Biosorption of heavy metal ions by the cell walls of yeast Saccharomyces cerevisiae in their combined presence

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Abstract. Stationary method ions biosorption Pb(II), Cd(II) and Cu(II) in di- and tri-ionic systems is studied. It is shown that the presence of extraneous ion in solution leads to a reduction (inhibition) of biosorbent sorption capacity. It is set that ion Pb (II) has the best adsorption capacity as in the case of individual ions, and in di- and tri-ionic systems. The explanation of this phenomenon from the point of the Lewis-Pearson theory of the nature of the specific binding of “hard” and “soft” ion-complex with the appropriate ligands - functionally active groups of biopolymers budding fungi cell walls is given. It is offered that the relative electronegativity of the element on the Pauling scale can be an indicator of the relative sorption capacity of heavy metal ions.

1 Introduction

The practice of applying engineering and technological methods of remediation of wastewater and surface waters confirms the advantage of sorption methods of its purification from heavy metal ions, radionuclides, organic substances and other pollutants [1,2]. At the same time, the problem of finding cheap and affordable sorbents from renewable raw materials that could compete with expensive and scarce synthetic sorbents is becoming more acute. In this regard sorbents based on waste from the food, agricultural and pharmaceutical industries can make a reasonable alternative to a range of synthetic and natural sorption materials. As studies of recent decades show, the use of sedimentary yeast Saccharomyces cerevisiae in biosorption technologies for the extraction of ecotoxicants from wastewater and surface waters does not find proper coverage, despite the fact that it is excess brewing yeast that is the most affordable, practically inexhaustible and inexpensive raw materials for creating biosorbents based on them [3,4,5,6]. Perhaps this is due to the fact that the researchers had other, more effective microorganisms at their disposal.

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should not be excluded that such recognized authorities in the field of biosorption technologies as B. Vašková, D. Kratochvíl, Z. Holan predicted the lack of demand for Saccharomyces cerevisiae yeast due to the mediocre, as they found, sorption capabilities of Saccharomyces in relation to heavy metal ions [7,8]. However, already at the beginning of the two thousandth years, Turkish [9], and then Chinese [10] and Indian [11,12] scientists have shown very acceptable biosorption capabilities for both living and dead cells of brewing yeast, in some cases even surpassing many natural and synthetic sorption materials.

Unfortunately, the vast majority of these studies considered the interactions of only an individual metal ion with a biosorbent in a heterogeneous solution–sorbent phase, which is practically not found in nature. Studies on the combined action of two or more heavy metal ions with a biosorbent are extremely few, and with the cell walls of yeast Saccharomyces cerevisiae there are none at all. In addition, the interaction of heavy metal ions with a sorbent in a multi-ion system cannot be predicted based on the results of biosorption studies of one type of heavy metal ions.

The aim of this work is to study the competitive sorption of heavy metals by the cell walls of yeast Saccharomyces cerevisiae in multi-ionic systems containing Cd(II), Cu(II) and Pb(II) ions.

2 Experimental

2.1 Materials and methods

2.1.1. Biosorbent

A biosorbent based on yeast cell walls was obtained from the sedimentary yeast Saccharomyces cerevisiae strain W-37, selected from a cylindrical-conical tank after filtration of the main product – beer. Sedimentary yeast was subjected to the following treatment: The biomass was centrifuged using a PC-6 centrifuge at 5000 rpm (~3600 g), the yeast precipitate was washed with water until a clear solution was obtained, autoclaved in the presence of 1-3% caustic soda solution in 70% ethyl alcohol at 120°C for 1.5 hours and dried in a vacuum cabinet at 65°C. The dried yeast biomass was crushed in an electric mill and sieved through a sieve with a hole diameter of 0.3–0.5 mm.

The physico-chemical properties of the biosorbent were characterized using elemental analysis, estimation of the sorption surface area by the BET method using CO₂ adsorption, as well as potentiometric and IR spectroscopic studies and described in our previously published works [2, 3].

2.1.2. Adsorbate

Initial solutions of lead (II), copper (II) and cadmium (II), (1000 mg/l) were prepared by dissolving salts of the pure for analysis Pb(NO₃)₂, Cu(NO₃)₂•3H₂O and Cd(NO₃)₂•5H₂O, respectively, in bidistilled water, and subsequently were diluted to the required concentrations. pH values of 5.5 were regulated by 0.1 n NaOH and 0.1 N HNO₃.

Double and triple mixtures of ions were obtained by mixing the initial solutions so that the concentration of each of the ions was 1.0 mM/L. The equilibrium concentrations of the studied ions in solutions were determined using an atomic absorption spectrophotometer "Aurora" in an air-acetylene flame.
2.2. Sorption experiments

The study of the sorption capacity of the biomass of yeast cell walls in relation to the ions of the studied metals was carried out by the method of equilibrium concentrations. To do this, 0.25 g of dry sorbent was introduced into a conical Erlenmeyer flask with 100 ml of a solution with a known concentration of metal ions and shaken on a horizontal shaker A V A-6S with a frequency of 150 rpm for 120 minutes. After the activation time, the contents of the flask were centrifuged at 4000 rpm and the residual concentration of metal ions in the filtrer fluid was determined. The sorption capacity of biomass was calculated by the difference in the concentrations of the initial and final solutions according to the formula:

\[
q = \frac{(C_0 - C_{eq}) \cdot V}{m}
\]

where:
- \(q\) is the sorbent capacity mg/g;
- \(C_0\) and \(C_{eq}\) – initial and final concentrations of metal ions in solution, mg/l;
- \(V\) is the volume of the solution, L;
- \(m\) is the mass of the sorbent, g.

According to the data obtained, adsorption isotherms were constructed and its parameters were calculated in Freundlich and Langmuir coordinates.

3 Results and discussion

3.1. Theoretical concepts of the sorption concentration of metal ions on the surface of the biosorbent. Specific and non-specific binding

The sorption concentration of heavy metal ions on the surface of yeast cell walls can be carried out by appropriate mechanisms of specific and non-specific binding. The first of them involves the chemical interaction of heavy metal cations with specific functional groups of biopolymers of yeast cell walls with the formation of ion-metal-sorbent complexes according to the scheme:

\[
M + aM + S \leftrightarrow K_MMS_{aM}
\]

where:
- \(M\) – metal ion (oxidation state not specified);
- \(S\) – monodentat binding site on yeast cell wall biopolymer;
- \(K_M\) is a binding constant, the value of which is determined by the affinity of a heavy metal ion to a specific functional group of a biopolymer;
- \(aM\) is the stoichiometric coefficient corresponding to the charge of the metal ion.

Plasinsky W. [13, 14], based on the admissibility of the mathematical description of biosorption, both by exchange and adsorption mechanisms, offers a formula for calculating \(K_M\),

\[
K_M = \frac{q_M}{C_M \left(N_S - \sum_i a_i q_{M_i}\right)^{a_M}}
\]

\[
M + aM + S \leftrightarrow K_MMS_{aM}
\]
Then the expression \( -\sum_i M_i S_i q a N \) represents the number of free binding sites on the surface of the sorbent. In the case of sorption in a multi-ionic system, this formula should also be supplemented with other equations similar to equation (2). Then, in the case of biosorption of two ions X and Y having close affinity with respect to homogeneous binding sites, equation (3) will take the form:

\[
K_X = \frac{q_{X(ads)}}{C_X \left(N_S - \sum_i a_i q_{M_i}\right)^{a_X}}
\]

\[
K_Y = \frac{q_{Y(ads)}}{C_Y \left(N_S - \sum_i a_i q_{M_i}\right)^{a_Y}}
\]

These equations express the amount of bound ion as a function of its concentration in solution and the number of free (unoccupied) binding sites on the biosorbent. Equation (2) is intuitive, but the stoichiometry of the specific binding reaction is not obvious even for a simple single-ion system. In addition, biopolymers of yeast cell walls contain various binding sites due to the presence of specific functional groups, each of which is chemically heterogeneous with respect to different ions, and therefore their specific contribution to the overall picture of biosorption is quite difficult to predict. For example, carboxyl and amino groups, which are found to be more responsible for biosorption, are capable of complexation by mono- and bidentate binding. At the same time, even for a relatively simple heterophase ion-metal system in an aqueous solution–biosorbent, the presence of ligands in the solution competing with the biosorbent for binding to the metal ion should be allowed. These can be water molecules that potentiate hydrolysis, and OH- ions at higher pH values, and the hydrolysis products themselves can be adsorbed on the surface of the sorbent. This picture can be further complicated by the biosorption of heavy metal ions from multicomponent solutions. It is obvious that both ions having the same affinity with respect to the binding site should have equal biosorption capabilities. On the other hand, the ion exchange of X and Y ions bound to the surface of the biosorbent and located in solution can be represented as:

\[
a_Y X + a_X Y S_{aY} \overset{k_i}{\longleftrightarrow} a_Y XS_{aX} + a_X Y
\]

\[
k = \frac{(K_X)^{a_Y}}{(K_Y)^{a_X}} = \frac{\left[\frac{q_{X(ads)}}{C_X} C_{aX}^{a_Y}\right]}{\left[\frac{q_{Y(ads)}}{C_Y}\right] C_{aY}^{a_X}}
\]
In addition to the specific binding of metal ions to the surface of the biosorbent, biosorption can be carried out by nonspecific binding, or physical sorption. Nonspecific sorption can be qualitatively characterized as an increase in the concentration of cations in the solid phase of the sorbent without the formation of a cation-sorbent complex. It is known that the surface of the cell walls of yeast Saccharomyces cerevisiae carries a negative charge of the order of \(-15\) to \(-18\) mV [15]. This causes the electrostatic attraction of positively charged metal cations.

According to the work [16] there is a relation:

$$\frac{[Z_{\text{sorb}}]}{[Z]} = \Lambda = \exp\left(\frac{-F\psi(I)}{RT}\right)$$

Here \(Z\) is the concentration of the ion carrying the charge \(Z\); \(\psi(I)\) is the Donnan potential (volts), which is a function of the ionic strength of the solution; \(F\) is the Faraday constant, 96500 coulomb.; \(R\) is the gas constant; \(T\) is the temperature, K.

\(\Lambda\) is a dimensionless quantity. For cations \(\Lambda > 1\); for anions \(\Lambda < 1\); for neutral particles \(\Lambda = 1\).

Davis [16] determined the value of \(\Lambda\) experimentally for Cd(II) ions and showed that the values of \(\Lambda\) can vary from 2.5 to 4.2 depending on the ionic strength of the solution.

This suggests that the concentration of the metal cation in the adsorption layer is significantly higher than the concentration of these cations in the entire volume of the solution. Since \(q = f(C_1, C_2, \ldots, C_i)\), then the above arguments presented in this article do not accurately characterize the real thermodynamic equilibrium between metal ions in solution and already sorbed on the biosorbent.

The consequence of this is that the constants \(K_M\), \(K_X\) and \(K_Y\) in equations (3), (4) and (6), designated by us as constants characterizing the affinity of metal ions to the biosorbent, can only be considered conditional. At the same time, it is practically an unsolvable task to isolate exclusively specific or nonspecific binding of heavy metal ions on the surface of the biosorbent, as well as their contribution to the \(q_{eq}\) equilibrium value.

Nonspecific sorption can also be complicated by the presence in the adsorbate of other anionic ligands competing with the biosorbent for binding to a metal ion, or, as already described above, the influence of \(\text{OH}^-\) ions, leading to the formation of metal precipitation with a small value of the solubility product of \(PR\).

Thus, summarizing, we come to the conclusion that the nonspecific sorption of heavy metal cations will be primarily due to the negative value of the sorbent surface potential, the charge of ions, their radius and hydration, concentration in solution, porosity and the nature of the pores of the sorbent.

3.2. Isotherms of sorption of heavy metal ions in multi-ionic systems

Figure 1 shows the adsorption isotherms for individual Cu(II) and Cd(II) ions, as well as their mixtures. From Figure 1, showing the dependence of the biosorption capacity of yeast cell walls on the equilibrium concentration of Cu (II) and Cd (II) ions, it follows that the process is characterized by classical sorption, accompanied by the formation of a monomolecular adsorbate layer on the surface of the adsorbent. At the same time, there is a significant decrease in the sorption efficiency in a binary mixture of metal ions both with respect to
Cd(II) and Cu(I) ions. This fact can be explained by the direct competition of metal ions for binding sites on the surface of the biosorbent, which are caused by the presence of specific functional active groups of biopolymers of yeast cell walls [17,18].

Fig. 1. Isotherms of adsorption of Cd(II) and Cu(II) ions by the cell walls of Saccharomyces cerevisiae yeast for a single ion and a binary system. Conditions: pH 5.5; biomass concentration 2.5 g/L; t = 25°C; shaking speed 150 rpm; activation time – 120 min.

Fig. 2 and 3 show the metamorphoses of adsorption isotherms in the linearized coordinate systems of the Freundlich and Langmuir sorption models.
Fig. 3. Isotherms (metamorphoses) of sorption for single Cd(II) and Cu(II) ions and their binary mixture by cell walls of yeast Saccharomyces cerevisiae in Langmuir coordinates. From the obtained graphical dependences, the main parameters characterizing the biosorption of individual Cu(II) and Cd(II) ions, as well as their mixtures, were calculated. The values of these parameters are shown in Table 1.

Table 1. Characteristic parameters of isotherms of adsorption of Cd(II) and Cu(II) ions by cell walls of yeast Saccharomyces cerevisiae in Freundlich and Langmuir coordinates

<table>
<thead>
<tr>
<th>Metal ion</th>
<th>Calculations based on the Freundlich equation</th>
<th>Calculations based on the Langmuir equation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$q_{eq} = K_F \frac{C}{n}$</td>
<td>$q = \frac{Q}{C} + \frac{bQ}{C}$</td>
</tr>
<tr>
<td>Cd (II)</td>
<td>2.35</td>
<td>2.88</td>
</tr>
<tr>
<td></td>
<td>3.417</td>
<td>3.670</td>
</tr>
<tr>
<td>Pb (II)</td>
<td>2.32</td>
<td>3.35</td>
</tr>
<tr>
<td></td>
<td>3.150</td>
<td>3.916</td>
</tr>
<tr>
<td>Cd (II) [Pb(II)]</td>
<td>2.35</td>
<td>2.32</td>
</tr>
<tr>
<td></td>
<td>3.417</td>
<td>3.150</td>
</tr>
<tr>
<td>Pb (II) [Cd (II)]</td>
<td>2.32</td>
<td>2.88</td>
</tr>
<tr>
<td></td>
<td>3.150</td>
<td>3.670</td>
</tr>
</tbody>
</table>

As can be seen from the table, the values of the $R^2$ regression coefficients of both models are close to each other, both for single metal ions and for their mixtures, which states the adequacy of the description of the experiment. At the same time, the Langmuir model is somewhat better suited for describing the biosorption process. The presence of an extraneous ion in the solution leads to a decrease in the biosorption capacity – $Q_{max}$ of the sorbent relative to the main component. Thus, the presence of Cd(II) ions reduces the sorption capacity of Cu(II) ions by ~ 36%, the presence of copper ions in the binary mixture reduces the sorbent capacity relative to Cd(II) ions by more than 40%.

The presence of an extraneous ion also leads to changes in other sorption parameters taken into account when describing the biosorption process: coefficient $b$, characterizing the sorption intensity for the Langmuir model, $K_F$ and $n$ for the Freundlich model.

Note: The above equations and table are placeholders for the actual mathematical expressions and data.
indicates that biosorption in a binary system of Cd(II) and Cu(II) ions can proceed by the same mechanism as for a single metal ion, and depends primarily on the affinity of the metal ions themselves to the functional active groups biopolymers of yeast cell walls, and from the initial concentration of ions.

We came to a similar conclusion in the case of studying the biosorption of other di-ion systems: Cu(II)–Pb(II) and Cd(II)–Pb(II). In the future, we have complicated the study of biosorption by applying the developed models for the triple Pb(II)–Cd(II)–Cu(II) system. The results of these studies are presented in Table 2.

Table 2. Sorption capacity of S. cerevisiae yeast cell walls with respect to Pb(II), Cd(II) and Cu(II) ions for single and multi systems

<table>
<thead>
<tr>
<th>Heavy metal ion</th>
<th>The maximum sorption capacity Qmax.</th>
<th>Total sorption capacity of metal ions in di- and triple systems, mmol/g</th>
<th>mg/g</th>
<th>mmol/g</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>single system (individual ions)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pb²⁺</td>
<td>125.0</td>
<td></td>
<td>0.603</td>
<td></td>
</tr>
<tr>
<td>Cd²⁺</td>
<td>34.96</td>
<td></td>
<td>0.311</td>
<td></td>
</tr>
<tr>
<td>Cu²⁺</td>
<td>27.93</td>
<td></td>
<td>0.439</td>
<td></td>
</tr>
<tr>
<td>binary system</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pb²⁺ + Cd²⁺</td>
<td>0.605</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pb²⁺</td>
<td>102.53</td>
<td></td>
<td>0.495</td>
<td></td>
</tr>
<tr>
<td>Cd²⁺</td>
<td>8.64</td>
<td></td>
<td>0.11</td>
<td></td>
</tr>
<tr>
<td>binary system</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pb²⁺ + Cu²⁺</td>
<td>0.628</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pb²⁺</td>
<td>92.83</td>
<td></td>
<td>0.448</td>
<td></td>
</tr>
<tr>
<td>Cu²⁺</td>
<td>11.43</td>
<td></td>
<td>0.18</td>
<td></td>
</tr>
<tr>
<td>binary system</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cd²⁺ + Cu²⁺</td>
<td>0.460</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cd²⁺</td>
<td>20.24</td>
<td></td>
<td>0.18</td>
<td></td>
</tr>
<tr>
<td>Cu²⁺</td>
<td>17.85</td>
<td></td>
<td>0.28</td>
<td></td>
</tr>
</tbody>
</table>

As can be seen from the table, Pb(II) ions have the best adsorption capacity both in the case of single and di- and tri-ion systems. The presence of foreign ions significantly reduces the adsorption of cadmium ions. In general, the adsorption of each of the ions in the mixture is less than for a single ion.
In the tri-ion system, there is also a competition of ions for binding sites, which is preferable for lead ions and partly copper, which obviously indicates a greater affinity of the functional groups of biopolymers of yeast cell walls to these ions. It also follows from Table 2 (last column) that the total molar adsorption capacity is close to or slightly higher (but within a statistical error of < 5%) than the maximum capacity of a single metal ion with preferred sorption (for Pb\(^{2+}\) ions in the bi-ion system and for Cu\(^{2+}\) ions in the Cd\(^{2+}\) system Cu\(^{2+}\)). For Cd\(^{2+}\) in the triple system, the presence of Pb\(^{2+}\) and Cu\(^{2+}\) inhibits the absorption of cadmium ions to an even greater extent, and therefore the total molar capacity for three ions is already noticeably less than for a single Pb\(^{2+}\) ion.

The theoretical explanation of this fact is as follows: specific binding is carried out due to the complexation of a metal ion with a ligand, which acts as one or more functionally active groups of biopolymers of the yeast cell wall. The effectiveness of the donor-acceptor interaction of the ligand and the complexing agent, that is, the bond strength, is determined by their polarizability—the ability to transform electronic shells under external influence. According to this feature, complexing ions and ligands, in accordance with the Lewis-Pearson theory of acid-base equilibrium, are conditionally divided into "hard", difficult to polarize, and "soft", easily polarizable [19]. "Soft" cations form more stable complexes with "soft" electron donors, and "hard" cations form with "hard" ones.

It is also generally recognized that the sorption capacity of sorbents in relation to ions carrying the same charge depends on their ionic radius [20]. Ions with a large radius exhibit a greater sorption capacity, since they are less prone to the formation of a hydrate shell, which reduces the forces of electrostatic attraction. Since lead has a larger ionic radius (1.19 Å) than copper (0.74 Å) and cadmium ions (0.95 Å), it is sorbed to the best extent on the polar sorbent, which is the cell walls of yeast.

According to the Lewis-Pearson theory, phosphate, sulfo-, carboxy- and hydroxo-groups of biopolymers of yeast cell walls should be referred to "hard" ligands, and sulfohydryl and amino groups should be referred to "soft" ones.

And, in accordance with this, Pb\(^{2+}\) ions, which are more related to "hard" cations, will be the first to form donor-acceptor bonds with "hard" ligands. When carrying out physical sorption, the dimensions of the radius of the hydrated ion, the pores of the sorbent surface themselves and their shape should also be taken into account. Thus, the hydrated radii of Pb\(^{2+}\), Cu\(^{2+}\) and Cd\(^{2+}\) ions are 4.01, 4.19 and 4.26, respectively. Therefore, hydrated Pb\(^{2+}\) ions, having a smaller radius, they have greater access to the biosorbent pores, compared with hydrated Cu\(^{2+}\) and Cd\(^{2+}\) ions.

In [20], the authors suggest that the relative electronegativity of an element can become an indicator for the comparative sorption capacity of heavy metal ions. This observation has its confirmation is also in our case: the relative electronegativity of elements on the Pauling scale decreases in the series Pb (2.33) > Cu (1.90) > Cd (1.69). Thus, lead has the greatest electronegativity in this series, and Pb\(^{2+}\) ions have the best sorption ability. In the triple system, Cd\(^{2+}\) ions are in a less favorable position for sorption.
4 Conclusions

1. The presence of an extraneous metal ion in the solution ads to a decrease in the sorption capacity of the sorbent.

2. Lead ions have the best sorption ability both in the case of an individual ion and in two- and three-ion systems, which can be explained by the nature of the specific binding of "hard" and "soft" complexing ions with the corresponding ligands - functionally active groups of biopolymers of yeast cell walls.

3. The relative electronegativity of a heavy metal on the Pauling scale can be used as a qualitative indicator of the comparative sorption capacity of the ion of this metal.

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