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COPPER BIOSORPTION ON A STRAIN OF SACCHAROMYCES CEREVISIAE ISOTHERM EQUILIBRIUM AND KINETIC STUDY

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ABSTRACT. In the present work, biosorption of copper ions from aqueous solutions on a strain of *Saccharomyces cerevisiae*, collected from the waste of a brewing industry, was studied in batch system for a better understanding of biosorption isotherm equilibrium, as well as biosorption kinetics. The influence of different sorbent dosages on the sorption of copper ions was investigated. Freundlich and Langmuir isotherm models were used for interpreting the copper biosorption equilibrium and the isotherm constants (i.e., for Freundlich isotherm model, $k = 10.454$ and $n = 3.017$) were determined by experimental data. Freundlich adsorption isotherm ($R^2 = 0.9642$) was found to be more suitable than the Langmuir isotherm ($R^2 = 0.8709$) for correlation of equilibrium biosorption data. Kinetics of biosorption for copper ions was investigated using the first- and second-order models. The kinetic constants were also determined. Second-order kinetics ($R^2 = 0.9937 – 0.9996$) was found to fit the experimental data better than the first-order model ($R^2 = 0.743$).

Keywords: *copper, biosoption, Saccharomyces cerevisiae, Freundlich and Langmuir models*

INTRODUCTION

Water pollution with heavy metals due to industrial activities such as mining, metal processing, electroplating and dyeing is an issue of great environmental concern [1]. Traditional treatments for these wastewaters include chemical precipitation, membrane processes, ion exchange, adsorption and reverse osmosis. Many of these approaches can be less cost effective or difficult for practical use. In an earlier work we have shown the possibility of heavy metals removal from acid mine wastewater using apatite, a calcium-phosphate mineral [2]. Minerals are being commonly applied in environment treatment, based on their properties, such as surface adsorption, high ionic exchange capacity, dissolution, hydration, and mineralogical-biological interactions [3, 4].

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In the last decade more studies referring to the removal of heavy metals from groundwater and wastewater researched natural products adsorption capacity, due to their availability in large quantities as waste or by-products from agricultural and biological processes [5, 6].

The adsorptive studies using treated and untreated waste baker's beer yeast have shown that yeast could be a promising adsorbent for ions such as Zn^{+2}, Cu^{+2}, Ni^{+2}, Pb^{+2} [7-10]. The advantages of *Saccharomyces cerevisiae* as biosorbent are: *S. cerevisiae* as a by-product is easier to get from fermentation industry, in comparison with other types of waste microbial biomass; is easy to cultivate at large scale; is generally regarded as safe; and is an ideal model organism to identify the mechanism of biosorption in metal ion removal.

Copper ion was chosen for the present study with the regard to its wide presence in the mine wastewaters [2]. In the same time copper is widely used as metal in our daily life, and as any other heavy metals it is potentially toxic for living organisms. The concentration limit of copper in wastewaters for discharge in aquatic media according to Romanian legislation is 0.1 mg/L [11].

The objectives of the present study were: to investigate the biosorption of Cu^{+2} from aqueous solutions on a strain of *Saccharomyces cerevisiae* yeast collected from the waste of a Romanian brewing industry – URSUS at different biosorbent yeast dosages (from 0.1 to 0.4 g dry yeast/100 ml copper solution), and then to apply the isotherm equilibrium models and the kinetics of biosorption to experimental data for a better understanding of biosorption mechanism of copper ions on *Saccharomyces cerevisiae* yeast.

EXPERIMENTAL SECTION

Materials

Biosorbent yeast waste *Saccharomyces cerevisiae* was collected from the Romanian brewery URSUS Cluj-Napoca (fermentation unit) and transported to the laboratory in plastic containers. The yeast was then washed several times with distilled water and separated by filtration using filter paper, dried in a hot air oven at 80℃ for 24 hours and stored for further use.

Stock artificial copper solutions of 1000 mg/L Cu^{+2} were prepared from $CuSO_4 \times 5H_2O$ of analytical grade and double distilled water. The solutions were diluted as required to obtain working solutions.

The pH of copper solutions was adjusted at 2.2, value which reproduces the pH of an acid mine wastewater, by addition of H_2SO_4 0.1 M. The pH values were measured using a digital pH-meter, (Thermo Electronic Corporation). Fresh dilutions were used for each biosorption study.

Methods

Batch adsorption experiments were carried out by shaking Erlenmeyer flasks on a rotary shaker at 150 rpm and at room temperature (20℃) for biosorptive experiments. The samples were then filtered using filter paper and the concentration of metal ions in the filtrate was analyzed using Varian Atomic Absorption Spectrophotometer SpectrAA-880 type with deuterium background correlation. Each determination was repeated three times and the results were given as average values. The standard deviation is less than 7%.

RESULTS AND DISCUSSION

Biosorptive isotherm of copper

The effect of contact time on copper biosorption at different *Saccharomyces cerevisiae* yeast dosages was studied and the results were shown in figure 1. As seen in figure 1, the equilibrium concentration was reached in about 120 minutes at lower concentration of yeast, but at higher concentration of yeast the biosorption took about 60 minutes.

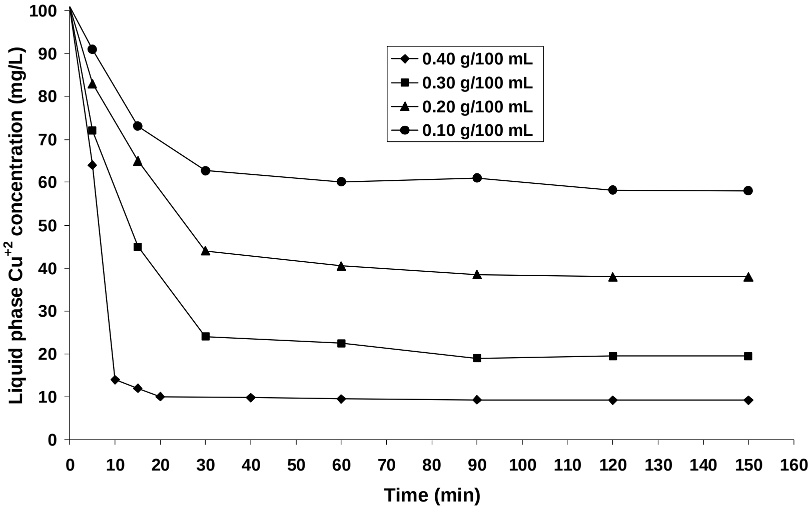


Figure 1. Biosorption of Cu^{+2} by *Saccharomyces cerevisiae* yeast at different dosages of yeast at pH = 2.2.

To determine the copper sorption mechanism on *Saccharomyces cerevisiae* yeast, experimental measurements were conducted using an initial copper concentration C_i = 100 mg/L and different concentrations of biosorbent (0.1 – 0.4 g/100 mL). The results of biosorption were plotted as figure 2 shown, where C_{eq} (mg/L) is the final equilibrium concentration of copper remaining in the solution and q (mg/g) is the metal uptake (equation 1).

$$q = V \cdot \left(C_i - C_{eq}\right) / S \tag{1}$$

The sorption isotherm relationship was than mathematically expressed using Freundlich model (equation 2) and Langmuir model (equation 3).

$$q = k \cdot C_{eq}^{(1/n)} \tag{2}$$

$$q = \left(q_{\max} \cdot b \cdot C_{eq}\right) \cdot \left(1 + b \cdot C_{eq}\right)^{-1} \tag{3}$$

where, k and n are Freundlich constants, q_{max} is the maximum adsorption capacity corresponding to complete monolayer coverage (mg/g), interpreted as the total number of binding sites available for biosorption, and b (L/mg) is the Langmuir constant related to the affinity between the sorbent and sorbate [12].

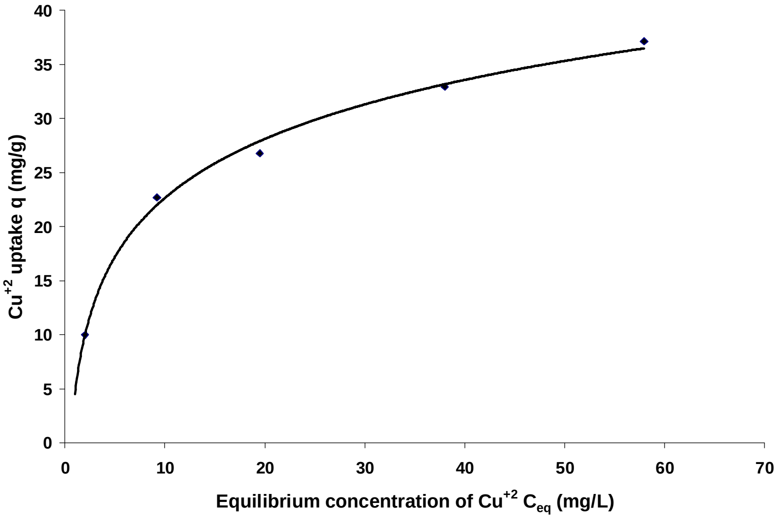


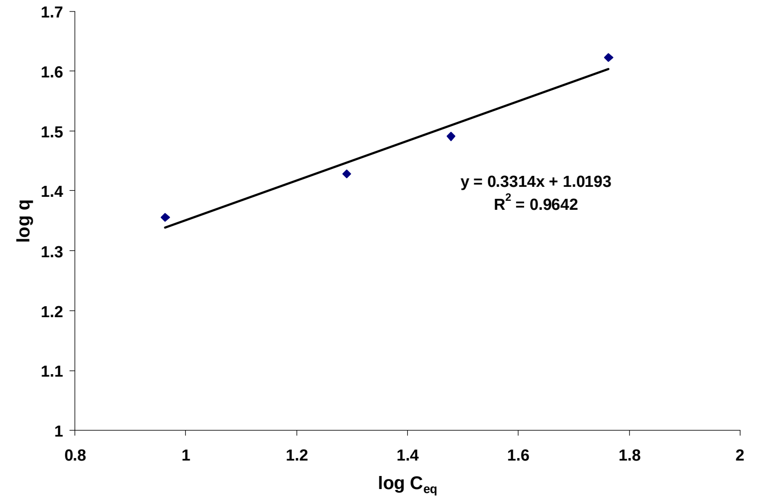
Figure 2. Adsorption isotherm of Cu^{+2} by *Saccharomyces cerevisiae* yeast at pH = 2.2.

The Freundlich equation which deals with heterogeneous surface adsorption can be linearized by plotting it in a log-log format (equation 4, figure 3a).

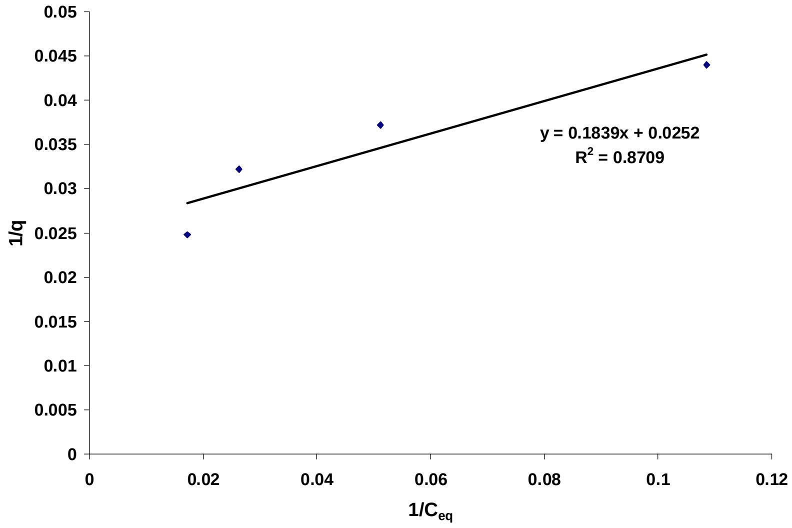
$$\log q = \log k + n^{-1} \cdot \log C_{eq} \qquad (4)$$

The Langmuir model was linearized as equation 5 shows (figure 3b):

$$1/q = \left(q_{\max} \cdot b\right)^{-1} \cdot \left(C_{eq}\right)^{-1} + \left(q_{\max}\right)^{-1} \qquad (5)$$



(a).



(b).

Figure 3. Application of adsorption models to experimental data: (a). Freundlich model, (b). Langmuir model.

The correlation coefficients obtained from Freundlich and Langmuir models were 0.9642, respetively 0.8709. The better correlation of Freundlich model with experimental data suggests heterogeneous surface adsorption. Freundlich and Langmuir parameters were estimated from the fitting of experimental points of copper biosorption (table 1).

Table 1.

Freundlich and Langmuir parameters estimated from experimental data.

FREUNDLICH	**LANGMUIR**
k (L/g) = 10.454	q_{max} (mg/g) = 40
n = 3.017	b (L/mg) = 0.137
S.D. = 0.07	S.D. = 0.06

Maximum biosorption capacity was calculated to be q_{max} = 40 mg Cu^{+2}/g yeast. From the Langmuir model a value of K = 1/b = 7.3 (mg/L) was determined for the affinity constant, comparable with literature data [9].

Kinetic models

Kinetic models can be helpful to better understand the mechanisms of metal biosorption and to evaluate performance of biosorbents for metal removal. Generally, the study of adsorption dynamics describes the solute uptake rate. The kinetics of copper sorption on the *S. cerevisiae* yeast was analyzed using pseudo-first-order and pseudo-second-order [13, 14] models. The conformity between experimental data and the model predicted values was expressed by the correlation coefficients (R^2).

The pseudo-first-order equation is generally expressed as follows:

$$\frac{d\,q_t}{d\,t} = k_1 \cdot (q_e - q_t) \tag{6}$$

where,

q_e and q_t are the adsorption capacity at equilibrium and at time t, (mg/g),

k_1 is the rate constant of pseudo first-order adsorption.

After integration and applying boundary conditions t = 0 to t = t and q_t = 0 to q_t = q_t, the integrated form of equation (6) becomes:

$$\ln(q_e - q_t) = \ln(q_e) - k_1 \cdot t \tag{7}$$

The plot of log (q_e - q_t) versus time should give a linear relationship from which k_1 (1/min) and q_e can be determined from the slope and intercept of the plot, respectively. The correlation coefficient obtained was R^2 = 0.743.

The pseudo-second-order adsorption kinetic rate equation is expressed as equation 8 shows:

$$\frac{d\,q_t}{d\,t} = k_2 \cdot (q_e - q_t)^2 \tag{8}$$

where,

k_2 is the rate constant of pseudo second-order adsorption (g/mg·min).

For the boundary conditions t = 0 to t = t and q_t = 0 to q_t = q_t, the integrated form of equation 8 becomes:

$$\frac{t}{q_t} = \frac{1}{k_2 \cdot q_e^{\,2}} + \frac{1}{q_e} \tag{9}$$

The correlation of experimental data using pseudo-second-order model for different sorbent dosages (0.1 – 0.4 g) is shown in figure 4. The high values of correlation coefficients (R^2 = 0.9937 – 0.9996) have shown that the biosorption of copper using as biosorbent *S. cerevisiae* yeast has followed a pseudo-second-order kinetic.

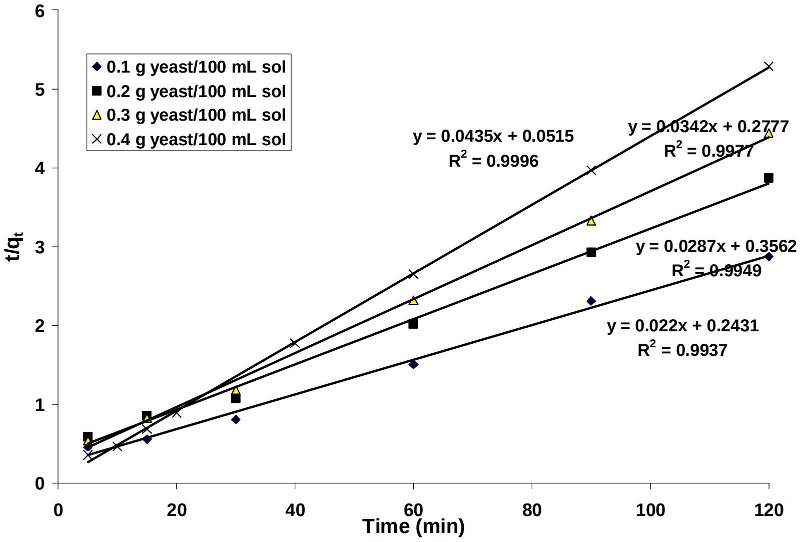


Figure 4. Correlation of experimental data using the pseudo-second-order model.

Sorption parameters and the correlation coefficients obtained from experimental data analyzed in terms of pseudo-second-order equation are given in table 2.

It easy to see that q_e was inversely related to the added yeast mass (S). While k_2 increased from 0.0019 to 0.036 (g/mg·min), h, increased from 2.790 to 19.04, as the yeast dosage increased from 0.1 to 0.4 g/100 mL solution. A similar behavior was reported by Vasudevan et al. in the case of biosorption of cadmium on Baker's yeast [8].

Table 2.

The effect of yeast dosages on copper sorption parameters

S (g/100 mL)	**R^2**	**q_e (mg/g)**	**k_2 (g/mg·min)**	**h (mg/g·min)**
0.1	0.9937	45.45	0.0019	3.925
0.2	0.9949	34.84	0.0023	2.790
0.3	0.9977	29.24	0.0042	3.590
0.4	0.9996	23.00	0.0360	19.04

where S is the yeast dosage; q_e - copper ion uptake capacity at equilibrium; k_2 – rate constant and $h = k_2 . q_e^2$ – initial adsorption rate.

CONCLUSIONS

Saccharomyces cerevisiae yeast collected from the waste of URSUS brewery has been successfully used as a potential biosorbent to treat wastewater contaminated with copper ions. The amount of sorbed copper ions at equilibrium was related to yeast ratio.

The biosorption was mathematical described using Freundlich and Langmuir models. The better correlation of Freundlich model with experimental data suggests a heterogeneous surface adsorption. Freundlich and Langmuir parameters were estimated from the fitting of experimental points of copper biosorption. The maximum biosorption capacity was q_{max} = 40 mg Cu^{+2}/g yeast. From the Langmuir model a value of K = 7.3 (mg/L) for the affinity constant was determined.

Kinetics of biosorption of copper ions was investigated by using the pseudo-first- and pseudo-second-order models and the kinetic parameters were determined. Second-order kinetics (R^2 = 0.9937 – 0.9996) was found to fit the experimental data better than the first-order model (R^2 = 0.727).

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