)	2.0	25	25-250	1.0	1.979	PCR	F	28
Rhizopus arrhizus		Cr(VI)	2.0	25 35-45	25-200	1.0	1.118 1.427	BSTR	L	34
Aspergillus niger		Co(II)	4-5	23	8.5-1000		1.612	BSTR		30
Rhizopus arrhizus		Co(II)	6.5	30	2.5	0.15	0.049			35
Aspergillus niger		Co(II)	6.5	30	2.5	0.15	0.041			35
Ganoderma lucidum	mushroom, alkali treated	Cu(II)	5	25±2	0-200	4.0	1.015	BSTR	L,F	36
Rhizopus arrhizus	immobilized in polyurethane foam sheet	Cu(II)	7	30	2	4.9	0.787-1.023 for 250 batches	BSTR	F	23
Rhizopus arrhizus	immobilized in stainless steel mesh sheet	Cu(II)	7	30	2	6.2	0.787-1.023 for 250 batches	BSTR		23
Rhizopus arrhizus	free-biomass	Cu(II)	4.0	25	25-250	1.0	0.754	PCR	F	28
Rhizopus arrhizus		Cu(II)	4.0	25	25-200	1.0	0.738	BSTRS, n=3	F	37
Fusarium flocciferum		Cu(II)	4.5 ±0.1	Room T	10-200	0.5	0.629-0.944	BSTR	Two-site L	11

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

Rhizopus arrhizus	Untreated, DCM-treated, immobilized in PVF	Cu(II)	4.0		0-70	1.0	0.400	BSTR	L	24
Rhizopus arrhizus		Cu(II)	4.0-5.0	25	50-500	1.0	0.353	CFST	L, LPSKM	38
Rhizopus arrhizus		Cu(II)	4.0	25	25-200	1.0	0.301	BSTR	F	37
Mucor mihei	Biocide-treated	Cu(II)	4.0		0-64	1.0	0.300	BSTR	L	24
Mucor mihei	Suspended in column	Cu(II)	4.0		64	0.76-8.80	0.300	PCR	TPFBAM	24
Cladosporium resinae		Cu(II)	5.5	25	1-320	1.0	0.252			39
Penicillium digitatum		Cu(II)	5.5	25	22.2-222.4	6.5	0.230	BSTR		31
Aspergillus oryzae	Acid-washed-Fungal mycelia	Cu(II)	5		0.064-8.9		0.217	BSTR	L, Two-site L	40
Rhizopus arrhizus	immobilized in PVF	Cu(II)	4.0		10	0.8 g	0.209	PCR	TPFBAM	24
Rhizopus oryzae	Acid-washed-fungal mycelia	Cu(II)	5		0.064-6.355		0.191	BSTR	L, Two-site L	40
Aspergillus niger	alkali treated	Cu(II)	5	25±2	0-200	4.0	0.159	BSTR	L,F	36
Penicillium chrysogenum		Cu(II)	4.5	23	0-100		0.134	BSTR		32

(continued)

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

Table I. Continued.

Fungal Biomass		Metal	pH	T (°C)	C_i (mg l^{-1})	X (g l^{-1})	q_{max} (mmol g^{-1})	Reactor Type	Isotherm or model	Reference
Aureobasidium pullulans		Cu(II)	5.5	25	1-320	1.0	0.094			39
Rhizopus oryzae		Cu(II)	5		3.18	0.98	0.046	BSTR		27
Aspergillus oryzae	Acid treated pellets	Cu(II)	5		3.18	0.98	0.026-0.056	BSTR, PCR		27
Aspergillus oryzae		Cu(II)	5		3.18	0.98	0.012	BSTR		27
Rhizopus arrhizus	free-biomass	Fe(III)	2.0	25	50-200	1.0	0.688	PCR	F	41
Rhizopus arrhizus		Fe(III)	2.0	25 35-45	25-200	1.0	0.622 0.931	BSTR	L	34
Penicillium digitatum		Fe(III)	5.5	25	19.6-195.5	6.5	0.270	BSTR		31
Penicillium chrysogenum		Pb(II)	4.5	23	2-20		0.560	BSTR		32
Rhizopus arrhizus		Pb(II)	5.0	35-45 25	25-300	1.0	0.439 0.332	BSTR	F	42
Rhizopus arrhizus		Pb(II)	5.0-7.0		10-600	3.0	0.270	BSTR	L	17
Rhizopus arrhizus		Pb(II)	5.0	25	50-500	1.0	0.236	CFST	L, LPSKM	38
Penicillium digitatum		Pb(II)	5.5	25	72.5-725.2	6.5	0.090	BSTR		31

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

Phanerochaete chryosponum	White-rot fungi	CH_3HgCl C_2H_5HgCl $HgCl_2$	7.0	25	5-500	4.0	0.394 0.334 0.304	BSTR	L	43
Rhizopus arrhizus		Ni(II)	5.0	25	50-500	1.0	1.274	CFST	L, LPSKM	38
Rhizopus arrhizus		Ni(II)	4.5	25	25-200	1.0	0.895	BSTRS, n=3	F	37
Fusarium flocciferum		Ni(II)	7.5-8.0	Room T	10-50	0.5	0.886	BSTR	L	11
Rhizopus arrhizus		Ni(II)	4.5	25	25-200	1.0	0.494	BSTR	F	37
Rhizopus arrhizus		Ni(II)	6.0-7.5		10-600	3.0	0.320	BSTR	L	17
Penicillium digitatum		Ni(II)	5.5	25	20.5-205.4	6.5	0.250	BSTR		31
Rhizopus arrhizus		Th(VI)	4-5	5-40	30-100		0.797	BSTR	F,L	4
Aspergillus niger		Th(VI)	0-1	25	100-700	0.3-9.0	0.698			44
Penicillium chrysogenum		Th(VI)	4-5	23	30-100		0.612	BSTR	F,L	4
Rhizopus arrhizus		Th(VI)	0-1	25	100-700	1-13	0.500			44
Aspergillus niger		Th(IV)	2-5	23	30-100		0.095	BSTR	F,L	4
Aspergillus terreus		Th(VI)	4-5	23	30-100		0.035	BSTR	F,L	4

(continued)

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

Table I. Continued.

Fungal Biomass		Metal	pH	T (°C)	C_i (mg l^{-1})	X (g l^{-1})	q_{max} (mmol g^{-1})	Reactor Type	Isotherm or model	Reference
Aspergillus niger	biomass pellets	U	5.8				0.924	FB		45
Rhizopus arrhizus		U	4-5	5-40	50-1000		0.756	BSTR	F,L	4
Penicillium chrysogenum		U	2-5	23	50-1000		0.693	BSTR	F,L	4
Rhizopus sp.	nine species	U	3.7-3.9	25	100-300	0.5-1.0	0.630-1.050	BSTR		46
Rhizopus arrhizus	immobilized biomass of *R. arrhizus* (MSR particles)	U	4		500		0.630	PCR		22
Rhizopus arrhizus	MSR particles	U	4		500-1000		0.504	BSTR	F, BRMTK	47
Rhizopus nigricans		U	4-5	23	8.5-1000		0.480	BSTR		30
Aspergillus oryzae		U	4-5	23	8.5-1000		0.290	BSTR		30
Rhizopus arrhizus	hydrated pellets	U	3.7-3.9	25	90	0.95 g	0.195	PCR		46
Aspergillus niger		U	4-5	23	50-1000		0.130	BSTR	F,L	4
Trichoderma reesii		U	4-5	23	8.5-1000		0.120	BSTR		30

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

Endothia parasitica	U	4-5	23	8.5-1000		0.100	BSTR		30
Penicillium digitatum	U	5.5	25	83.3 -833.1	6.5	0.042	BSTR		31
Aspergillus terreus	U	2-5	23	50-1000		0.004	BSTR	F,L	4
Aspergillus oryzae	Zn(II)			5-200	1.4	0.270	BSTR	L	5
Penicillium digitatum	Zn(II)	5.5	25	22.9-228.9	6.5	0.260	BSTR		31
Trichoderma reesii	Zn(II)			5-200	1.0	0.240	BSTR	L	5
Rhizopus nigricans	Zn(II)			5-200	1.7	0.220	BSTR	L	5
Aspergillus niger	Zn(II)			5-200	1.2	0.210	BSTR	L	5
Rhizopus arrhizus	Zn(II)	6.0-7.5		10-600	3.0	0.210	BSTR	L	17
Rhizopus arrhizus	Zn(II)	4.0-5.0		5-250	1.0	0.195	BSTR	L,F,RP	48
Endothia parasitica	Zn(II)			5-200	0.8	0.150	BSTR	L	5
Penicillium chrysogenum	Zn(II)	4.5	23	0-100		0.095	BSTR		32

Isotherm- Langmuir=L, Freundlich=F, Redlich-Peterson=RP, Mathematical model- Lumped parameter simple kinetic model incorporated with continuous system mass balance=LPSKM, Two-parameter fixed bed adsorption model=TPFBAM, Batch reactor mass transfer kinetic model=BRMTK.

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

when in excess. A wide variety of free-immobilized, treated-untreated fungal biomasses has been used for Cu biosorption in different reactor systems and a wide range of capacities for Cu ions has been observed. The biosorption capacities vary from 1.015 mmol g^{-1} for *Ganoderma lucidum*, a mushroom, to 0.012 mmol g^{-1} for *A. oryzae*. The Cu(II) biosorption capacities of *R. arrhizus* obtained in batch stirred tank reactor (BSTR)[37], continuous-flow stirred-tank contactor (CFST)[38], batch stirred-tank reactors in series (BSTRS)[37] (when three reactor was used in series), packed column (or fixed bed) reactor[28] (PCR) at exactly same operating conditions have been found to be 0.301, 0.353, 0.738, 0.754 mmol g^{-1}, respectively. Brady *et al*[24] have reported that in continuous-flow columns *R. arrhizus* and *M. mihei* adsorbed copper (0.400 and 0.300 mmol g^{-1}, respectively) to levels equal or approaching the batch uptake values. The Ni(II) biosorption capacities of *R. arrhizus* obtained in BSTR[37], BSTRS[37] (n=3), CFST[38] have been determined as 0.494, 0.895, 1.274 mmol g^{-1}, respectively. The most widely used contacting device for sorption processes is the packed column reactor configuration and its modifications. A maximum uranium uptake of 0.924 mmol g^{-1} by *A. niger* pellets has been reached in a compartmentalized fluidized bed (FB) reactor[45]. When the biosorption of uranium ions by immobilized biomass of *R. arrhizus* has been studied in a PCR[22] instead of BSTR[47], uranium uptake has increased from 0.504 to 0.630 mmol g^{-1}. The weight of Cr(VI) adsorbed per unit dry weight of *R. arrhizus* in PCR[28] (1.979 mmol g^{-1}) was considerably higher than that in BSTR[34] (1.118 mmol g^{-1}), whereas the weight of Fe(III) adsorbed per unit dry weight of *R. arrhizus* in PCR[41] (0.688 mmol g^{-1}) was approximately equal to than that in BSTR[34] (0.622 mmol g^{-1}).

Mechanisms of Metal Biosorption on Fungal Cells

The complexity of the microorganism' s structure implies that there are many ways for the metal to be captured by the cell. Biosorption mechanisms are therefore various and in some cases they are still not very well understood. According to the dependence on the cells' metabolism, biosorption mechanisms can be divided into:

1. Metabolism dependent (active metal uptake): Transport across cell membrane, precipitation. It is an energy-driven process.
2. Non-metabolism dependent (passive metal uptake): Precipitation, physical adsorption, ion exchange, complexation[6].

Dead cells sequester metals through chemical functional groups of the material comprising the cell and particularly the cell wall which constitutes a large percentage of the cellular dry weight. The passive metal uptake may be present even when the cell is metabolically active and, conversely, it may be suppressed by ac-

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

tive metal exclusion processes. Passive metal uptake is relatively rapid and can be reversible[6,9].

According to the location where the metal removed from the solution is found, biosorption may also be classified as:

1. extracellular accumulation/precipitation;
2. cell surface sorption/precipitation: ion exchange, complexation, physical adsorption, precipitation;
3. intracellular accumulation: transport across cell membrane[6];

The chemical makeup of the fungal cell wall and its structural organization is such that metals can become deposited either on its surface or within its structure before they penetrate into the cellular interior where they could be bound by other compounds and organelles which are part of the cytoplasm. Fungal cell surfaces can be regarded as a mosaic of different functional groups where coordination complexes with metals can be formed. Among those groups are carboxyl (-COOH), amide (-NH_2), thiol (-SH), phosphate (PO_4^{3-}), and hydroxide (-OH). Phosphate groups are present mainly in glycoproteins and are believed to play an important role in biosorption because they can exhibit a negative charge above pH 3[49]. In fungal cells, metal ions can bind to the amino groups of chitin (R_2-NH) and chitosan (R-NH_2), chitin and its associated proteins contain many carboxylate groups with pKa 4 to 5. Aspartate, glutamate, and cysteine are also believed to play an important role in metal chelation[11,40,50].

Tsezos and Volesky[51,52] were of the opinion that amino-nitrogen of chitin was the main component responsible for uranium and thorium biosorption on *R. arrhizus*. They have reported a three process-mechanism for uranium biosorption, based on uranium coordination and physical adsorption by the cell wall chitin structure and precipitation of uranylhydroxide within the chitin microcrystalline cell wall structure[51]. Muraleedharan and Venkobachar[53] have showed that copper ions chemically coordinate to *G. lucidum.* They have not identified the specific groups responsible for biosorption but have concluded that these groups were neither protein nor chitin. Electrostatic interactions have been demonstrated to be responsible for chromium biosorption by *G. lucidum* and *A. niger*[54]. Phosphodiester and carboxyl groups present confer the electrical surface potential to the fungal cell wall[15]. Physical adsorption is furthermore responsible for copper[8], nickel, zinc, cadmium and lead[17] biosorption by *R. arrhizus*. The removal of heavy metal cations by most biomass types decreases as the pH of the metal solutions decreases from pH 6 to 2.5 (Table I). Because most of the heavy metals precipitate at pH$>$5.5, at higher pH values, the metals might accumulate inside the cells and/or the cell walls by a combined sorption-microprecipitation mechanism. However, experiments performed in batch systems without pH adjustment showed that the sorption of heavy metals onto acid-treated biomass led to a decrease in the pH of the liquid[55]. Based on this findings, a hypothesis of ion ex-

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

change between protons and heavy metals has been formulated[3]. Treen-Sears et al[46] have shown that uranium biosorption on *R. arrhizus* resulted in exchange of hydrogen ions from biomass for uranyl ions. It needs to be emphasized that biosorption of heavy metals on different fungi may involve different functional groups to varying extents. The typical dependence of metal uptake on pH points to the weakly acidic carboxyl groups R-COOH (pKa in the range 3.5-5.5) of fungal cell-wall constituents. However, the pH values at which the metal uptake increases sharply and reaches its maximum are generally higher for the amino groups than for the carboxyl groups[3]. The role played by various functional groups in the cell wall of *A. niger* in biosorption of lead, cadmium and copper has been investigated by Kapoor and Viraraghavan[56]. They have suggested that both carboxyl and amine groups played an important role in biosorption of lead, cadmium and copper. On the other hand, phosphate groups and the lipids fraction of the biomass did not not play a significant role in biosorption of the metal ions studied. They have also shown that biosorption of metal ions on *A. niger* released potassium ions, in addition to calcium and magnesium ions, indicating that biosorption took place as a result of an ion-exchange process.

Scant information is available about the accumulation of metals in their complexed forms, as they are usually present in cyanide-containing industrial solutions. Some studies mainly focus on biodegradation of metal cyanides. In recent studies, *Cladosporium cladosporioides* biomass has been shown to be a highly efficient biosorbent of copper cyanide(TCC) and nickel cyanide(TCN) from aqueous solutions[57]. *C. cladosporioides* biomass had maximum loading capacity for TCC (0.040 mmol g^{-1}) and TCN(0.034 mmol g^{-1}) which was higher than the activated charcoal (0.030 mmol g^{-1} for TCC and 0.0275 mmol g^{-1} for TCN), *Aspergillus fumigatus* (0.028 mmol g^{-1} for TCC), *Aureobasidium pullulans* (0.026 mmol g^{-1} for TCC and 0.013 mmol g^{-1} for TCN) and chitin (0.010 mmol g^{-1} for TCC and 0.008 mmol g^{-1} for TCN)[57]. Gomes *et al*[58] have attempted to elucidate the nature of cyano-metal complexes-cell interaction of an *A. niger* strain during metal uptake from an industrial cyanide-containing solution by the light of solution chemistry and microanalysis (Electron microscopy, X-ray energy dispersion spectra analysis and Fourier-transform infrared analysis) of the metal-containing bio-material. They have reported that *A. niger* actively transformed cyano-metal complexes into insoluble metal compounds that were then adsorbed onto the cell wall. The metabolism-dependent and-independent processes occurred simultaneously during the metal uptake by *A. niger*.

Metal Biosorption Mechanism of Chitin and Chitosan

Chitosan, poly(β-(1 → 4)-2-amino-2-deoxy-D-glucopyranose(is a polymer composed of partially deacetylated (1 → 4)-2-acetamide-2-deoxy-β-D-glucose. It

Marcel Dekker, Inc.
270 Madison Avenue, New York, New York 10016

can be easily made by deacetylating chitin, poly(β-(1 → 4)-2-acetamido-2-deoxy-D-glucopyranose) (Figure 1). The natural source of chitin is the shell of crustaceans (lobsters, shrimps, etc.) or the broth from industrial fungal processes. Several studies have demonstrated that its interactions with metals are always much more important compared to those of chitin due to the higher number of free amine groups in the chitosan molecule (Table II). Chitosan is selective for metal ions, it only uptakes the transition and post transition metals but does not adsorb for the alkali and alkaline earth metals. The formation of a coordination complex between the metal and the chitin nitrogen or oxygen has been suggested. Ion exchange has also been suggested as a process that may be active in certain metals' uptake by chitin or chitosan, however, chitin/chitosan-metal biosorption mechanism has still not yet been fully explained. In contrast, the sorption efficiency for the soluble chitosan with a large number of metal ions and their chelating properties have been found to obey the Irving-Williams and Mellor-Maley series[9,73 -75].

Since chitosan can be dissolved in acidic media, crosslinking of chitosan is necessary for the purpose of insolubilization. The capacity of metal adsorption is known to become relatively small due to crosslinking between the polymer chains

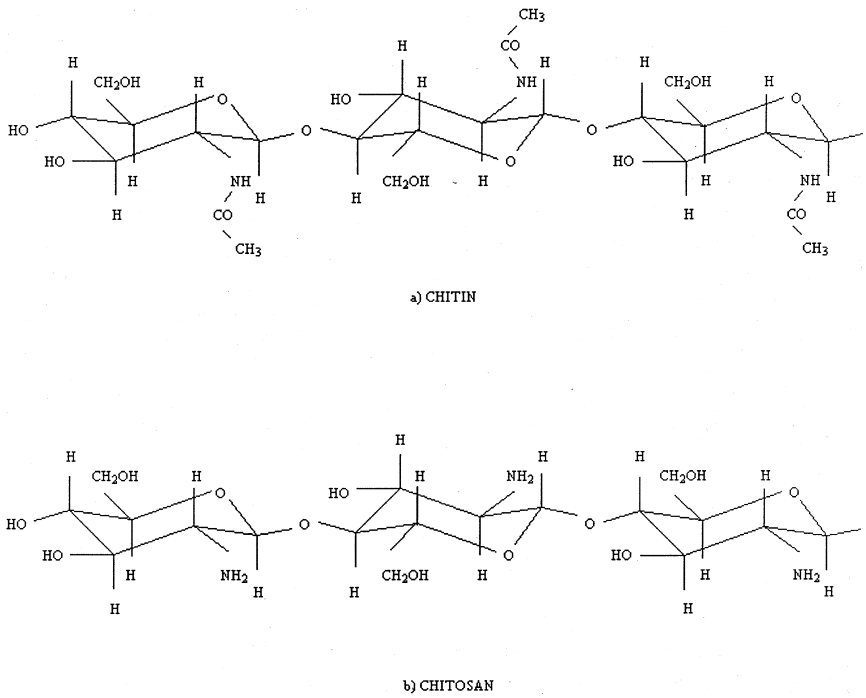


Figure 1. Molecular repeating units of a) chitin and b) chitosan.

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

Table II. Comparison of Biosorption Capacities of Chitin and Chitosan

Biosorbent		Metal	pH	T (°C)	C_i (mg l^{-1})	X (g l^{-1})	q_{max} (mmol g^{-1})	Reactor Type	Isotherm or model	Reference
Chitosan	cross-linked chitosan gel beads with GA	Cd(II)	6.5	25	2000	20	0.890	BSTR		59
Chitin derivative	ChAA-*co*-Am graft copolymer	Cd(II)	3.5	25		20	0.186	BSTR		60
Chitin derivative	ChAA graft copolymer	Cd(II)	3.5	25		20	0.177	BSTR		60
Chitin derivative	ChAm-*co*-AN graft copolymer	Cd(II)	3.5	25		20	0.160	BSTR		60
Chitin derivative	ChAA-*co*-Am graft copolymer	Cr(III)	3.5	25		20	2.125	BSTR		60
Chitin derivative	ChAA graft copolymer	Cr(III)	3.5	25		20	1.904	BSTR		60
Chitin derivative	ChAm-*co*-AN graft copolymer	Cr(III)	3.5	25		20	1.221	BSTR		60

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

Chitin	with 46.8% of DD	Cr(VI)	3.0	25	0-100	0.5	2.054	BSTR	L	61
Chitosan	Crab shells	Cr(VI)	3.0-4.0	25±2	5-50	0.5	0.671	BSTR	L,F	62
Chitosan	Prawn shell	Cu(II)		25-40	0-300	2	3.493	BSTR	L	63
Chitin derivative		Cu(II)			0.1 mol l^{-1}	1 g	1.553			64
Chitosan	PSC resin	Cu(II)	5.5-7.5	30	0-500	2.5	1.480	BSTR	L	65
Chitin derivative	ChAA-*co*-Am graft copolymer	Cu(II)	3.5	25		20	1.125	BSTR		60
Chitosan	CLC resin	Cu(II)	5.7	30	0-500	2.5	0.950	BSTR	L	65
Chitosan	Prawn shell	Cu(II)	4.2	25-60	0-200	0.059	0.629	BSTR	L,F, EMTDM	66
Chitin derivative	ChAA graft copolymer	Cu(II)	3.5	25		20	0.485	BSTR		60
Chitin derivative	ChAm-*co*-AN graft copolymer	Cu(II)	3.5	25		20	0.472	BSTR		60
Chitin		Cu(II)	6.5	25	0-136	1.7	0.20±0.02	BSTR	L	67
Chitosan	Prawn shell	Cu(II)	6.2		100	0.2 g	0.074	PCR		68
Chitin derivative	ChAA-*co*-Am graft copolymer	Fe(III)	3.5	25		20	0.376	BSTR		60
Chitin derivative	ChAA graft copolymer	Fe(III)	3.5	25		20	0.162	BSTR		60
Chitin derivative	ChAm-*co*-AN graft copolymer	Fe(III)	3.5	25		20	0.051	BSTR		60
Chitin	Crab shell	Pb(II)	5.5	25	100	7.5	0.236	BSTR		69

(continued)

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

Table II. Continued.

Biosorbent		Metal	pH	T (°C)	C_i (mg l^{-1})	X (g l^{-1})	q_{max} (mmol g^{-1})	Reactor Type	Isotherm or model	Reference
Chitosan	Prawn shell	Hg(II)		25	0-600	2	4.063	BSTR	L	63
Chitosan	Prawn shell	Ni(II)		25-60	0-300	2	2.794	BSTR	L	63
Chitosan	CLC resin	Pd(II)		30	0-1500	2.5	2.790	BSTR	L	65
Chitosan	PSC resin	Pd(II)		30	0-1500	2.5	1.720	BSTR	L	65
Chitosan	Fe(III)-templated oxine type of chemically modified chitosan, in the presence of Sn(II)	Rh(III)		30	0-100	3.333	0.920	BSTR	L	70
Chitosan		U	6.5-7.5		$3x10^{-5}$ mol l^{-1}	0.12	0.294	BSTR		71
Chitin		U	6.5-7.5		$3x10^{-5}$ mol l^{-1}	0.10	0.053	BSTR		71
Chitosan		V(VI)	4.0	20±1	25-100	0.1	7.843	BSTR	L,F, EMTDM, IMTDM	72
Chitosan	Prawn shell	Zn(II)		25-60	10-400	2	1.147	BSTR	L	63

Isotherm- Langmuir=L, Freundlich=F, Mathematical model- External mass transfer diffusion model= EMTDM, Intraparticular mass transfer diffusion model= IMTDM.

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

of chitosan as metallic ions normally adsorb onto the amino and hydroxyl groups of chitosan[65]. The saturation adsorption capacity of Cd(II) ions onto cross-linked chitosan gel beads exponentially decreased from 2.224 to 0.890 mmol of Cd(II) g^{-1} of chitosan as the extent of cross-linking increased from 0 to 1.3 mol of GA/mol of $-NH_2$. At higher extents of cross-linking, the saturation adsorption capacity remained at 0.890 mg of Cd/g of chitosan[59]. An alternative approach is to find a degree of deacetylation in chitin which could produce an optimal balance between its maximum sorption and stability in the acidic condition. The deacetylated chitins with 46.8% DD were generally the most effective in removal of Cr(VI) ions at pH 3 and stability of highly deacetylated chitin was increased at low pH conditions due to a crosslinking effect[61]. The chitin thiocarbonate-Fe(II)-H_2O_2 redox system has been investigated as the initiator for the graft copolymerization of acrylonitrile and acrylic acid monomers onto chitin powder. Reactions of chitin-acrylonitrile graft copolymer with hydroxyl amine hydrochloride, as well as, sodium hydroxide have been conducted in order to obtain chitin-(amidoxime-*co*-acrylonitrile) (ChAm-*co*-AN) and chitin-(acrylate-*co*-acryl-amide) graft copolymers, respectively. Among these derivatives, the product with $-NH_2$ and -COONa groups, chitin -(acrylate-*co*-acrylamide) (ChAA-*co*-Am) graft copolymer, showed higher adsorption amounts for metal cations, which is attributed not only to the adsorption capacity of the functional groups, but also to the hydrophilicity of the main chain and the pendant of coordination sites which form chelate rings with metal ions[60]. A novel chitosan-supported sulfonic acid resin modified by propane sultone has been prepared and the adsorption characteristics of metal ions have been examined by using a crosslinked chitosan-supported sulfonic acid resin (PSC) and a crosslinked chitosan resin (CLC). The maximum adsorption capacity for PSC in the case of adsorption of copper is 1.6 times that of CLC[65] (Table II).

Using pure commercial chitin gave a copper binding capacity of 0.20 ± 0.02 mmol g^{-1} chitin[67]. *R. arrhizus* exhibited maximum copper uptake of 0.787-1.023 mmol g^{-1} [23] while *A. oryzae*, a sorbent devoid of chitin, removed 0.217 mmol Cu(II) g^{-1} [40]. Piron[71] has observed a chitin uptake of 0.053 mmol U g^{-1}, while maximum uranium uptake capacities of nine species of *R. arrhizus* and *A. oryzae* have been reported as 0.630-1.050 mmol g^{-1} [46] and 0.290 mmol g^{-1} [30], respectively. According to the uranium and thorium uptake mechanism suggested by Tsezos and Volesky[51,52], substituted amino groups of the cell wall chitin network act initially as uranium coordination sites. Coordinated uranium function subsequently as nucleation sites for sequestering of additional uranium. Therefore, although the pure chitin uranium uptake capacity is very small, chitin may play an important role in the uranium biosorption by *R. arrhizus*. On the other hand, Sağ[42] has reported that *R. arrhizus* reached uptake value of 0.332 mmol Pb(II) g^{-1}. Fourest[17] has measured uptake amount of 0.270 mmol Pb(II) g^{-1} for *R. arrhizus*. Ashkenazy[69] has reported similar experimental result for the uptake of Pb(II) (0.236 mmol g^{-1}) ions by pure chitin. Thus, pure chitin has a lead uptake capacity close to that of the

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

whole *R. arrhizus* cells, as observed previously for *Saccharomyces uvarum*[69]. In particular, in case of Cu(II), maximum metal uptake capacities of chitosan and chitin derivatives reported in the literature[63-65] are generally higher than those of pure whole cell cultures[11,23,36] (Tables I and II).

Competitive Metal Biosorption by Fungal Cells and Antagonistic-Synergistic Interactions

Up to now, the research on biosorption of heavy metals has mainly focused on either the adsorption efficiencies and equilibria for different biosorbent materials or the development of batch or continuous biosorption processes. However, relatively less work has been contributed to elucidate the details of the biosorption behavior in multi-metal systems, which are normally the composition of the industrial effluents. The interactive effects of a metal mixture on an aquatic organism are extremely complex and depend on species of microorganisms, number of metals competing for binding sites, metal combination, levels of metal concentration, order of metal addition, residence time and test criterion (i.e. cell number, cell growth, cell volume, dissolved oxygen, metal uptake, etc.). When dead cells are used in the biosorption studies, the other test criteria are eliminated. Three types of responses may be produced by an organism: i) The effect of the mixture is greater than that of each of the individual effects of the constituents in the mixture (synergism); ii) the effect of the mixture is less than that of each of the individual effects of the constituents in the mixture (antagonism); iii) the effect of the mixture is no more or less than that of each of the individual effects of the constituents in the mixture (noninteraction)[1,76,77].

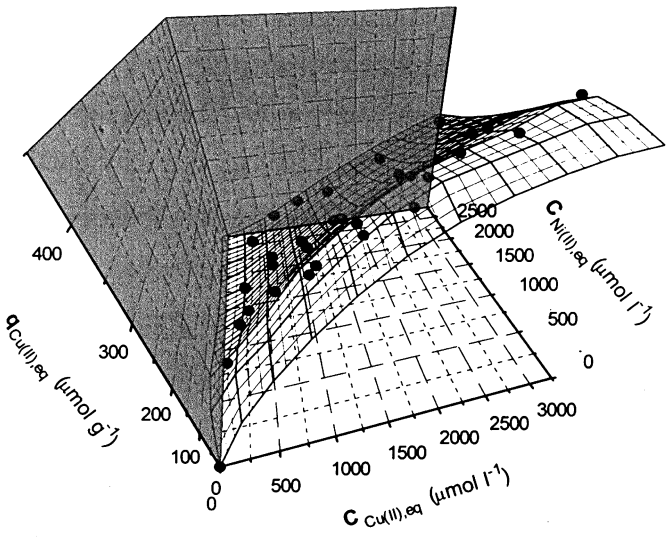
The uptake of Cu(II) and Cr(VI) ions from binary mixtures by *R. arrhizus* has been described as a function of ion concentration, pH and temperature by Sağ and Kutsal[77]. The combined action of Cu(II) and Cr(VI) on *R. arrhizus* has been generally found to be antagonistic at pH 2.0 and Cr(VI) dominated the competitive binding. The most logical reason for the antagonistic action is claimed to be the competition for adsorption sites on the cells and/or a screening effect by the second metal ion. The increasing concentrations of metal ions that are not adsorbed can mask preferentially adsorbed metal ions. The screening effect of the presence of the second metal ion in the biosorption medium can also give rise to mixed synergism and antagonism toward biosorption. The screening effect can induce synergism mutually ameliorating their individual toxic effects and masking the antagonism. Since the total uptake of metal ions were higher than those of the single-metal systems, the total interactive effects of Cu(II) and Cr(VI) ions on *R. arrhizus* were thought to be synergistic at pH 4.0. This can be attributed to the fact that increases in the total metal-ion concentration in the multi-metal mixtures result in a strong driving force or a large difference in concentration between ad-

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

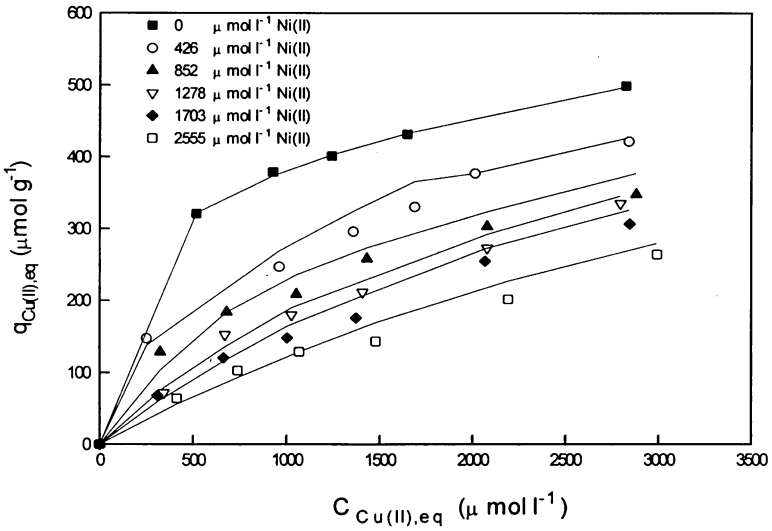
sorbent surface and metal solution, and further uptake of the competing metal ions. The ability of the fungal biomass *R. arrhizus* to bind three metals-Cr(VI), Fe(III), Cu(II)-simultaneously in solution has also been investigated[78]. Although Cr(VI) ions, in agreement with the single and dual component data, were adsorbed selectively from the ternary metal mixtures, Fe(III) ions competed strongly with Cr(VI) ions to bind to active sites on the fungus. On the other hand, the simultaneous biosorption of Cu(II) ions at pH 2.0 appeared to be significantly low. Tsezos *et al*[22] have indicated that an 18% reduction in the uranium uptake capacity of immobilized *R. arrhizus* occurred when mine leachate solutions instead of synthetic uranyl nitrate solutions were used. Tsezos *et al*[79] have also suggested that Al(III) interfered with the uranium biosorptive uptake capacity of *R. arrhizus* by the precipitation of a metastable amorphous hydroxy polymeric precipitate through a mechanism referred to as steric competition.

Simple sorption isotherm curves enable quantitative evaluation of sorption performance of different biosorbent materials for only one metal at a time. When more than one metal is present in the biosorption system, the evaluation, interpretation, and representation of biosorption results become much more complicated. Often the prediction of sorption equilibria is also complicated by the presence of several sorbed ions, requiring the use of multi-component isotherm equations. With two metals in the solution, instead of a two-dimensional sorption isotherm curve, the sorption system evaluation results in a series of three-dimensional sorption isotherm surfaces[2,3,80,81]. The correct and most illustrative way of representing the biosorption equilibrium of a two-metal system is to constract a 3-D sorption isotherm plot whereby the metal uptake is plotted as a function of the final equilibrium concentrations of the two metals. The computer program MATLAB 4.0 is capable of plotting a 3-D diagram based on randomly generated experimental data, fitting a smooth surface to the data according to the appropriate input equation, which represents the surface. The input equation is a multi-component sorption equilibrium model and a binary Langmuir-type equation was generally used in the literature[1,2]. This approach is illustrated in Figure 2 a)-e) for the simultaneous biosorption of Cu(II) and Ni(II) ions by using 3-D isotherm-surface plotting. In order to create the biosorption isotherm surfaces an empirical extension of the Freundlich model, restricted to binary mixtures, was used. Depending on the $q_{i,eq}$ value calculated and used, there could be three different sorption-isotherm surface plots: 1) for the uptake of metal 1, yielding the effect of metal 2 on metal 1 (Figure 2 a); 2) for the uptake of metal 2, yielding the effect of metal 1 on metal 2 (Figure 2 c); and 3) for the total uptake (metal 1 + metal 2) (Figure 2 e). All the $C_{i,eq}$ values and their corresponding $q_{i,eq}$ values belong to the same isotherm surface, and so it can be cut by selected isoconcentration parallel planes at chosen second metal $C_{i,eq}$, yielding (in projection) a series of isotherms for the first metal as affected by the presence of increasing concentrations of the second metal (Figure 2 b,d). The effect of different levels of Ni(II) on the biosorbent up-

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016



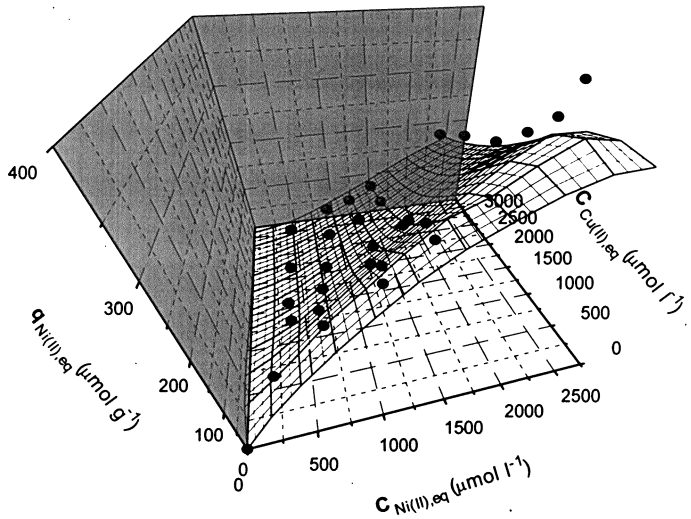
a)



b)

Figure 2. a) A three-dimensional biosorption surface for the simultaneous biosorption of Cu(II) and Ni(II) on *R. arrhizus* from binary mixtures: Cu(II) uptake. b) The effect of Ni(II) on equilibrium uptake of Cu(II) by *R. arrhizus* is derived by 'cutting' the isotherm surface with Ni(II) isoconcentration planes and plotting the resulting curves.

Marcel Dekker, Inc.
270 Madison Avenue, New York, New York 10016



c)

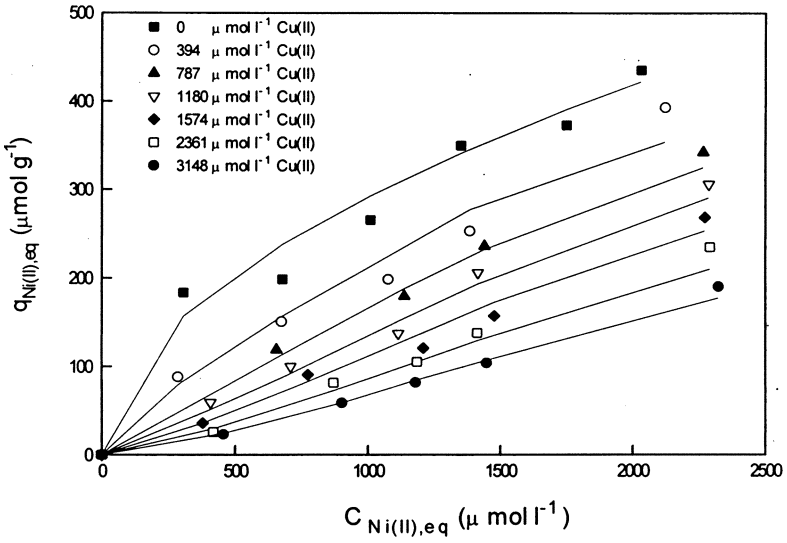
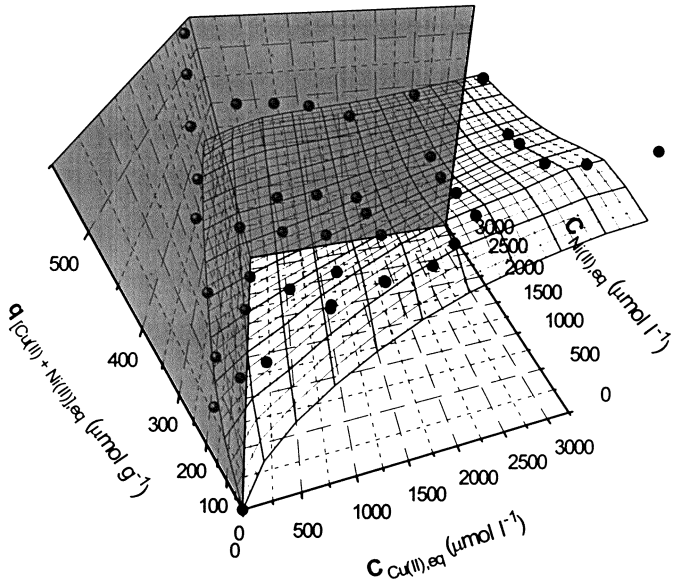


Figure 2. Continued. c) A three-dimensional biosorption surface for the simultaneous biosorption of Cu(II) and Ni(II) on *R. arrhizus* from binary mixtures: Ni(II) uptake. d) The effect of Cu(II) on equilibrium uptake of Ni(II) by *R. arrhizus* given with the two-dimensional biosorption isotherm curves. e) A three-dimensional sorption surface for the Cu(II)-Ni(II)-*R. arrhizus* biosorption system: total metal uptake.

(*continued*)

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016



e)

Figure 2. Continued.

take of Cu(II) is quantitatively much better demonstrated in Figure 2 b), showing how the biosorption uptake of Cu(II) decreases in the presence of Ni(II). The curves in Figure 2 b) represent series of Ni(II) 'isoconcentration cuts' of the Cu(II) biosorption surface in Figure 2 a). Figure 2 c) and d) summarizes the effect of Cu(II) on the uptake of Ni(II). In the range of low equilibrium Ni(II) concentrations the Ni(II) uptake is more severely affected by the presence of Cu(II). However, equilibrium uptake of Ni(II) ions increases when Ni(II) concentration and/or ratio of Ni(II) ion concentration is increased with respect to total metal-ion concentration. In Figure 2 e), the two main planes (x-z and y-z) show the single-metal biosorption isotherms for Cu(II) and Ni(II), respectively. One type of the metal ion present interfere with the uptake of another one in the system, although the overall total metal uptake is not necessarily lowered. Figure 2 e) shows that, with high levels of overall metal concentration present in the solution, the biosorbent easily reaches the saturation level demonstrated by a wide plateau of the surface. Since the experimental points for the surface are likely to exhibit a certain degree of scattering, the experimental surface has to be smoothed. To do this in 3-D plots requires more calculating power, which is now with the use of computers, which

can also fit a suitable mathematical model to the surface; the availability of an appropriate mathematical model is essential for the surface-cutting exercise.

Although this method can be extended to represent three-metal sorption equilibria (by a series of three dimensional 3-D plots whereby the residual concentration of one of the metals is taken as a parameter), a ternary system is represented in a triangular equilibrium diagram whereby the effect of the third ion is not ignored[1]. To use the triangular diagram, the equilibrium data are converted into their respective dimensionless forms by using mole fractions. The final residual concentrations in solution, $C_{i,eq}$, and the metal uptakes, $q_{i,eq}$, are converted to metal fractions in solution, X_i, and mole fractions in the biosorbent, Y_i, respectively. Use of a triangular diagram to graphically depict the equilibrium data of the ternary Cr(VI)+Cu(II)+Fe(III) system is illustrated in Figure 3 a)-c). In the triangular diagram, the equidistant axes refer to the mole fractions of the respective metal species on the biosorbent. Superimposed on these axes are contour lines or parametric lines which, in Figure 3 a)-c), correspond to the mole fractions of Cr(VI), Cu(II) and Fe(III) in solution, respectively. Due to the preference of *R. arrhizus* for the metals examined which was Cr(VI)>Fe(III)>Cu(II), the experimental points tend to cluster toward the Cr(VI) corner with a noticeable void in the Cu(II) corner of the triangular diagram. It is possible to see the diagrams also as pseudo-4D plots (the result of projecting/viewing a series of the surfaces over the Gibbs triangle[82,83] from above).

Equilibrium Sorption Models

Single-Component Sorption Models

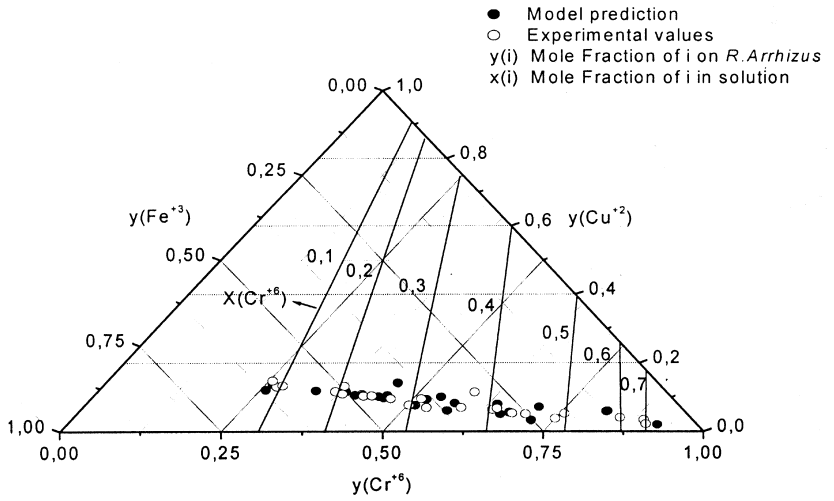
To design equipment, the investigation of the performance of free cells is fundamental for the industrial application of biosorption, because it gives information about the equilibrium of the process. The most widely used isotherm equation for modeling of the biosorption equilibrium data is the Langmuir equation[84,85].

$$q_{eq} = \frac{aC_{eq}}{1 + bC_{eq}} \tag{1}$$

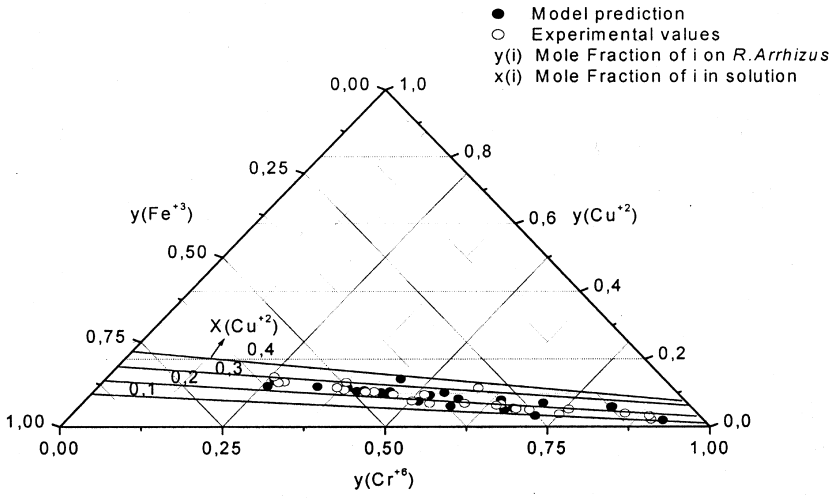
Where C_{eq} is the metal concentration in solution and $a=Q_m b$. The constants a and b are the characteristics of the Langmuir equation and can be determined from a linearised form of Eq. (1). The Langmuir equation obeys Henry's Law at low concentrations.

Langmuir model assumes that all sites are energetically equivalent. By taking into account the energetic heterogeneity, the bi-Langmuir model has been derived. This model is based on the coexistence of two independent non-cooperative sites and is formulated as follows[86].

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016



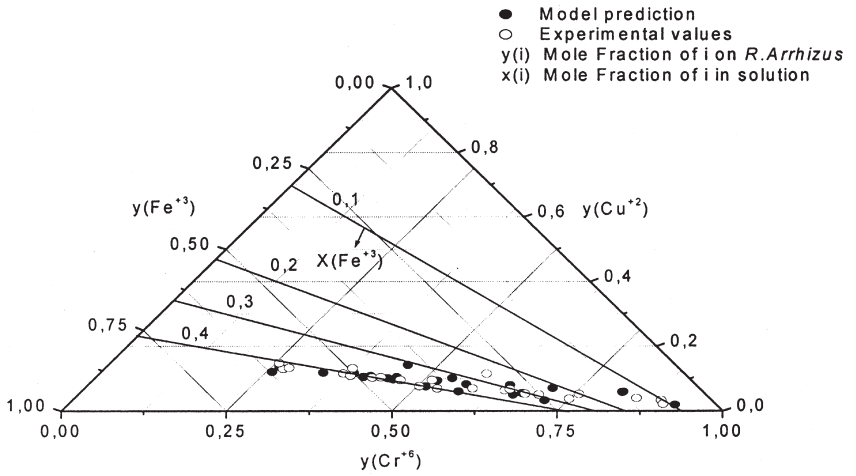
a)



b)

Figure 3. The simultaneous biosorption of Cr(VI), Cu(II) and Fe(III) ions on *R. arrhizus* from ternary mixtures. a) Biosorption isotherms of the constant Cr(VI) fraction in the solution (——). b) Biosorption isotherms of the constant Cu(II) fraction in the solution (——). Biosorption isotherms of the constant Fe(III) fraction in the solution (——).

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016



c)

Figure 3. Continued.

$$q_{eq} = \frac{a_1 C_{eq}}{1 + b_1 C_{eq}} + \frac{a_2 C_{eq}}{1 + b_2 C_{eq}} \tag{2}$$

The bi-Langmuir model has been applied to the biosorption of Cu(II), Cd(II) and Ni(II) on *F. flocciferum* and Cu(II) biosorption equilibrium data have exhibited a very good correlation with the bi-Langmuir model[11].

The Freundlich expression is an empirical equation based on sorption on a heterogeneous surface. The Freundlich equation is commonly presented as[84,85]:

$$q_{eq} = a^0 C_{eq}^{b0} \tag{3}$$

and the equation may be linearised by taking logarithms.

A further empirical isotherm has been developed by Redlich and Peterson (RP), incorporating three parameters[86]:

$$q_{eq} = \frac{K_R C_{eq}}{1 + a_R C_{eq}^{\beta}} \tag{4}$$

where the exponent β, lies between 0 and 1. When β=1, the Redlich-Peterson equation reduces to the Langmuir equation. When β=0, the Henry's Law form results. Although the Langmuir and Freundlich models have been widely used to define equilibrium parameters of fungal biosorption, the application of the Redlich-Peterson equation to biosorption is scarce in the literature. The Redlich-Peterson isotherm has been demonstrated to provide a good correlation for the biosorption of Cu(II) and Zn(II) ions on *R. arrhizus*[48].

Multi-Component Sorption Models

Competitive isotherms, describing multi-component sorption, are classified according to the relationship they have with single component isotherms[86]:

Competitive Isotherms Related to the Individual Isotherm Parameters Only

The extension of the basic Langmuir model to competitive adsorption is based on the same hypotheses as for the single-component Langmuir model and assumes, in addition, identical saturation capacities for all components[86]. It is written as

$$q_{i,eq} = \frac{a_i C_{i,eq}}{1 + \sum_{j=1}^{N} b_j C_{j,eq}} \tag{5}$$

where the a_i and b_i are derived from the corresponding individual Langmuir isotherm equations. The competitive Langmuir model has been shown to be consistent with the observed uptake of Cr(VI) and Fe(III) ions on *R. arrhizus* from binary mixtures[34].

The bi-Langmuir isotherm to describe the adsorption of binary mixtures has been modified. It is written as follows[86]:

$$q_{i,eq} = \frac{a_{i,1} C_{i,eq}}{1 + b_{i,1} C_{i,eq} + b_{j,1} C_{j,eq}} + \frac{a_{i,2} C_{i,eq}}{1 + b_{i,2} C_{i,eq} + b_{j,2} C_{j,eq}} \tag{6}$$

The two-site model has been successfully employed for describing competitive adsorption equilibrium data of Cu(II) ions and protons on *A. oryzae* and *Rhizopus oryzae*[40].

The three parameter isotherm of Redlich-Peterson that has been empirically developed for multi-component mixtures is given as[86]:

$$q_{i,eq} = \frac{K_{R,i} C_{i,eq}}{1 + \sum_{j=1}^{N} a_{R,i} C_{j,eq}^{\beta j}} \tag{7}$$

Competitive Isotherms Related to the Individual Isotherm Parameters and to Correction Factors

Better accuracy may be achieved by extracting additional coefficients from experimental competitive isotherms. An interaction term η_i , which is a charac-

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

teristic of each species and depends on the concentrations of the other components, has been added in the competitive Langmuir model. The modified competitive Langmuir isotherm becomes[86]

$$q_{i,eq} = \frac{a_i(C_{i,eq}/\eta_i)}{1 + \sum_{j=1}^{N} b_j(C_{j,eq}/\eta_j)} \tag{8}$$

where the a_i and b_i are given by the individual Langmuir isotherms, and the η_i are estimated from competitive adsorption data. As mentioned above, the competitive Langmuir model has been employed to describe adsorption data of Cr(VI) and Fe(III) ions on *R. arrhizus*[34]. However, positive deviations from the competitive Langmuir model have been observed at low total metal ion concentrations. To obtain an excellent fit, the modified competitive Langmuir model has also been applied to multi-component adsorption equilibria of Cr(VI) and Fe(III) ions. The correction factors for both metal ions have been found to be 0.894, validating the proposed models for adsorption data[87].

Sheindoref *et al*[88] have derived a Freundlich type multi-component adsorption isotherm. The adsorption isotherm for component i in a k-component system expressed in terms of weight of sorbate, is written in the form:

$$q_{i,eq} = a_i^0 C_{i,eq}\left(\sum_{j=1}^{k} a_{ij} C_{j,eq}\right)^{b_{i-1}^0} \tag{9}$$

The pre-exponential coefficient a_i^0 and the exponent b_i^0 can be determined from the mono-component systems. The competition coefficients a_{ij} describe the inhibition to the adsorption of component i by component j, and can be determined from thermodynamic data, or more likely, from experimental data of bicomponent systems[89,90].

Fritz and Schluender[91] have considered another approach and proposed an empirical extension of the Freundlich model, restricted to binary mixtures:

$$q_{1,eq} = \frac{a_1^0 C_{1,eq}^{b_1^0 + b_{11}}}{C_{1,eq}^{b_{11}} + a_{12} C_{2,eq}^{b_{12}}} \tag{10a}$$

$$q_{2,eq} = \frac{a_2^0 C_{2,eq}^{b_2^0 + b_{22}}}{C_{2,eq}^{b_{22}} + a_{21} C_{1,eq}^{b_{21}}} \tag{10b}$$

where the a_i^0 and b_i^0 are derived from the individual Freundlich isotherms. The six new parameters to be derived experimentally in bisolute adsorption tests are correction coefficients[86,90]. The bicomponent biosorption of Cu(II)-Zn(II), Pb(II)-Cu(II) and Pb(II)-Zn(II) on *R. arrhizus* in batch stirred reactors[92] has been shown to be represented by the empirical extension of the Freundlich model.

Ion-Exchange Isotherms

More recent studies with fungal biomass and seaweed in particular have indicated a dominant role of ion exchange metal binding. As ion exchange is the predominant metal-ion-binding mechanism the classical ion-exchange concept based on exchange-equilibrium constants and separation factors[93,94] can be applied to this case. For a generalized ion-exchange reaction for dissolved species A exchanging for a bound species B, with underlining representing the bound species,

$$bA^{+a} + a\underline{B}^{+b} \Leftrightarrow b\underline{A}^{+a} + aB^{+b} \tag{11}$$

the equilibrium constant K_{AB} and the separation factor r_{AB} are given as follows, for the case of ideal behaviour of the exchanging species (1:1 ion exchange, activity= 1) in both of the phases:

$$K_{AB} = \frac{q_A^b C_{Bf}^a}{C_{Af}^b q_B^a} = \left(\frac{y_A^b x_B^a}{x_A^b y_B^a}\right)\frac{C_o^{a-b}}{Q^{a-b}} \tag{12}$$

$$\gamma_{AB} = \frac{y_A x_B}{x_A y_B} \tag{13}$$

For the binary ion-exchange system, the value of the equilibrium constant K_{AB} can be determined from the slope of the plot of q_A/q_B versus C_A/C_B. Biosorbents can also be prepared in different ionic forms[95] and the sorption analysis is often reduced to considering a series of simple binary ion-exchange systems. By eliminating q_B through substitutions[95],

$$\frac{q_{\underline{A}}}{Q} = \frac{1}{1 + \dfrac{C_B}{K_{AB}C_A}} \tag{14}$$

As $q_{\underline{A}}/Q$ represents the fraction of the binding sites occupied by A, this equation may be used to evaluate the decrease of the equilibrium uptake of the species A by the biosorbent caused by the presence of species B. Using simple dimensionless concentration fractions as variables, Eq(14) can be re-written:

$$y_A = \frac{1}{1 + \dfrac{x_B}{K_{AB}x_A}} \tag{15}$$

This equation is the most generalized description of the ion-exchange sorption equilibrium for binary systems[3]. Modeling multi-metal ion exchange in biosorption has rarely been applied to fungal biosorption while for the brown alga *Sargassum fluitans*, which contains the carboxyl groups of alginate and the sulfate groups of fucoidan, an ion-exchange-based two-site model has been developed[96] and extended to describe multi-site and multi-ion system behavior[97].

Marcel Dekker, Inc.
270 Madison Avenue, New York, New York 10016

Modeling of Fungal Biosorption in BSTR

Tsezos *et al*[21] have modeled the uranium biosorptive behavior of MSR biosorbent particles using a batch reactor mass transfer kinetic model (BRMTK). According to the model, a typical MSR particle is spherical, consisting of a uniform non-biomass outer layer and a uniform biomass, porous inner core. The hydrodynamic boundary layer, the non-biomass layer and the intraparticle transport have been considered the major factors controlling the observed overall rate of biosorption from the bulk solution. The model has been developed expressing the mass balance for the metal across each of the assumed mass transport resistances.

A mass balance of the solute in the biomass core of an immobilized biomass particle is as follows:

$$\lambda \frac{\partial c}{\partial t} + \rho \frac{\partial q}{\partial t} = D_p \lambda \left(\frac{\partial^2 c}{\partial r^2} + \frac{2}{r} \frac{\partial c}{\partial r} \right) \tag{16}$$

A mass balance of the solute across the non-biomass layer is given by

$$\frac{4\pi (KR)^2 D_m}{\delta} (c_{m,Kr} - c_{m,R}) = 4\pi R^2 D_p \lambda \frac{\partial c}{\partial r} \Big|_{r=R} \tag{17}$$

A mass balance of the solute in the external fluid film is given by

$$k_f (c_b - c_{b,kR}) = \frac{D_m}{\delta} (c_{m,KR} - c_{m,R}) \tag{18}$$

The overall mass transfer coefficient, k_0, the effective solute diffusivity in the pore of the biomass core, D_p, and the effective metal diffusivity in the non-biomass layer, D_m, have been estimated using a non-linear least-squares procedure. Detailed derivation can be found in Tsezos *et al*[21].

$$k_0 = \frac{1}{\left(\frac{1}{k_f} + \frac{\delta}{D_m} \right)} \tag{19}$$

Modeling of Fungal Biosorption in CFST

For the prediction of the performance of a continuous-flow stirred-tank contactor (CFST) for mono and multi-component biosorption of heavy metal ions on *R. arrhizus*, Sağ *et al* [38] have used a mathematical model based on mass balances for liquid and solid phases. The lumped parameter simple kinetic model assumes that the adsorption can be taken as a reversible mass transfer process in which free adsorbate becomes bound to the adsorbent[98-100]. Adsorption reaction is given as

follows:

$$C \underset{K_2}{\overset{K_1(Qm-q)}{\rightleftharpoons}} q$$

where C is the metal concentration in solution and q is the adsorbed metal ion quantity per unit weight of dried biomass. The constants K_1 and K_2 are the forward and backward rate constants, respectively. Q_m is the amount of adsorbate per unit weight of adsorbent to form a complete monolayer on the surface.

From a mass balance for C:

$$\frac{dC}{dt} = -K_1C(Q_m - q) + K_2q \tag{20}$$

and from a mass balance for q:

$$\frac{dq}{dt} = K_1C(Q_m - q) - K_2q \tag{21}$$

At equilibrium:

$$\frac{dC}{dt} = 0 \quad \text{and} \quad \frac{dq}{dt} = 0$$
$$\text{therefore} \quad K_1C(Q_m - q) = K_2q \tag{22}$$

$$\text{or} \quad q_{eq} = \frac{Q_mC_{eq}}{C_{eq} + K_d} \tag{23}$$

The Langmuir equation given by Eq. (23) is the most widely used isotherm equation for modeling adsorption equilibrium data. K_d is the dissociation constant, $K_d = 1/b = K_2/K_1$. From the adsorption isotherm curve, Q_m is the value that q tends to asymptotically as C tends to a high value, and K_d is the value of C in equilibrium with $q = Q_m/2$.

For multi-component adsorption, to model competition, Q_j, the free capacity for species j, is given by Eq. (24)[98]:

$$Q_j = Q_{m,j}\left(1 - \sum_{i=1}^{n} \frac{q_i}{Q_{m,i}}\right) \tag{24}$$

where $Q_{m,i}$ is the maximum capacity for i, q_i is the solid phase concentration for i and is given by the Eq. (25):

$$qi = \frac{C_{i,0} - C_i}{x_0} \tag{25}$$

In this Eq. $C_{i,0}$ shows the initial metal ion concentration for i and x_0 denotes microorganism concentration. For multi-component adsorption, the adsorption reac-

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

tion becomes:

$$C_j \underset{K_2}{\overset{K_1 Q_j}{\rightleftharpoons}} q_j$$

which must be solved numerically.

For CFST, the mass balance is given by the Eq. (26):

$$V\frac{\partial C_j}{\partial t} = \nu_0 C_{j,0} - \nu_0 C_j - \frac{\partial q_j}{\partial t} V x_i \tag{26}$$

and

$$\frac{\partial q_j}{\partial t} = K_1 C_j Q_j = K_2 q_j \tag{27}$$

The differential Eqs. (26) and (27) have been solved simultaneously by using the Runga-Kutta method. The solution has been writtten in Visual Basic Program and modified in Excel 7.0. The biosorption of Pb(II), Ni(II) and Cu(II), in single component, binary and ternary systems has been studied using *R. arrhizus* in the CFST[38]. Comparing simulated concentration curves from the lumped parameter simple kinetic model incorporated with continuous system mass balance (LP-SKM) with experimental results, the proposed model has been shown to correlate well with single and multi-component adsorption data.

Modeling of Fungal Biosorption in PCR

The most optimal configuration for continuous flow-biosorption is the packed-bed column which gets gradually saturated from the feed to the solution exit end. The breakthrough curves for the single- and multi-component biosorption of metal ions are measured as a function of flow rate and inlet metal ion concentration. In the breakthrough curves the normalized concentration, defined as the measured concentration divided by the inlet concentration, is plotted against volumes of synthetic aqueous solutions treated. Breakthrough occurs when that metal appears in the effluent. The general position of the breakthrough curve along the volume axis depends on the capacity of the column with respect to the feed concentration. This is set by the equilibrium. The breakthrough curves are evaluated in terms of the maximum (equilibrium) capacity of the column, $C_{i,max}$ (mg), the amount of metal loading on the biomass surface, $q_{i,eq}$ (mg g^{-1}), and the adsorption yield (adsorbed metal percentage), $\%Y_i$. The maximum (equilibrium) capacity of the column for a given feed concentration is equal to the area under the plot of the adsorbed metal ion concentration $C_{i,ads}$ (mg l^{-1}) vs. time (min) or the area behind the breakthrough curve[25,28,41].

$$C_{i,max} = \nu_0 \int_0^a C_{i,ads} dt \tag{28}$$

The amount of metal that remains in the effluent, $C_{i,eq}$, is the area behind the adsorption curve or the area under the breakthrough curve[25,28,41].

$$C_{i,eq} = \frac{C_i t - \int_0^a C_{i,ads} dt}{t} \quad or \quad C_{i,eq} = \frac{W_i - q_{i,eq} X}{\nu_0 t} \tag{29}$$

The amount of metal loading on the biomass surface is calculated from the weight of metal adsorbed per unit dry weight of biomass in the column (that is, the ratio of the maximum capacity of the column to the amount of microorganism filled in the column) [28,41].

$$q_{i,eq} = \frac{C_{i,max}}{X} \tag{30}$$

The adsorption yield is the ratio of the maximum capacity of the column to the amount of metal loading into the column, W_i (mg) [28,41].

$$Y_i = \frac{C_{i,max}}{W_i} \ .100 \tag{31}$$

Where the amount of metal loading into the column is $W_i = C_i \nu_0 t$. In multi-metal mixtures total adsorption yield[28,41]:

$$Y_T = \frac{\sum_{i=1}^{n} C_{i,max}}{\sum_{i=1}^{n} W_i} \cdot 100 \tag{32}$$

In multi-metal mixtures, when the column capacity is approached, the metal with a higher affinity displaces the metal with lower affinity. The adsorption and displacement of metal ions is the reason for the outlet concentrations sometimes rising to values greater than the inlet concentrations, giving a negative accumulation. Usually, only the toxic metal with the high concentration is targeted for removal. However, owing to the competitive ion exchange taking place in the column, one or more of the metals present even at trace levels may overshoot the acceptable limit in the column effluent well before the breakthrough point of the targeted metal, thereby considerably reducing the service time of the column[3]. Although output-concentration overshoots have been observed experimentally[28,41], their occurrence and impact on heavy metal removal has not, until recently, been discussed, analyzed or even considered. The simultaneous biosorption of Cr(VI) and Cu(II) [28], Cr(VI) and Fe(III)[41] on free *R. arrhizus* from binary metal mixtures in a

packed column operated in the continuous mode has been investigated. The competitive-empirical Freundlich model for binary metal mixtures has been shown to represent most the column adsorption equilibrium data of Cr(VI) and Cu(II)[28], Cr(VI) and Fe(III)[41] on *R. arrhizus* satisfactorily.

The movement of a solute in a column type reactor is generally described by the following equation[101-103]:

$$\frac{\partial C}{\partial t} = D_h \frac{\partial^2 C}{\partial z^2} - \nu_z \frac{\partial C}{\partial z} - \rho_s \frac{(1-\varepsilon)}{\varepsilon} \frac{\partial q}{\partial t} \tag{33}$$

The most important term of this material balance equation, is the rate of solute uptake by the biosorbent, $\partial q / \partial t$. If it is assumed that mass transfer limitation in the liquid and solid phase is negligible and the sorption reaction is rapid, this approach yields the local equilibrium models (LEM), given by the Eq (34)[102]:

$$\frac{\partial C}{\partial t} = D_h \frac{\partial^2 C}{\partial z^2} - \nu_z \frac{\partial C}{\partial z} - \rho_s \frac{(1-\varepsilon)}{\varepsilon} \frac{\partial q}{\partial C} \frac{\partial C}{\partial t} \tag{34}$$

The most simple local equilibrium model assumes that the equilibrium distribution between the solid phase and the fluid phase is linear.

$$q = K_p C \tag{35}$$

$$\frac{dq}{dC} = K_p \tag{36}$$

The linear local equilibrium model (LLEM) is given by the Eq (37) [102]:

$$\frac{\partial C}{\partial t} = D_h \frac{\partial^2 C}{\partial z^2} - \nu_z \frac{\partial C}{\partial z} - \rho_s \frac{(1-\varepsilon)}{\varepsilon} K_p \frac{\partial C}{\partial t} \tag{37}$$

If the Freundlich isotherm is used to describe the sorption term, then a local equilibrium model is obtained by substituting the term $\partial q/\partial C$ by the Eq. (27)[102]:

$$q = a^0 C^{b^0} \tag{38}$$

$$\frac{dq}{dC} = a^0 b^0 C^{b^0 - 1} \tag{39}$$

$$\frac{\partial C}{\partial t} = D_h \frac{\partial^2 C}{\partial z^2} - \nu_z \frac{\partial C}{\partial z} - \rho_s \frac{(1-\varepsilon)}{\varepsilon} a^0 b^0 C^{b0-1} \frac{\partial C}{\partial t} \tag{40}$$

Similarly, for the case of Langmuir isotherm the term $\partial q/\partial C$ can be substituted by the derivative of Langmuir isotherm:

$$q = \frac{aC}{1 + bC} \tag{41}$$

$$\frac{dq}{dC} = \frac{a}{(1 + bC)^2} \tag{42}$$

$$\frac{\partial C}{\partial t} = D_h \frac{\partial^2 C}{\partial z^2} - \nu_z \frac{\partial C}{\partial z} - \rho_s \frac{(1 - \varepsilon)}{\varepsilon} \frac{Q_m b}{(1 + bC)^2} \frac{\partial C}{\partial t} \tag{43}$$

For the case of first order reversible sorption[98,99,102]

$$\frac{\partial C}{\partial t} = D_h \frac{\partial^2 C}{\partial z^2} - \nu_z \frac{\partial C}{\partial z} - K_1 C + \rho_s \frac{(1 - \varepsilon)}{\varepsilon} K_2 q \tag{44}$$

This equation is the analogous the combined form of the Eqs. (26) and (27) given for CFST and can be modified for multi-component sorption systems by the method defined Section (2.9.).

For the case of equilibrium and first order sorption/desorption, the local equilibrium model (LEM) becomes[102]:

$$\frac{\partial C}{\partial t} = D_h \frac{\partial^2 C}{\partial z^2} - \nu_z \frac{\partial C}{\partial z} - \rho_s \frac{(1 - \varepsilon)}{\varepsilon} \frac{\partial q}{\partial C} \frac{\partial C}{\partial t} - K_1 C + \rho_s \frac{(1 - \varepsilon)}{\varepsilon} K_2 q \tag{45}$$

Although the analytical and numerical solutions of the fixed bed column equation for many special cases are available elsewhere[98,99,101,102,104-106], the mathematical modeling of biosorption columns particularly in case of multicomponent biosorption is still scarce in literature.

Brady *et al*[24]have tested Cu(II) biosorption capacities of laboratory cultured, immobilized *R. arrhizus* and industrial waste *M. miehei* in continuous-flow column systems. The two parameter fixed-bed adsorption model (TPFBAM) described by Belter *et al*[107] has been applied to the data from each of the fixed bed biosorption systems. The model relates change in effluent solution concentration (C_e) to column residence time (t) through two parameters : a characteristic time (t_0) and a standard deviation (σ).

$$\frac{C_e}{C_i} = \frac{1}{2}\left(1 + erf\left[t - \frac{t_0}{\sigma t_0 \sqrt{2}}\right]\right) \tag{46}$$

Breakthrough curve data were tested and untested operating conditions were generated by the two parameter model and agreed closely with experimental values[24].

CONCLUSIONS AND FUTURE DIRECTIONS

Fungal cell walls and their components have a major role in biosorption and also take up suspended metal particulates and colloids. Fungi are ubiquitous in the

natural environment and play important roles in decomposition, nutrient cycling and transformation of toxic metals between soluble and insoluble forms including volatile derivatives. Application of fungal biomass to remove heavy metal from industrial waste water and/or to recover economically valuable metals is attractive for industry. Food and industrial fermentation processes can provide a cheap and constant supply of fungal biomass or the biomass can be cultured using inexpensive growth media and unsophisticated fermentation techniques. The byproducts or products of the above processes can be used economically and successfully in the selective removal of heavy metal ions from waste waters. Moreover, as particle size can be optimized, fungi can be used in column-type reactors without immobilization. Industrial solutions commonly contain multimetal systems or several organic and inorganic substances that form complexes with metals at relatively high stability forming a very complex environment. Metal uptake by fungi has been widely described by several authors, however, when real industrial solutions are used in the experiments, most of these works reveal inconclusive and very speculative results as of an indication of the nature of metal-microorganism interaction. This is most probably due a lack of results supported by analytical data. By the beginning of 1990's, the research work in the field of biosorption has focused again on the better explanation and understanding of biosorption mechanisms, such as the competing ions effect and selectivity, rather than on the design of biosorption process. Applied microbiology needs to clarify the composition of microbial cell walls which are mainly responsible for sequestering the metals. When the metal-fungal biomass interaction mechanisms are reasonably understood, it opens the possibilities of optimizing the biosorption process on the molecular level and manipulating the biosorption properties of biomass when it is growing. This could be achieved by the extensive application of advanced instrumental analyses combined to the study of the chemical composition of the solutions, before and after contact with the fungal cells. Use of genetically modified strains for specific industrial applications can become one of the main subjects of biosorption engineering in the future. At least economically attractive analogous sorbent materials can be developed. Intrabiotechnological hybrid technologies can be integrated with other non biotechnology based processes, e.g. chemical precipitation, electrochemical processes. The combination of biosorption along with metabolically mediated processes such as bioreduction and bioprecipitation, called intrabiotechnological hybrid technologies, is possible inside novel single reactor designs. Therefore, the fundamental research into the better understanding of the mechanism of biosorption on what drives the selectivity of biosorptive and bioaccumulative processes must be continued. A major consideration preceding the implementation of any sorption operation is the equilibrium distribution of ionic components between the solid and liquid phases. When several components are present, interference and competition phenomena for sorption sites occur and lead to a more complex mathematical formulation of the equilibrium. The complex overlapping breakthrough curves for multi-component mixtures where dis-

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

persive and nonequilibrium effects are important cannot be described easily. Apart from the difficulty of evaluating such systems, the experimental volume increases enormously with each additional ionic component present. In this stage, mathematical models play a key role in transferring technologies from the laboratory to a full-scale application. Good models cannot only help in analyzing and interpreting experimental data but also in predicting the process performance under different conditions. Computer simulations can then replace numerous tedious and costly experiments. Mathematical modeling and computer simulation is essential for process design and optimization where the equilibrium and dynamic test information comes together representing a multivariable system. The dynamic nature of columns and flow-through contactors makes computer modeling obligatory. When reaction kinetics is combined with mass transfer which is also dependent on the particle and fluid properties, advanced computer simulations will be required. Advanced computer modeling/simulation techniques can also be used in modeling of molecules, their parts and interactions. As mentioned above, 'seeing' how the biosorbent works on a molecular level would aim at preparing a better biosorbent. While significant advances have been recorded in explaining protein and nucleic acid structures and their behavior, carbohydrate chemistry which appears to play a predominant role in the biosorption mechanisms still has not significantly benefited from these advanced computer modeling techniques.

NOMENCLATURE

c	: Solute concentration in the pore of the biomass core (mg l^{-1})
c_b	: Solute concentration in the bulk solution (mg l^{-1})
c_m	: Solute concentration in the non-biomass layer (mg l^{-1})
C	: For fixed bed adsorbers, solution phase solute concentration (mg of solute / cm^3 of solution)
C_i	: Metal ion concentration range studied, for fixed bed adsorbers influent metal ion concentration (mg l^{-1} or mmol l^{-1})
$C_{i,eq}$ or C_{eq}	: Unadsorbed metal ion concentration in solution at equilibrium, (mg l^{-1})
C_0	: Normality of the solution (meq l^{-1})
ChAA	: Chitin-acrylic acid
C_{ML}	: Concentration of species M in liquid phase (mmol l^{-1})
DCM	: Dichloromethane
DD	: Deacetylation
D_h	: Hydrodynamic dispersion coefficient (cm^2 min^{-1})
GA	: Glutaraldehyde
k_f	: External fluid film mass transfer coefficient (cm s^{-1})
K_P	: Partitioning coefficient

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

KR : Radius of immobilized biomass particle (cm)
n : Reactor number
q : Solute concentration in the biomass (mg g^{-1} or mmol g^{-1}), for fixed bed adsorbers, volume averaged sorbed-phase solute mass per solid-phase mass (mg solute/g sorbent)
$q_{i,eq}$ or q_{eq} : Adsorbed metal ion quantity per unit weight of dried biomass at equilibrium (mmol g^{-1} or mg g^{-1})
q, q_A, q_B : Sorption uptake, and uptake of species A or B (mmol g^{-1})
Q : Equilibrium uptake of M at C_{ML} (meq l^{-1})
r : Radial variable in the biomass core (cm)
R : Radius of the biomass core (cm)
t : Time (min)
T : Temperature
TCC : Tetracyanocuprate(II) [$K_2Cu(CN)_4$]
TCN : Tetracyanonickelate(II) [$K_2Ni(CN)_4$]
v_z : One dimensional fluid phase interstitial velocity (cm min^{-1})
v_0 : Volumetric flow rate (ml min^{-1})
x_A, x_B : Equivalent fractions of species A and B in liquid phase
X : Microorganism concentration (g l^{-1}) or amount of microorganism filled in the column (mg)
y_A, y_B : Equivalent fractions of species A and B in solid phase
z : Space direction (cm)

Greek Letters

λ : Apparent biomass core porosity
ρ : Apparent biomass core density (g cm^{-3})
ρ_s : Biosorbent material density (g cm^{-3})
$\rho_s(1-\varepsilon)$: Fixed density of the bed (biosorbent mass per unit bed volume, g cm^{-3})
ε : Bed porosity, void volume per unit total volume (dimensionless)
δ : Non-biomass layer thickness (KR-R) (cm)

REFERENCES

1. K. H. Chong and B. Volesky, Biotechnol. Bioeng., 49, 629 (1996).
2. M. M. Figueira, B. Volesky and V. S. T. Ciminelli, Biotechnol. Bioeng., 54, 344 (1997).
3. D. Kratochvil and B. Volesky, Trends Biotechnol., 16, 291 (1998).

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

4. M. Tsezos and B. Volesky, Biotechnol. Bioeng., 23, 583 (1981).
5. B. Volesky, FEMS Microbiol., Rev., 14, 291 (1994).
6. F. Veglio and F. Beolchini, Hydrometallurgy, 44, 301 (1997).
7. C. J. Williams, D. Aderhold and R. G. J. Edyvean, Wat. Res., 32, 216 (1998).
8. J. L. Zhou and R. J. Kiff, J. Chem. Tech. Biotechnol., 52, 317 (1991).
9. B. Volesky, "Biosorption by Fungal Biomass. In Biosorption of Heavy Metals," B. Volesky, ed., CRC Press, Boca Raton, Florida, 1990, p. 139.
10. D. Brady, A. Stoll and J. R. Duncan, Environ. Technol., 15, 429 (1994).
11. A. Delgado, A. M. Anselmo and J. M. Novais, Water Environ. Res., 70, 370 (1998).
12. J. E. Bailey and D. F. Ollis, "Biochemical Engineering Fundamentals," Mc Graw-Hill, New York, 1977.
13. M. L. Shuler and F. Kargi, "Bioprocess Engineering: Basic Concepts," Prentice Hall, Englewood Cliffs, New Jersey, 1992.
14. S. Bartnicki-Garcia, "Fungal Cell Wall Composition. In CRC Handbook of Microbiology," Vol 2, A. I. Laskin and H. A. Lechevalier, eds., CRC Press, Boca Raton, Florida, 1973, p. 201.
15. J.Remacle, "The Cell Wall and Metal Binding. In Biosorption of Heavy Metals," B. Volesky, ed., CRC Press, Boca Raton, Florida, 1990, p.83.
16. L. Yerushalmi, "Propagation of Biosorbents by Fermentation Processes. In Biosorption of Heavy Metals," B. Volesky, ed., CRC Press, Boca Raton, Florida, 1990, p.341.
17. E. Fourest and J-C. Roux, Appl. Microbiol. Biotechnol., 37, 399 (1992).
18. B. E. Holbein, "Immobilization of Metal-Binding Compounds. In Biosorption of Heavy Metals," B. Volesky, ed., CRC Press, Boca Raton, Florida, 1990, p.327.
19. M Tsezos and A. A. Deutschmann, J. Chem. Tech. Biotechnol., 48, 29 (1990).
20. M Tsezos, S. H. Noh and M. H. I. Baird, Canadian Patents and Development Ltd., Patent file 265-861 (1987).
21. M Tsezos, S. H. Noh and M. H. I. Baird, Biotechnol. Bioeng., 32, 545 (1988).
22. M Tsezos, Z. Georgousis and E. Remoudaki, J. Chem. Tech. Biotechnol., 70, 198 (1997).
23. R. Ileri, F. Mavituna, M. Parkinson and M. Turker, "Proceedings of AP-BioChEC '90: Repeated Use of Immobilized Dead *Rhizopus Arrhizus* for the Removal of Heavy Metal Contaminants from Waste Water," Kuyungju, Korea, 1990, p. 564.
24. J. M. Brady, J. M. Tobin and J-C Roux, J. Chem. Tech. Biotechnol., 74, 71 (1999).
25. F.H. Arnold, H.W. Blanch, C.R. Wilke, Chem. Eng. J., 30, B9 (1985).

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

26. M. Mutlu, Y. Sağ and T. Kutsal, Chem. Eng. J., 65, 81 (1997).
27. C. Huang and C. P. Huang, Wat. Res. 30, 1985 (1996).
28. Y. Sağ, I. Ataçoğlu and T. Kutsal, Separ. Sci. Technol., 34, 3155 (1999).
29. E. Fourest, C. Canal and J-C. Roux, FEMS Microbiol., Rev., 14, 325 (1994).
30. N. Kuyucak and B. Volesky, Biotechnol. Lett., 10, 137 (1988).
31. M. Galun, E. Galun, B. Z. Siegel, P. Keller, H. Lehr and S. M. Siegel, Water Air Soil Poll., 33, 359 (1987).
32. H. Niu, X. S. Xu, J. H. Wang and B. Volesky, Biotechnol. Bioeng., 42, 785 (1993).
33. R. J. Kiff and D. R. Little, "Biosorption of Heavy Metals by Immobilized Fungal Biomass. In Immobilization of Ions by Biosorption," H. H. Eccles and S. Hunt, eds., Ellis Horwood, Chichester, West Sussex, 1986, p. 71.
34. Y. Sağ and T. Kutsal, Process Biochem., 31, 573 (1996).
35. T. Sakaguchi and A. Nakajima, "Accumulation of Heavy Metals such as Uranium and Thoruim by Microorganisms. In Mineral Bioprocessing," R. W. Smith and M. Misra, eds., The Minerals, Metals and Materials Society, Pennsylvania, 1991, p. 85.
36. C. R. N. Rao, L. Iyengar and C. Venkobachar, J. Environ. Eng. Division, Proceed. Amer. Soc. Civil Eng., 119, 369 (1993).
37. Y. Sağ and T. Kutsal, Chem. Eng. J., 58, 265 (1995).
38. Y. Sağ, A. Yalçuk and T. Kutsal, Process Biochem., 35, 787 (2000).
39. G. M. Gadd and L. de Rome, Appl. Microbiol. Biotechnol., 29, 610 (1988).
40. C. Huang, C. P. Huang and A. L. Morehart, Wat. Res., 25, 1365 (1991).
41. Y. Sağ, I. Ataçoğlu and T. Kutsal, Hydrometallurgy, 55, 165 (2000).
42. Y. Sağ, D. Özer and T. Kutsal, Process Biochem., 30, 169 (1995).
43. N. Sağlam, R. Say, A. Denizli, S. Patir and M. Y. Arica, Process Biochem., 34, 725 (1999).
44. G. M. Gadd, C. White and L. De Rome, "Heavy Metal and Radionuclide Uptake by Fungi and Yeasts. In Biohydrometallurgy," P. R. Norris and D. P. Kelly, eds., A. Rowe, Chippenham, Wilts., 1988, p. 104.
45. N. A. Yakubu and A. W. L. Dudeney, "Biosorption of uranium with Aspergillus niger. In Immobilization of Ions by Biosorption," H. H. Eccles and S. Hunt, eds., Ellis Horwood, Chichester, West Sussex, 1986, p.183.
46. M. E. Treen-Sears, B. Volesky and R. J. Neufeld, Biotechnol. Bioeng., 26, 1323 (1984).
47. M Tsezos and A. A. Deutschmann, J. Chem. Tech. Biotechnol., 53, 1 (1992).
48. Y. Sağ, A. Kaya and T. Kutsal, Hydrometallurgy, 50, 297 (1998).
49. J. M. Tobin, D. G. Cooper and R. J. Neufeld, Appl. Environ. Microbiol., 74, 821 (1984).
50. D. Brady, A. D. Stoll, L. Starke and J. R. Duncan, Biotechnol. Bioeng., 44, 297 (1994).

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

51. M. Tsezos and B. Volesky, Biotechnol. Bioeng., 24, 385 (1982).
52. M. Tsezos and B. Volesky, Biotechnol. Bioeng., 24, 955 (1982).
53. T. R. Muraleedharan and C. Venkobachar, Biotechnol. Bioeng., 35, 320 (1990).
54. C. Venkobachar, Water Sci. Technol., 22, 319 (1990).
55. R. H. Crist, K. Oberholser, D. Schwartz, J. Marzorff, D. Ryder and D.R. Crist, Environ. Sci. Technol., 22, 755 (1988).
56. A. Kapoor and T. Viraraghavan, Bioresource Technol., 61, 221 (1997).
57. Y. B. Patil and K. M. Paknikar, Biotechnol. Lett., 21, 913 (1999).
58. N. C. M. Gomes, M. M. Figueira, E. R. S. Camargos, L. C. S. Mendonça-Hagler, J. C. T. Dias and V. R. Linardi, Biotechnol. Lett., 21, 487 (1999).
59. T-Y. Hsien and G. L. Rorrer, Ind. Eng. Chem. Res., 36, 3631 (1997).
60. A. S. Aly, B. D. Jeon and Y. H. Park, J. Appl. Polym. Sci., 65, 1939 (1997).
61. C. Y. Kim, H-M. Choi and H. T. Cho, J. Appl. Polym. Sci., 63, 725 (1997).
62. P. Udaybhaskar, L. Iyengar and A. V. S. P. Rao, J. Appl. Polym. Sci., 39, 739 (1990).
63. G. McKay, H. S. Blair and A. Findon, Indian J. Chem., 28A, 356 (1989).
64. V. E. Tikhonov, L. A. Radigina and Y. A., Carbohyd. Res., 290, 33 (1996).
65. K. Kondo, S-I. Nakagawa, M. Matsumoto, T. Yamashita and I. Furukawa, J. Chem. Eng. Jpn., 30, 846 (1997).
66. A. Findon, G. McKay and H. S. Blair, J. Environ. Sci. Health, A28, 173 (1993).
67. M. T. S. D. Vasconcelos, M. A. O. Azenha and J. P. S. Cabral, Environ. Toxicol. Chem., 16, 2029 (1997).
68. W. S. W. Ngah and I. M. Isa, J. Appl. Polym. Sci., 67, 1067 (1998).
69. R. Ashkenazy, L. Gottlieb and S. Yannai, Biotechnol. Bioeng., 55, 1 (1997).
70. M. S. Alam, K. Inoue, Y. Yoshizuka and H. Ishibashi, Separ. Sci. Technol., 33, 655 (1998).
71. E. Piron and A. Domard, Int. J. Biol. Macromol., 21, 327 (1997).
72. M. Jansson-Charrier, E. Guibal, J. Roussy, B. Delanghe and P. Le Cloirec, Wat. Res., 30, 465 (1996).
73. L. E. Macaskie and A. C. R. Dean, "Metal-Sequestering Biochemicals. In Biosorption of Heavy Metals," B. Volesky, ed., CRC Press, Boca Raton, Florida, 1990, p.199.
74. G. McKay, Y. S. Ho and J. C. Y. Ng, Separ. Purif. Method., 28, 87 (1999).
75. H. Jiang, J. Liang, J. T. Grant, W. Su, T. J. Bunning, T. M. Cooper and W. W. Adams, Macromol. Chem. Phys., 198, 1561 (1997).
76. Y. P. Ting, F. Lawson and I.G. Prince, Biotechnol. Bioeng., 37, 445 (1991).
77. Y. Sağ and T. Kutsal, Process Biochem., 31, 561 (1996).

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

78. Y. Sağ and T. Kutsal, Process Biochem., 33, 571 (1998).
79. M. Tsezos, Z. Georgousis and E. Remoudaki, Biotechnol. Bioeng., 55, 16 (1997).
80. R. P. de Carvalho, K.-H. Chong and B. Volesky, Biotechnol. Prog., 11, 39 (1995).
81. B. Volesky and Z. R. Holan, Biotechnol. Prog., 11, 235 (1995).
82. V. S. Soldatov and V. A. Bichkova, Separ. Sci. Technol., 15, 89 (1980).
83. V. S. Soldatov and V. A. Bichkova, React. Polym., 3, 199 (1985).
84. D. O. Hayward and B. M. W. Trapnell, "Chemisorption," 2nd edn., Butterworth, London, 1964.
85. J. M. Smith, "Chemical Engineering Kinetics," 3rd edn., McGraw-Hill, New York, 1981.
86. J. C. Bellot and J. S. Condoret, Process Biochem., 28, 365 (1993).
87. Y. Sağ, Ü. Açikel, Z. Aksu and T. Kutsal, Process Biochem., 33, 273 (1998).
88. C. H. Sheindorf, M. Rebhun and M. Sheintuch, J. Colloid Interf. Sci., 79, 136 (1981).
89. C. Sheindorf, M. Rebhun and M. Sheintuch, Wat. Res., 16, 357 (1982).
90. M. Sheintuch and M. Rebhun, Wat. Res., 22, 421 (1988).
91. W. Fritz and E.-U. Schluender, Chem. Eng. Sci., 29, 1279 (1974).
92. Y. Sağ, A. Kaya and T. Kutsal, Appl. Microbiol. Biotechnol., 53, 338 (2000).
93. T. Vermeulen, G. Klein and N. K. Heister, "In Chemical Engineers' Handbook," 5th edn., R. H. Perry and C. H. Chilton, eds., McGraw-Hill, New York, p.16-1.
94. M. Shallcross, C. C. Herrmann and B. J. McCoy, Chem. Eng. Sci., 43, 279 (1988).
95. D. Kratochvil, B. Volesky and G. Demopoulos, Wat. Res., 31, 2327 (1997).
96. S. Schiewer and B. Volesky, Environ. Sci. Technol., 29, 3049 (1995).
97. S. Schiewer and B. Volesky, Environ. Sci. Technol., 30, 2921 (1996).
98. H. A. Chase, J. Chromatogr., 297, 179 (1984).
99. G. H. Cowan, I. S. Gosling, J. F. Laws and W. P. Sweetenham, J. Chromatogr., 363, 37 (1986).
100. G. H. Cowan, "Development of Physical and Mathematical Modelling Methods for Scale-up of Batch Stirred Tank and Packed-Bed Column Adsorption and Chromatographic Units. In Adsorption: Science and Technology," A.E. Rodrigues, M.D. LeVan and D. Tondeur, eds., NATO ASI Series, 158, Kluwer Academic Publishers, London, 1988, p. 517.
101. D. M. Ruthven, "Principles of Adsorption and Adsorption Processes," Wiley Interscience, New York, 1984.
102. W. J. Jr. Weber, P. M. McGinley and L. E. Katz. Wat. Res., 25, 499 (1991).

103. G. Doğu, "Diffusion Limitations for Reaction in Porous Catalysts, In Handbook for Heat and Mass Transfer Operations," N. P. Cheremisinoff, ed.,Gulf, 1986, p.401.
104. H. C. Thomas, J. Amer. Chem. Soc., 66, 1664 (1944).
105. H. K. S. Tan and I. H. Spinner, Can. J. Chem. Eng., 72, 330 (1994).
106. D. J. Wiblin, S. D. Roe and R. G. Myhill, J. Chromatogr. A, 702, 81 (1995).
107. P. A. Belter, E. L. Cussler and W. S. Hu, "Bioseparations, Downstream Processing for Biotechnology," John Wiley and Sons, New York, 1988.

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

Request Permission or Order Reprints Instantly!