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# Adsorption of Heavy Metals by Biomass

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**Abstract** The discharge of heavy metals into aquatic ecosystems has become a matter of concern in India over the last few decades. These pollutants are introduced into the aquatic systems significantly as a result of various industrial operations. Industrialization in India gained a momentum with initiation of five year developmental plan in the early 50's. The pollutants of concern include lead, chromium, mercury, uranium, selenium, zinc, arsenic, cadmium, gold, silver, copper and nickel. The main objective of the work is to remove the heavy metal by using biomass.

***Keywords:*** *biological, biosorption, biomass, chemical, heavy metal*

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## 1. Introduction

Effluent treatment is nowadays one of the most important targets for industry and other institutions, mainly those where the effluent contains different contaminant species. Different alternatives for treating effluents are described in the literature, including chemical precipitation, carbon adsorption, ion exchange, and membrane separation process, among others (Juang and Shiau, 2000; Lacour et al., 2001; Yan and Viraraghavan, 2001). The most common of these alternatives is chemical precipitation. However, some limitations in this process can be pointed out, such as cost, low efficiency, labor-intensive operation, and lack of selectivity of the precipitation process (Lee et al., 1998). New approaches for removing metals based on biosorption using algae or bacteria have been reported (Dos Santos and Lenzi, 2000). Although these materials present binding sites, including amines, carboxyl and thiol groups, and their use for effluent treatment purposes may not be suitable due to their poor natural abundance. The second option is use of natural materials, such as peanut shells, soybean hulls and corncobs, which are available in large quantities, may present higher potentials as inexpensive sorbents for effluent treatment (Vaughan et al., 2001). In addition, although the use of these materials is still not very common, in general, they present good adsorption capacity (Dushenkov et al., 1995). Bailey et al. (1999) have presented an interesting review, which focuses on the potential of a wide variety of low cost sorbents for heavy metals. According to these authors, a low cost sorbent can be assumed if it requires less prior processing, is abundant in nature, or is either a by-product or waste material from another industry. These materials could be alternatives for expensive treatment processes.

In this sense, biological methods of metal removal, defined as biosorption, have been recommended as cheaper and more effective techniques. In biosorption, either live or dead microorganisms or their derivatives are used, which complex metal ions through the action of ligands or functional groups located on the outer surface of the cell (Aksu and Kutsal, 2011). Microorganisms including bacteria, algae, fungi and yeast are found to be capable of efficiently accumulating heavy-metal ions. Microbial biomass is produced in fermentation processes to synthesize valuable products such as antibiotics, enzymes, flavoring agents and organic acids. In such processes, a large amount of byproducts is generated, which can be used in biosorption of heavy metals. In the case of fungal biomass, removal of metal ions from aqueous solutions has been studied with strains of Penicillium, Rhizopus arrhizus, Rhizopus oryzae and Aspergillus oryzae, and Aspergillus niger (Fourest and Volesky, 2006). Limited information is available on the removal of some metal ions such as copper, silver and lanthanum by Mucor rouxii, a representative soil fungus, but information on its ability to remove lead, cadmium, nickel and zinc from aqueous solution is not available (Kapoor and Viraraghavan, 2012). The main objective of study is to represent the effectiveness of M. rouxii for removal of heavy metals. The research work focus on effect of pH on the sample, metabolic effects, Elution, regeneration and reuse.

## 2. Material and Methods

A laboratory strain of Mucor rouxii (ATCC 24905) was routinely maintained on Bacto potato dextrose agar (PDA). For experimental purposes, a liquid medium (YPG) (Bartnicki-Garcia and Nickerson, 1962) with a pH value adjusted to 4.5 was prepared, which comprises (in g·1-1) the following: yeast, 3; peptone, 10; glucose (replaced by dextrose), 20. The cultures were grown at 23°C in the medium in conical flasks kept on a rotary shaker agitated at 125 r·min-1. All culture work was conducted aseptically (Butter et al., 2008). The fungi grew in a filamentous (mold like) form under air, with fragmentation of some hyphae into spherical cells. They were harvested after 3 d of growth by filtering the growth media through a 150 μm sieve. The harvested biomass was washed with generous amounts of deionised water. The live biomass so obtained will be referred to as Type A hereinafter. 50 g (wet mass) of Type A was then pretreated in different ways (Huang and Huang, 2006).

The biomass after each pretreatment was washed with generous amounts of deionised water, and then dried at 60°C for 24 h in a drying oven. In addition, prior to being autoclaved, biomasses that had been pretreated with alkali chemical such as NaOH, Na2CO3 and NaHCO3 were washed with deionised water until the pH of the wash solution was in near neutral range (pH 6.8 to 7.2). Dried biomass was ground in a mortar and pestle. Bioadsorption experiments were conducted using separate solutions containing $Pb^{2+}$, $Cd^{2+}$, $Ni^{2+}$ and $Zn^{2+}$ added in the form of $Pb(NO_3)_2$, $Cd(NO_3)_2.4H_20$, $Ni(NO_3)_2.6H_20$, and $Zn(NO_3)_2.6H_20$ respectively. The solution prepared using distilled water had an initial metal concentration of 10 $mg^{-1}$ and a pH of 5.0. Known amounts of biomass were contacted with each metal solution. The reaction mixture was agitated at 125 r·min-1 on a rotary shaker (Loaec et al., 2007).

After 15 h of contact time, filtrate was obtained by filtering the reaction mixture through an 0.45 μm polycarbonate filter and analysed for metal concentration. Metal concentrations were measured using a Varian AA-10 atomic absorption spectrophotometer. Bioadsorption experiments were carried out in duplicate and average values were used in the analysis. Bioadsorption capacity, i.e. amount of metal ion (mg) bioadsorbed per g (dry mass) of biomass, was calculated using the following equation (Mullen et al., 2002):

$$Q= (C_i\text{-}C_f/m)\ V$$

Where:

Q = mg of metal ion bioadsorbed per g of biomass;
Ci = initial metal ion concentration, $mg^{-1}$;
Cf = final metal ion concentration, $mg^{-1}$;
m = mass of biomass in the reaction mixture, g;
V = volume of the reaction mixture, L.

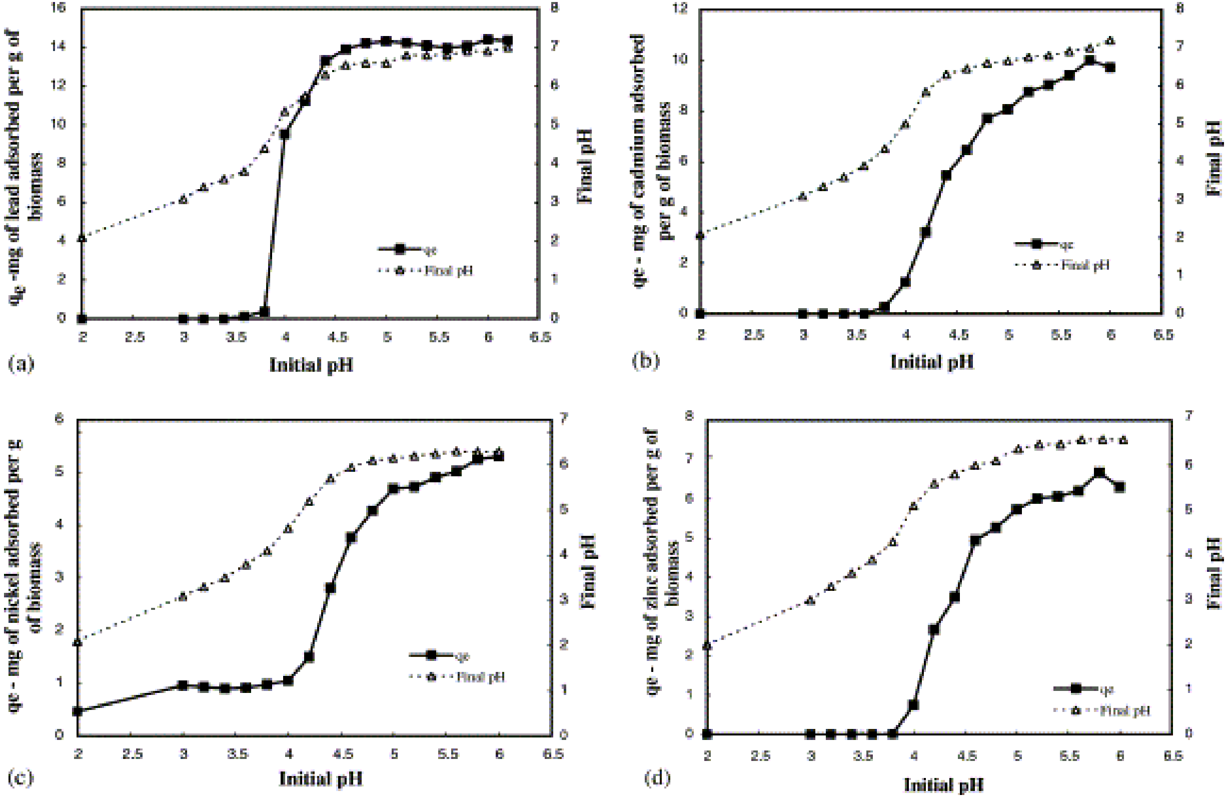

**Figure 1.** Effect of pH on biosorption of (a) lead (b) cadmium (c) nickel and (d) zinc on pretreated M. rouxii biomass

# 3. Result and Discussion

## 3.1. Effect of pH on Removal of Heavy Metal

Properties of adsorbent, pH, concentration of adsorbate, and the presence of co-ions in solution affect the biosorption of metal ions from aqueous solutions. NaOH-pretreated M. rouxii biomass (0.05 g) was contacted with $Pb^{2+}$, $Cd^{2+}$, $Ni^{2+}$ and $Zn^{2+}$ ions in separate solutions (75 ml) at a metal ion concentration of approximately 10 mg/l for 14 h, with an initial pH value of the solutions ranging from 2.0 to 6.0. Figure 1 (a)–Figure 1 (d) show the effect of pH on biosorption of $Pb^{2+}$, $Cd^{2+}$, $Ni^{2+}$ and $Zn^{2+}$ ions. At an initial pH 4.0 or lower, little biosorption occurred. Especially at pH 2.0, almost no biosorption was observed (except for nickel). A sharp increase in biosorption capacity took place in the pH range of 4.0–5.0. Above pH 5.0, biosorption of lead was found to be relatively constant; biosorption of cadmium and nickel still increased but to a lesser extent. Thus, different metals have different pH optima, due to the different solution chemistry of the metals. The low biosorption capacity at pH values below 4.0 was attributed to hydrogen ions that compete with metal ions on the sorption sites. In other words, at lower pH, due to protonation of the binding sites resulting from a high concentration of protons, negative charge intensity on the sites was reduced, resulting in the reduction or inhibition of the binding of metal ions. In fact, most microbial surfaces are negatively charged because of the ionization of functional groups, thus contributing to the metal binding. Generally, fungal surfaces have a negative charge in the pH range of 2–6 examined in this study. At low pH, some functional groups will be positively charged and may not interact with metal ions. For example, removal of copper by P. spinulosum decreased at lower pH. Mullen et al. (2009) found that biosorption of Pb, Cd, Ni and Zn by Penicillium digitatum was severely inhibited when pH was below 3. Rhizopus nigricans also had a significantly low sorption of lead at pH values below 3. Zinc biosorption on Saccharomyces cerevisiae occurred above pH 4. Therefore, biosorption of metal ions is dependent to a larger extent on pH of metal ion solution. The pH plays an important role mainly by its influence on metal or cell wall chemistry. The increase observed in final pH values of reaction mixtures could be either from the adsorption of hydrogen ions from aqueous solutions by fungal biomass or neutralization of H+ with OH− released from the biomass. Kapoor and Viraraghavan (2012) also observed such an increase in pH for copper biosorption on alalkali-treated A. niger.

## 3.2. Metabolic Effect on Removal of Heavy Metal

In the Figure 2 (a)–Figure 2 (d) show the experimental data points for biosorption of lead, cadmium, nickel and zinc. Lead, cadmium and nickel removal capacities of live biomass were higher than those of pretreated biomass obtained at pH 4.0 and 5.0, but lower at pH 6.0. For zinc, removal capacity of live biomass was higher than that of pretreated biomass at pH 4.0, but lower than those obtained at pH 5.0 and 6.0 (Tobin and Roux, 2008). The higher adsorption of the live biomass within some pH range might be explained by the fact that biosorption of metal ions on live biomass is due to surface binding followed by intracellular uptake. The intracellular uptake could account for a substantial part in total uptake for some fungal stains of live biomass, while the biosorption of metal ions on dead biomass is achieved via only surface and wall binding, which is non-metabolic. This surface binding involves specific chemical sites or functional groups on the cell wall, performance of which is affected by pH and other ions. This may explain why biosorption capacity of the dead NaOH-pretreated biomass exceeded that of live biomass for certain pH values. Biosorption data for all the four metal ions at pH 4.0 were not described by both models as biosorption capacity at pH 4.0 increased with a decrease in final equilibrium concentration, which is contrary to the condition for favorable adsorption. The Langmuir model was able to describe the experimental data for biosorption of all metal ions at pH 5.0 by live biomass and only Pb ion by pretreated biomass at pH 5.0 and 6.0 (Huang et al., 2010). The Freundlich model explained the data better for biosorption of Cd, Ni and Zn by pretreated biomass at pH 6.0. It was also observed that the final pH of the reaction mixture using live biomass was higher than the initial pH values. This is due to the growth property of M. rouxii which, under aerobic condition, tends to neutralize the medium with pH less than 7.0. Even though no substrate was added to the reaction mixture in the experiment, the biomass was still active to some extent, possibly due to endogenous respiration.

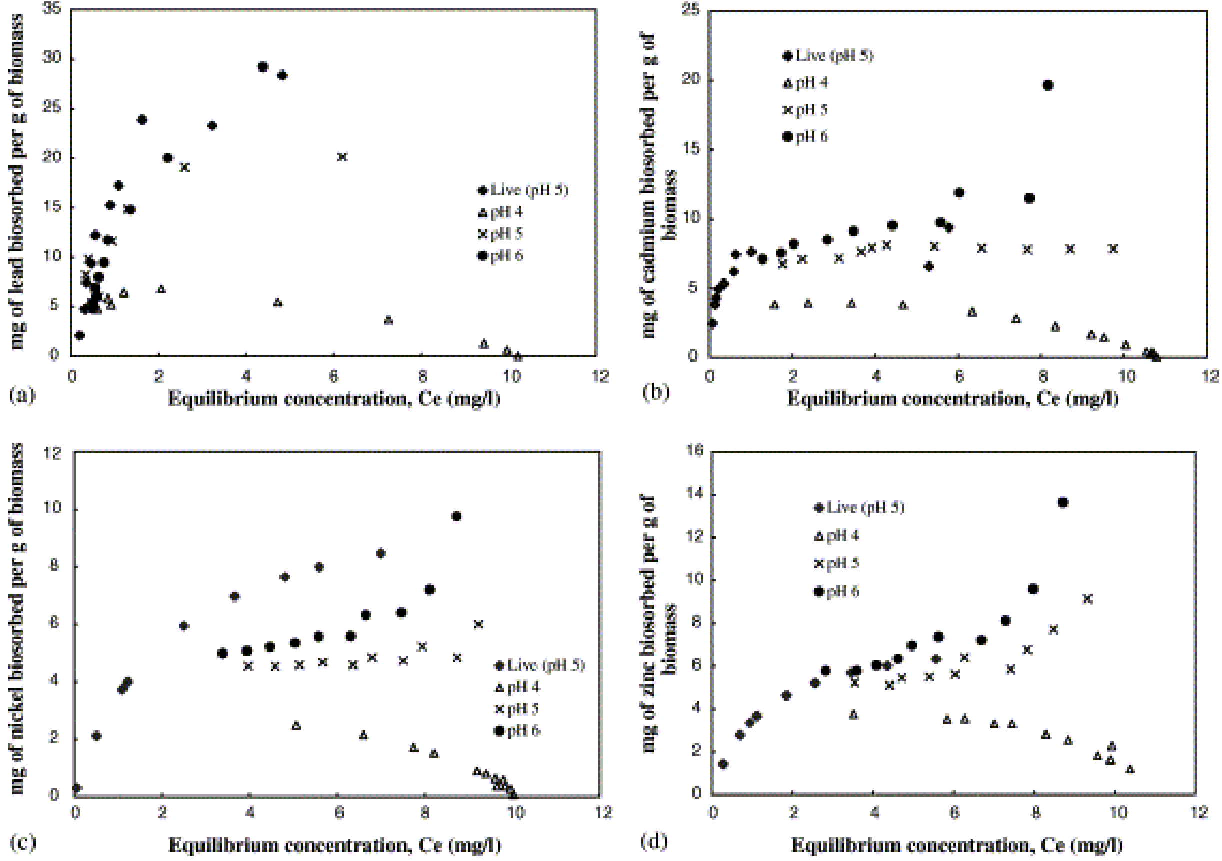

**Figure 2.** Biosorption of (a) lead (b) cadmium (c) nickel and (d) zinc on M. rouxii biomass at various pH values

### 3.3. Elution, Regeneration and Reuse Studies

Various elutants were used to desorb the metal ions loaded on pretreated biomass. 3 shows the results of desorption tests. The effectiveness of an elutant was expressed as a percentage of ions desorbed from biomass to that biosorbed on biomass (Atkinson et al., 2008). $HNO_3$ proved to be a more effective elutant than $CaCl_2$ and NaCl, with more than 90% elution for $Pb^{2+}$, $Cd^{2+}$, $Ni^{2+}$ and $Zn^{2+}$, while deionized water exhibited negligible desorption capability. Spinti et al.(2005) reported that more than 80% of lead could be desorbed from non-living R. nigricans with the use of mineral acids i.e. HCl and HNO3. The mineral acids are proton-exchange agents, which dislodge high valence metal ions from biomass. Tobin and Roux showed the effectiveness of H2SO4 in eluting biosorbed chromium from M. meihi biomass.

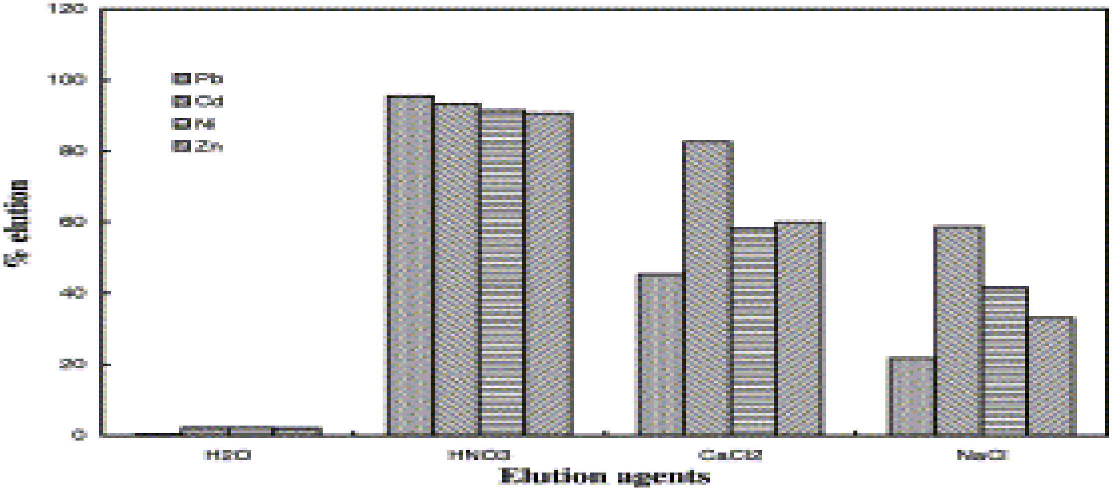

**Figure 3.** Effectiveness of metal in desorption from M. rouxii biomass using various elutants

The NaOH-pretreated M. rouxii biomass showed a high adsorption capability for the removal of lead, cadmium, nickel and zinc from aqueous solution. It exhibited good biosorption capacity in bi- or multi-metal ion systems in terms of total adsorption capability. pH was found to be critical in biosorption, with an optimum pH being 6.0 or higher (Brierley et al., 2009). High recovery of biosorbed metal ions could be achieved with acid elution. Caustic regeneration of eluted biomass rehabilitated the metal ion biosorption capacity of the biomass even after five cycles of reuse (Whistler and Daniel, 2005).

## 4. Conclusion

It was concluded that biosorption show good performance for the removal of heavy metal. The effect of pH 4.0 to 5.0 of sample was found to be good. the experimental data points for biosorption of lead, cadmium, nickel and zinc. Lead, cadmium and nickel removal capacities of live biomass were higher than those of pretreated biomass obtained at pH 4.0 and 5.0, but lower at pH 6.0. $HNO_3$ proved to be a more effective elutant than $CaCl_2$ and NaCl, with more than 90% elution for $Pb^{2+}$, $Cd^{2+}$, $Ni^{2+}$ and $Zn^{2+}$, while deionized water exhibited negligible desorption capability.

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