EXAMINING THE PROPERTIES OF DRY MAGNETICALLY CONTROLLED BIOSORBENT, OBTAINED BY THE METHOD OF MECHANICAL AND MAGNETOHYDRODYNAMIC AGITATION

S. Gorobets
Doctor of technical sciences, Professor, Head of Department*
E-mail: pitbm@ukr.net

O. Gorobets
Doctor of Physical and Mathematical Sciences, Professor*

O. Kovalyov
Postgraduate Student*
E-mail: alexej.covalew@yandex.ua

K. Hetmanenko*
E-mail: getmanenko.ka@ukr.net

S. Kovalyova

Kollegium № 11
Miry ave., 137, Chernigiv, Ukraine, 14033
E-mail: Svitlayak@gmail.com

*Department of bioinformatics
National Technical University of Ukraine
"Igor Sikorsky Kyiv Polytechnic Institute"
Peremohy ave., 37, Kyiv, Ukraine, 03056

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1. Introduction

In recent years, methods for the removal of ions of heavy metals and radionuclides from the waste water and the concentration of precious and rare metals from ores by microorganisms have been widely used. The accumulation of cations of heavy metals from aqueous solutions by microorganisms is attained by biosorption. It is known that microbial biomass may retain a significant amount of ions of metals, more than needed for their metabolism, which defines the prospect of wide use of microorganisms in the biotechnological methods of water purification from heavy metals, toxins, radionuclides, and the use of microorganisms in biometallurgy [1]. Yeast Saccharomyces cerevisiae has significant potential to accumulate a wide range of cations of metals, in particular, ions of Cd$^{2+}$, Cr$^{3+}$, Cr$^{6+}$, Cu$^{2+}$, Pb$^{2+}$ and Zn$^{2+}$ [1, 2].

The use of the magnetically tagged cells of yeast for the biosorption of heavy metals ions on the model solutions has been studied over twenty years [2, 3]. The problems of creation of magnetically-controlled biosorbent are related to a decrease in its sorption capacity due to the competition

Досліджено ефективність вилучення іонів Cu$^{2+}$ сухим магнітокерованим біосорбентом (МКБС), виготовленим методом магнітокерованих магнітних полях. Визначено сорбційну ємність, стабільність магнітних властивостей сухого МКБС у скрещених електричному та магнітному полях, з різною концентрацією магнітних наноміток. Показано, що ступінь вилучення іонів міді сухого МКБС, виготовленого методом МГДП у скрещених електричному та магнітному полях, з 22 % більше, ніж сухого МКБС, виготовленого методом механічного перемішування.

Ключові слова: сухий МКБС, біосорбція, наночастики магнетиту, механічне перемішування, МГДП у скрещених електричному та магнітному полях.

Исследована эффективность удаления ионов Cu$^{2+}$ сухим магнитоуправляемым биосорбентом (МКБС), изготовленного методом магнитогидродинамического перемешивания (МГДП) в скрещенных электрическом и магнитном полях. Определена сорбционная емкость, стабильность магнитных свойств сухого МКБС в скрещенных электрическом и магнитном полях, с разной концентрацией магнитных наноприемоток. Показано, что степень удаления ионов меди сухим МКБС, изготовленного методом МГДП в скрещенном электрическом и магнитном полях, на 22 % выше, чем сухого МКБС, изготовленного методом механического перемешивания.

Ключевые слова: сухой МКБС, биосорбция, наночастицы магнетита, механическое перемешивание, МГДП в скрещенном электрическом и магнитном полях.

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of magnetic nanoparticles and heavy metals ions for binding sites at the surface of the resulting biosorbent [4].

Magnetically tagged yeast cells might be used as biosensors and biocatalysts and are used in the microfiltration of toxic substances, as well as effective adsorbents of different types of organic and inorganic xenobiotics [5].

Laboratory study of the sorption of ions Cu$^{2+}$ by magnetically tagged yeast demonstrated that sorption capacity of magnetically tagged biosorbent, prepared with the help of multi-vortex MHDS, does not decrease compared to native yeast [4, 6].

MCBS is obtained with the use of mechanical and multi-vortex MHDS of *Saccharomyces cerevisiae* yeast biomass with magnetic nanoparticles (magnetic fluid).

An alternative to using dry MCBS for wastewater treatment is the ion exchange resin, the price of which is 10–15 times higher than the price of dry MCBS [7]. Traditional methods of using biosorbents in aerotanks, tanks and biofilters, where constant support for their living activity is needed, require additional costs [8].

### 2. Literature review and problem statement

In recent years, the process of biosorption has become economic and ecological alternative to the technology of purification of drinking water and industrial wastewater. In this regard, a number of biosorbents were developed, which are successfully applied for the cleaning from a variety of pollutants, including ions of metals, dyes, phenols, fluoride and medicines in solutions (aqueous or oil) [6]. These materials provide the basis for an entirely new technology of removing and restoring the ions of heavy metals [9].


An effective way to remove ions of Pb(II) from aqueous solution using adsorbent from Aspergillus Niger was also investigated [14]. The biomass of native yeast *Saccharomyces CERVISIAE* is used to remove lead, mercury and nickel in the form of ions, dissolved in water [15]. There is an interesting study [16] to use *S. cerevisiae* as a biosorbent to restore the phenolic compounds. A biosorbent based on native yeast *Saccharomyces CERVISIAE* is also effectively used for the biosorption of manganese from ground water [17].

The above mentioned papers address biosorption by native and native modified magnetic biosorbents. Analyzing materials of the given articles, there is a remaining unresolved issue of uneven magnetic tagging, which reduces the effectiveness of cleaning and removal of modified magnetic biosorbents by magnetic filters. Hence a promising question of exploring the properties of dry MCBS manufactured in the crossed electric and magnetic fields to improve the processes of biosorption of heavy metals ions and other contaminants, and the extraction of modified magnetic biosorbents by magnetic filters.

### 3. The aim and tasks of the study

The aim of the study is to compare the properties of dry MCBS obtained by different methods of stirring and manufactured with different concentration of magnetic nanotags.

To achieve the aim, the following tasks were to be solved:

- to determine the optimum conditions for manufacturing dry MCBS in the crossed electric and magnetic fields and by the method of mechanical stirring;
- to examine a dependence of the size of the clusters, which are formed in the process of manufacturing dry MCBS in the crossed electric and magnetic fields and by the method of mechanical agitation with different concentration of magnetic nanotags on the sorption capacity of the Cu$^{2+}$ ions;
- to determine stability of magnetic properties and the degree of extraction of copper ions by dry MCBS in the crossed electric and magnetic fields and by the method of mechanical agitation, made with different concentration of magnetic nanotags;
- to study sorption capacity of dry MCBS manufactured with different concentration of nanotags and obtained by different methods of agitation.

### 4. Materials and methods of research

#### 4.1. Method of obtaining dry MCBS using mechanical agitation

We used pressed baking yeast *Saccharomyces cerevisiae* made by PrAT “Company Enzyme” (Ukraine) during experiments.

For the preparation of MCBS based on yeast *Saccharomyces cerevisiae*, to a glass cup with capacity 200 cm$^3$ we added 4 g of yeast, which was dissolved in 99.33 ml of distilled water, then we introduced 0.67 ml of magnetic liquid and stirred using a mixer with rotation frequency 180 min$^{-1}$ [18]; in this case, the solution pH is 5.5, during 10 minutes. Weighing the sample of yeast was carried out using analytical scales Radwag AS-60/220/S (Fig. 1). Measurement of pH indicator was carried out by the ionomer І-160МІ; in this case, the solution pH is 5.5, during 10 minutes. Weighing the sample of yeast was carried out using analytical scales Radwag AS-60/220/S (Fig. 1). Measurement of pH indicator was carried out by the ionomer І-160МІ (Fig. 2). We obtained a suspension of yeast of concentration 100 mg/dm$^3$. This suspension was filtered through the filter “white ribbon” and took the sediment into heat-resistant ceramic mortars and dried in a drying chamber at temperature 105 °C for 3–4 hours until maintaining constant weight. The resulting dry MCBS was carried over to a glass crucible and stored in a desiccator.

![Image](fig1.png)

Fig. 1. General view of the analytical scales AS Radwag-60/220/S
4. 2. Method of obtaining dry MCBS at MHDS in the crossed electric and magnetic fields

MCBS was received by mixing yeast biomass Saccharomyces cerevisiae with the solution of magnetite so that the ratio of mass of biosorbent to the mass of magnetite is 100:1; in this case, the concentration of yeast cells equaled \(8 \times 10^9\) cells/dm\(^3\) (100 mg of dry yeast per 1 dm\(^3\)), and the concentration of particles of magnetite in the original solution – 1 mg/dm\(^3\). We reduced the solution pH by nitric acid to 2.5 [19] and prepared modified biosorbent in external electric and magnetic fields [20] for 6 minutes at magnetic field intensity 240 kA/m and electric current 0.5 V.

Next, the mixture of MCBS based on yeast Saccharomyces cerevisiae was fractioned through highly gradient ferromagnetic caps in magnetic field at 3500 E in portions of 100 ml. What remained at the caps in the filter was washed out with a small amount of distilled water. Then the received suspension was filtered through the “white ribbon” filter and the sediment was carried over into the heat-resistant ceramic cups and dries in the drying chamber at temperature 105 °C for 3–4 hours to gaining constant weight to obtain completely dry substance (CDS). The resulting dry MCBS was moved into a glass crucible and stored in a desiccator.

4. 3. Method for determining the effectiveness of dry MCBS

Dry MCBS was ground by electric mill. Then dry MCBS was fractioned using the sieves of different diameter (0.1 mm; 1.0 mm; 2.0 mm) and the sorption capacity of each fraction of MCBS was tested in relation to the Cu\(^{2+}\) ions.

Biosorption of dry MCBS was conducted at mechanical agitation of the solution during 60 min. The concentrations of dry MCBS comprised 0.2; 0.6; 1.0 g/dm\(^3\). The starting concentration of the Cu\(^{2+}\) ions was 50 mg/dm\(^3\).

After every 10 min., the sample was selected and passed through a paper filter (pore diameter is 10 nm) for the removal of magnetically tagged yeast cells. Then we calculated the cleaning effect from the ions of copper. By the effect of cleaning the solution from the ions of copper, we draw a conclusion on the effectiveness of MCBS.

4. 4. Method of determining residual amount of copper ions after conducting the biosorption with dry MCBS, obtained by the method of mechanical and MHDS

A residual concentration of the Cu\(^{2+}\) copper ions in the solution after conducting the process of sorption with dry MCBS, received by the mechanical and MHDS method based on baking yeast S. cerevisiae, was determined by evaluating the number of ammonia complexes in the working solution (spectrophotometric determining method).

4. 5. Method of simulated biosorption to study the stability of magnetic favorability of dry MCBS

After obtaining dry MCBS by the MHDS method in the crossed electric and magnetic fields, we tested the stability of magnetic favorability for establishing the optimal time of stirring when obtaining dry MCBS. This was carried out by the process of mechanical agitation of the resulting dry MCBS at the parameters of the system, which recreate (simulate) the process of biosorption of heavy metals ions without adding the copper ions: pH=5.5, concentration of yeast biomass – 4 g/dm\(^3\); agitation velocity – 180 min\(^{-1}\); maximum time of agitation is 50 minutes. After every 10 min, the sample was taken and was centrifuged (the centrifuge CLMN-R10-01 “Elecon”, rotor rotation frequency is 1500 min\(^{-1}\)). The magnetite, which was desorbed from the surface of dry MCBS in the stirring process (that is, in the process of simulation of the copper ions sorption), remained in the supernatant fluid, which was examined for the magnetic favorability.

4. 6. Method for determining the dry MCBS magnetic favorability

Magnetic favorability was measured by the experiment installation [21] for radio resonance method of investigating magnetic favorability of the samples.

The installation includes an oscillograph, an electronic computing cymometer, Q meter and LC-circuit. The LC-circuit consists of a capacitor and the solenoid made of copper wire. Inside the solenoid is a cylindrical container for the sample. A signal from the generator of Q meter arrives at the LC-circuit. Using the oscillograph, visual observation of the signal is conducted. The cymometer determines the magnitude of the resonance frequency of the circuit. Determining the magnetic favorability is performed at frequencies 12–20 MHz with error not exceeding 0.2 % [21].

4. 7. Method for measuring the dry MCBS sorption capacity

Determining the concentration of the copper ions was performed by using the spectrophotometer ULAB 102 (Fig. 3). The copper solution at concentration to 50 mg/dm\(^3\) is a colorless liquid. A method for determining the existence of Cu\(^{2+}\) ions in the solution is based on the reaction between this metal and the aqueous solution of ammonia:

\[
\text{Cu}^{2+} + 4\text{NH}_3 \rightarrow [\text{Cu} (\text{NH}_3)_{4}]^{2+},
\]

as a result of which the solution takes on a blue shade.

25 ml of each of the solutions (or of the examined sample) was added with 10 ml of the ammonia solution and 15 ml of distilled water. We determined optical density using the spectrophotometer ULAB 102 at absorption wavelength 590 nm [18].
5. Results of studying dry MCBS, obtained by various methods of agitation

5.1. Study of particle size of dry MCBS after grinding

The study of clusters dispersibility of MCBS was carried out using the optical microscope REMT-100 with magnification ×20. For this purpose, we prepared MCBS by the following parameters:

- mechanical agitation, concentration of magnetic nanotags – 1.0 %, 0.6 %, 0.2 %, drying temperature 105 °C, Fig. 4, a, b, d, f;
- MHDS in the crossed electric and magnetic fields, pH=2.5, U=0.5 V, the concentration of magnetic nanotags – 1.0 %, 0.6 %, 0.2 %, drying temperature 105 °C, Fig. 4, a, c, e.

After drying to constant mass, BS was ground, sorbed, then we prepared the samples that were coated with a nanofilm.

Using the IMAGEJ software, we defined mean size of the particles of dry biosorbent after grinding. Results are presented in Table 1.

Dimensions of the MCBS particles, manufactured by the MHDS method in the crossed electric and magnetic fields, at the corresponding concentrations of magnetic nanotags, are 6 times smaller than the size of the MCBS particles fabricated at mechanical agitation.

<table>
<thead>
<tr>
<th>Concentration of magnetic nanotags</th>
<th>Type of agitation</th>
<th>Quantity of particles</th>
<th>Mean size, mm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2 %</td>
<td>Mechanical agitation</td>
<td>451</td>
<td>0.006</td>
</tr>
<tr>
<td></td>
<td>MHDS in the crossed electric and magnetic fields</td>
<td>1353</td>
<td>0.002</td>
</tr>
<tr>
<td>0.6 %</td>
<td>Mechanical agitation</td>
<td>239</td>
<td>0.012</td>
</tr>
<tr>
<td></td>
<td>MHDS in the crossed electric and magnetic fields</td>
<td>736</td>
<td>0.002</td>
</tr>
<tr>
<td>1.0 %</td>
<td>Mechanical agitation</td>
<td>186</td>
<td>0.016</td>
</tr>
<tr>
<td></td>
<td>MHDS in the crossed electric and magnetic fields</td>
<td>2162</td>
<td>0.003</td>
</tr>
</tbody>
</table>

Fig. 4. Images of MCBS, manufactured by mechanical agitation and the MHDS method in the crossed electric and magnetic fields with different content of magnetite: a – MHDS in the crossed electric and magnetic fields (0.2 % magnetite); b – mechanical agitation (0.2 % magnetite); c – MHDS in the crossed electric and magnetic fields (0.6 % magnetite); d – mechanical agitation (0.6 % magnetite); e – MHDS in the crossed electric and magnetic fields (1.0 % magnetite); f – mechanical agitation (1.0 % magnetite)

5.2. Examining magnetic favorability of dry MCBS manufactured by mechanical agitation and the MHDS method in the crossed electric and magnetic fields

In order to examine magnetic favorability, we prepared dry MCBS according to the following parameters:

- mechanical agitation, concentration of magnetic nanotags – 1.0 %, 0.6 %, 0.2 %, drying temperature 105 °C;
- MHDS in the crossed electric and magnetic fields, pH=2.5, U=0.5 V, the concentration of magnetic nanotags – 1.0 %, 0.6 %, 0.2 %, drying temperature 105 °C.

After drying to constant mass, BS was ground, simulated sorption was carried out and we determined magnetic favorability of the solution after agitation.

The value of magnetic favorability of MCBS manufactured by the MHDS method in the crossed electric and magnetic fields is 2 times larger than the magnetic favorability of MCBS manufactured at mechanical agitation.

The mean deviation of magnetic favorability during simulated biosorption for MCBS manufactured by the MHDS
method in the crossed electric and magnetic fields is 2–4 %. The mean deviation of magnetic favorability for MCBS manufactured at mechanical agitation is 28–34 %.

5. 3. Examining the sorption capacity of dry magnetic-controlled biosorbent manufactured at mechanical agitation and by the MHDS method in the crossed electric and magnetic fields

In order to examine the sorption capacity, we prepared dry MCBS at such parameters:

- mechanical agitation, the concentration of magnetic nanotags – 1.0 %, 0.6 %, 0.2 %, drying temperature 105 °C.
- MHDS in the crossed electric and magnetic fields, pH=2.5, U=0.5 V, the concentration of magnetic nanotags – 1.0 %, 0.6 %, 0.2 %, drying temperature 105 °C.

After drying to constant mass, BS was ground; we conducted sorption and determining the residual amount of the Cu²⁺ ions in the solution after agitation.

The effectiveness of dry MCBS manufactured by the MHDS method in the crossed electric and magnetic fields is larger than that of dry MCBS manufactured by the method of mechanical agitation.

6. Discussion of results of examining dry MCBS obtained by different methods of stirring

Magnetic favorability of dry MCBS obtained by MHDS in the combined electric and magnetic field is 2 times larger than the magnetic favorability of MCBS manufactured at mechanical agitation. With a regard to this, it was concluded that MCBS, obtained by using MHDS in the combined electric and magnetic field, possesses more stable magnetic characteristics.

Magnetic favorability of dry MCBS, obtained by using mechanical agitation, was lower than that of the dry MCBS, obtained by using MHDS in the crossed electric and magnetic fields. Thus, MCBS, obtained by mechanical agitation, demonstrates less stable magnetic characteristics.

Dry MCBS manufactured by the MHDS method in the crossed electric and magnetic fields, under according concentrations of magnetic nanotags, forms clusters that are 1.5–3 times smaller than the dry MCBS manufactured at mechanical agitation.

That is why dry MCBS manufactured by the MHDS method in the crossed electric and magnetic fields possesses a larger surface area, therefore, more binding sites for the ions of heavy metals and large sorption capacity.

Dry MCBS, obtained by using mechanical agitation, possesses a larger degree of clustering and a smaller surface area with free bind-

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Table 2

<table>
<thead>
<tr>
<th>Concentration of magnetic nanotags</th>
<th>Type of agitation</th>
<th>Effectiveness of removal of the copper ions, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,0 %</td>
<td>Mechanical agitation</td>
<td>60</td>
</tr>
<tr>
<td>0,6 %</td>
<td>Mechanical agitation</td>
<td>76</td>
</tr>
<tr>
<td>0,2 %</td>
<td>MHDS in the crossed electric and magnetic fields</td>
<td>60</td>
</tr>
<tr>
<td>1,0 %</td>
<td>MHDS in the crossed electric and magnetic fields</td>
<td>82</td>
</tr>
<tr>
<td>0,6 %</td>
<td>MHDS in the crossed electric and magnetic fields</td>
<td>60</td>
</tr>
<tr>
<td>0,2 %</td>
<td>MHDS in the crossed electric and magnetic fields</td>
<td>82</td>
</tr>
</tbody>
</table>
ing plots of the ions of heavy metals and, therefore, lower absorption capacity.

Fig. 6 demonstrates that there is a larger sorption capacity for dry MCBS received by the MHDS method in the crossed electric and magnetic fields at magnetite concentration of 0.2–0.6 %. Lower sorption capacity is observed for dry MCBS obtained by mechanical agitation at the concentration of magnetite 0.6 %. The results correlate with the conclusion that increasing the degree of clustering in the already mentioned dry MCBS leads to the reduction in sorption capacity for biosorbent, obtained by means of mechanical agitation. But, as it was demonstrated, the degree of clustering for dry MCBS, obtained by using mechanical agitation, much is much larger than that of the dry MCBS received using MHDS in the crossed electric and magnetic fields.

After 10 minutes into the process of sorption, using dry MCBS obtained in the crossed electric and magnetic fields, the absorption of copper ions from the solution is 60 % higher than when using dry MCBS received by mechanical agitation. It is obvious (Fig. 6) that sorption capacity reaches 82 % of the initial concentration of the Cu²⁺ ions in the solution after 20 minutes.

As demonstrated in the patent [20], native MCBS, obtained by using MHDS in the crossed electric and magnetic fields, has a larger efficiency of extraction of the ions of copper by 8 % than dry MCBS, obtained by the same method. An advantage of dry MCBS, obtained by using MHDS in the crossed electric and magnetic fields, is in the storage and transportation. The study is useful by the fact that the dry MCBS, obtained by using MHDS in the crossed electric and magnetic fields may be removed under rapid mode using magnetic separation. It might also be applied to remove heavy metals from the wastewater of electroplating enterprises. Further research may be devoted to increasing the degree of extraction of copper ions from the solution.

### 7. Conclusions

1. The optimum conditions for the manufacture of dry magnetic-controlled biosorbent: pH of the solution – 2.5, magnetic field intensity – 240 kA/m and voltage of electric current – 0.5 V, agitation period – 6 min., temperature drying – 105 °C.

2. Mean dimensions of the MCBS clusters manufactured by the MHDS method in the crossed electric and magnetic fields are 3 times smaller than the average size of clusters of MCBS manufactured at mechanical agitation.

3. Sorption capacity of dry MCBS manufactured by the MHDS method in the crossed electric and magnetic fields is 30–40 % larger than that of dry MCBS manufactured at mechanical stirring. Stability of magnetic favorability of the magnetic-controlled biosorbent, manufactured by the MHDS method in the crossed electric and magnetic fields is maintained in the process of agitation within 2–4 %, while that of the MCBS manufactured with mechanical agitation – within 28–34 %.

4. The efficiency of extraction of the ions of copper by dry MCBS, manufactured by the MHDS method in the crossed electric and magnetic fields, is 82 %, and for the dry MCBS, manufactured by the method of mechanical agitation, is 60 %. That is, sorption capacity of the dry MCBS, manufactured by the MHDS method in the crossed electric and magnetic fields is 1.4 times larger than that of dry MCBS manufactured at mechanical stirring.

### References


