IMMOBILIZATION OF Cu(II) IONS FROM AQUEOUS SYSTEMS INTO ECO-FRIENDLY, LOW-COST BIOMATERIAL

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Această lucrare analizează capacitatea drojdiei uscate de panificație, Saccharomyces cerevisiae (de tip comercial) de a adsorbi ionii de Cu(II) din soluții apoase sintetice. Datele obținute la echilibru au fost corelate conform modelelor Langmuir, Freundlich, Redlich-Peterson şi Temkin. Rezultatele experimentale obținute pentru capacitatea de adsorbție (Q_{max}=15.6 mg Cu(II)/g) şi randamentul de îndepărtare (Y_{max}=73.02%), confirmă faptul că S. cerevisiae reprezintă un biosorbent eficient pentru îndepărtarea ionilor de Cu(II) din soluții apoase sintetice.

This paper analysis the ability of dry Baker's yeast Saccharomyces cerevisiae (commercial type) for adsorbing Cu(II) ions from synthetic aqueous solutions. The copper biosorption equilibrium was described using the Langmuir, Freundlich, Redlich-Peterson and Temkin models. The experimental results obtained for the adsorption capacity (Q_{max}=15.6 mg Cu(II)/g) and removal efficiency, respectively (Y_{max}=73.02%), confirmed that S. cerevisiae represents an effective biosorbent for the removal of Cu(II) ions from synthetic aqueous solutios .

Keywords: Cu(II), aqueous systems, biosorption, biomaterials, *S. cerevisiae.*

1. Introduction

The natural capacity of microrganisms, yeasts, fungi, algae and plants to uptake inorganic contaminants and, in some cases, to promote their conversion to less toxic forms has received increasing attention from scientists during the past decades [1, 2].

Biosorption is the property of living and non-living biomass (biosorbents) to uptake and concentrate inorganic or organic compounds even from very diluted aqueous solutions, to the surface of cellular wall or membrane in an equilibrium process [1,3]. More recently, it has been discovered that biosorption is the physical or chemical interaction between metal ions and the functional groups

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present in the structure of the biomass. That is why, biosorption can be classified as a typical adsorption process [3].

Biosorption is a metabolically-passive process that covers the immobilization of heavy metals as well as rare earth elements and radionuclides or metalloids, but the research and applications extended to the removal of organic compounds (dyes) and for the recovery of high-value proteins, steroids, pharmaceuticals and drugs [1,2].

There are various classes of biosorbents: by-products or waste materials, naturally grown and collected biomass, and especially propagated biomass. The biomaterials used in the field of biosorption can be of microbial *(B. subtillis, E. coli)*, fungal *(R. arrhizus, A. niger)*, yeast *(S. cerevisae*), seaweed *(S. natans, A. sargassum)*, plant *(L. stolonifera, S. nigrum)* or animal (*eggshells, bones*) origin [3-9].

The presence of toxic metals (such as Hg, Cr, Pb, Zn, Cu, Ni, Cd, As, Co, Sn, etc.) and radionuclides (such as U, Th, Ra, Am, etc.) in the environment is not desired, therefore their emission by the industry is regulated by law [3, 4, 10, 11].

Heavy metals represent an important environmental problem due to their potential toxic effects, and their accumulation throughout the food chain leads to serious ecological and health problems.

It is difficult to employ conventional methods to remove metal ions below the level of ppm since these methods if applied at such low concentrations cause that the final costs of the process become more expensive and highly energy consuming [3]. These disadvantages of conventional technologies created the need to elaborate a new generation of efficient methods of environmental prevention, protection and restoration, as well as monitoring [3].

Compared to conventional wastewater decontamination techniques, the advantage of biosorption. not only in that it can be operated under a extensive range of conditions (pH, temperature, concentration) but especially that it appears to be economically attractive due to the low-cost biological materials that can be used as biosorbents, which can be easily regenerated and reused [12]. The method also offers efficient removal and recovery of metal(s) from aqueous solution, minimization of chemical/biological sludge, and has no requirement of additional nutrients [13].

Of the many sort of biosorbents recently investigated for the biosorption ability of heavy metals, *S. cerevisiae* has proven to be one of the most promising, as well as reliable and effective for the removal of heavy metal ions from large volume and low concentration solutions, because it is easy to get from fermentation industry as a by-product, safe, easy to identify the molecular mechanism of biosorption and can be produced in large quantities [1].

S. cerevisiae cell wall consists of a number of polymers involved in the adsorption process, such as: β-glucan (28.8%), mannan (31%), proteins (13%),

lipids (8.5%), chitin/ chitosan (2%) and it also contains inorganic ions (Ca^{2+}, Mg^{2+}, 2%) [14, 15].

Some data regarding the adsorption capacities of *S. cerevisiae* and other sorbent materials for Cu(II) ions is presented in Table1.

Table 1

Adsorption capacities of different sorbent materials for copper ions [3-5, 10]

Metal	Sorbent material	Adsorption capacity[1], mg/g
Cu(II)	*Saccharomyces cerevisiae*	1 – 25.4
	Ganoderma lucidum	10
	Penicillium spinulosum	2 - 6
	Penicillium chrysogenum	9
	Penicillium italicum	0.4 - 2
	Phanerochaete chrysosporium	20.23
	Aspergillus niger	0.7 – 15.6
	Rhizopus oryzae	6.06
	Rhizopus arrhizus	10.8
	Sargassum natans	2
	Bacillus sp.	16.3
	Candida sp	4.80
	Chitin	0.438
	Tea leaves	27
	Oil-palm fibre	1.98
	Rice hulls	3.58
	Peat	16.4
	Activated sluge	5.54
	Activated carbon	9.22

[1]Adsorption capacity is not necessarily maximum

The aim of this study was to assess the ability of dry Baker's yeast (commercial type) to remove Cu(II) ions from synthetic aqueous solutions under different operating conditions. The Cu(II) adsorption capacity, removal efficiency and adsorption equilibrium were determined in order to describe the biosorption process. The effects of initial concentration and contact time on Cu(II) adsorption capacity by the dry Baker's yeast biomass was also studied.

2. Experimental

2.1. Chemicals

Commercial dry Baker's yeast (*S. cerevisiae* strain) available from local commercial company, was prepared as non-living biomass by drying in a hot air oven at 105ºC for 24 h.

Copper stock solution of 1000 mg/L was prepared using $CuSO_4 \cdot 5H_2O$ of analytical reagent grade. Copper solutions of different concentrations (10, 26, 50, 105, 150 and 196 mg/L) were obtained by diluting the stock solution.

The pH of the solutions was adjusted by addition of H_2SO_4 0.1 M or NaOH 0.1M solutions.

2.2. Equipments

The aqueous samples were analyzed for Cu(II) final concentration using an UNICAM PAY SP9 Atomic Absorption Spectrophotometer. The pH values were measured with an ORION 290 A pH-meter. The batch experiments were carried out using an HEILDORPH VIBRAMAX 100 orbital shaker.

2.3. Methods

Metal ions biosorption studies were realised under batch conditions with continuously stirring (200 rpm), at room temperature (20 °C), pH=4.5, by adding a constant dose of dry Baker's yeast biomass of 0.5g/ 100 mL sample, for 30 minutes.

Experiments to evaluate the effect of initial Cu(II) concentration were conducted in the range of 10–196 mg/L. Further experiments were proceeded in order to investigate the effect of contact time, during which samples were withdrawn after 30, 60, 90, 120, 150, 180, 360 and 1440 min. After that, the metal loaded biomass was separated from the metal solutions by decantation and the liquid phase was analyzed for Cu(II) final concentrations by atomic absorption spectrophotometry (AAS).

The adsorption isotherms were obtained using a similar procedure as for the biosorption experiments previously mentioned.

The equilibrium adsorption capacity was determined by means of equation (1) [16]:

$$Q_e = \frac{(C_0 - C_e) \times V}{m \times 1000} \tag{1}$$

The removal efficiency Y% was determined by means of equation (2) [16]:

$$Y = \left(1 - \frac{C_e}{C_0}\right) \times 100 \tag{2}$$

The isotherm parameters were determined by means of the following expressions (3 – 5):

The general form of the Langmuir equation can be expressed as [11, 17]:

$$Q_e = \frac{Q \max K_L C_e}{1 + K_L C_e} \tag{3}$$

The essential characteristics of Langmuir isotherm can be explained in terms of a dimensionless constant separation factor (R_L), defined by:

$$R_L = \frac{1}{1 + K_L C_0} \tag{4}$$

The value of R_L indicates the type of Langmuir isotherm: irreversible (R_L = 0), favorable ($0 < R_L < 1$), linear ($R_L = 1$), or unfavorable ($R_L > 1$) [17].

The Freundlich equation is a semi-empirical one [11, 16, 17] employed to describe heterogeneous systems, and can be expressed as:

$$Q_e = K_F C_e^{1/n} \tag{5}$$

3. Results and discussion

3.1. Adsorption equilibrium models

The copper biosorption equilibrium was described using the Langmuir, Freundlich, Redlich-Peterson and Temkin models (Figure 1 - 5), which are widely used to fit adsorption data.

The analysis of equilibrium data is important for developing a model that can be used for the design of biosorption systems [18].

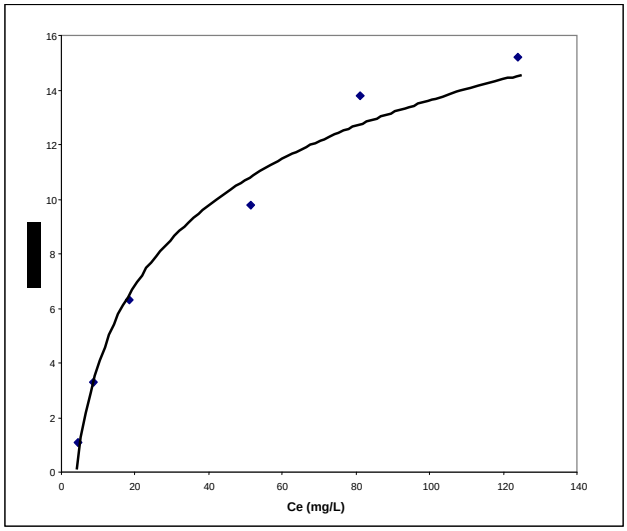

Fig. 1. Adsorption isotherm of Cu(II) biosorption on dry Baker's yeast biomass at pH 4.5

The equilibrium adsorption data are satisfactorily fitted in the order:
Langmuir > Freundlich >Redlich-Peterson > Temkin (Fig. 2 - 5).

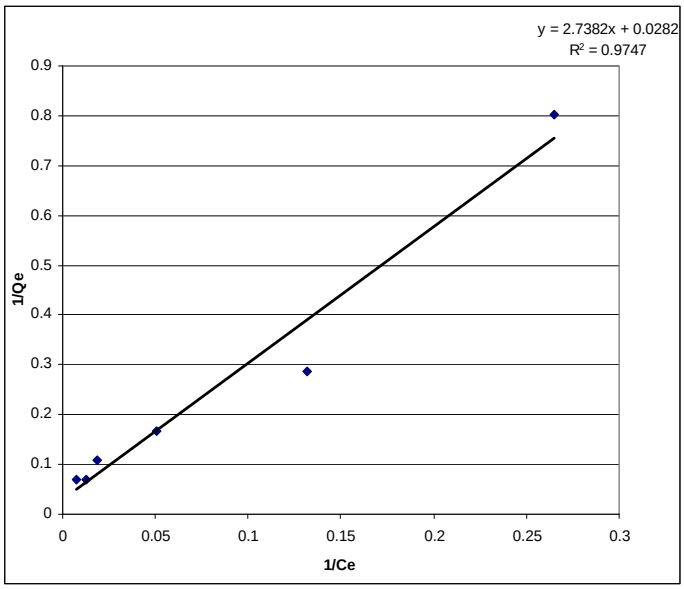

Fig. 2. Langmuir adsorption model of Cu(II) biosorption on dry Baker's yeast biomass

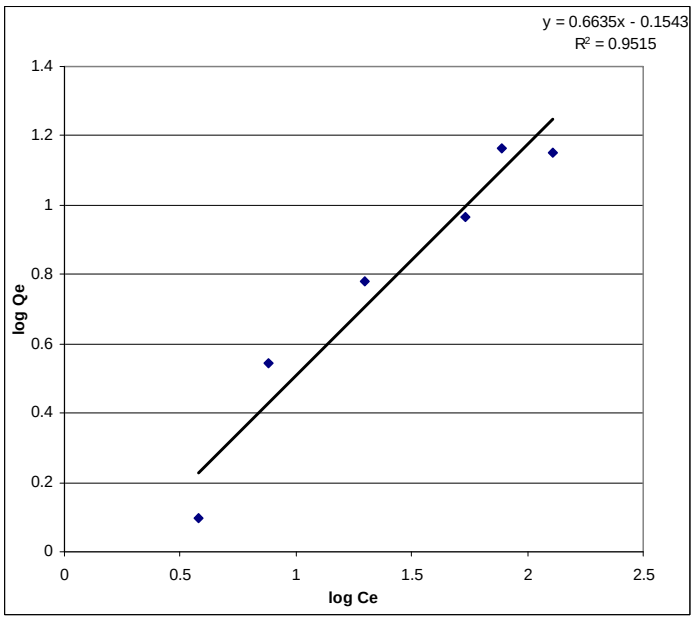

Fig. 3. Freundlich adsorption model of Cu(II) biosorption on dry Baker's yeast biomass

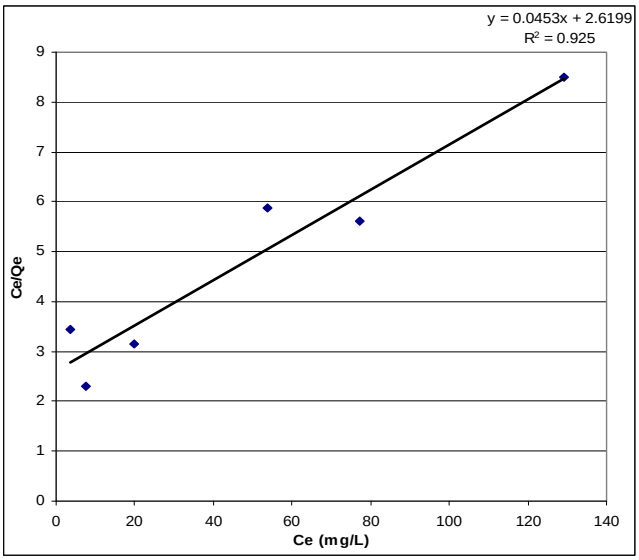

Fig. 4. Redlich-Peterson adsorption model of Cu(II) biosorption on dry Baker's yeast biomass

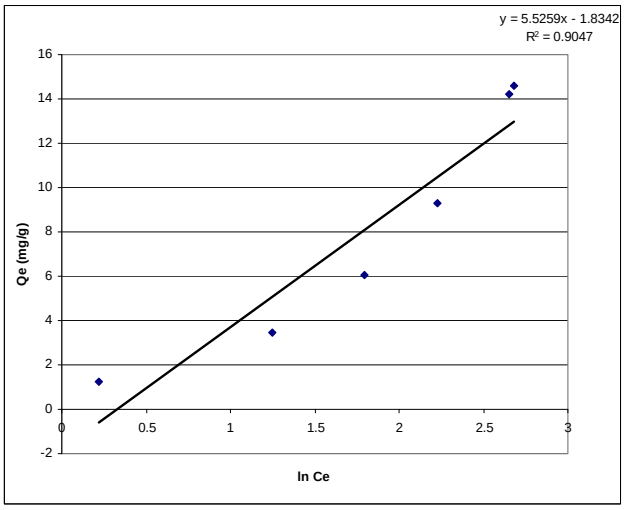

Fig. 5. Temkin adsorption model of Cu(II) biosorption on dry Baker's yeast biomass

From the linear log Qe vs. log Ce plot (Fig. 3), a correlation coefficient (R^2) of 0.9515 was determined, which is smaller than that obtained for the Langmuir model (Fig.2), 0.9747. Therefore, it was concluded that Cu(II) biosorption on dry Baker's yeast biomass followed a Langmuir isotherm. Since the values of the correlation coefficients for Redlich-Peterson and Temkin models were much smaller (0.9250 and 0.9047, respectively), they were not considered.

3.2. Isotherm parameters for Cu(II) biosorption on dry Baker's yeast biomass

The isotherm parameters for both Langmuir and Freundlich isotherms are presented in Table 1.

Table 1

Isotherm parameters for Cu(II) biosorption on dry Baker's yeast biomass

Langmuir isotherm				Freundlich isotherm		
K_L(L/mg)	Q_{max}(mg/g)	R_L	R^2	K_F	*1/n*	R^2
2.7382	15.2	0.0072	0.9747	0.6206	0.6635	0.9515

Q_{max} and K_L were determined from the slope and intercept of the Langmuir isotherm plot (Fig. 2) and were found to be 15.2 mg/g and 2.7382 L/mg respectively. The value of R_L was 0.0072, therefore it indicates that the Langmuir isotherm was favorable.

K_F and $1/n$ were calculated from the slopes of the Freundlich plots (Fig. 3) and were found to be 0.6206 and 0.6635 respectively. The value of n is related to the distribution of bonded ions on the biosorbent surface.

3.3. Influence of initial concentration and contact time on the adsorption capacity

The effect of initial concentration on the adsorption capacity at pH 4.5 with increasing contact time is presented in Fig. 6.

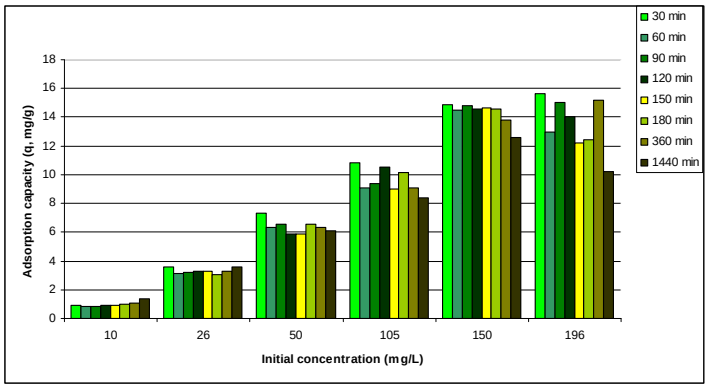

Fig. 6. Effects of initial concentration and contact time on the adsorption capacity of the dry Baker's yeast biomass

From Fig. 6 it can be observed that the adsorption of Cu(II) on the dry Baker's yeast biomass increased with the increase of the initial concentration. Maximum adsorption capacities at pH=4.5, after 30 min. contact time increased

from 1.347 mg $Cu^{2+}g^{-1}$ for an initial copper concentration of 10 mg/L to 15.6 mg $Cu^{2+}g^{-1}$ for an initial concentration of 196 mg/L.

Fig. 6, also shows that the adsorption capacity of Cu(II) on the dry Baker's yeast biomass increases with the increase of the contact time and initial concentration for the diluted samples and in case of the more concentrated samples the adsorption capacity decreased with increase of contact time (due to the fact that with increasing contact time the process becomes reversible, and desorption occurs, due to the saturation of the biomass).

3.4. Influence of contact time on the removal efficiency

The effect of contact time on the removal efficiency of Cu(II) by the dry Baker's yeast biomass is summarized in Fig. 7.

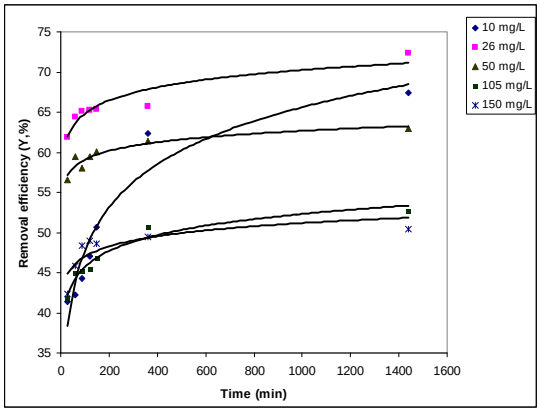

Fig. 7. Effect of contact time on Cu(II) removal efficiency by dry Baker's yeast biomass for different initial concentrations

The contact time was varied from 30 min. to 1440 min.(24 h). Fig. 7 shows that the Cu(II) removal from synthetic aqueous solutions by the dry Baker's yeast biomass was rapid in the first minutes.

3.5. Influence of the initial concentration on the maximum removal efficiency

The results of maximum percentage removal efficiency of Cu(II) at pH 4.5 with increasing initial concentration are presented in Fig. 8.

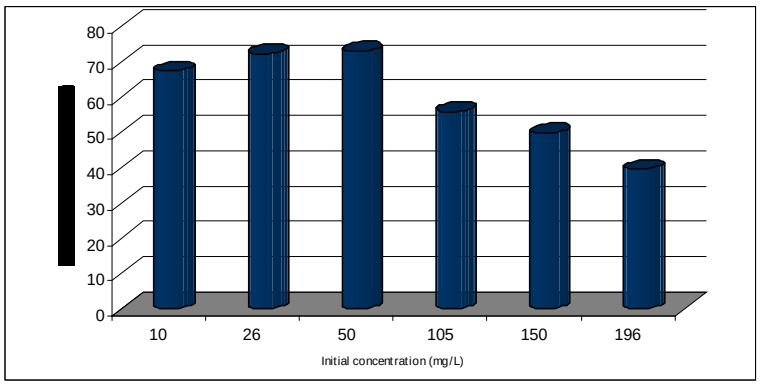

Fig. 8. Influence of the initial concentration on maximum removal efficiency (Y max) obtained during Cu(II) adsorption experiments

The maximum values of the percentage removal efficiency were 72.36% and 73.02% reached for an initial concentration of 26 mg/L and 50 mg/L respectively. Fig. 8, also illustrates that for the most diluted samples, the removal efficiency of Cu(II) by the dry Baker's yeast biomass increased with the increase of the initial concentration. On the contrary, for the most concentrated samples, the removal efficiency slightly decreased with the increase of the initial concentration. At higher concentrations, more Cu(II) ions are left unabsorbed in solution due to the saturation of the biomass, as a consequence to the increase of the number of ions competing for the available binding sites [17].

4. Conclusions

This study confirmed that eco-friendly, low-cost biomaterials, such as *S. Cerevisiae* (commercial type) can efficiently remove Cu(II) ions from synthetic aqueous solutions. The biosorption performances are strongly affected by operating parameters, such as contact time and initial metal concentration. Langmuir, Freundlich, Redlich-Peterson and Temkin adsorption models were used to correlate the equilibrium adsorption data. Based on the correlation coefficients, it was concluded that the Langmuir isotherm is more suitable to describe the equilibrium data of Cu(II) biosorption on dry Baker's yeast. The adsorption capacity of copper increased with increasing initial metal concentration. The maximum value of the adsorption capacity was 15.6 mg Cu(II)/g reached for an initial concentration of 196 mg/L. A maximum value of the removal efficiency of 73.02% was reached.

Further investigations will be conducted, in order to diminuate the concentration of Cu(II) after biosorption to the limits imposed by the

environmental laws and to reach maximum removal efficiency, through a biosorption-flotation process.

Acknowledgment

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List of symbols

Q_e	- equilibrium adsorption capacity (mg/g);
Q_{max}	- maximum adsorption capacity (mg/g);
Y	- removal efficiency (%);
C_0 and C_e	- initial, respectively final metal concentrations in the solution (mg/L);
V	- volume of the sample (mL);
m	- weight of the dried biosorbent (g);
K_L	- Langmuir constant (L/mg);
R_L	- separation factor;
K_F	- relative adsorption capacity;
n	- intensity of adsorption.

R E F E R E N C E S

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