Biosorption of monovalent and divalent ions on baker's yeast

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Abstract

Biosorption of monovalent ions Na+ and K+ by deactivated protonated yeast (Saccharomyces cerevisiae) at controlled pH, was compared with biosorption of divalent ions Ca2+ and Mg2+ to help to understand the underlying binding mechanisms. The adsorption for monovalent ions was accompanied by H+ release. Divalent ions were sorbed by proton displacement, and also an additional mode not accompanied by release of H+. The sorption uptake of both monovalent and divalent metal ions increased with pH in the range 3-7 peaking at 6.75. Equilibrium sorption isotherms at pH = 6.75 showed that the total maximum biosorptive capacity for metal ions decreased in the following order: Ca > Mg > Na > K.

Keywords: Biosorption; Metal ions; Mechanism; Wastewater treatment; Yeast

1. Introduction

There has been considerable interest in the use of a complex mixture of microorganisms both dead and living, for removal of heavy metal ions from effluents. A review (Vasudevan et al., 2001) of literature on metal biosorption by inactive cells of bacteria, algae and fungi shows that these generally pertain to the native biomass as the sorbent, as obtained immediately after deactivation. In many cases, raw data on sorption capacity are reported at only one concentration without studying the reproducibility of the data. Only in some recent papers the biomass has been characterised (Yang and Volesky, 1999; Pagnanelli et al., 2000). Complexation, coordination, microprecipitation and ion exchange, are believed to be involved in biosorption (Kuyucak and Volesky, 1989; Avery and Tobin, 1993), besides physical adsorption. However, less attention has been paid to separate these effects for a better understanding and optimization of conditions of sorption.

Baker's yeast, which is an inexpensive and easily available source of biomass, was selected for the present study on the biosorption of monovalent and divalent ions. Na and K ions were chosen as typical monovalent ions and Ca and Mg ions as typical divalent ions. Since yeast bioaccumulates these ions from the media in which it is grown, it was of interest to compare the amounts of these ions present in the live cell sample of yeast initially taken, with the amounts biosorbed by deactivated cells from metal ion solution.

2. Methods

2.1. Preparation and characterization of sorbent

The yeast biomass procured from SAF yeast, Chembur, Mumbai, India, was deactivated by heating in an oven at 80 °C for 24 h (Schiewer and Volesky, 1995). The finely ground deactivated native biomass (Saccharomyces cerevisiae) was taken and eluted with acids in the following different ways to determine the amount of cations present in it.

(a) Treating 0.1 g of deactivated yeast with 10 ml of 3 M HNO₃ for 20 min.
(b) Ashing of 0.1 g deactivated yeast at 600 °C for 2 h followed by treatment with 10 ml of 3 M HNO₃ for 20 min.
(c) Treating 0.1 and 10 g of deactivated yeast with 10 and 1000 ml of 0.1N HCl solution, respectively for 24 h.

The cations (Na, K, Ca and Mg) present in the eluates were determined. The biomass residue from
2.3.1. Effect of pH

2.2. Chemicals

Metal solutions were prepared by taking NaCl, KCl, CaCl2 and MgSO4 (Qualigens fine Chem.) of analytical grade and dissolving in appropriate amounts of distilled water.

2.3. Metal binding experiments

2.3.1. Effect of pH

Experiments were conducted by contacting 0.1 g of deactivated and protonated biomass (referred to as sorbent) with 100 ml of NaCl [4.34 and 43.4 mmol/l (i.e., 100 and 1000 ppm, respectively)] and CaCl2 [2.5 and 25 mmol/l (i.e., 100 and 1000 ppm, respectively)] solutions. The solutions were shaken on a rotary shaker (Neolab Instruments, Mumbai, India) at 120 rpm. The pH of the solution was kept constant with addition of 0.01 N NaOH or 0.01 N HCl as needed and studies were conducted at pH = 3, 4, 5, 6, 6.75 and 7. The biosorbent was then removed from the solution by centrifugation and filtration. The solution was analysed for residual metal concentration according to Standard Methods (APHA, 1985). The collected sorbent was dried and the metal ions, leached out with 10 ml of 3 M HNO3 for 20 min and analysed. Thus the amounts biosorbed could be determined both from the loss from solution and elution of amount bound by the sorbent.

2.3.2. Biosorption studies

Equilibrium sorption experiments were carried out at a pH of 6.75 by contacting 0.1 g of sorbent with 100 ml each of either NaCl, KCl, CaCl2 and MgSO4 solutions. The concentrations were varied over the range 1-100 mmol/l. The pH was constantly measured and adjusted using 0.01 N NaOH/HCl. The biosorbent was separated from the solutions after 24 h. The metal ions in the solution and the sorbent were estimated. All experiments were conducted at room temperature. Blanks and triplicates were also run simultaneously. The maximum variation in metal sorption data between triplicate experiments was 5%. Mean value for the replicates was used for comparisons.

3. Results and discussion

3.1. Metal content and acidity of deactivated yeast biomass

Three different batches of yeast (I, II, III), bought in different months were examined for the amount of light metal ions released (Table 1) by different methods a, b and c (Section 2.1). For the batch (I), the total cations released from the native yeast by process a (A) and process b (B) were found to match more closely than that by process c (C). Between the eluates by process c of 0.1 g (C) and 10 g samples (C1) of batch (I), there was some variation in the amount of ions released. The differences between the eluates from C and C1 (10 g samples from batch (III) eluted by process c) reflected some level of heterogeneity within the same batch. As can be seen from the average values in the last column of Table 1, the percentage variation relative to the mean taken over samples for all the batches and processes for the amount of K and Ca ions released were smaller than for Na and Mg ions released. While the Na ion eluted from different batches was at least one or more orders less than K ion, the Mg ion released was about two to

Table 1
Metal ions in untreated yeast

<table>
<thead>
<tr>
<th>Metal ion</th>
<th>Bound in mL sorbent (meq/g)</th>
<th>I (September 1999)</th>
<th>II (January 2000)</th>
<th>III (May 2000)</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
<td>B</td>
<td>C</td>
<td>C</td>
<td></td>
</tr>
<tr>
<td>Na</td>
<td>0.069</td>
<td>0.0043</td>
<td>0.013</td>
<td>0.0043</td>
<td>0.023</td>
</tr>
<tr>
<td>K</td>
<td>0.242</td>
<td>0.256</td>
<td>0.200</td>
<td>0.200</td>
<td>0.215</td>
</tr>
<tr>
<td>Ca</td>
<td>0.200</td>
<td>0.239</td>
<td>0.200</td>
<td>0.200</td>
<td>0.200</td>
</tr>
<tr>
<td>Mg</td>
<td>0.457</td>
<td>0.427</td>
<td>0.905</td>
<td>0.641</td>
<td>0.838</td>
</tr>
<tr>
<td>Total cations</td>
<td>0.968</td>
<td>0.922</td>
<td>1.358</td>
<td>1.045</td>
<td>1.217</td>
</tr>
</tbody>
</table>

1Elution of 0.1 g yeast with 3 M HNO3 (method a).
2Ashing of 0.1 g yeast followed by elution with HNO3 (method b).
3Elution of 0.1 g yeast with 0.1 N HCl (method c).
4Elution of 10 g yeast with 0.1 N HCl (method c).
3.3. Proton release during biosorption

During sorption experiments with protonated biomass the pH was measured after every hour. Generally, pH variations occurred in the first six hours after which it became constant. The fall in pH (6.75-5.8) was compensated by the addition of NaOH. The H⁺ released in the experiment was determined from the total amount of NaOH added. The H⁺ released was taken to be indicative of the cation sorption by exchange with protons (Crist et al., 1981; Holan et al., 1993; Schiewer and Volesky, 1995).

3.4. Metal biosorption studies

The metal ion biosorbed was calculated in two ways, namely, based on the metal ion decrease in solution and based on metal ion eluted from the sorbent. Also metal ion exchanged for H⁺ was calculated from pH change. Adsorption isotherms of the type qₑ vs Cₑ, under constant pH values were plotted (Figs. 2 and 3) where qₑ represents the amount of metal ion sorbed per unit weight of biomass and Cₑ the metal ion concentration remaining in solution at equilibrium. In the case of monovalent ions the dashed line in Fig. 2 is the isotherm for biosorption measured in terms of pH change. The solid lines represent the values obtained by elution of the cations from the sorbent after equilibration. The two curves overlap for Na (line A) and K (line B) ions indicating that the mechanism of biosorption is essentially by proton displacement. The total amounts of Na and K ions biosorbed were found to be 0.125 and 0.1 meq/g, respectively.

In the case of divalent ions, biosorption with pH change was of the order of 0.13 meq/g (Fig. 3 dashed line, E) for both Ca and Mg ions. However, the total sorption as determined by elution was much higher (Fig. 3 solid lines, C and D). The total maximum adsorption

![Graph showing pH reading vs Volume of NaOH added](image)
capacity for divalent ions was thus higher (Table 2) than that for monovalent ions and was in the order

$$\text{Ca}^{2+} \text{meq/g} > \text{Mg}^{2+} \text{meq/g} > \text{Na}^{+} \text{and } \text{K}^{+} \text{meq/g}.$$  

It was noted that biosorption with proton exchange (column 1 of Table 2) was of the same order for all the four ions (0.12 meq/g). This matched with the value of 0.1 meq/g for capacity obtained by pH titration. Thus, the total sorption values for the monovalent ions Na and K were same (column 2, Table 2) as the sorption determined by pH change. On the other hand, the total sorption of Ca and Mg ions were higher than that obtained by pH change, by the amounts shown in parenthesis. The additional amounts sorbed was by a mechanism without proton release.

Ion exchange has been shown as the predominant sequestering mechanism in algae (Kuyucak and Volesky, 1989; Crist et al., 1994), particularly for seaweed-based metal biosorption systems (Schiewer et al., 1995; Fourest and Volesky, 1996). In the case of yeast, biosorption mechanisms have been related to different cell wall constituents (Murray and Kidby, 1975; Norris and Kelly, 1977; Tsezos and Volesky, 1982a,b; White and Gadd, 1987; Muraleedharan and Venkobachar, 1990). In fungi, the cell wall is a multilamine, microfibrillar structure consisting of up to 90% polysaccharide. In S. cerevisiae mannan-b-glucan is the main structural polymer (Remacle, 1990). The other components of yeast cell wall include proteins, lipids, chitin and chitosan. The functional groups responsible for metal adsorption include carboxylate, phosphate, sulphhydryl and amine moieties present in proteins and lipids (Shumate and Strandberg, 1985).

### 3.5. Comparison of cations biosorbed with the amounts available in native biomass

Comparison of Tables 1 and 2 showed that while the amounts of ions bound in native biomass were in the order Mg > K > Ca > Na, the amounts bound by biosorption by protonated biomass were in the order Ca > Mg > Na P K. The amounts of Ca ion biosorbed on protonated biomass was maximum at 1 meq/g which was interestingly equal to the order of total cations bound in the native sorbent (last row, Table 1). Thus while the total sites available in yeast for metal ion binding may be in the range 0.9-1.3 meq/g, the metal ion distribution in activated sorption by live cells during the growth of yeast may be quite different from that obtained on deactivated protonated yeast. Few studies conducted on live and wet cells of some strains of yeast (Avery and Tobin, 1992) have also brought out differences between metabolism dependent and metabolism independent adsorption in the same strain and also variations in the pattern of sorption between different strains.

### 4. Conclusions

The following were the major conclusions of the study. The average amount of cations bound in the baker's yeast strain studied was in the range of 0.9-1.3 meq/g with the distribution Mg > K > Ca > Na. This would depend on the composition of growth medium as well as preferences of the sites for the cation. On the other hand sorption of these cations on protonated (acid washed) deactivated yeast was Ca > Mg > Na P K in the solution concentration range of 1-100 mmol/l. For Na and K (monovalent ions) the total biosorption by protonated yeast was of the order of 0.12 meq/g, and this occurred with pH change. The total biosorption in the case of Ca and Mg ions was 1.0 meq/g and 0.36 meq/g respectively. Out of this 0.13 meq/g of sorption occurred with pH change. Thus in the case of divalent ions there is an additional mechanism possibly involving coordination and electrostatic interactions.
References


