Screening of Tropical Wood-Rotting Mushrooms for Copper Biosorption

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Fruiting bodies (mushrooms) of nine nonedible macrofungi were screened for copper(II) uptake potential. The maximum uptake potentials (Q_{max}s) derived from equilibrium studies indicated that all nine species exhibited higher Q_{max}s at pH 4.0 than that of Filtrasorb-400, a generally used adsorbent for metal removal. Wide variation in Q_{max} was observed among the species and ranged from 0.048 to 0.383 mmol per g of sorbent. The uptake capacity of *Ganoderma lucidum*, which exhibited the highest Q_{max}, was higher than those of other microbial biosorbents reported in the literature.

The use of adsorbents of biological origin has emerged in the last decade as one of the most promising alternatives to conventional heavy metal management strategies (3, 5, 11, 15). Because of the absence of a rational method for a priori prediction of the biosorption potential of a microorganism, the only method for identifying and developing newer and efficient biosorbents is the sustained screening of microbes.

Most studies of biosorption for metal removal have involved the use of either laboratory-grown microorganisms or biomass generated by the pharmacologic and food-processing industries or wastewater treatment units (2, 6, 8, 9, 14, 16). The presence of extensive biodiversity available in tropical forests has been identified as the treasure box for the emerging field of biotechnology (1). Many species of commercial interest in other areas of biotechnology, such as agriculture and the pharmaceutical industry, were identified in the vast genetic pool of tropical forests (7). It was therefore considered appropriate to conduct an exploratory search for the presence of naturally occurring biosorbents in tropical forests. Because of the vast number of species available, the scope of the search was demonstrative rather than comprehensive.

Fruiting bodies of macrofungi (mushrooms) were considered ideal for the purpose of evaluation as biosorbents, because it has been demonstrated that many fungal species exhibit high biosorptive potentials (6, 9, 14, 16). Mushrooms grow prolifically and are found in many parts of the world (12). They are large, have a tough texture, and have other conducive characteristics required for their development into sorbents, thus obviating the need for immobilization or deployment of specialized reactor configuration as required with other microbial sorbents (2, 5, 15, 17). In this study, fruiting bodies of nine nonedible fungal species were evaluated for copper(II) uptake on the basis of saturation uptake potential.

Mushrooms were collected during the postmonsoon period (September and October) from forests and plantations in Kerala, India. The fruiting bodies were detached from the rotting wood and sun dried for 2 or 3 days before being transported to the laboratory. Biosorbents were prepared by pulverizing the sun-dried fruiting bodies in a hand grinder. Particles passing through 1,200-μm-aperture sieves and retained on 600-μm-aperture sieves were collected, washed with distilled water to remove the fines, and dried at 50°C overnight. This material, which was used as the biosorbent, was stored at room temperature until use.

Adsorption experiments were carried out with copper(II) added in the form of $CuSO_4$. All solutions used in adsorption experiments were prepared in double-distilled water. The initial concentration of the metal was varied from 0.2 to 2.0 mM for the equilibrium uptake studies. The reaction mixture consisted of 100 ml of adsorbate solution buffered at pH 4.0 with 0.1 M acetate buffer (5 ml per 100-ml solution) and 2.5 g of adsorbent per liter. The mixture was agitated at 30 rpm on an end-on-end rotary shaker. After 3 h of contact time, the adsorbent was separated by gravity settling (10 min), and the supernatant was analyzed for copper. Estimation of copper was carried out by inductively coupled plasma atomic emission spectroscopy on an ICPAES (Labtam). Adsorption experiments were conducted in triplicate, and the average supernatant metal concentration is reported. The variation was found to be within 5%.

For identification of the mushrooms, representative specimens from visibly different groups of mushrooms were soaked in 1% formaldehyde for 24 h to prevent biodegradation. These samples were then dried at 40°C overnight, packed in polyethylene bags, and sent to the Royal Botanical Garden (Kew, United Kingdom) for identification. A list of the fungi examined is given in Table 1.

The equilibrium sorption curves for all sorbents followed the typical saturation profile. The sorption curve for *Ganoderma lucidum*, which exhibited the maximum copper uptake among the nine fungal species screened, is shown in Fig. 1.

The Langmuir relationship (4) has been extensively used for the evaluation and comparison of metal uptake capacities of biosorbents (13, 17). The general form of the Langmuir relationship follows:

$$q_e = \frac{Q_{max}bC_e}{1 + bC_e} \qquad (1)$$

where q_e is millimoles of Cu(II) bound per gram of sorbent at the equilibrium concentration of C_e, Q_{max} is the maximum metal binding capacity (in millimoles per gram of sorbent), and b is a constant.

The following three linearized forms of equation 1 have been used generally for the evaluation of the constants:

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TABLE 1. Q_{max}s of different fungal species

Species	Q_{max} (mmol/g)	b^a (liter/mmol)
Coriolopsis strumosa	0.115	3.95
Daedalea tenuis	0.109	27.80
Lentinus strigosus	0.167	11.98
Lenzites malaccensis	0.143	5.26
Phellinus xeranticus	0.173	23.12
Rigidoporus lineatus	0.173	14.45
Rigidoporus microporus	0.104	2.40
Trametes lactenia	0.048	8.33
Ganoderma lucidum	0.375	8.89

^{a} b is a constant.

TABLE 2. Copper(II) uptake capacities of some reported biosorbents

Species	Q_{max} (mmol/g)	Reference
Activated sludge	0.125	8
Aspergillus niger	0.120	6
Cladosporium resinae	0.120	9
Penicilium italicum	0.150	9
Penicilium spinulosum	0.040	14
Rhizopus arrhizus	0.250	13
Ganoderma lucidum	0.383	This study
Filtrasorb-400	0.030	This study

$$\frac{1}{q_e} = \frac{1}{Q_{max}} + \frac{1}{bC_e} \quad (2)$$

$$\frac{C_e}{q_e} = \frac{C_e}{Q_{max}} + \frac{1}{bQ_{max}} \quad (3)$$

$$q_e = Q_{max} - \frac{q_e}{bC_e} \quad (4)$$

Rubin and Mercer (10) have reported that equation 2 generally results in a lower coefficient of correlation than the other two equations, because it involves two reciprocal quantities prone to experimental errors. In this study, equation 3 was used to evaluate the copper binding constants, because this relationship resulted in a better linearization for all sorbents. Table 1 gives Q_{max}s for different adsorbents.

Results indicated that all species could bind copper(II), but there was considerable variation in the extent of metal uptake (Table 1). *Trametes lactenia* took up only 0.048 mM Cu(II) per g, whereas *G. lucidum* could bind as much as 0.383 mM/g under identical conditions. Other species that were screened exhibited uptake values between these two values. It will be relevant here to compare the copper uptake potentials of mushroom species with those of other biosorbents reported in literature, which are presented in Table 2. *G. lucidum* exhibited an uptake capacity far exceeding all the other biosorbents. Among nine mushroom species investigated in this study, eight exhibited metal uptake capacities of more than 0.1 mM/g, which is comparable with some biosorbents, and all were better
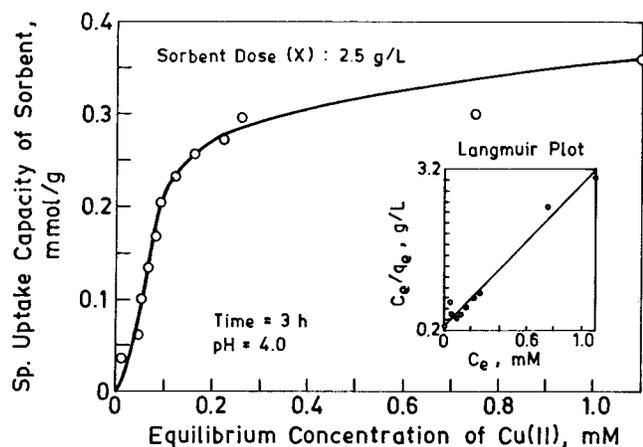
than Filtrasorb-400, which is generally employed for heavy metal removal.

Results of this study have shown that there exists a positive potential for developing promising biosorbents from the fruiting bodies of naturally occurring macrofungi. Their capacities are comparable to those of other reported biosorbents and have an edge over other microbe-based sorbents, because they obviate the immobilization step required to employ these sorbents in column reactors. The rationale behind the screening is thus vindicated.

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FIG. 1. Equilibrium sorption curve for Cu(II) by *G. lucidum*.