

Inga ZINICOVSCAIA<sup>1,2\*</sup>, Nikita YUSHIN<sup>1</sup>, Dmitrii GROZDOV<sup>1</sup>, Konstantin VERGEL<sup>1</sup>  
Tatiana OSTROVNAYA<sup>1</sup> and Elena RODLOVSKAYA<sup>3</sup>

## METAL REMOVAL FROM COMPLEX COPPER CONTAINING EFFLUENTS BY WASTE BIOMASS OF *Saccharomyces cerevisiae*

**Abstract:** *Saccharomyces cerevisiae*, waste biomass originated from beer fermentation industry, was used to remove metal ions from four copper-containing synthetic effluents: Cu-Fe, Cu-Fe-Ni, Cu-Fe-Zn, and Cu-Fe-Ni-Zn. The characterization of the biomass surface was investigated by Scanning Electron Microscopy and Fourier-transform Infrared Spectroscopy. The adsorption behavior of *Saccharomyces cerevisiae* for copper, iron, nickel and zinc ions in aqueous solution was studied as a function of pH, initial copper concentration, equilibrium time, and temperature. Langmuir, Freundlich, Temkin and Dubinin-Radushkevich equilibrium models have been assessed to describe the experimental sorption equilibrium profile, while pseudo-first order, pseudo-second order, Elovich and the intra-particle diffusion models were applied to describe experimental kinetics data. Maximum sorption capacities have been calculated by means of Langmuir equilibrium model and mean free sorption energies through the Dubinin-Radushkevich model. Thermodynamic analysis results showed that the adsorption of copper, iron and zinc was spontaneous and endothermic in nature, while of nickel exothermic. *Saccharomyces cerevisiae* can be successfully applied for complex wastewater treatment.

**Keywords:** biosorption, copper, iron, nickel, *Saccharomyces cerevisiae*, zinc

### Introduction

With the industrial and population advances, the generation of effluents containing heavy metals has grown a lot [1]. Copper is a widely used metal in various industries such as plating, mining and smelting, brass manufacture, electroplating industries, chemicals, fertilizers and pigments production, petroleum refining, and in agriculture [1-3]. Presence of copper in water in concentrations above 1.3 mg/dm<sup>3</sup> is associated with changes in the nervous system, gastrointestinal irritation, depression and lung cancer [4].

To deal with metal-contaminated effluents different techniques have been suggested including adsorption, chemical precipitation, ion exchange, coagulation, electrolysis, solvent extraction, reverse osmosis, filtration and membrane processes [2, 5]. Oftentimes, the application of these methods is limited due to their high cost, low applicability for diluted effluents, and generation of secondary waste products [3].

Biological techniques are usually considered as an alternative to traditional techniques and can significantly reduce the quantity of heavy metals in aqueous solutions [5]. Among

<sup>1</sup> Joint Institute for Nuclear Research, Joliot-Curie Str., 6, 1419890 Dubna, Russia

<sup>2</sup> Horia Hulubei National Institute for R&D in Physics and Nuclear Engineering, 30 Reactorului Str. MG-6, Bucharest - Magurele, Romania

<sup>3</sup> A.N. Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Sciences, Vavilova Str., 28, 119991, Moscow, Russia

\* Corresponding author: zinikovskaia@mail.ru

biological techniques, biosorption technique is the most common and cost-effective, since biosorbents are available in abundance, renewable, non-toxic, cheap, main part of them can be regenerated and reused [6]. Application of biosorbents for wastewater treatment requires less investment in terms of both initial cost and operational cost in comparison with conventional techniques, simple design, easy operation and no effect of toxic substances [3].

Among microorganisms, yeast *Saccharomyces cerevisiae* have been actively used as a biosorbent [5, 7, 8] due to its high removal efficiency and low procurement cost [8]. *Saccharomyces cerevisiae* is widely used in food industry and can be easily obtained in comparison with other types of waste microbial biomass [9]. Biosorption of copper ion using treated and untreated immobilized *Saccharomyces cerevisiae* from aqueous solution was investigated by Raffar et al. [10]. The capacities of live and heat-killed cells of *Saccharomyces cerevisiae* at for the removal of copper, nickel and zinc from the solution were compared by Machado et al. [11]. Laboratory and brewing strains of *Saccharomyces cerevisiae* were used for metabolism-independent and-dependent  $\text{Sr}^{2+}$  uptake. Strontium uptake levels were greater in denatured (dried and ground) yeast [12]. Brady and Duncan [13] determined the capacity and selectivity of yeast cell walls for binding of copper, cobalt and cadmium ions. Nascimento et al. [1] studied the effect of different parameters on copper ions removal by *Saccharomyces cerevisiae*.

*Saccharomyces cerevisiae* was mainly applied for metal removal from single component systems, while real industrial effluent usually contains various compounds, including metal cations and anions. Presence of impurities in effluents additional to the ions of interest can influence significantly the process of metal biosorption. Heat-inactivated cells of a flocculent strain of *Saccharomyces cerevisiae* were used in the bioremediation, in a batch mode, of a real electroplating effluent containing Cu, Ni, and Cr [14].

In the present study *Saccharomyces cerevisiae* (*S. cerevisiae*), waste biomass originated from beer fermentation industry, was used to remove metal ions from four copper containing synthetic effluents with the following composition: Cu(II)-Fe(III), Cu(II)-Fe(II)-Ni(II), Cu(II)-Fe(III)-Zn(II) and Cu(II)-Fe(III)-Ni(II)-Zn(II). The influence of several parameters such as initial pH, contact time, copper concentration and temperature on the yeast sorption capacity is investigated. The kinetic data were fitted to pseudo-first, pseudo-second, Elovich, intra-particle diffusion models, while the isotherm equilibrium data were fitted to Langmuir, Freundlich, Temkin and Dubinin-Radushkevich models. Thermodynamics parameters were evaluated from biosorption data.

## Material and methods

### Reagents and materials

All the chemicals used for biosorption experiments ( $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ,  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Cu}(\text{NO}_3)_2 \cdot 5\text{H}_2\text{O}$ ,  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , nitric acid, sodium hydroxide) were purchased from Sigma-Aldrich and were of analytical grade. Stock solutions of  $1000 \text{ mg/dm}^3$  metal ions were prepared by dissolution of the respective salts in deionized water. The solutions were diluted as required to obtain working solutions.

### Preparation of adsorbent

As sorbent the yeast *Saccharomyces cerevisiae* (*S. cerevisiae*) obtained from company Efes Vitanta Moldova Brewery (Chisinau, Republic of Moldova) were used. Obtained

biomass was rinsed twice with deionized water and then dried in an oven at 80 °C for 48 h. Then the biomass was homogenized in a homogenizer at 400 rpm for 10 min and afterwards used in the experiments.

### Biosorption experiments

In present work, metal removal from the following systems was studied: Cu-Fe, Cu-Fe-Ni, Cu-Fe-Zn, Cu-Fe-Ni-Zn. The concentration of copper in studied systems was 10 mg/dm<sup>3</sup>, of iron, nickel and zinc 5, 2 and 2 mg/dm<sup>3</sup>, respectively. The batch mode adsorption experiments were conducted to investigate the influence of pH, time, copper concentration and temperature on metal removal from complex systems. All the experiments were carried out using a Unimax 1010 shaker (Heidolph, Germany) at a fixed agitation speed at 200 rpm.

The effect of pH on metal biosorption was studied at the pH range 2-7. The initial solution was adjusted to the desired pH with diluted or concentrated HNO<sub>3</sub> and NaOH solutions before being mixed with the biosorbent. To determine the contact time required for the sorption equilibrium experiments, samples were withdrawn at predetermined time intervals (5, 15, 30, 60 and 120 min). All the experiments were carried out under ambient conditions at 20 °C, except for the thermodynamic studies at temperature 20, 30, 40 and 50 °C.

The equilibrium experiments were performed at initial copper concentrations in the range of 10-100 mg/dm<sup>3</sup>, while the iron, zinc and nickel concentrations in each biosorption medium was held constant. In all experiments the working volume was 50 cm<sup>3</sup> and sorbent dosage 0.5 g. All the experiments were conducted in triplicate and the averages of the measurements for each treatment were used.

The metal uptake  $q$  was calculated using the following equation:

$$q = \frac{V(C_i - C_f)}{m} \quad (1)$$

and sorption removal efficiency,  $E$  [%] from the equation:

$$E = \frac{C_i - C_f}{C_i} \cdot 100 \quad (2)$$

where  $q$  is the amount of metal ions adsorbed on the biosorbent [mg/g];  $V$  is the volume of solution [cm<sup>3</sup>];  $C_i$  is the initial concentration of metal in [mg/dm<sup>3</sup>],  $C_f$  is the final metal concentration in the solution [dm<sup>3</sup>], and  $m$  is the mass of sorbent [g].

### Desorption experiment

In desorption experiments *S. cerevisiae* biomass was firstly exposed to working solutions. Next, the biomass was separated from the solution by centrifugation. The obtained metal-loaded biosorbent was then brought in contact with 50 cm<sup>3</sup> of HNO<sub>3</sub> (0.1 M), EDTA (0.1 M) and distilled water for 1 h on an orbital shaker at 200 rpm.

### Methods

Copper concentration in solution was determined by applying atomic absorption spectrometry (Thermo Scientific iCE 3400 series) with electrothermal atomization. The calibration solutions were prepared from a 1 g/dm<sup>3</sup> stock solution (AAS standard solution; Merck, Germany). To determine the content of Fe, Ni and Zn biosorbent samples

were irradiated at the pulsed fast reactor IBR-2 (Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research, Dubna, Russia) for 3 days under at a neutron flux of  $1.8 \cdot 10^{11} \text{ cm}^{-2} \text{ s}^{-1}$ . The iron content in the samples was determined by a  $\gamma$ -line with the energy of 1099.25 keV of isotope  $^{59}\text{Fe}$ , nickel by a  $\gamma$ -line with the energy of 810.57 keV of isotope  $^{58}\text{Co}$  and zinc by a  $\gamma$ -line with the energy of 1115.54 keV of isotope  $^{65}\text{Zn}$ . The description of the irradiation channels and the pneumatic transport system REGATA of the IBR 2 is given in [15]. The quality control of the analytical measurements was carried out using certified reference materials: NIST SRM 1566b - Oyster tissue, NIST SRM 2710a - Montana I Soil Highly Elevated Trace Element Concentrations, and IAEA SRM 433 - Marine Sediment, which were irradiated under the same experimental conditions as the samples. For method precision and accuracy determination, NIST SRM 2710a, because of the large number of elements with certified values, was used. The precision, expressed as the percentage standard deviation of the mean of three determinations, was below 10 % for all elements. The accuracy, given as the percentage deviation from the certified value material, varied between 1 and 12 %.

Fourier-transform infrared spectroscopy was used to confirm the presence of the functional groups in the samples of *S. cerevisiae* and to observe the chemical modification after metal biosorption. Infrared spectra were recorded in the range of  $4,000\text{-}400 \text{ cm}^{-1}$  using a Nicolet 6700 spectrometer (Thermo Scientific, Germany). Scanning Electron Microscopy (SEM) characterization was performed using S3400N (Hitachi) microscope.

## Results and discussion

### Sorbent characterization

SEM and FTIR techniques were used to characterize native and metal loaded *S. cerevisiae* biomass.

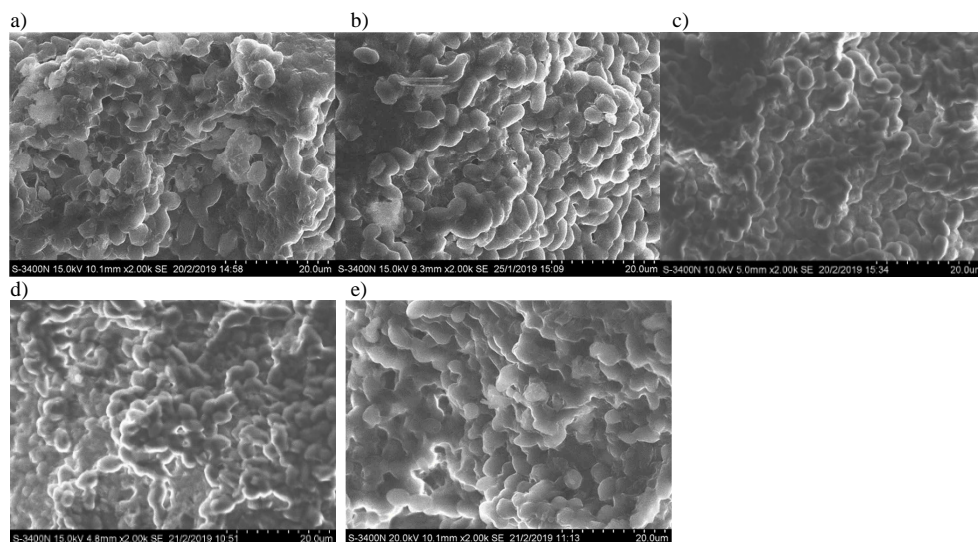


Fig. 1. The SEM images of *S. cerevisiae*: a) control, b) system Cu-Fe, c) system Cu-Fe-Ni, d) system Cu-Fe-Ni-Zn, e) system Cu-Fe-Ni-Zn

The SEM images (Fig. 1) show that the morphology of *S. cerevisiae* cells did not change significantly after metal ions sorption, indicating that biosorption has place on the yeast surface.

The cell wall of *S. cerevisiae* is the first cellular structure to be in contact with metal ions and is composed of three major components:  $\beta$ -glucans, chitin, and mannoproteins [11]. According to [11] the brewer's yeast contains the sugar component, the nucleic acids; protein component;  $-\text{OH}$  and  $-\text{NH}$  groups and hydrogen bonding; chitin, glucan,  $\text{C}-\text{N}$ ,  $\text{N}-\text{H}$ ,  $\text{OH}$  and  $\text{C}=\text{O}$  groups. Hlihor et al. [16] showed presence of  $\text{OH}$ ,  $\text{N}-\text{H}$ ,  $\text{C}-\text{H}$ ,  $\text{C}=\text{O}$ ,  $\text{N}-\text{O}$ ,  $\text{C}-\text{C}$ ,  $\text{COOH}$  and  $\text{P}=\text{O}$  groups in dried *S. cerevisiae* biomass.

FTIR spectrum of native *S. cerevisiae* biomass (Fig. 2) indicates on strong absorption bands in the regions  $1036$  and  $1518\text{ cm}^{-1}$ , which corresponds to  $\text{OH}$ -groups. Peak at  $1214\text{ cm}^{-1}$  was related to the stretching vibration of  $\text{C}=\text{O}$  groups, whereas peaks at  $1393$  and  $2950\text{ cm}^{-1}$  represent the stretching vibration of alkyl groups ( $-\text{CH}_3$  or  $\text{CH}_2$ ). Peak at  $1518\text{ cm}^{-1}$  is related to the vibration of aromatic groups, and absorption band at  $1626\text{ cm}^{-1}$  corresponds to  $\text{CH}=\text{CH}$  groups. The band at  $3288\text{ cm}^{-1}$  is relevant to standard absorption band of amido group  $\text{HN}=\text{O}$ .

After biomass interaction with solution containing  $\text{Cu(II)}$  and  $\text{Fe(III)}$  ions the IR spectra revealed a slight shift of bands  $1036$ ,  $1393$  and  $3288\text{ cm}^{-1}$  indicating on their involvement of  $\text{OH}$ ,  $\text{CH}=\text{CH}$ ,  $\text{C}=\text{O}$  and  $\text{N}=\text{O}$  groups in metal binding. In case of  $\text{Cu(II)-Fe(III)-Zn(II)}$  system, shifting of bands observed at  $1034$ ,  $1390$  and  $1620\text{ cm}^{-1}$  could be due to the involvement of  $\text{CH}=\text{CH}$  and  $\text{OH}$  groups in metal biosorption. For  $\text{Cu(II)-Fe(III)-Ni(II)}$  and  $\text{Cu(II)-Fe(III)-Zn(II)-Ni(II)}$  no significant changes in metal loaded biomass spectra were observed. The transmittance of the peaks in the metal loaded biomass was lower than the control sample indicating on the occurrence of bond stretching to a lesser degree due to the presence of metals [17].

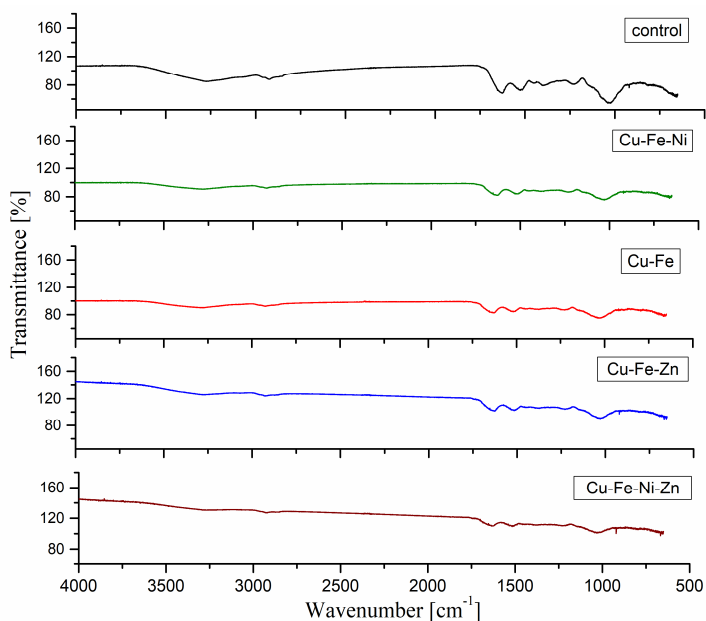


Fig. 2. FTIR spectrum of *S. cerevisiae* biomass before and after metal biosorption

### The influence of pH on metals adsorption

The pH is the critical factors that influences adsorption of metal ions since it affects the metal and functional groups chemistry [18]. The effect of pH on the metal ions biosorption was studied in the range 2.0-7.0. As it can be seen from the data presented in Figure 3 increases of the pH lead to the increase of Cu(II), Zn(II) and Ni(II) removal efficiency. The maximum removal of copper (60-72 %) was achieved at pH = 3.0 in all studied systems. Nickel maximum removal (61 %) in Cu(II)-Fe(III)-Ni(II) system was achieved at pH 3.0-4.0, while in Cu(II)-Fe(III)-Zn(II)-Ni(II) (53 %) at pH = 3.0. In Cu(II)-Fe(III)-Zn(II) system zinc removal efficiency (94 %) was constant in the pH range 4.0-7.0, while in Cu(II)-Fe(III)-Zn(II)-Ni(II) system maximum amount of Zn(II) ions removal (87 %) was achieved at pH 6.0.

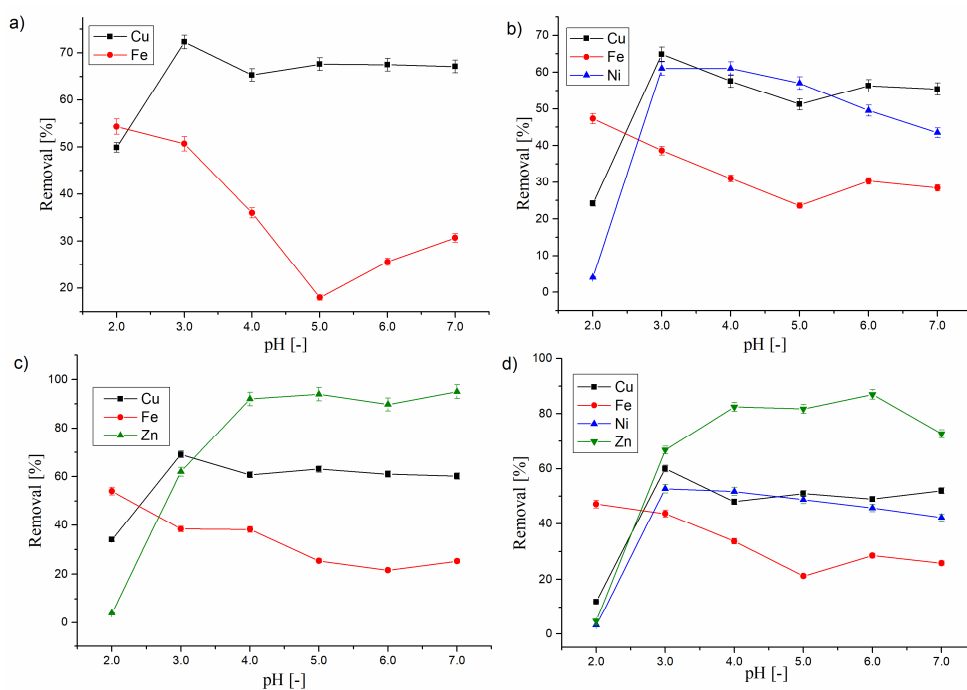


Fig. 3. Removal of metal ions at different initial pH (at  $T = 20\text{ }^{\circ}\text{C}$ ; sorbent dosage  $0.5\text{ g/dm}^3$ ; adsorption time 1 h): a) Cu-Fe, b) Cu-Fe-Ni, c) Cu-Fe-Zn, d) Cu-Fe-Ni-Zn systems

The mechanism of metal ions adsorption by *S. cerevisiae* include both the ion exchange and the surface complexation [19]. Thus, in [1] it was shown the decrease of the potassium content in *S. cerevisiae* biomass after its interaction with copper ions. Under pH 6.0, the dominant copper specie was Cu(II) which as normally included in the adsorption process [20]. Brady and Duncan [13] showed that carboxyl and amino groups play important role in Cu(II) ions binding. The blocking of amino, carboxyl or hydroxyl groups of the cell walls reduced the yeast accumulation capacity toward Cu(II) ions. Machado et al. [11] suggests the involvement of carboxyl, amino, hydroxyl and amide groups of protein and carbohydrate fractions (most likely of mannoproteins, glucans and chitin) of the cell

wall in the yeast copper, nickel and zinc ions uptake. These results are in agreement with those obtained by Padmavathy et al. [21], who suggested that mannoproteins and glucans present on the cell wall were responsible for the sorption of Ni(II) ions. According to Basak et al. [22] carboxyl, phosphate, sulfhydryl, hydroxyl and nitrogen-containing groups of yeast biomass surface participated in the removal of Zn(II) ion. Gerlach et al. [27] have found that OH groups play the main role in iron ions binding.

At highly acidic pH values low metals removal is explained by competition of metal cations and protons for binding sites on cell wall. With the pH increase more ligands, carrying negative charges are available for metallic ions with positive charges binding [3, 4]. However, when the pH is higher than a certain value, OH<sup>-</sup> groups interact with metal cations leading to the formation of metal hydroxides and the decrease of the adsorption capacity [5].

Iron ions were more effectively adsorbed at pH = 2.0. In Cu(II)-Fe(III) and Cu(II)-Fe(III)-Zn(II) systems maximum Fe(III) removal constituted 54 %, while in Cu(II)-Fe(III)-Ni(II) and Cu(II)-Fe(III)-Zn(II)-Ni(II) systems 47 % of iron ions were removed from the solution. It can be concluded that Ni(II) ions inhibit Fe(III) ions removal. Results obtained for iron are in good agreement with data reported by Sag and Kutsal [24] and Aksu and Gulen [25], who studied iron removal by *Rhizopus arrhizus* from single and multicomponent systems. The decrease of iron removal with the pH increase is because iron(III) ions precipitated with the increase of the concentration of OH<sup>-</sup> ions in the adsorption medium [26].

Several researchers have investigated the effect of pH on biosorption of copper by *S. cerevisiae*. Han et al. [27] showed maximum copper removal by beer yeast at pH = 6.0, while in Nascimento et al [1] study the best biosorption efficiency of yeast for copper was found at pH 5.0. In Wang and Chen [9] review is reported that the optimal pH value for copper removal by *S. cerevisiae* is 5.0-9.0. At pH up to 6.0, the *S. cerevisiae* biomass batch leads to a removal of 52 % of Ni(II) and 78 % of Cu(II) from industrial effluents [14].

The maximum capacity of Cu(II) absorption by immobilized *S. cerevisiae* occurs at pH = 4.5 [5]. Since the pH = 3.0 was found as optimal for Cu(II) ions removal all further experiments were performed at pH = 3.0.

### Effect of copper ions concentration on metals adsorption

The effect of initial Cu(II) concentration on metal biosorption was studied by maintaining constant the concentration of interfering metals (Fe, Zn and Ni) and varying copper concentration from 10 and 100 mg/dm<sup>3</sup>. In all studied systems (Fig. 4) the adsorption of Cu(II) ions on *S. cerevisiae* increased with increasing Cu(II) ion concentrations up to 100 mg/dm<sup>3</sup>. The maximum adsorption was found to be 4.96 mg/g in Cu(II)-Fe(III) system, 5.07 mg/g in Cu(II)-Fe(III)-Ni(II) system, 5.22 mg/g in Cu(II)-Fe(III)-Zn(II) system and 5.7 mg/g in Cu(II)-Fe(III)-Zn(II)-Ni(II) system.

Increase of Cu(II) concentration resulted in the decrease of the adsorption of Fe(III), Ni(II) and Zn(II) ions. Increase of copper concentration from 10 to 100 mg/dm<sup>3</sup> resulted in the decrease of Ni(II) removal from 83 to 42 % in Cu(II)-Fe(III)-Ni(II), and from 73 to 44 % in Cu(II)-Fe(III)-Zn(II)-Ni(II) system. Zinc removal was most affected by increase of copper concentration in solution. In Cu(II)-Fe(III)-Zn(II) system Zn(II) sorption was reduced from 98 to 8.5 %, while in quaternary system at copper concentration in solution higher than 40 mg/dm<sup>3</sup> Zn(II) ions was not removed from solution by *S. cerevisiae*

biomass. It can be concluded that Cu(II) and Zn(II) ions compete for the same binding sites. Iron adsorption was less affected by increase of copper concentration.

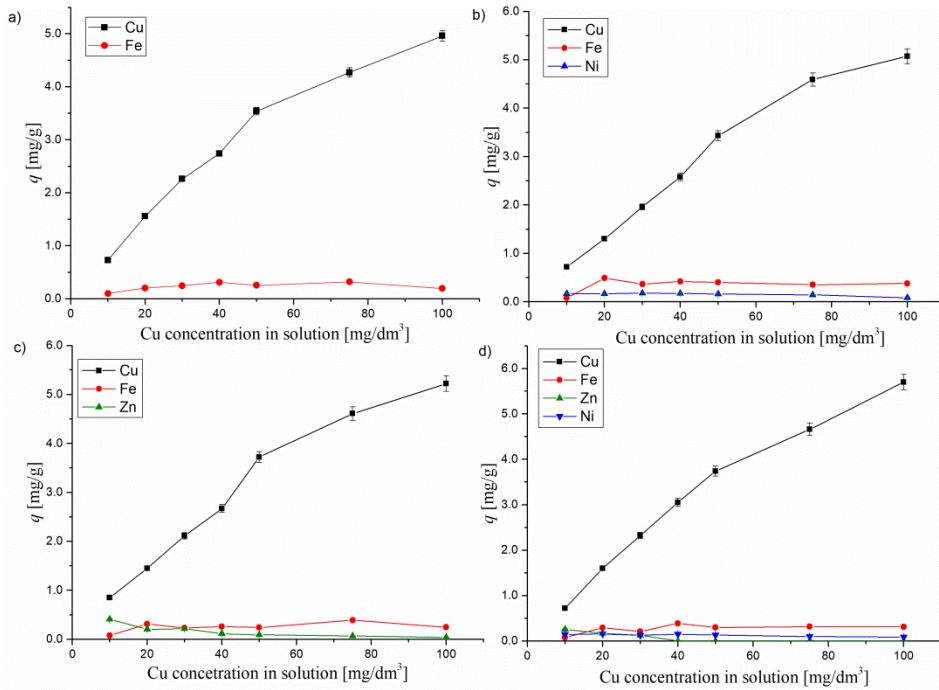


Fig. 4. Removal of metal ions at different copper concentration in solution (at  $T = 20\text{ }^{\circ}\text{C}$ ; sorbent dosage  $0.5\text{ g/dm}^3$ ; adsorption time 1 h): a) Cu-Fe, b) Cu-Fe-Ni, c) Cu-Fe-Zn, d) Cu-Fe-Ni-Zn systems

### Biosorption isotherms

The equilibrium data were described using following equilibrium models: Langmuir, Freundlich, Temkin and Dubinin-Radushkevich. The description of the model can be found elsewhere [28].

The Langmuir model suggests a monolayer adsorption and is expressed by the formula:

$$q_e = \frac{q_m b C_e}{1 + b C_e} \quad (3)$$

where:  $C_e$  is metal ions concentration at equilibrium [ $\text{mg/dm}^3$ ],  $q_e$  is amount of metal adsorbed at equilibrium [ $\text{mg/g}$ ],  $q_m$  is maximum adsorption capacity of the sorbent [ $\text{mg/g}$ ] and  $b$  is Langmuir adsorption constant [ $\text{dm}^3/\text{mg}$ ].

The mathematical expression of Freundlich isotherm model is presented by formula (9):

$$q_e = K_F C_e^{\frac{1}{n}} \quad (4)$$



where  $q_e$  is amount of metal adsorbed at equilibrium [mg/g],  $C$  is concentration of metal ions in aqueous solution at equilibrium [mg/dm<sup>3</sup>];  $K_F$  and  $n$  are Freundlich constants that include factors that affect adsorption capacity and adsorption intensity, respectively.

The Dubinin-Radushkevich isotherm mode is expressed by equation:

$$q_e = q_m \exp(-K_{DR} \varepsilon^2) \quad (5)$$

where  $K_{DR}$  is a constant related to adsorption energy [mol<sup>2</sup>/kJ<sup>2</sup>],  $q_m$  is a constant that indicates the sorption capacity of sorbent [mg/g].

Polanyi potential,  $\varepsilon$ , was calculated with the equation:

$$\varepsilon = RT \ln \left( 1 + \frac{1}{C_e} \right) \quad (6)$$

where  $R$  is the universal gas constant (8.314 J · K<sup>-1</sup> · mol<sup>-1</sup>) and  $T$  is the temperature [K].

The free adsorption energy ( $E$ ) was calculated using the following expression:

$$E_s = (-2K_{DR})^{-1/2} \quad (7)$$

The Temkin isotherm model is given below:

$$q_e = \frac{RT}{b} \ln(a_T C_e) \quad (8)$$

$1/b$  indicates the sorption potential of the sorbent, and  $a_T$  [dm<sup>3</sup>/g] is Temkin constant.

The results of adsorption isotherms are shown in Figure 5 and Table 1.

For all studied systems Langmuir model provide the best representation of the experimental equilibrium data, with the maximum adsorption capability varying from 10.6 mg/g for Cu(II)-Fe(III)-system to 15.1 mg/g in Cu(II)-Fe(III)-Ni(II) system. For quaternary system experimental data well Langmuir as well as Freundlich model, with coefficients of determination  $R^2 = 0.99$ , showing that several functional groups may be involved in copper ions binding. The  $1/n$  value calculated from Freundlich isotherm model was less than unity for all systems, indicating that the biosorption of Cu(II) onto *S. cerevisiae* biomass is favorable.

Dubinin-Radushkevich isotherm models showed low correlation coefficients for all systems. Similar to Freundlich isotherm, Dubinin-Radushkevich isotherm is used to describe adsorption on the heterogeneous solid surfaces [2]. The mean free energy  $E$  values calculated from Dubinin-Radushkevich model were in the range of 0.06 to 0.07 kJ/mol, indicating that physical adsorption play main role in the copper adsorption process [29]. It should be mentioned, that  $q$  values calculated from Dubinin-Radushkevich model were most approximate to experimental data. Temkin model was not applicable for Cu(II)-Fe(III)-Ni(II) system, while determination coefficients were other systems were rather high. The positive value of  $b$  indicates on endothermic character of Cu(II) biosorption [30].

Copper and lead removal by *S. cerevisiae* was better described by Langmuir model [27]. Nascimento et al. [1] demonstrate that the Langmuir model adjusted better to study copper biosorption by *S. cerevisiae*, while models Freundlich and Dubinin-Radushkevich had lower coefficients.

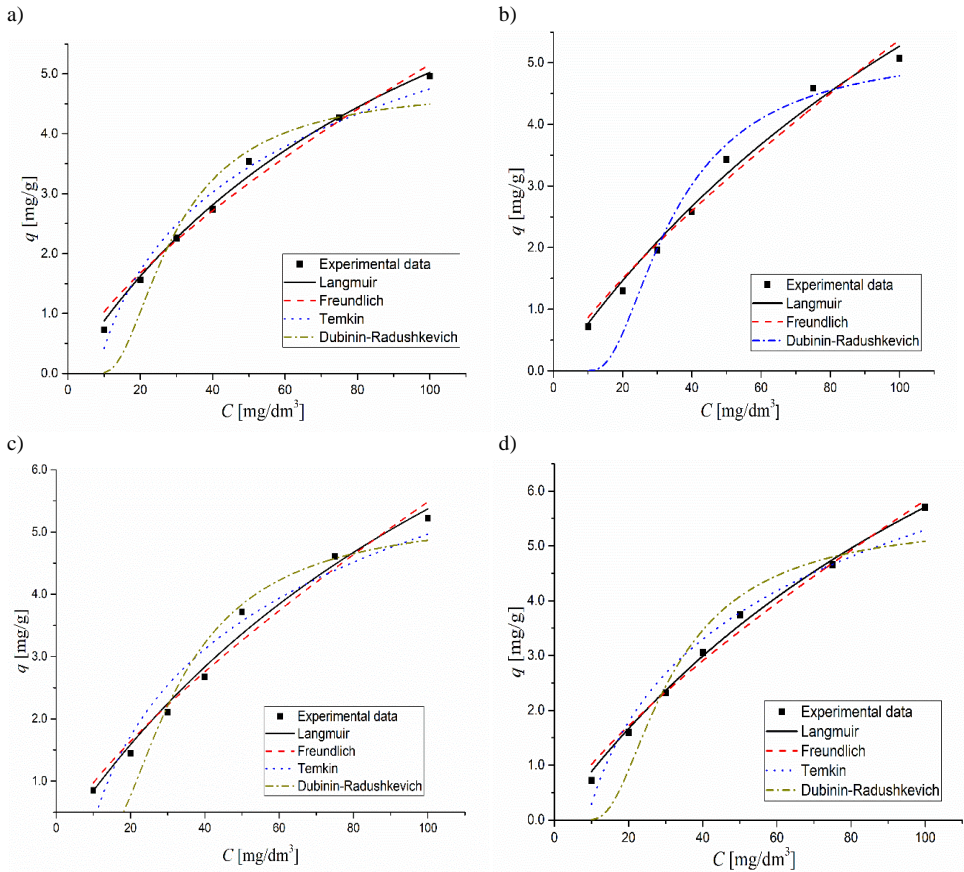


Fig. 5. The adsorption isotherms: a) Cu-Fe, b) Cu-Fe-Ni, c) Cu-Fe-Zn, d) Cu-Fe-Ni-Zn systems

Table 1

The constants and correlation coefficients,  $R^2$  of the adsorption isotherms

Model	Parameters	System			
		Cu-Fe	Cu-Fe-Ni	Cu-Fe-Zn	Cu-Fe-Ni-Zn
Langmuir	$q_m$ [mg/g]	10.6	15.1	13.30	14.50
	$b$ [dm <sup>3</sup> /mg]	0.009	0.005	0.007	0.006
	$R^2$ [-]	0.99	0.98	0.98	0.99
Freundlich	$K_F$ [mg/g]	0.21	0.14	0.17	0.18
	$1/n$ [-]	0.7	0.79	0.75	0.75
	$R^2$ [-]	0.98	0.97	0.97	0.99
Temkin	$a_T$ [dm <sup>3</sup> /g]	0.13	n.a.*	0.12	0.11
	$B$ [J/mol]	1875	n.a.	1934	2176
	$R^2$ [-]	0.97	n.a.	0.93	0.96
Dubinin-Radushkevich	$q_{DR}$ [mg/g]	4.8	5.2	5.5	5.5
	$\beta$ [mol <sup>2</sup> /kJ <sup>2</sup> ]	108	152	137	127
	$R^2$ [-]	0.88	0.90	0.88	0.89
	$E$ [kJ/mol]	0.07	0.06	0.06	0.06

\* n.a.- not applicable

### The effect of contact time on metal biosorption

Time required for maximum removal of metals from industrial effluents is an important parameter. The effect of time on studied metal biosorption is shown in Figure 6. In system Cu(II)-Fe(III) maximum amount of copper was adsorbed after 60 min of interaction (68 %), while of iron (51 %) after 30 min of sorbent-sorbate interaction. In Cu(II)-Fe(III)-Ni(II) system metal removal efficiency changed in the following order: Ni (74 %) > Cu (66 %) > Fe (43 %). In Cu(II)-Fe(III)-Zn(II) system maximum amount of metal ions was removed in 30-45 min of interaction. Yeast biomass showed high affinity for zinc ions, 82 % of zinc was removed by biomass during 45 min. Copper and iron removal efficiency constituted 69 and 66 %, respectively. In four component system biomass showed high affinity for nickel and copper was on the level of Cu(II)-Fe(III)-Ni(II) system: 74 and 65 %, respectively. At the same time zinc removal efficiency in quaternary system was reduced by 30 % in comparison with Cu(II)-Fe(III)-Zn(II) system. Iron removal efficiency firstly increased up to 52 % and after 45 min of interaction it was reduced to 43 %. Decrease of iron and zinc removal efficiency can be explained by their competition for binding sites with nickel ions, since copper removal efficiency did not change significantly in studied system.

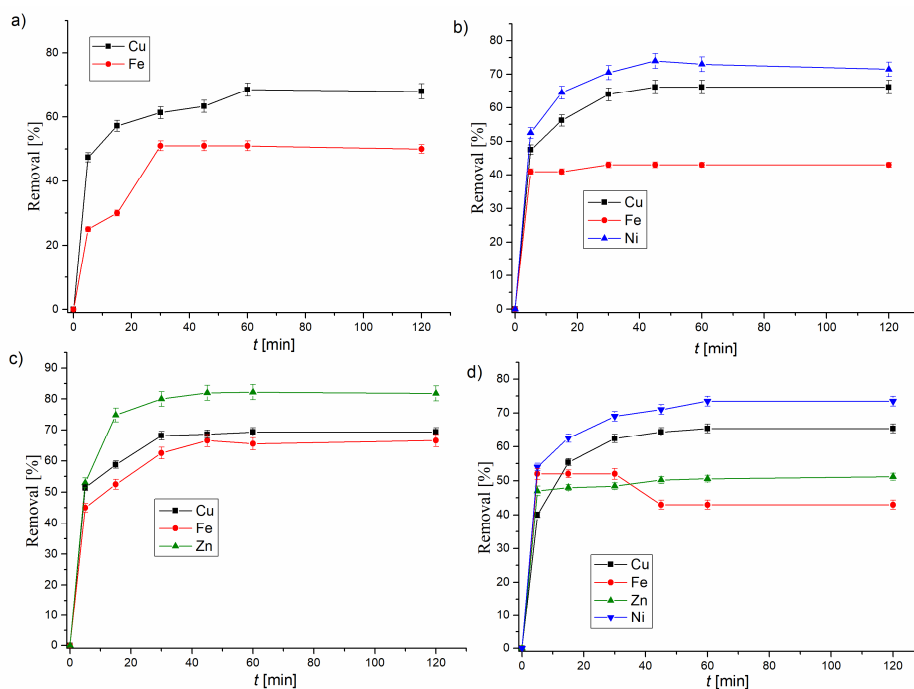


Fig. 6. Adsorption of metal ions on *S. cerevisiae* as the function of time (at  $T = 20$  °C; sorbent dosage  $0.5 \text{ g/dm}^3$ ): a) Cu-Fe, b) Cu-Fe-Ni, c) Cu-Fe-Zn, d) Cu-Fe-Ni-Zn systems

As it was shown in Han et al. [27] study the biosorption of Cu(II) and Pb(II) onto waste beer yeast was rapid for first 10 min and equilibrium was nearly reached after 60 min.

### Adsorption kinetic models

Four models pseudo-first order (PFO), pseudo-second order (PSO), Elovich model (EM) and the intra-particle Weber and Morris diffusion model (IPM) were applied to describe experimental data. The description of the models can be found in Albadarin et al. [28] and Ahmad et al. [29] studies.

The models are expressed by the following formulas (9)-(12):

Pseudo-first order model:

$$q = q_e (1 - e^{-k_1 t}) \quad (9)$$

where  $q_e$  and  $q$  are the amounts of metal [mg/g] adsorbed at equilibrium and at  $t$  time [min], respectively, and  $k_1$  is the rate constant of pseudo-first order [1/min].

Pseudo-second order model:

$$q = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \quad (10)$$

where  $k_2$  is the rate constant of second order [g/(mg·min)].

Elovich model:

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln(t) \quad (11)$$

where  $\alpha$  [mg/g·min] and  $\beta$  [g/min] are the Elovich equation constants.

Weber and Morris intra-particle diffusion model:

$$q = k_{diff} \cdot t^{0.5} + C_i \quad (12)$$

where  $k_{diff}$  is rate parameter of the  $i$  step [mg/(g·min<sup>1/2</sup>)],  $C_i$  is intercept of  $i$  step, giving an idea about the thickness of the boundary layer.

The experimental kinetic data were described according to the indicated models (Figs. 7-10) and the coefficients of determination as well as the kinetic parameters of metal sorption on yeast are given in Table 2.

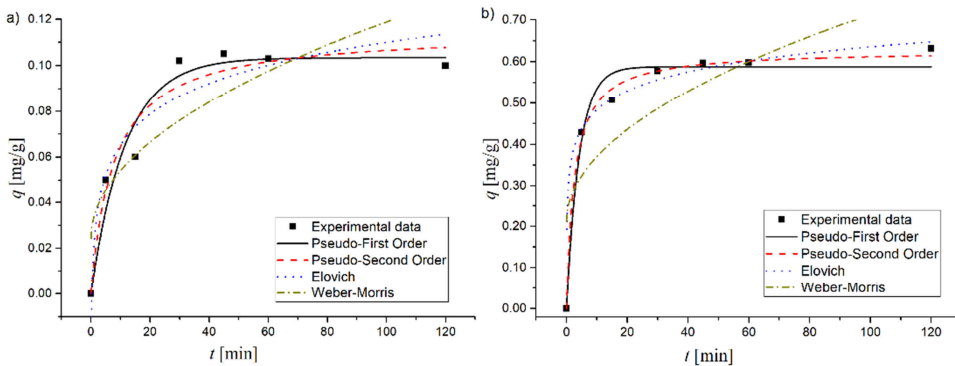


Fig. 7. Kinetics of the metal adsorption using *S. cerevisiae* in Cu-Fe system: a) Cu, b) Fe

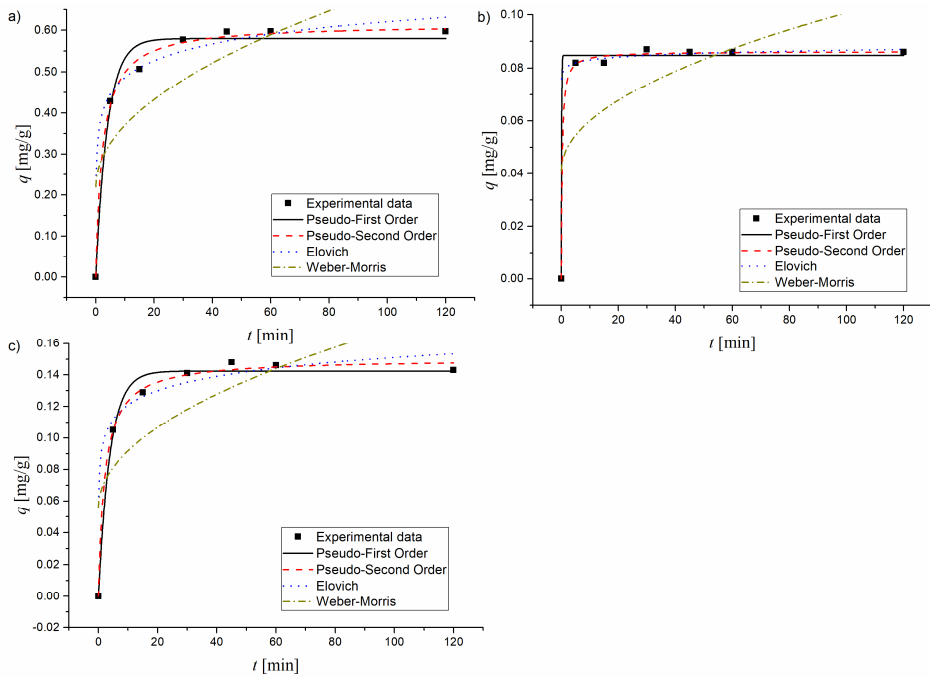


Fig. 8. Kinetics of the metal adsorption using *S. cerevisiae* in Cu-Fe-Ni system: a) Cu, b) Fe, c) Ni

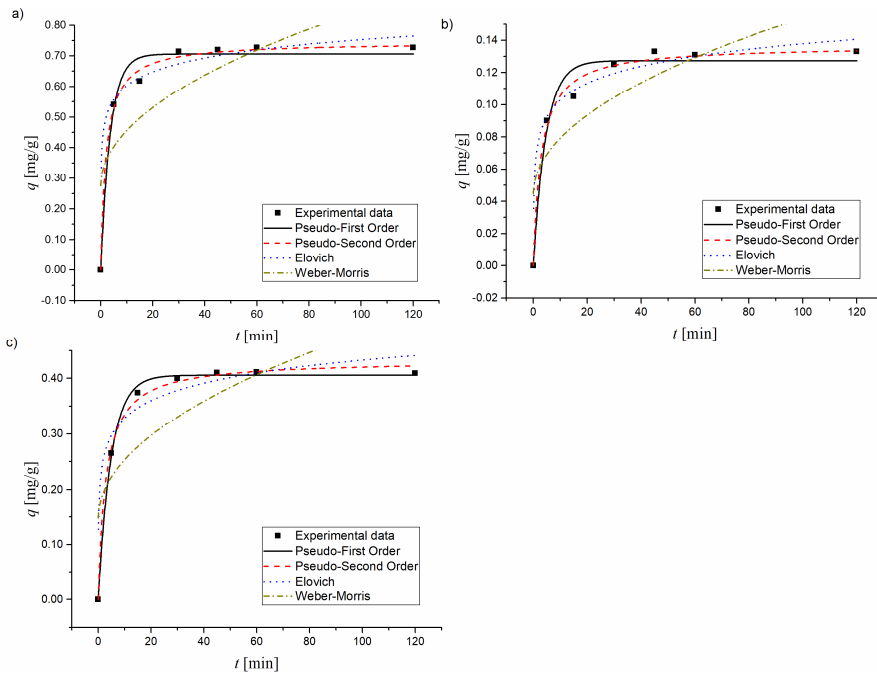


Fig. 9. Kinetics of the metal adsorption using *S. cerevisiae* in Cu-Fe-Zn system: a) Cu, b) Fe, c) Zn

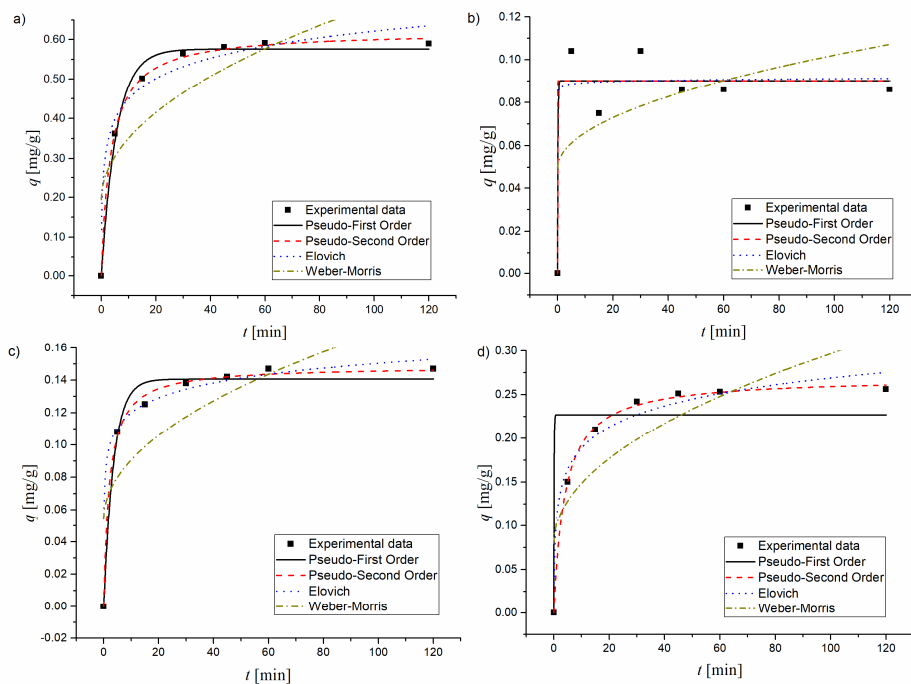


Fig. 10. Kinetics of the metal adsorption using *S. cerevisiae* in Cu-Fe-Ni- Zn system: a) Cu, b) Fe, c) Ni, d) Zn

In Cu(II)-Fe(III) system, the PSO and EM fit well the experimental values obtained for copper. PSO model assumes that the biosorption process occurs in two reactions, the first one is fast and reaches equilibrium quickly and the second is slow and keeps going for a long time period [30]. The Elovich equation, is used to describe the chemical adsorption processes and is suitable for systems with heterogeneous adsorbing surfaces [31, 32]. As can be seen from Table 1, for iron the theoretical  $q_e$  values in the case of the PFO and PSO agree well with the experimental values. The pseudo-first order rate equation is obtained under the ideal assumption of a totally homogenous adsorption surface [32].

In Cu(II)-Fe(III)-Ni(II) system experimental data obtained for Cu(II) were well described by PSO and EM, while data obtained for Fe(III) and Ni(II) by PFO and PSO models. In case of Cu(II)-Fe(III)-Zn(II) system PSO and EM were suitable to describe experimental values for Cu(II) and Fe(III). Data obtained for Zn(II) were more adequately described by PFO and PSO models. In quaternary system data for Cu(II) and Fe(III) well with PFO and PSO models. Data obtained for Ni(II) were better described by PSO and EM, while for Zn(II) by PSO model. Since PSO and EM were applicable for the main part of experimental data it can be suggested that chemisorption mechanism plays an important role in the adsorption of studied ions on the *S. cerevisiae*.

For the intra-particle diffusion model the correlation coefficients are relatively low lying between 0.07 and 0.7.

Table 2

The constants and correlation coefficients ( $R^2$ ) of the kinetic models

		Model							
		PFO				PSO			
	Metal	$q_{exp}$ [mg/g]	$q_e$ [mg/g]	$k_1$ [min <sup>-1</sup> ]	$R^2$ [-]	$q_e$ [mg/g]	$k_2$ [g/(mg·min)]	$R^2$ [-]	
Systems	Cu-Fe	Cu	0.6	0.59	0.24	0.97	0.63	0.62	0.99
		Fe	0.1	0.10	0.09	0.94	0.11	1.12	0.94
	Cu-Fe-Ni	Cu	0.6	0.58	0.25	0.98	0.61	0.69	0.99
		Fe	0.09	0.08	10	0.99	0.09	3.81	0.99
		Ni	0.14	0.14	0.25	0.99	0.15	3.08	0.99
	Cu-Fe-Zn	Cu	0.72	0.71	0.27	0.98	0.75	0.65	0.99
		Fe	0.13	0.13	0.21	0.96	0.14	2.48	0.99
		Zn	0.4	0.4	0.2	0.99	0.43	0.79	0.99
	Cu-Fe-Ni-Zn	Cu	0.59	0.58	0.18	0.99	0.62	0.46	0.99
		Fe	0.09	0.09	23	0.93	0.09	0.12	0.93
		Ni	0.14	0.14	0.28	0.98	0.14	3.285	0.99
		Zn	0.25	0.22	10	0.80	0.26	0.9	0.99

		Model							
		EM				IPM			
	Metal	$q_{exp}$ [mg/g]	$\alpha$ [mg/(g·min)]	$\beta$ [g/min]	$R^2$ [-]	$k_{diff}$ [mg/(g·min <sup>1/2</sup> )]	$C_i$ [-]	$R^2$ [-]	
Systems	Cu-Fe	Cu	0.6	10.37	15.21	0.99	0.05	0.21	0.62
		Fe	0.1	0.06	51.54	0.91	0.009	0.024	0.70
	Cu-Fe-Ni	Cu	0.6	24.7	17.2	0.99	0.05	0.22	0.57
		Fe	0.09	n.a.	n.a.	n.a.	0.006	0.04	0.34
		Ni	0.14	13.51	76.41	0.98	0.01	0.06	0.53
	Cu-Fe-Zn	Cu	0.72	67.3	15.3	0.99	0.06	0.28	0.55
		Fe	0.13	1.3	65.8	0.99	0.01	0.04	0.62
		Zn	0.4	6.28	22.03	0.97	0.03	0.15	0.57
	Cu-Fe-Ni-Zn	Cu	0.59	3.07	13.39	0.98	0.05	0.19	0.62
		Fe	0.09	3.13	11.7	0.92	0.005	0.05	0.07
		Ni	0.14	11	75.3	0.99	0.01	0.05	0.56
		Zn	0.25	0.7	28	0.97	0.02	0.08	0.65

### Effect of temperature on metal biosorption

The effect of temperature on the adsorption of metals onto *S. cerevisiae* was studied at 293, 303, 313, and 323 K. From the data presented in Figure 11, it is seen that in Cu(II)-Fe(III), Cu(II)-Fe(III)-Ni(II) and Cu(II)-Fe(III)-Zn(II) systems with the temperature rising, the removal of copper by *S. cerevisiae* increased approximately from 60 to 80 %. In quaternary system, copper removal was almost not dependent of temperature.

Iron removal increased significantly in systems: Cu(II)-Fe(III), Cu(II)-Fe(III)-Ni(II) and Cu(II)-Fe(III)-Ni(II)-Zn(II), while in Cu(II)-Fe(III)-Zn(II) system increase of temperature did not affect its removal. Significant increase of zinc removal with temperature increase was observed in in both systems: in Cu(II)-Fe(III)-Zn(II) (from 49 to 70 %) and in Cu(II)-Fe(III)-Ni(II)-Zn(II) (from 71 to 95 %) systems. The rise in sorption capacity with temperature increase can be explained by the increase in collision frequency

between the sorbent and the sorbate, which results in increased sorption on the surface of biosorbent [33].

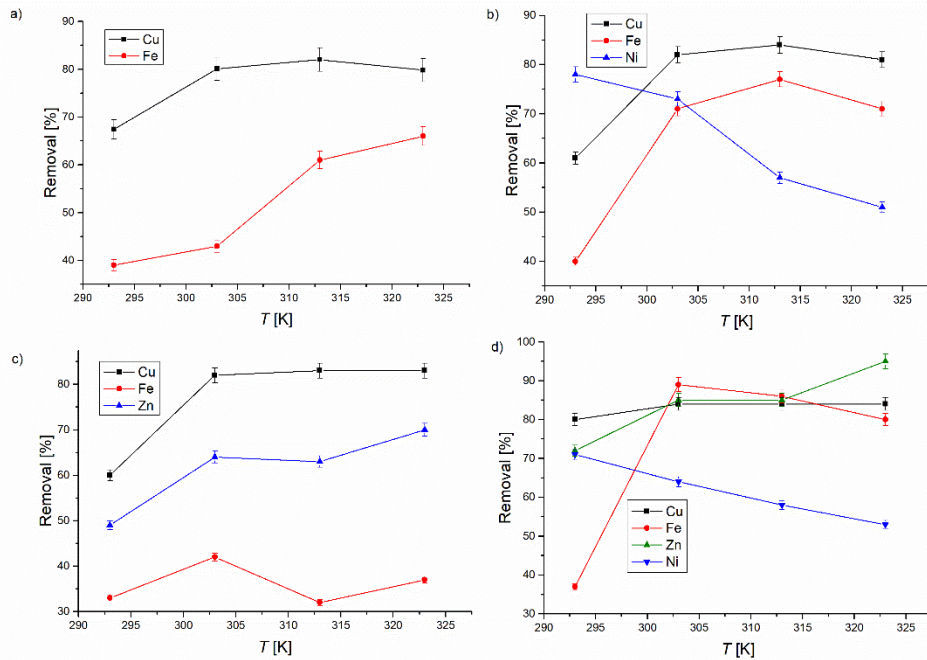


Fig. 11. Effect of temperature on the sorption of metal ions by *S. cerevisiae* biomass (at  $T = 20\text{ }^{\circ}\text{C}$ ; sorbent dosage  $0.5\text{ g/dm}^3$ ; adsorption time 1 h): a) Cu-Fe, b) Cu-Fe-Ni, c) Cu-Fe-Zn, d) Cu-Fe-Ni-Zn systems

Nickel removal by *S. cerevisiae* decreased approximately by 20 % in both studied systems with the increase of the temperature. Obtained results showed that the nickel adsorption by *S. cerevisiae* has an exothermic character, while for copper, and endothermic for copper, iron and zinc ions.

Zinicovscaia et al. [7] found that temperature increase from 20 to 40  $^{\circ}\text{C}$  lead to decrease of copper removal by yeast from 37 to 16 %. Han et al. [27] showed that adsorption of copper ions by beer yeast was increasing, but for lead it was decreasing with temperature increase.

### Thermodynamic parameters of adsorption

To understand the nature of biosorption process the Gibbs free energy change,  $\Delta G^{\circ}$ , enthalpy ( $\Delta H^{\circ}$ ) and entropy ( $\Delta S^{\circ}$ ) values were calculated according to formula presented in Zinicovscaia et al. [34] work.

$$\ln K_d = \frac{\Delta S^{\circ}}{R} - \frac{\Delta H^{\circ}}{RT} \quad (13)$$

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} \quad (14)$$



where  $K_d$  is the distribution coefficient and it is calculated according to equation:

$$K_d = \frac{(C_0 - C_e)V}{mC_e} \quad (15)$$

where  $C_0$  is initial concentration of metal ions [ $\text{mg}/\text{dm}^3$ ],  $C_e$  is metal concentration in aqueous solution at equilibrium [ $\text{mg}/\text{dm}^3$ ],  $V$  is the volume of aqueous solution [ $\text{dm}^3$ ], and  $m$  is sorbent mass [g].

The standard enthalpy and entropy changes of biosorption determined from the  $\ln K_d$  versus  $1/T$  plot (Fig. 12). Calculated thermodynamic parameters are presented in Table 3.

Table 3

Thermodynamic parameters for metal biosorption on *S. cerevisiae*

		System					
		Cu-Fe		Cu-Fe-Ni			Cu-Fe-Zn
Parameter	T [K]	Cu	Fe	Cu	Fe	Ni	Cu
$\Delta G^0$ [kJ/mol]	293	-10.2	-8.7	-10.4	-9.3	-10.73	-9.9
	303	-10.7	-9.6	-11.0	-10.1	-10.66	-10.6
	313	-11.1	-10.4	-11.5	-11.0	-10.59	-11.2
	323	-11.6	-11.3	-12.1	-11.8	-10.52	-11.8
$\Delta H^0$ [kJ/mol]		3.9	16.3	6.1	15	-12.7	8.8
$\Delta S^0$ [J/mol·K]		48.2	85.6	56.5	83.1	-6.8	64
		System					
		Cu-Fe-Zn		Cu-Fe-Ni-Zn			
Parameter	T [K]	Fe	Zn	Cu	Fe	Ni	Zn
$\Delta G^0$ [kJ/mol]	293	-8.6	-9.4	-10.7	-9.3	-10.4	-10.5
	303	-8.9	-10.0	-11.1	-10.2	-10.5	-11.1
	313	-9.2	-10.6	-11.5	-11.2	-10.5	-11.7
	323	-9.5	-11.2	-11.8	-12.2	-10.6	-12.2
$\Delta H^0$ [kJ/mol]		0.2	8.9	0.7	19	-8.1	6.8
$\Delta S^0$ [J/mol·K]		29.9	62.3	39	97.2	7.9	59

The negative values of  $\Delta G^0$  observed for all studied systems indicate that the sorption process is feasible and spontaneous. With the increase of temperature, the  $\Delta G$  value was gradually decreased which showed that the increase of temperature was favorable to the adsorption process [33, 36]. The negative  $\Delta H^0$  value indicates on the exothermic character of the reaction, while positive value indicates on the endothermic one. Positive  $\Delta H^0$  values were obtained for all elements in studied systems, except nickel. According to Xu et al. [35] significant variation of  $\Delta H^0$  values for metal ions in studied system indicate on complex character of metal ions interaction with biosorbent surface.

The negative  $\Delta S^0$  values calculated for nickel indicate on the decrease in the degree of freedom of the adsorbed species. The positive values of  $\Delta S^0$  obtained for the remainder elements confirm the increased randomness at the solid-solution interface during biosorption [36].

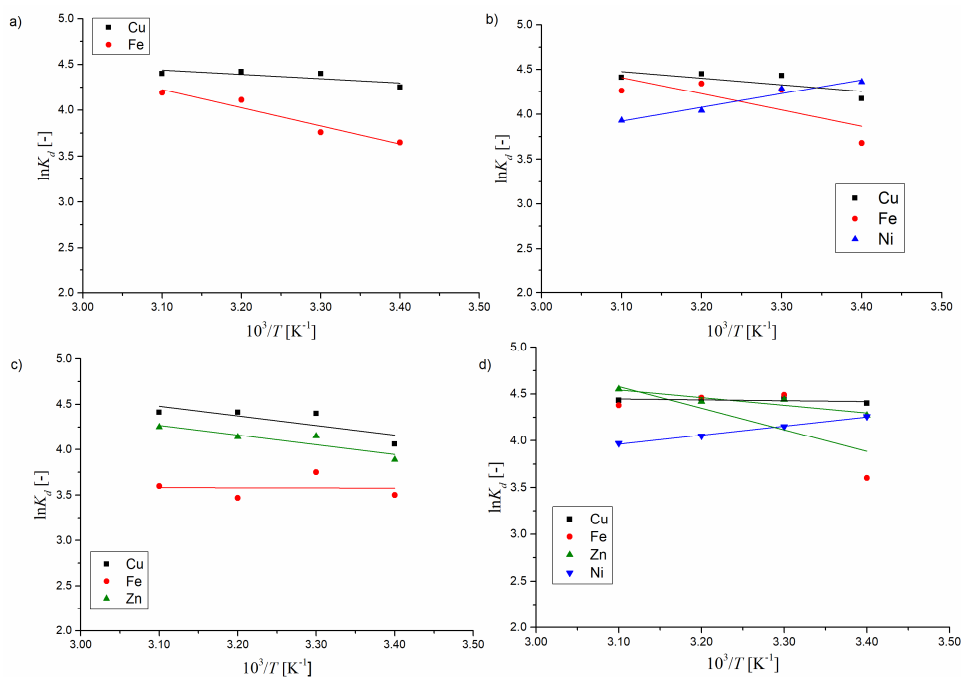


Fig. 12. The van't Hoff plot of  $\ln K_d$  vs.  $1/T$  for the estimation of thermodynamic parameters for metal sorption by *S. cerevisiae* biomass: a) Cu-Fe, b) Cu-Fe-Ni, c) Cu-Fe-Zn, d) Cu-Fe-Ni-Zn systems

## Desorption study

In order to implement biomass for industrial application, it is important to estimate metal desorption behaviour of biomass. In the present study three desorbing agents distilled water, 0.1M  $\text{HNO}_3$  and 0.1 M EDTA were used for metal desorption from yeast biomass. Data presented in Figure 7 showed that in all studied systems metal ions desorption with distilled water was almost negligible. EDTA and  $\text{HNO}_3$  showed to be more efficient desorbents.

In Cu(II)-Fe(III) system 68 % of Cu(II) ions were desorbed by  $\text{HNO}_3$  and 63 % by EDTA. EDTA was more efficient for Fe(III) desorption (88 %) and only 10 % of Fe(III) ions were desorbed by  $\text{HNO}_3$ . In Cu(II)-Fe(III)-Ni(II) system metal ions desorption by EDTA changed in the following order: Fe (96 %) > Cu (88 %) > Ni (71 %).  $\text{HNO}_3$  was efficient for Cu(II) (86 %) and Ni(II) (68 %) desorption, while Fe(III) ions were not desorbed by nitric acid. In Cu(II)-Fe(III)-Zn(II) system EDTA and  $\text{HNO}_3$  more efficiently desorbed Zn(II) ions, followed by Cu(II) and Fe(III) ions. In quaternary system EDTA and  $\text{HNO}_3$  desorption efficiency changed in the following order Cu > Zn > Ni, while for Fe(III) ions it was zero.

Chojnacka et al. [37] studied the desorption of Cr, Cd and Cu from *Spirulina sp.* biomass using 0.1 M EDTA, 0.1 M  $\text{HNO}_3$  and deionised water. Nitric acid was the most efficient desorbent followed by EDTA and deionised water.

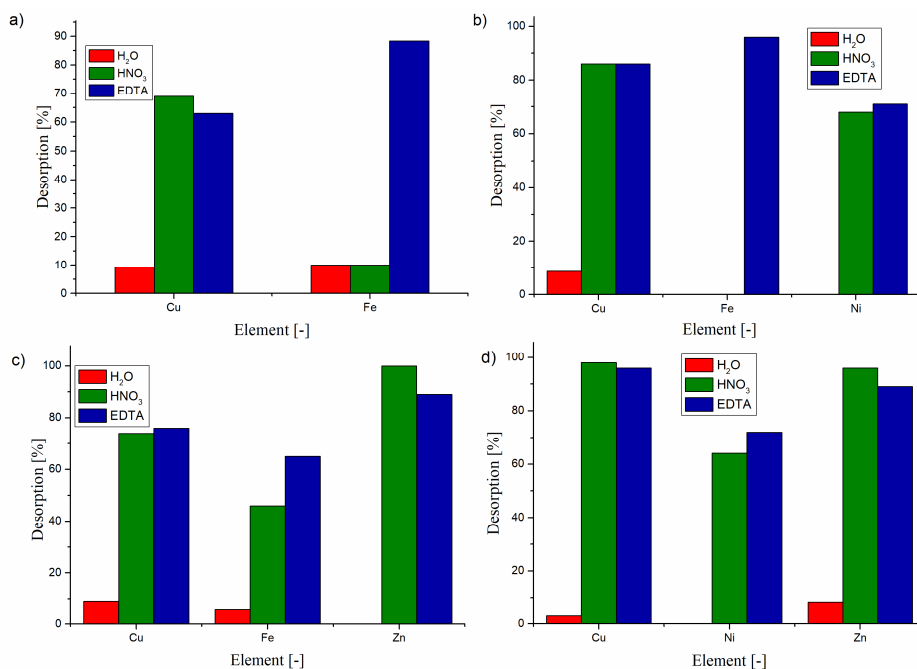


Fig. 13. Desorption of metal ions by different eluents: EDTA, nitric acid and distilled water: a) Cu-Fe, b) Cu-Fe-Ni, c) Cu-Fe-Zn, d) Cu-Fe-Ni-Zn

## Conclusion

The results of present study showed that the *S. cerevisiae* waste biomass is suitable biosorbent for complex effluents treatment. Different optimal pH values determined for metal present in studied systems indicate on possibility of selective metal biosorption from binary, ternary and quaternary systems. The experimental data of copper adsorption in complex systems fit well to Langmuir model followed by Freundlich, Temkin and Dubinin-Radushkevich models. The maximum adsorptive quantity of beer yeast for Cu(II) was 10.6 mg/g in Cu(II)-Fe(III) system, 15.1 mg/g in Cu(II)-Fe(III)-Ni(II) system, 13.3 mg/g in Cu(II)-Fe(III)-Zn(II) system and 14.5 mg/g in Cu(II)-Fe(III)-Ni(II)-Zn(II) system. All the experimental data showed better correlation with chemisorptions kinetic models. The adsorptive process for Cu(II), Fe(III), Zn(II) and Ni(II) ions was feasible and spontaneous. The biosorption of Cu(II), Fe(III), Zn(II) ions was endothermic in nature, while of Ni(II) ions exothermic. Using different eluents, it is possible to recover from biomass metals of interest. Yeast biomass obtained after biosorption experiments can be applied as additive in cement production and at road construction.

## Acknowledgements

This work was supported by the Russian Foundation for Basic Research (RFBR) [grant numbers 18-29-25023-MK].

## References

- [1] do Nascimento JM, de Oliveir JD, Rizzo ACL, Leite SGF. Biosorption Cu(II) by the yeast *Saccharomyces cerevisiae*. *Biotechnol Rep.* 2019;21:e00315. DOI: 10.1016/j.btre.2019.e00315.
- [2] Demiral H, Güngör C. Adsorption of copper(II) from aqueous solutions on activated carbon prepared from grape bagasse. *J Clean Prod.* 2016;124:103-13. DOI: 10.1016/j.jclepro.2016.02.084.
- [3] Yargıç AS, Yarbay Sahin RZ, Ozbay N, Onal E. Assessment of toxic copper(II) biosorption from aqueous solution by chemically-treated tomato waste. *J Clean Prod.* 2015;88:152-9. DOI: 10.1016/j.jclepro.2014.05.087.
- [4] Moreira VR, Lebron YAR, Freire SJ, Santos LVS, Palladino F, Jaco RS. Biosorption of copper ions from aqueous solution using *Chlorella pyrenoidosa*: Optimization, equilibrium and kinetics studies. *Microchem J.* 2019;145:119-29. DOI: 10.1016/j.microc.2018.10.027.
- [5] Peng Q, Liu Y, Zeng G, Xu W, Yang C, Zhang J. Biosorption of copper(II) by immobilizing *Saccharomyces cerevisiae* on the surface of chitosan-coated magnetic nanoparticles from aqueous solution. *J Hazard Mater.* 2010;177:676-82. DOI: 10.1016/j.jhazmat.2009.12.084.
- [6] Zinicovscaia I, Yushin N, Abdusamadzoda D, Grozdov D, Shvetsova M. Efficient removal of metals from synthetic and real galvanic zinc-containing effluents by brewer's yeast *Saccharomyces cerevisiae*. *Materials.* 2020;13:3624. DOI: 10.3390/ma13163624.
- [7] Zinicovscaia I, Grozdov D, Yushin N, Abdusamadzoda D, Gundorina S, Rodlovskaya E, et al. Metal removal from chromium containing synthetic effluents by *Saccharomyces cerevisiae*. *Desalin Water Treat.* 2020;178:254-70. DOI: 10.5004/dwt.2020.24987.
- [8] De Rossi A, Rigon MR, Zapparoli M, Braido RD, Colla LM, Dotto GL, et al. Chromium(VI) biosorption by *Saccharomyces cerevisiae* subjected to chemical and thermal treatments. *Environ Sci Pollut Res Int.* 2018;25:19179-86. DOI: 10.1007/s11356-018-2377-4.
- [9] Wang J, Chen C. Biosorption of heavy metals by *Saccharomyces cerevisiae*: A review. *Biotechnol Adv.* 2006;24:427-51. DOI: 10.1016/j.biotechadv.2006.03.001.
- [10] Raffar NIA, Rahman NNA, Alrozi R, Senusi F, Chang SH. Potential immobilized *Saccharomyces cerevisiae* as heavy metal removal. *AIP Conf Proc.* 2015;1660:070093. DOI: 10.1063/1.4915810.
- [11] Machado MD, Janssens S, Soares HMVM, Soares EV. Removal of heavy metals using a brewer's yeast strain of *Saccharomyces cerevisiae*: advantages of using dead biomass. *J Appl Microbiol.* 2009;106:1792-804. DOI: 10.1111/j.1365-2672.2009.04170.x.
- [12] Avery SV, Tobin JM. Mechanisms of strontium uptake by laboratory and brewing strains of *Saccharomyces cerevisiae*. *Appl Environ Microbiol.* 1992;58(12):3883-9.
- [13] Brady D, Duncan JR. Binding of heavy metals by the cell walls of *Saccharomyces cerevisiae*. *Enzyme Microb. Technol.* 1994;16:633-8. DOI: 10.1016/0141-0229(94)90131-7.
- [14] Machado MD, Soares HMVM, Soares EV. Removal of chromium, copper, and nickel from an electroplating effluent using a flocculent brewer's yeast strain of *Saccharomyces cerevisiae*. *Water Air Soil Pollut.* 2010;212:199-204. DOI: 10.1007/s11270-010-0332-1.
- [15] Frontasyeva MV. Neutron activation analysis for the life sciences. *Phys Part Nucl.* 2011;42:332-78. DOI: 10.1134/S1063779611020043.
- [16] Hlihor RM, Diaconu M, Fertu D, Chelaru C, Sandu I, Tavares T. Bioremediation of Cr(VI) polluted wastewaters by sorption on heat inactivated *Saccharomyces cerevisiae* biomass. *Int J Environ Res.* 2013;7(3):581-94. DOI: 10.22059/ijer.2013.638.
- [17] Oves M, Saghir Khan M, Zaidi A. Biosorption of heavy metals by *Bacillus thuringiensis* strain OSM29 originating from industrial effluent contaminated north Indian soil. *Saudi J Biol Sci.* 2013;20:121-9. DOI: 10.1016/j.sjbs.2012.11.006.
- [18] Al-Homaidan AA, Al-Houri HJ, Al-Hazzani AA, Elgaaly G, Moubayed NMS. Adsorptive removal of cadmium ions by *Spirulina platensis* dry biomass. *Saudi J Biol Sci.* 2015;22:795-800. DOI: 10.1016/j.sjbs.2015.06.010.
- [19] Rajfur M, Klos A, Kříž J. Translocation of cations during sorption of copper in the system solution - algae (*Spirogyra* sp.). *Ecol Chem Eng S.* 2014;21(3):425-33. DOI: 10.2478/eces-2014-0031.
- [20] Yildiz S. Kinetic and isotherm analysis of Cu(II) adsorption onto almond shell (*Prunus dulcis*). *Ecol Chem Eng S.* 2017;24(1):87-106. DOI: 10.1515/eces-2017-0007.
- [21] Padmavathy V, Vasudevan P, Dhingra SC. Biosorption of nickel(II) ions on Baker's yeast. *Process Biochem.* 2003;38:1389-95. DOI: 10.1016/S0032-9592(02)00168-1.
- [22] Basak G, Preethy Chandran LV, Das N. Removal of Zn(II) from electroplating effluent using yeast biofilm formed on gravels: batch and column studies. *J Environ Health Sci Eng.* 2014;12:8. DOI: 10.1186/2052-336X-12-8.

- [23] Gerlach M, Trautwein AX, Zecca L, Youdim MBH, Riederer P. Moessbauer spectroscopic studies of purified neuromelanin isolated from the substantia nigra. *J Neurochem.* 1995;65:923-6. DOI: 10.1046/j.1471-4159.1995.65020923.x.
- [24] Sag Y, Kutsal T. Fully competitive biosorption of chromium(VI) and iron(III) ions from binary metal mixtures by *R. arrhizus*: Use of the competitive Langmuir model. *Proc Biochem.* 1996;31:573-85. DOI: 10.1016/S0032-9592(96)00003-9.
- [25] Aksu Z, Gulen H. Binary biosorption of iron(III) and iron(III)-cyanide complex ions on *Rhizopus arrhizus*: modelling of synergistic interaction. *Process Biochem.* 2002;38:161-73. DOI: 10.1016/S0032-9592(02)00062-6.
- [26] Sag Y, Kutsal T. The simultaneous biosorption of Cr(VI), Fe(III) and Cu(II) on *Rhizopus arrhizus*. *Proc Biochem.* 1998;33:571-9. DOI: 10.1016/S0032-9592(98)00020-X.
- [27] Han R, Li H, Li Y, Zhang J, Xiao H, Shi J. Biosorption of copper and lead ions by waste beer yeast. *J Hazard Mater.* 2006;137:1569-76. DOI: 10.1016/j.jhazmat.2006.04.045.
- [28] Albadarin AB, Al-Muhtase AH, Al-laqtah NA, Walker GM, Allen SJ, Ahmad MNM. Biosorption of toxic chromium from aqueous phase by lignin: mechanism, effect of other metal ions and salts. *Chem Eng J.* 2011;169:20-30. DOI: 10.1016/j.cej.2011.02.044.
- [29] Ahmad MA, Ahmad Puad NA, Bello OS. Kinetic, equilibrium and thermodynamic studies of synthetic dye removal using pomegranate peel activated carbon prepared by microwave-induced KOH activation. *Water Res Ind.* 2014;6:18-35. DOI: 10.1016/j.wri.2014.06.002.
- [30] Kula I, Ugurlu M, Karaoglu H, Celik A. Adsorption of Cd(II) ions from aqueous solutions using activated carbon prepared from olive stone by  $ZnCl_2$  activation. *Bioresource Technol.* 2008;99:492-501. DOI: 10.1016/j.biortech.2007.01.015.
- [31] Riahi K, Chaabane S, Thayer BB. A kinetic modeling study of phosphate adsorption onto *Phoenix dactylifera* L. date palm fibers in batch mode. *J Saudi Chem Soc.* 2017;2:143-52. DOI: 10.1016/j.jscs.2013.11.007.
- [32] Wu FC, Tseng RL, Juang RS. Characteristics of Elovich equation used for the analysis of adsorption kinetics in dye-chitosan systems. *Chem Eng J.* 2009;150:366-73. DOI: 10.1016/j.cej.2009.01.014.
- [33] Saini AS, Melo JS. Biosorption of uranium by melanin: Kinetic, equilibrium and thermodynamic studies. *Bioresource Technol.* 2013;149:155-62. DOI: 10.1016/j.biortech.2013.09.034.
- [34] Zinicovscaia I, Yushin N, Shvetsova M, Frontasyeva M. Zinc removal from model solution and wastewater by *Arthrospira* (*Spirulina*) *platensis* biomass. *Int J Phytoremediation.* 2018;20:901-8. DOI: 10.1080/15226514.2018.1448358.
- [35] Xu L, Zheng X, Cui H, Zhu Z, Liang J, Zhou J. Equilibrium, kinetic, and thermodynamic studies on the adsorption of cadmium from aqueous solution by modified biomass ash. *Bioinorg Chem Appl.* 2017;3695604. DOI: 10.1155/2017/3695604.
- [36] Pahlavanzadeh H, Keshtkar AR, Safdari J, Abadi Z. Biosorption of nickel(II) from aqueous solution by brown algae: equilibrium, dynamic and thermodynamic studies. *J Hazard Mater.* 2010;304-10. DOI: 10.1016/j.jhazmat.2009.10.004.
- [37] Chojnacka K, Chojnacki A, Górecka H. Biosorption of  $Cr^{3+}$ ,  $Cd^{2+}$  and  $Cu^{2+}$  ions by blue-green algae *Spirulina* sp.: kinetics, equilibrium and the mechanism of the process. *Chemosphere.* 2005;75-84. DOI: 10.1016/j.chemosphere.2004.10.005.