Biosorption of mercury on magnetically modified yeast cells

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Abstract

Brewer’s yeast (bottom yeast, Saccharomyces cerevisiae subsp. uvarum) cells were magnetically modified using water based magnetic fluid stabilized perchloric acid. The magnetically modified yeast cells were characterized by scanning electron microscopy (SEM) and electron spin resonance (ESR). Hg2+ biosorption-desorption properties of magnetically modified yeast cells from synthetic solutions were utilized in batch system. The biosorption process was fast; 80% of biosorption occurred within 60 min and equilibrium was achieved at around 90 min. The maximum Hg2+ biosorption capacity was obtained to be 114.6 mg/g at 35 °C. The suitability of the Langmuir, Freundlich and Redlich-Peterson adsorption models to the equilibrium data was investigated for mercury-biosorbent system. The results were well fitted to the Langmuir isotherm. The applicability of two kinetic models including pseudo-first order and pseudo-second order model was estimated on the basis of comparative analysis of the corresponding rate parameters, equilibrium capacity and correlation coefficients. Results suggest that chemisorption processes could be the rate-limiting step in the biosorption process. The yeast biomass can be easily regenerated by 0.1 M HNO3 with higher effectiveness. Biosorption of heavy metal ions from artificial wastewater was also studied. The biosorption capacities are 29.9 mg/g for Cu2+, 76.2 mg/g for Hg2+, 14.1 mg/g for Ni2+ and 11.8 mg/g for Zn2+.

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1. Introduction

Heavy metal pollution represents an important environmental problem due to the toxic effects of metals, and their accumulation throughout the food chain leads to serious ecological and health problems [1]. Mercury, as one of the most dangerous heavy metals, in any form introduced to the natural environment from a variety of sources is converted into more toxic form, i.e., methylmercury chloride by aquatic living-organisms, and accumulated in the tissue of fishes and birds [2]. The illness, which came to be known as Minamata disease, was caused by mercury poisoning as a result of eating contaminated fish [3]. Mercury has very high tendency for binding to proteins and it mainly affects the renal and nervous systems [4]. In humans, the initial symptoms include numbness of the lips and limbs. As the sickness progresses, permanent damage is done to the central nervous system, and the victim experiences visual constriction, loss of motor coordination, and, in the final stages prior to death, loss of memory, speech, hearing and taste.

Because of these reasons, mercury must be removed to very low levels from wastewater generated in industries such as metal smelting and caustic-chlorine production in mercury cells, metal processing, plating and metal finishing. These effluents require chemical treatment before they can be discharged. Different treatment techniques have been developed to remove either or both dissolved and suspended heavy metal ions from industrial wastewaters. A number of traditional treatment techniques included precipitation-neutralization, ultra-filtration, reverse osmosis, electro-deposition, solvent extraction, foam-flotation, cementation, complexation/sequestration, filtration and evaporation [5]. The necessity to reduce the amount of heavy metal ions in wastewater streams has led to an increasing interest in selective supports [6–8].

Magnetic separation techniques have recently found many interesting applications in various areas of biosciences and biotechnology. Magnetic nano- and microparticles have been used for immunomagnetic separation of prokaryotic and eukaryotic cells [9], magnetic separation of various biologically active
compounds [10], removal of xenobiotics [11] and in various biomedical applications [12]. Conventional adsorption techniques based on the use of classical chromatographic methods are very time consuming. Magnetically stabilized fluidized bed enables the use of magnetic processing for rapid and selective removal [13]. Magnetic separation has several potential advantages over conventional approaches. Magnetically stabilized fluidized bed cartridges require high flow-rates with a much lower operating pressure than a packed bed column. Especially, when dealing with highly viscous mediums such as wastewater contact with the magnetic adsorbent in a magnetically stabilized fluidized bed is desirable because of high convective transport rates without clogging. In this technique, heavy metal ions to be separated can be directly transported by convection to the binding sites on the surface of the adsorbent (i.e., magnetically modified yeast cells), higher throughput and faster processing times onto the magnetic yeast particles can be achieved. Due to these reasons, we prepared magnetic yeast cells for selective removal of heavy metal ions [14,15].

It was observed that yeast cells could be magnetically modified after contact with appropriate water-based magnetic fluid [16–18]. Physiological conditions of the treated cells influence substantially the localization of magnetic nanoparticles. In case non-growing cells are magnetically modified, majority of magnetic nanoparticles is localized on the outer surface of the cell wall. On the contrary, growing cells accumulated magnetic nanoparticles inside the periplasmic space [17]. In this study, magnetic yeast cells were prepared. Hg$^{2+}$ biosorption/desorption properties of magnetic yeast cells from aqueous medium and artificial wastewater were studied. Here we present preparation of the magnetic yeast cells, and potential for their use in Hg$^{2+}$ biosorption/desorption studies.

2. Methods

2.1. Materials

Water based ionic ferro-fluids (stabilized either with perchloric acid or tetramethylammonium hydroxide) were prepared using the standard procedure [19]. The ferrofluids were composed of magnetite nanoparticles with the diameter ranging between 10 and 20 nm (electron microscopy measurement). The relative ferrofluid concentration (19.2 mg/ml) is given as the magnetite content determined by a colorimetric method [20]. All standard and reagents were prepared in ultra-pure water produced in a Barnstead (Dubuque, IA) ROpure LP® reverse osmosis unit with a high flow cellulose acetate membrane (Barnstead D2731) followed by a Barnstead D3804 NANOpure® organic/colloid removal and ion exchange packed-bed system.

2.2. Brewer’s yeast

Suspension of brewer’s yeast (bottom yeast, *Saccharomyces cerevisiae* subsp. uvarum) was obtained in Samson brewery (Ceske Budejovice, Czech Republic) from reservoirs in a fermentation room; the yeast was used in the fermentation process up to three times and usually non-significant bacterial contamination was observed. The suspension of yeast cells was stored in water at 4°C.

2.3. Magnetic modification of the yeast cells

Magnetic adsorbent based on non-cultivated yeast cells was prepared as follows: the yeast suspension obtained from the brewery was centrifuged and the sedimented yeast cells (2 ml, sedimented volume) were resuspended in 6 ml of saline (0.85% NaCl). Centrifugation and washing with saline were repeated three times to remove impurities from the yeast cells. After the last centrifugation, yeast cells were suspended in 2 ml of glycine–HCl buffer, pH 2.2 and the suspension was mixed. After 15 min, 0.6 ml of perchloric acid stabilized ferrofluid was added to 1.8 ml of the cell suspension. After 30 min mixing on a rotary mixer (Dynal, Norway) the magnetic suspension was washed with water. After that the suspension was heated in a boiling water bath for 15 min and washed with water again. The prepared material was stored at 4°C.

2.4. Characterization of the magnetically modified yeast cells

The surface morphology of the magnetically modified yeast cells was examined using a scanning electron microscope (SEM). The samples were initially dried in air at 25°C for 7 days before being analyzed. A fragment of the dried cells was mounted on a SEM sample mount and was sputter coated for 2 min. The magnetic yeast sample was then mounted in a scanning electron microscope (Model: JSM 5600, Jeol, Japan). The surface of the yeast sample was then scanned at the desired magnification to study the morphology of the yeast cells.

The degree of magnetism of the yeast cells was measured in a magnetic field by using a vibrating-sample magnetometer (Princeton Applied Research, Model 150A, USA). The presence of ferrofluids in the magnetically modified yeast structure was investigated with an electron spin resonance (ESR) spectrophotometer (EL 9, Varian, USA).

2.5. Hg$^{2+}$ biosorption/desorption studies

Biosorption of Hg$^{2+}$ ions from aqueous solutions and from artificial wastewater was investigated in batch experiments. Effects of the equilibrium Hg$^{2+}$ concentration and pH of the medium on the biosorption rate and capacity were studied. Fifty milliliter of an aqueous solution were stirred with 100 mg of dry magnetic yeast cells at 100 rpm. Nitrate salt was used as the source of Hg$^{2+}$ ions. The biosorption experiment was repeated three times. The concentration of the Hg$^{2+}$ ions in the aqueous phase, after the desired treatment periods was measured by using a flame atomic absorption spectrophotometer (Shimadzu Model AA-6800 Flame, Japan). For mercury determinations, MVU-1A (mercury-vapor unit) was employed. Deuterium background correction was applied throughout the experiments and the spectral slit width was 0.5 nm. The instrument response was periodically checked with a known Hg$^{2+}$ solution standard. The
biosorption experiments were performed in replicates of three and the samples were analyzed in replicates of three as well. For each set of data present, standard statistical methods were used to determine the mean values and standard deviations. Confidence intervals of 95% were calculated for each set of samples in order to determine the margin of error. The amount of metal biosorption per unit mass of the magnetic yeast cells was evaluated by using the concentration difference.

Desorption of Hg$^{2+}$ ions was studied in 0.1 M HNO$_3$ solution. Hg$^{2+}$ loaded magnetically modified yeast cells were placed in the desorption medium and stirred (at a stirring rate of 100 rpm) for 3 h at room temperature. The final concentration of Hg$^{2+}$ ions in the aqueous phase was determined by using a graphite furnace atomic absorption spectrophotometer. The desorption ratio was calculated from the amount of Hg$^{2+}$ ions adsorbed on the magnetic yeast cells and the final concentration of Hg$^{2+}$ ions in the desorption medium. In order to evaluate the reusability of the magnetically modified yeast cells, biosorption–desorption cycles were repeated 20 times by using the same modified yeast.

2.6. Heavy metal biosorption from artificial wastewater

Biosorption of heavy metal ions from artificial wastewater was carried out in a batch system. A solution (20 ml) containing 0.5 mmol/L from each metal ions [i.e., Cu$^{2+}$, Ni$^{2+}$ and Hg$^{2+}$] was incubated with the magnetically modified yeast cells at a pH of 7.0 at room temperature, in the flasks stirred magnetically at 600 rpm. Artificial wastewater also contains Zn$^{2+}$, Fe$^{3+}$, Co$^{2+}$, Cd$^{2+}$, Cr$^{3+}$ and Al$^{3+}$. Concentration of each metal ions in artificial wastewater is 0.5 mmol/L. Artificial wastewater solution was prepared according to the European Union Directive 91/271/EEC. In order to adjust salinity, NaCl was added to the artificial wastewater (700 ppm). After biosorption, the

Fig. 1. SEM photographs of the magnetic yeast cells.
concentration of the metal ions in the remaining solution was determined as described above.

3. Results and discussion

3.1. Characterization of the magnetically modified yeast cells

Microscopy observations showed the magnetically modified yeast cells surface is quite rough, providing a large exposed surface area for biosorption of mercury ions (Fig. 1). The porous nature of the magnetic structure reduces diffusional resistance and facilitate mass transfer.

The presence of magnetite material (i.e., ferrofluid) in the modified yeast structure was confirmed by ESR. The intensity of the magnetite peak against magnetic field is shown in Fig. 2. The application of an external magnetic field may generate an internal magnetic field in the sample which will add to or subtract from the external field. The local magnetic field generated by the electronic magnetic moment will add vectorially to the external magnetic field ($H_{\text{ext}}$) to give an effective field ($H_{\text{eff}}$) (Eq. (1)).

$$H_{\text{eff}} = H_{\text{ext}} + H_{\text{local}} \quad (1)$$

As seen in Fig. 2, magnetically modified yeast cells have a relative intensity of 100. This value shows that yeast cell structure has a local magnetic field because of ferrofluid in its structure. The $g$ factor can be considered as quantity characteristic of the molecules in which the unpaired electrons are located, and it is calculated from Eq. (2). The measurement of the $g$ factor for an unknown signal can be a valuable aid in the identification of a signal. In the literature the $g$ factor for Fe$^{3+}$ is determined between 1.4–3.1 for low spin and 2.0–9.7 for high spin complexes [21]. In this study, the $g$ factor was found to be 3.8 for magnetically modified yeast cells structure.

$$g = \frac{h \nu}{\beta H_r} \quad (2)$$

here, $h$ is the Planck constant ($6.626 \times 10^{-27}$ erg/s); $\beta$ is Universal constant ($9.274 \times 10^{-21}$ erg/G); $\nu$ is frequency ($9.707 \times 10^9$ Hz) and $H_r$ is resonance of magnetic field (G).

Magnetic properties of the magnetically modified yeast cells structure were presented using electron mass unit (EMU), showing the behaviour of magnetic yeast cells in a magnetic field using a vibrating magnetometer, in Fig. 3, and $H_r$ value, is defined as the external magnetic field at resonance. In EMU spectrum and from $H_r$ value, 4500 Gauss magnetic field was found sufficient to excite all of the dipole moments present in 1.0 g magnetic yeast cells sample. These values will be an important design parameter for a magnetically stabilized fluidized bed or for magnetic filtration using these magnetic sample. The value of this magnetic field is a function of the flow velocity, particle size and magnetic susceptibility of solids to be removed. In the literature, this value was found to change from 8 kG to 20 kG for various applications, thus magnetically modified yeast cells presented in this study will need less magnetic intensity in a magnetically stabilized fluidized bed or for a magnetic filter system [22].

3.2. Biosorption of Hg$^{2+}$ ions

3.2.1. Effect of incubation time

The biosorption kinetic properties of the Hg$^{2+}$ ions by the magnetically modified yeast cells are important for assessment of the suitability of this magnetic material to serve as an adsorbent in a through flow column. Fig. 4 shows biosorption rates of Hg$^{2+}$ on the magnetically modified yeast cells from aqueous solutions containing different amounts of Hg$^{2+}$ (in the range of 25–200 mg/L) at constant pH of 6.0. As seen here, mercury biosorption capacity increases with the time during the first 90 min and then levels off toward the equilibrium biosorp-
tion capacity. In addition, biosorption of Hg^{2+} was quite fast especially when the Hg^{2+} concentration was high. This is due to the high complexation rate between Hg^{2+} ions and reactive functional groups on the surface of yeast cells. Mass transfer limitations were also overcome by high driving force, which was the concentration difference of Hg^{2+} between the liquid and the solid phases, in the case of high Hg^{2+} concentration. It should be also mentioned that the biosorption is not a diffusion-controlled process since the biosorption seems to be faster for Hg^{2+} for all concentrations which studied.

3.2.2. Effect of Hg^{2+} concentration

Fig. 5 shows the effects of equilibrium concentration of Hg^{2+} onto the biosorption capacity of the magnetically modified yeast cells. Hg^{2+} biosorption capacity of the magnetically modified yeast cells increased first with the increasing of equilibrium concentration of Hg^{2+} then reached a plateau value at about an equilibrium Hg^{2+} concentration of 150 mg/L, which represents saturation of the active binding sites of the reactive functional groups (which are available for Hg^{2+}) on the magnetically modified yeast cells. The cell wall of yeast has only 1–3% of chitin with mannoproteins, β-glucan (85–90%) and lipids (2–5%) [23]. The cell wall components provide metal-binding groups including amino, carboxyl groups and sulphate, phosphate moieties. According to the study on the hard and soft metals, soft metal Hg form more stable bonds with nitrogen- or sulphur-containing (soft) ligands [24]. The maximum Hg^{2+} biosorption capacity is 114.6 mg/g for magnetically modified yeast cells. It should be also noted that Hg^{2+} uptake amount on unmodified yeast cells was found to be 114.2 mg/g.

3.2.3. Effect of pH

The ability of microbial biomass to bind metals in solution has been shown to be a function of pH [25]. The differences in biosorption mechanisms may be explained by the ionic state of metal in solution. In the absence of complexing chemical substances, the precipitation of the heavy metal ion is affected by the concentration. As discussed in literature [26], precipitation of mercury ions becomes significant at pH 8.0. For example, the theoretical and the experimental precipitation curves showed that precipitation begins above this pH, which also depends on the concentration of Hg^{2+} in the medium. In this study, in order to establish the effect of pH on the biosorption of Hg^{2+} onto the magnetically modified yeast cells, we repeated the batch biosorption studies at different pH in the range of 2.0–7.0. Fig. 6 shows the effect of pH on the biosorption of Hg^{2+}. As seen here, biosorption of Hg^{2+} increased with increasing pH and then reached almost a plateau value around pH 5.0. The magnetically modified yeast cells exhibited a low affinity for Hg^{2+} in acidic condition (pH < 4.0), somewhat higher affinity between pH 5.0 and 7.0, and an increase of biosorption above pH 4.0. The
increasing pH of the solution favors complex formation between the reactive groups on the yeast cells and Hg²⁺. Biosorption of Hg²⁺ via the reactive functional groups on the magnetically modified yeast was 82.5 mg/g biomass.

3.3. Biosorption isotherm

Two important physico-chemical aspects for evaluation of the biosorption process as a unit operation are the kinetics and the equilibria of adsorption. Modelling of the equilibrium data has been done using the Langmuir, Freundlich and Redlich-Peterson isotherms [27]. The Langmuir and Freundlich isotherms are represented as follows Eqs. (3) and (4), respectively.

\[
\frac{1}{q_e} = \left( \frac{1}{q_{\text{max}}} \right) + \left( \frac{1}{q_{\text{bmax}}} \right) \left( \frac{1}{C_e} \right)
\]

\[
\ln q_e = \ln C_e + \ln K_F
\]

where, \( b \) is the Langmuir isotherm constant, \( K_F \) is the Freundlich constant, and \( n \) is the Freundlich exponent. \( 1/n \) is a measure of the surface heterogeneity ranging between 0 and 1, becoming more heterogeneous as its value gets closer to zero. The ratio of \( Q_o \) gives the theoretical monolayer saturation capacity of magnetically modified yeast cells.

The Redlich–Peterson equation describes adsorption on heterogeneous surfaces, as it contains the heterogeneity factor \( \beta \). This equation has three parameters, \( A \), \( B \) and \( \beta \). Parameter \( \beta \) ranges between 0 and 1. It can be reduced the Langmuir equation as \( \beta \) approaches 1. \( A \), \( B \) and \( \beta \) were determined by curve fitting.

\[
\frac{C_e}{Q_e} = \left( \frac{B}{A} \right) + \left( \frac{1}{A} \right) C_e^\beta
\]

Table 1 Biosorption parameters obtained from Langmuir, Freundlich and Redlich–Peterson isotherm

<table>
<thead>
<tr>
<th>( T ) (°C)</th>
<th>Langmuir</th>
<th>Freundlich</th>
<th>Redlich–Peterson</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( Q ) (mg/g)</td>
<td>( b ) (1/mg)</td>
<td>( R^2 )</td>
</tr>
<tr>
<td>4</td>
<td>48.3</td>
<td>0.147</td>
<td>0.991</td>
</tr>
<tr>
<td>15</td>
<td>74.1</td>
<td>0.172</td>
<td>0.989</td>
</tr>
<tr>
<td>25</td>
<td>93.4</td>
<td>0.158</td>
<td>0.992</td>
</tr>
<tr>
<td>35</td>
<td>133.3</td>
<td>0.119</td>
<td>0.995</td>
</tr>
</tbody>
</table>

Table 2 Equilibrium association constants and free energies

<table>
<thead>
<tr>
<th>( T ) (°C)</th>
<th>( 1/T \times 10^3 )</th>
<th>( \ln b )</th>
<th>( \Delta G^o ) (kJ/mol)</th>
<th>( \Delta H^o ) (J/mol)</th>
<th>( \Delta S^o ) (J/mol K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>277</td>
<td>3.61</td>
<td>−1.91</td>
<td>−4.90</td>
<td>−0.0665</td>
<td>0.0175</td>
</tr>
<tr>
<td>288</td>
<td>3.47</td>
<td>−1.75</td>
<td>−5.09</td>
<td></td>
<td></td>
</tr>
<tr>
<td>298</td>
<td>3.36</td>
<td>−1.84</td>
<td>−5.26</td>
<td></td>
<td></td>
</tr>
<tr>
<td>308</td>
<td>3.25</td>
<td>−2.12</td>
<td>−5.44</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The essential characteristic of the Langmuir equation can be expressed in terms of dimension factor, \( R_L \), which was defined by McKay et al. [28] as:

\[
R_L = \frac{1}{(1 + K_L C_o)}
\]

where, \( C_o \) is the highest initial metal concentration (mg/L). The value of \( R_L \) indicates the nature of adsorption as unfavourable \((R_L > 1)\), linear \((R_L = 1)\), favourable \((0 < R_L < 1)\) or irreversible \((R_L = 0)\). The \( R_L \) values are 0.0433 for 4°C, 0.0371 for 15°C, 0.0404 for 25°C and 0.0529 for 35°C. The obtained \( R_L \) values show that biosorption behaviour of mercury ions onto biologically modified yeast cells are favourable \((R_L < 1)\).

Thermodynamic parameters such as free energy \((\Delta G^o)\), enthalpy \((\Delta H^o)\) and entropy \((\Delta S^o)\) changes for the process can be estimated using the following equations:

\[
\Delta G^o = −RT \ln b
\]
\[
\Delta G^o = \Delta H^o − T \Delta S^o
\]

where, \( b \) is Langmuir constant. The plot of \( \ln b \) versus \( 1/T \) for the biosorption process was found to be linear. Table 2 shows the maximum biosorption capacities \((Q_{\text{max}})\), the equilibrium association constant and free energies \((\Delta G^o)\) calculated from the experimental data at different temperatures.

The negative change in free energy \((\Delta G^o < 0)\) indicated that the biosorption of mercury ions on the magnetically modified yeast cells was a thermodynamically favorable process (Table 2).

3.4. Biosorption dynamics

In order to quantify the extent of uptake in adsorption kinetics, a pseudo-first-order as suggested by Ho and McKay was used [29]:

\[
\log(q_e − q_t) = \log(q_{\text{t(cal)}}) − \frac{(k_1 t)}{2.303}
\]
The first- and second-order kinetic constants

<table>
<thead>
<tr>
<th>Concentration (mg/ml)</th>
<th>Exp Q (mg/g)</th>
<th>First-order kinetic</th>
<th>Second-order kinetic</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>k₁ (1/min)</td>
<td>q₁cal (mg/g)</td>
</tr>
<tr>
<td>25</td>
<td>38.5</td>
<td>0.051</td>
<td>32.3</td>
</tr>
<tr>
<td>50</td>
<td>49.6</td>
<td>0.061</td>
<td>76.5</td>
</tr>
<tr>
<td>100</td>
<td>79.6</td>
<td>0.056</td>
<td>146.6</td>
</tr>
<tr>
<td>200</td>
<td>82.4</td>
<td>0.062</td>
<td>120.8</td>
</tr>
</tbody>
</table>

where \( q_e \) is the experimental amount of mercury ions adsorbed at equilibrium (mg/g); \( q_t \) is the amount of mercury adsorbed at time \( t \) (mg/g); \( k_1 \) is the equilibrium rate constant of first order biosorption (1/min); and \( q_{1cal} \) is the biosorption capacity calculated by the pseudo-first-order model (mg/g).

The rate constant for the second-order biosorption could be obtained from the following equation:

\[
\left( \frac{t}{q_t} \right) = \left( \frac{1}{k_2q_{2cal}} \right) + \left( \frac{1}{q_{2cal}} \right) t \tag{10}
\]

where \( k_2 \) is the equilibrium rate constant of pseudo-second-order biosorption (g/mg min); \( q_{2cal} \) is the biosorption capacity calculated by the pseudo-second-order kinetic model (mg/g).

According to the values in Table 3, the optimum results are for both the second and first order models, with the second order mechanism \( R^2 \) values being the highest. These results suggest that the pseudo-second order mechanisms is predominant and that chemisorption might be the rate-limiting step that controls the biosorption process. The rate-controlling mechanism may vary during the course of the biosorption process three possible mechanisms may be occurring [30]. There is an external surface mass transfer or film diffusion process that controls the early stages of the biosorption process. This may be followed by a reaction or constant rate stage and finally by a diffusion stage where the biosorption process slows down considerably [31].

The pore diffusion coefficient, \( D \), for the removal of mercury ions have been calculated using the following equation, assuming spherical shape geometry for the biosorbent particles.

\[
t_{1/2} = 0.03 \frac{r_o^2}{D} \tag{11}
\]

where \( t_{1/2} \) is time for half biosorption, \( r_o \) is diameter of magnetically modified yeast cells, and \( D \) is the pore diffusion constant cm²/s. The values of the pore-diffusion coefficient of mercury ions were found 9.23 × 10⁻¹¹ cm²/s. Thus, the value of pore diffusion rate constant was found to be on the order of 10⁻⁹ cm²/s for mercury ions, indicating that the pore diffusion is not significant.

3.5. Regeneration

Regeneration of the adsorbed \( \text{Hg}^{2+} \) ions from the magnetic yeast cells was also studied in a batch experimental set-up. The magnetically modified yeast cells loaded (at pH 5.0) with \( \text{Hg}^{2+} \) ions was placed within the desorption medium containing 1.0 M HNO₃ and the amount of \( \text{Hg}^{2+} \) ions desorbed in 5 min was measured. When HNO₃ is used as a desorption agent, the coordination spheres of chelated mercury ions is disrupted and subsequently \( \text{Hg}^{2+} \) ions are released from the solid surface into the desorption medium. The desorption ratio was then calculated by using the difference. The results indicated that the regeneration of the magnetically modified yeast cells by strong acids is feasible. Desorption ratio was very high (up to 98%). It is obvious that metal-chelate forming interactions between reactive functional-groups on the modified yeast cells and \( \text{Hg}^{2+} \) ions are weaker with decreasing pH. It must be pointed out that in metal chelation systems, biosorption is completely reversible. The biosorption capacity of the recycled magnetically modified yeast cells can still be maintained at 98% level at the 20th cycle.

3.6. Biosorption from artificial wastewater

The biosorption capacities of the magnetic yeast cells from artificial waste-water for \( \text{Hg}^{2+}, \text{Ni}^{2+} \) and \( \text{Cu}^{2+} \) are shown in Table 4. The biosorption capacities are 29.9 mg/g for \( \text{Cu}^{2+} \), 76.2 mg/g for \( \text{Hg}^{2+} \), 14.1 mg/g for \( \text{Ni}^{2+} \) and 11.8 mg/g for \( \text{Zn}^{2+} \). Magnetically modified yeast cells exhibits the following metal ion affinity sequence: \( \text{Hg}^{2+} > \text{Cu}^{2+} > \text{Ni}^{2+} > \text{Zn}^{2+} \). In this case, magnetically modified yeast cells adsorbed other metal ions also [i.e., \( \text{Cu}^{2+}, \text{Fe}^{3+}, \text{Co}^{2+}, \text{Al}^{3+} \) and \( \text{Cr}^{3+} \)]. The presence of other metal ions in the artificial wastewater decreases the biosorption capacities of magnetically modified yeast cells for \( \text{Cu}^{2+}, \text{Ni}^{2+} \) and \( \text{Hg}^{2+} \). The interactive effects of a metal mixture on a biomass are extremely complex and depend on biomass type, number of metals competing for binding sites, metal combination, levels of metal concentration, residence time and experimental conditions. Three types of responses may be occured: (a) the effect of the mixture is greater than that of each of the individual effects.

<table>
<thead>
<tr>
<th>Ions</th>
<th>Adsorbed ion (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Hg}^{2+} )</td>
<td>76.2 ± 1.12</td>
</tr>
<tr>
<td>( \text{Cu}^{2+} )</td>
<td>29.8 ± 0.74</td>
</tr>
<tr>
<td>( \text{Ni}^{2+} )</td>
<td>14.1 ± 0.80</td>
</tr>
<tr>
<td>( \text{Zn}^{2+} )</td>
<td>11.8 ± 0.66</td>
</tr>
<tr>
<td>( \text{Fe}^{2+} )</td>
<td>5.0 ± 0.72</td>
</tr>
<tr>
<td>( \text{Cd}^{2+} )</td>
<td>12.3 ± 0.89</td>
</tr>
<tr>
<td>( \text{Co}^{2+} )</td>
<td>8.2 ± 0.46</td>
</tr>
<tr>
<td>( \text{Cr}^{3+} )</td>
<td>6.2 ± 0.49</td>
</tr>
<tr>
<td>( \text{Al}^{3+} )</td>
<td>4.1 ± 0.57</td>
</tr>
</tbody>
</table>

Table 4
Biosorption of heavy metal ions from artificial wastewater on the magnetic yeast cells: concentration of each metal ions: 0.5 mmol/L; pH 7.0, biosorption time: 60 min
of the constituents in the mixture (synergism); (b) the effect of the mixture is less than that of each of the individual effects of the constituents in the mixture (antagonism); (c) the effect of the mixture is no more or less than that of each of the individual effects of the constituents in the mixture (non-interaction) [32]. It is worth noting that the biosorption capacities of the biologically modified yeast cells from synthetic wastewater for all metal ions were much lower than the single solutions. The most logical reason for the antagonistic action is claimed to be the competition for the binding sites on the cell surface and/or a screening effect by the other metal ions.

4. Conclusions

Biosorption process for the removal of soluble metals has become an important option in the integrated approach in aqueous waste treatment [33]. Magnetically modified yeast cells were used for biosorption/desorption of Hg\(^{2+}\) ions from synthetic solutions. High biosorption rates are observed at the beginning of biosorption process, and then plateau values (i.e., biosorption equilibrium) are gradually reached in about 90 min. Maximum Hg\(^{2+}\) biosorption capacity of the magnetic yeast cells was found to be very high (114.6 mg/g). Biosorption amounts of Hg\(^{2+}\) ions increased with increasing pH and reached almost a plateau value around pH 5.0. Desorption was performed by using 0.1 M HNO\(_3\) and very high desorption ratios were achieved up to 95%. Further, we have shown that the magnetic yeast cells can be used for heavy metal removal from artificial wastewater. The biosorption capacities are 76.2 mg/g for Hg\(^{2+}\), 29.9 mg/g for Cu\(^{2+}\), 14.1 mg/g for Ni\(^{2+}\) and 11.8 mg/g for Ni\(^{2+}\). From the results presented in this paper it can be concluded that the magnetic yeast cells may effectively be used (mean with high biosorption rates and capacities) for specific removal of Hg\(^{2+}\) ions from aqueous solutions including wastewater.

References