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Metal removal from chromium containing synthetic effluents by *Saccharomyces cerevisiae*

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ABSTRACT

Yeast *Saccharomyces cerevisiae* (*S. cerevisiae*), was used to remove metal ions from four complex effluents with the following composition: Cr(VI)-Fe(III), Cr(VI)-Fe(III)-Ni(II), Cr(VI)-Fe(III)-Ni(II)-Zn(II), and Cr(VI)-Fe(III)-Ni(II)-Zn(II)-Cu(II). Biosorbent was characterized using scanning electron microscopy and Fourier-transform infrared spectroscopy. The effect of pH, chromium concentration, contact time, and temperature on metal biosorption was investigated. Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich equilibrium models have been used to describe the experimental sorption equilibrium data, while the kinetics of the sorption was explained by pseudo-first-order, pseudo-second-order, Elovich, and the intra-particle diffusion models. The maximum amount of chromium sorbed by biomass has been calculated from the Langmuir isotherm. To estimate biosorption nature $\Delta G°$, $\Delta H°$ and $\Delta S°$ values were calculated. *S. cerevisiae* can be successfully applied for complex wastewater treatment.

Keywords: Saccharomyces cerevisiae; Chromium; Iron; Nickel; Zinc; Copper; Biosorption

1. Introduction

Industrialization and technological advancement have led to the discharge of large amounts of wastewater containing hazardous pollutants in natural waters [1]. Heavy metal due to their non-degradable nature and bioaccumulation in living organisms is considered one of the most dangerous environmental pollutants. Metals find their way into water bodies via wastewater from mining, electroplating, chemical, textile industries, leather industry, refineries, steelwork foundries, pigment manufacturing, textile, and photographic and cosmetics industry, and fertilizer production [2–4]. A large number of chemical and physical techniques such as chemical precipitation, ion exchange, chemical oxidation/reduction, reverse osmosis, electrodialysis, ultra-filtration, etc. can be used for metal removal from wastewater [3,5]. However, the application of such processes is often restricted because of technical and/or economic limitations [6].

Biosorption can be considered an eco-friendly alternative to the conventional methods for the removal of metals from industrial effluents [7]. Biosorption is the result of physicochemical interaction between the metal ions and the functional groups present on the microbial cell surface. The main advantages of biosorption are cost-effectiveness,

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good removal capacity, ability to purify large volumes of wastewater, and the possibility of sorbent regeneration [6,7].

Yeast *Saccharomyces cerevisiae* (*S. cerevisiae*) is one of the economical biosorbents obtained as a by-product of the fermentation industry, which is widely applied for metal removal from aqueous solutions [7–9]. The cell wall of *S. cerevisiae* is the first cellular structure to be in contact with metal ions. The cell wall is composed of three major components: β-glucans, chitin, and mannoproteins [10,11]. According to [11] the brewer's yeast contains the sugar component, the nucleic acids; protein component; –OH and –NH groups and hydrogen bonding; chitin, glucan, C–N, N–H, OH, and C=O groups. Infrared spectra of two yeast species *Candida rugosa* and *Cryptococcus laurentii* point at present in the structure of hydroxyl, ethylene group, carboxyl group, carboxylic group, C–O–C, and C–O [12]. Hlihor et al. [5] showed the presence of OH, N–H, C–H, C=O, COOH and P=O groups in dried *S. cerevisiae* biomass. José et al. [20] showed the presence of the N–H, O–H, C–H, C=O, N, N–O and C–C groups in yeast biomass.

Today, the main part of the biosorption studies is devoted to metal removal from single-metal solutions. In such systems, metal removal is mainly affected by specific surface properties of the organism and the physicochemical parameters of the solution. Since industrial effluents present multi-metal solution metal ions biosorption also depends on the number of metal ion present in effluent and their concentration [13,14].

In the present study the effect of pH, contact time, chromium concentration and temperature on metal ions removal from synthetic chromium-containing effluents by *S. cerevisiae* was studied. The kinetic data were described using pseudo-first, pseudo-second, Elovich, intra-particle diffusion models, while the isotherm equilibrium data were analyzed by Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich (DR) models. Thermodynamics parameters were evaluated from biosorption data.

2. Materials and methods

2.1. Reagents and materials

All the chemicals used for biosorption experiments (CrO_3, $Fe(NO_3)_3{\cdot}9H_2O$, $Ni(NO_3)_2{\cdot}6H_2O$, $Cu(NO_3)_2{\cdot}5H_2O$, $Zn(NO_3)_2{\cdot}6H_2O$, nitric acid, sodium hydroxide) were purchased from Sigma-Aldrich (Germany) company and were of analytical grade.

2.2. Preparation of adsorbent

As the sorbent, the yeast *S. cerevisiae* obtained from company Efes Vitanta Moldova Brewery (Chișinău, Republic of Moldova) was used. Yeast was dried in an oven at 80°C for 48 h, then the biomass was homogenized at 400 rpm for 10 min and afterward used in the experiments.

2.3. Biosorption experiments

The concentration of chromium in studied systems was 10 mg L^{-1}, of iron 5 mg L^{-1} and nickel, zinc and copper –2 mg L^{-1}. The effect of pH (2.0–6.0), time (5–120 min), temperature (20°C–50°C) and chromium concentration (10–100 mg L^{-1}) on metal biosorption was studied. In all experiments, the working volume was 50 mL and sorbent dosage 0.5 g. Experiments were conducted in triplicate and the averages of the measurements for each treatment were used.

The metal uptake q was calculated from the mass balance using the following equation:

$$q = \frac{V\left(C_i - C_f\right)}{m} \tag{1}$$

and sorption removal efficiency, R (%) from the equation:

$$R = \frac{C_i - C_f}{C_i} \times 100 \tag{2}$$

where q is the amount of metal ions adsorbed on the biosorbent, mg g^{-1}; V is the volume of solution, ml; C_i is the initial concentration of metal in mg L^{-1}, C_f is the final metal concentration in the solution, mg L^{-1}, and m is the mass of sorbent, g.

2.4. Methods

Copper concentration in solution was determined by applying atomic absorption spectrometry (Thermo Scientific iCE 3400, USA) with electrothermal atomization. The calibration solutions were prepared from a 1 g L^{-1} stock solution (AAS standard solution; Merck, Germany). To determine the content of Cr, 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 d under at a neutron flux of 1.5×10^{12} cm^{-2} s^{-1}. Iron content in the samples was determined by a γ-line with the energy of 1,099.25 keV of isotope ^{59}Fe, nickel by a γ-line with the energy of 810.57 keV of isotope ^{58}Co and zinc by a γ-line with the energy of 1,115.54 keV of isotope ^{65}Zn.

Fourier-transform infrared spectroscopy (FTIR) 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 4,000–400 cm^{-1} using a Nicolet 6700 spectrometer (Thermo Scientific, USA). Scanning electron microscopy (SEM) characterization was performed using the S3400N (Hitachi, Japan) microscope. Zeta potential of biomass was measured using Zetasizer Nano ZSP (Malvern, UK). X-ray diffraction (XRD) patterns of the samples were carried out on an X-ray diffractometer EMPYREAN (firm PANalytical, The Netherlands) in Cu-Kα radiation $\lambda = 1.541874$ Å.

3. Results and discussion

3.1. Sorbent characterization

The *S. cerevisiae* was characterized using SEM and FTIR techniques. Fig. 1 presents SEM images of *S. cerevisiae* before and after interaction with metal ions. The yeast cells before interaction with metals were oval and smooth. The surface

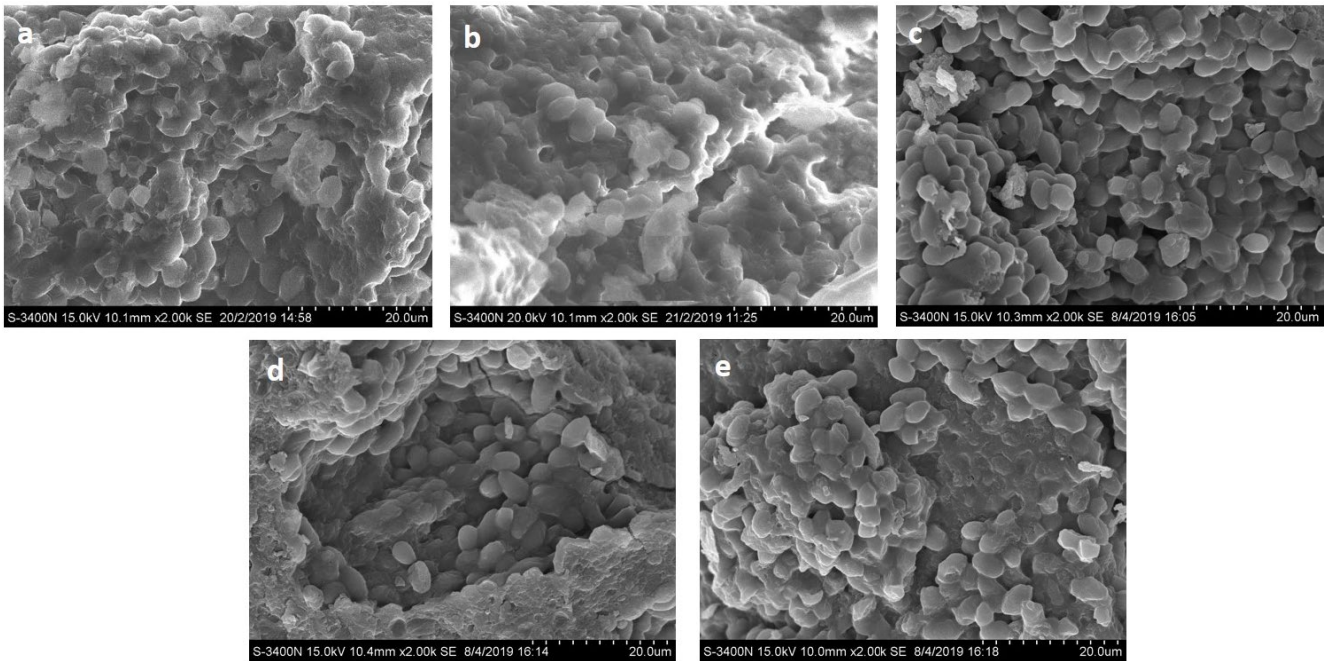

Fig. 1. SEM images of *Saccharomyces cerevisiae*: (a) control, (b) system Cr(VI)-Fe(III), (c) system Cr(VI)-Fe(III)-Ni(II), (d) system Cr(VI)-Fe(III)-Ni(II)-Zn(II), and (e) system Cr(VI)-Fe(III)-Ni(II)-Zn(II)-Cu(II).

morphology of the biomass did not change significantly after biomass interaction with metal ions, indicating that metal ions biosorption occurs at the surface of the biosorbent.

The presence of metal ions on the biomass surface was confirmed by energy dispersive analysis (Table 1).

According to the data presented in Table 1 Cr(VI), Fe(III), Ni(II), Zn(II), and Cu(II) were not detected in control biomass. However, they were determined in metal-loaded biomass. The decrease of the content of Mg, Al, and K in metal-loaded biomass indicates their participation in the metal exchange process. As it was shown in [15–17] decrease of the Mg and Al content in biomass can be associated with presence of Fe(III) and Cu(II) ions in the system, while *K* decrease can be explained by its replacement by Ni(II), Cu(II) and Zn(II) ions.

FTIR spectrum of native *S. cerevisiae* biomass (Fig. 2) indicates strong absorption bands in the regions 1,036 and 1,518 cm^{-1}, which corresponds to OH-groups. The peaks at 1,214 and 1,740 cm^{-1} are related to the stretching vibration of carboxyl (C=O) groups, whereas the peaks at 1,393 and 2,950 cm^{-1} represent the stretching vibration of alkyl groups ($–CH_3$ or CH_2). The peak at 1,518 cm^{-1} is related to the vibration of aromatic groups, an absorption band at 1,626 cm^{-1} corresponds to CH=CH groups. The peak of symmetrical stretching vibration of the phosphodiester group ($–PO_2^-$)

Table 1
Composition of control and metal-loaded *Saccharomyces cerevisiae* biomass

Element,%	Control	Cr(VI)-Fe(III)	Cr(VI)-Fe(III)-Ni(II)	Cr(VI)-Fe(III)-Ni(II)-Zn(II)	Cr(VI)-Fe(III)-Ni(II)-Zn(II)-Cu(II)
C	41.8	41.6	41.2	40.9	41.8
N	11.5	11.9	12.5	10.4	10.7
O	45.1	41.6	44.9	46.8	45.9
Mg	0.11	n.d.	0.02	0.01	n.d.
Al	0.89	0.37	0.56	0.77	0.36
P	0.41	1.1	0.58	0.74	0.79
S	0.16	0.38	0.18	0.23	0.28
K	0.08	0.02	0.02	0.04	0.01
Cr	n.d.	0.07	0.06	0.04	0.08
Fe	n.d.	0.04	0.03	0.03	0.08
Ni	n.d.	n.d.	0.003	0.001	0.001
Zn	n.d.	n.d.	n.d.	0.002	0.003
Cu	n.d.	n.d.	n.d.	n.d.	0.003

n.d. – not detected.

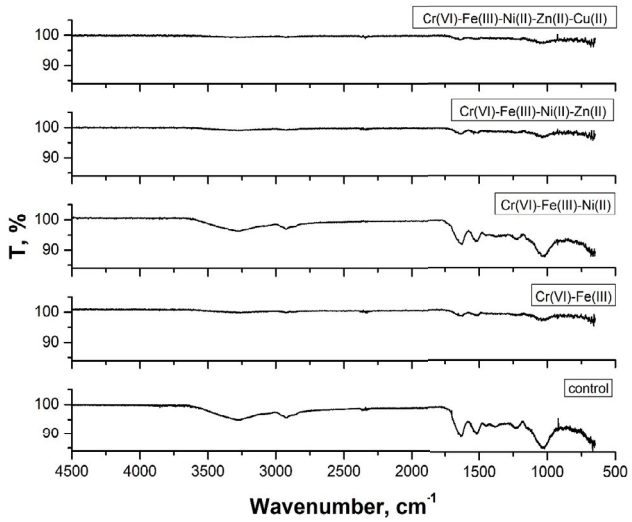

Fig. 2. FTIR spectrum of *Saccharomyces cerevisiae* biomass before and after metal biosorption.

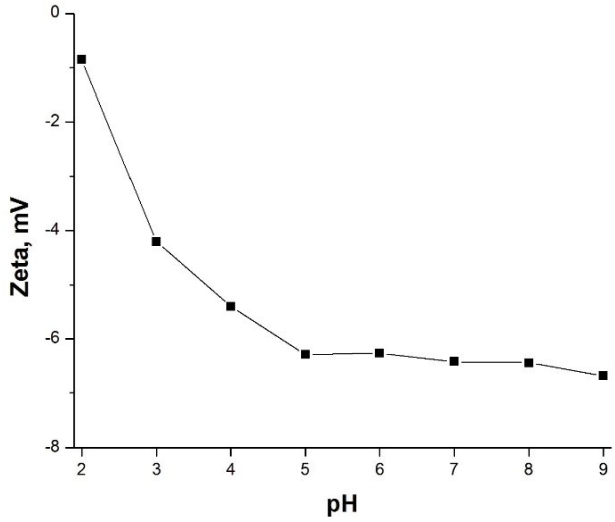

Fig. 3. Zeta potential of *Saccharomyces cerevisiae* as the function of pH.

centered at wavenumber 1,092 cm^{-1}, and the vibration absorption band of polysaccharide skeleton at wavenumber 1,043 cm^{-1} were observed.

The strong boarded peak at wavenumber area 3,600–3,200 cm^{-1} could be attributed to hydroxyl (–OH) and amine (–NH) functional groups. The presence of methyl (–CH) stretching vibrations could be confirmed by the adsorption peak at wavenumbers region 2,950–2,800 cm^{-1}. The band at 3,288 cm^{-1} is relevant to the standard absorption band of the amido group (HN=O).

In addition, –C–O, –C–C, and –C–OH stretching vibrations could be found at the adsorption peaks of the 1,650–1,200 cm^{-1} region or the strong bands in this area could also correspond to the amide I–III bands of polypeptide/proteins.

After biomass interaction with solution containing Cr(VI) and Fe(III) ions, the IR spectra revealed a slight shift of bands 1,036, 1,518 and 3,288 cm^{-1} indicating on the involvement of OH, CH=CH, C=OH N=O groups in metal binding. In case of Cr(VI)-Fe(III)-Ni(II), Cr(VI)-Fe(III)-Ni(II)-Zn(II) and (VI)-Fe(III)-Ni(II)-Zn(II)-Cu(II) no significant changes in metal loaded biomass spectra were observed. However, the transmittance of the peaks in the metal loaded biomass was lower than in the control sample. Reduction of peak transmittance can be explained by metal binding to biomass that leads to occurrence of bond stretching to a lesser degree [18].

The zeta potential of *S. cerevisiae* was investigated at the pH range 2.0–9.0. The results presented in Fig. 3 indicated that the zeta potential of biomass was negative at all pH values. In the pH range, 5.0–9.0 zeta potential value constituted –6.0 and it was independent of pH. The results were very similar to the data obtained by Lin et al. [19] for yeast *P. pastoris* and *S. cerevisiae*.

The structural transformation and the morphological change of raw and metal-loaded *S. cerevisiae* have been determined by XRD analyses (Fig. 4). The broad peak around $2\theta = 20°$ corresponds to the amorphous phase of biomass. These results are in agreement with other studies [20,21].

3.2. Influence of pH on metals adsorption

The pH is an important parameter for biosorption processes since it affects the speciation of the metal, the stability of the biomass and the chemical state of its reactive groups [22]. In the present study, the effect of pH on metal removal from complex systems was studied in the pH range 2.0–6.0 (Fig. 5), since at pH > 7.0 precipitation of metal cations takes place.

In Cr(VI)-Fe(III) system maximum removal of both elements was achieved at pH 2.0:97.7% for Cr(VI) and 98.1% for Fe(III). With pH increase, the removal of Cr(VI) ions was significantly reduced and at pH > 4.0 it constituted 30%. Depending on pH and concentration, Cr(VI) ions exist in solution in several forms: chromic acid (H_2CrO_4) at pH ≥ 1, hydrogen chromate ($HCrO_4^-$) and dichromate ($Cr_2O_7^{2-}$) at pH range of 1–7 and chromate (CrO_4^{2-}) at pH range of 7–14 [23]. The maximum Cr(VI) removal at pH 2.0 can be explained by the protonation of functional groups on the yeast surface and presence of chromium in solution in anionic form. Iron(III) ions were also more effectively adsorbed at low values of pH. Hlihor et al. [5] showed the involvement of carbonyl, amide and phosphate groups in Cr(VI) binding by *S. cerevisiae*. Amide, O–H and C=O groups were involved in Cr(VI) uptake by *S. cerevisiae* immobilized in multi-walled carbon nanotubes [24]. The anionic species of Cr(VI) can also be linked to the microbial surface trough electrostatic interaction with amines, which are positively charged [25].

Fe(III) exists in ionic form in a very narrow range of pH [26]. Gerlach et al. [27] have found that OH groups play the main role in iron ions binding. The decrease of Fe(III) ions removal with the pH increase can be explained by its precipitation caused by the increase of concentration of OH– ions in the adsorption medium. The present results are in good agreement with the data presented in Sag and Kutsal [2] and Aksu and Gülen [28], who showed that optimum pH for the biosorption of Cr(VI) and Fe(III) ions by *R. arrhizus* was 2.0.

In Cr(VI)-Fe(III)-Ni(II) system maximum Cr(VI) and Fe(III) removal occurred at pH 2.0: 88% and 98%, respectively. The pH 3.0 was found to be optimal for maximum Ni(II) ions removal (70%). In Cr(VI)-Fe(III)-Ni(II)-Zn(II) system pH 2.0 was optimal for Cr(VI) and Fe(III) ions removal, while Ni(II) and Zn(II) maximum removal was achieved at pH 3.0 and 4.0, respectively. The presence of Zn(II) ions in the system leads to the reduction of Ni(II) and Fe(III) ions removal. According to Basak et al. [12] carboxyl, phosphate, sulfhydryl, hydroxyl and nitrogen-containing groups of yeast biomass surface participated in the removal of Zn(II) ion. Thus, the reduction of Ni(II) and Fe(III) ions removal can be explained by their competition with Zn(II) ions for the same binding sites on the yeast surface. The reduction of Ni(II) removal at a pH ≥ 4.0 in all analyzed systems is explained by the formation of insoluble nickel hydroxide [29]. Padmavathy et al. [30] showed maximum removal of Ni(II) at pH of 6.75 and suggested that mannoproteins and glucans present on the cell wall were responsible for the sorption of Ni(II) ions by yeast.

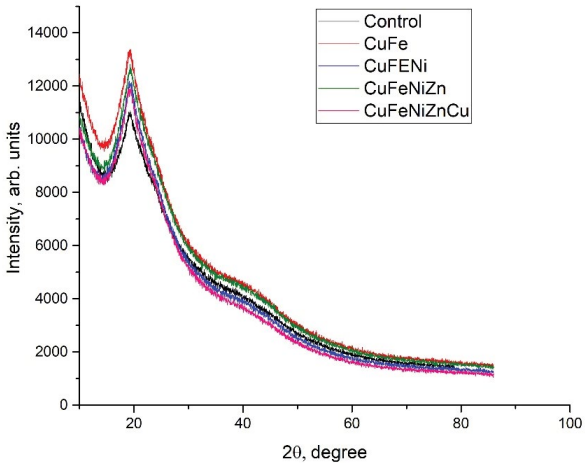

Fig. 4. XRD patterns of the original yeast and metal-loaded *Saccharomyces cerevisiae* biomass.

In Cr(VI)-Fe(III)-Ni(II)-Zn(II)-Cu(II) system at pH 2.0 83% of Cr(VI) and 69% of Fe(III) ions were removed from the solution. pH 3.0 was optimum for Ni(II) (71%) and Cu(II) (60%) ions removal, while at pH 5.0 maximum removal of Zn(II) ions (58%) was achieved. At the addition of Cu(II) ions in the systematic removal of Fe(III) and Zn(II) ions was reduced, while of nickel was maintained on the level of Cr(VI)-Fe(III)-Ni(II) system. Brady and Duncan [31] had shown the participation of amino, carboxyl and hydroxyl

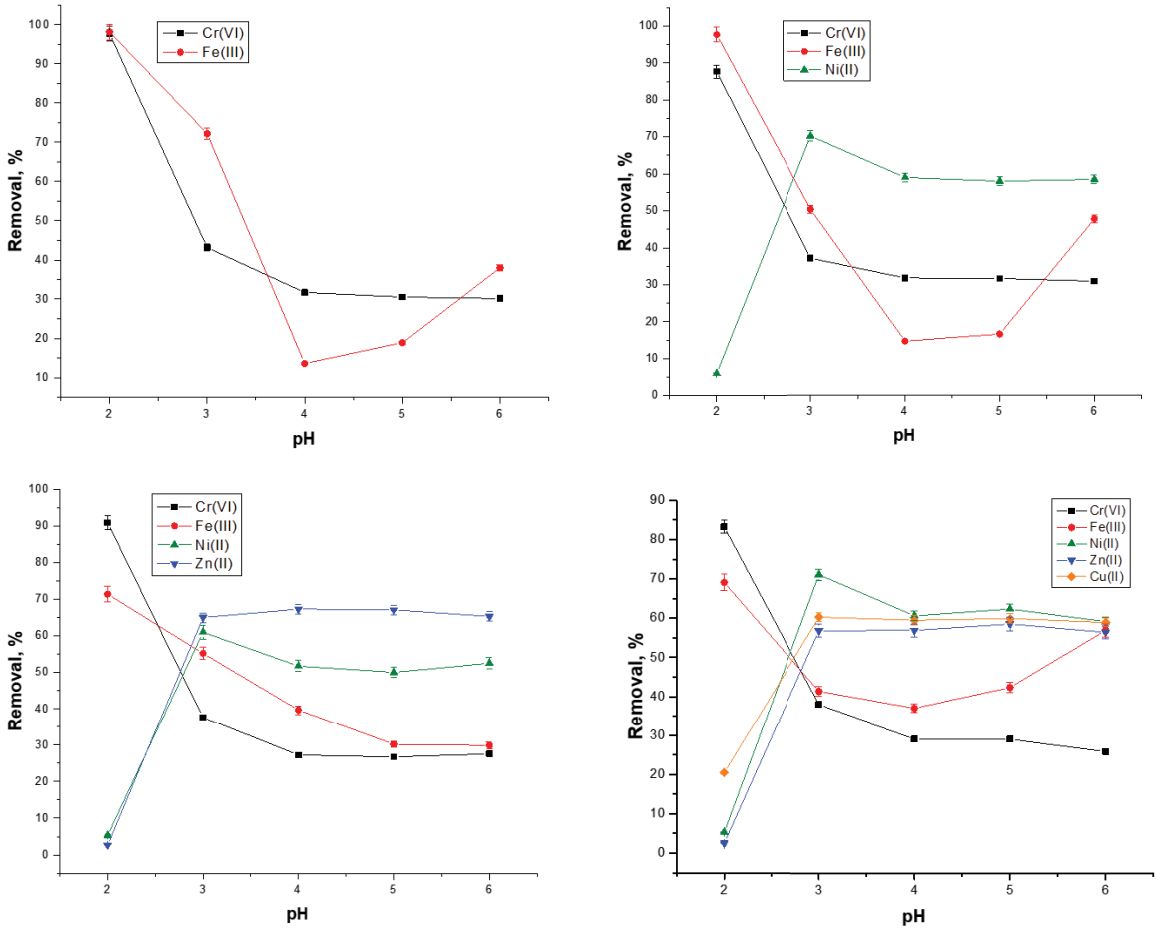

Fig. 5. Removal of metal ions at different initial pH (at *T*: 20°C; sorbent dosage: 0.5 g L^{-1}; and adsorption time: 1 h).

groups of the cell walls in Cu(II) binding. According to Guler and Sarioglu [32] in *S. cerevisiae* hydroxyl and carbonyl groups are involved in Cu(II) binding, while Ni(II) biosorption occurs in the hydroxyl, amine, and carboxylate groups of the polysaccharides on the peptidoglycan layer. Machado et al. [33] showed 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 *S. cerevisiae* in Cu(II), Ni(II) and Zn(II) uptake.

The obtained results are consistent with those reported by Liu et al [34], Mohapatra and Gupta [35] where the biosorbent exhibited reference for Cu(II) ions over Zn(II). The presence of Ni(II) or Ni(II) and Cu(II) in the system resulted in a significant decrease in zinc biosorption onto *Chlorella kessleri* [18].

Low Ni(II), Zn(II) and Cu(II) removal at pH 2.0 are attributed to the positive charge of biomass surface and high concentration of protons in the solution.

In Hlihor et al. [5] study it was shown that Cr(VI) was completely removed from the aqueous solution by 5 g L^{-1} yeast biomass at pH 1.0, while pH 2.0 was selected as optimum pH. Maximum Cr(VI) ions removal by *S. cerevisiae* at pH 2.0 was achieved in [36]. Due to the acidic nature of chromium-containing industrial effluents, further experiments were performed at pH 2.0. Brewing strain of *S. cerevisiae* was used to remove Cr(VI), Ni(II) and Cu(II) ions from electroplating effluent. 98% of Cr(VI) ions were removed at pH 2.0, while pH 6.0 was found to be optimal for Ni(II) (52%) and Cu(II) ions (78%) removal [33]. In Cherlys Infante et al. [37] study the biomass of *S. cerevisiae* removed a higher percentage of lead (86.4%) from solution as compared to mercury and nickel (69.7% and 47.8%, respectively).

3.3. Effect of temperature on metal biosorption

The effect of temperature on metal removal by *S. cerevisiae* was studied in the temperature range 20°C–50°C. Even pH 2.0 was most suitable for Cr(VI) and Fe(III) ions removal the effect of temperature on Ni(II), Zn(II) and Cu(II) ions were also traced. As it can be seen from the data presented in Fig. 6 increase of temperature did not affect significantly Cr(VI) removal in Cr(VI)-Fe(III), Cr(VI)-Fe(III)-Ni(II) and Cr(VI)-Fe(III)-Ni(II)-Zn(II) systems, while in Cr(VI)-Fe(III)-Ni(II)-Zn(II)-Cu(II) system the decrease of Cr(VI) removal from 73% to 65% with the increase of the temperature was observed.

Maximum removal of Fe(III) in Cr(VI)-Fe(III) (92%) and Cr(VI)-Fe(III)-Ni(II) (96%) systems was achieved at 40°C. At the addition of Zn(II) ions in the system maximum Fe(III)

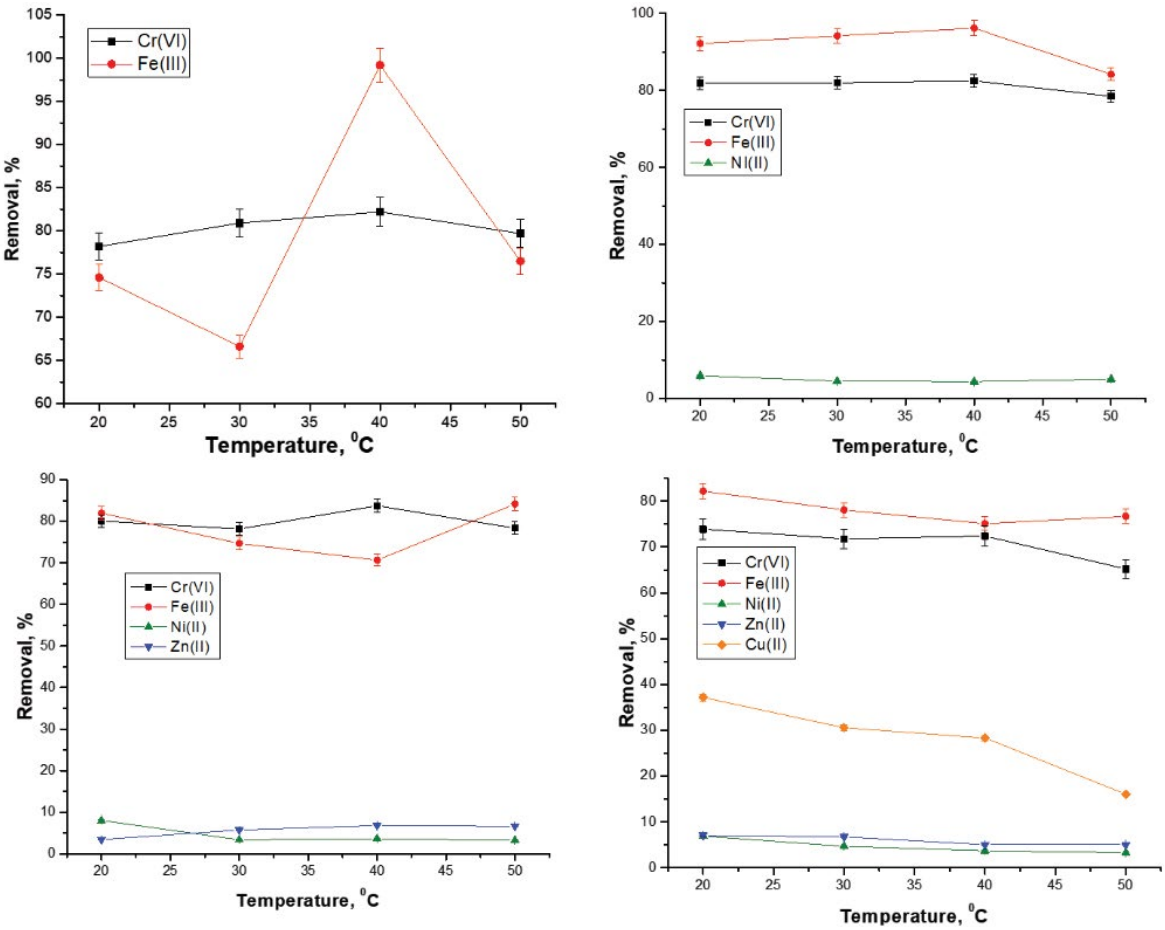

Fig. 6. Effect of temperature on the sorption of metal ions by *Saccharomyces cerevisiae* biomass (at *T*: 20°C; sorbent dosage: 0.5 g L^{-1}; and adsorption time: 1 h).

ions removal occurred at 50°C, while in Cr(VI)-Fe(III)-Ni(II)-Zn(II)-Cu(II) system at 20°C. Nickel ions removal in all studied systems decreased with temperature increase. In Cr(VI)-Fe(III)-Ni(II)-Zn(II) system maximum Zn(II) ions adsorption was at 40°C, while in Cr(VI)-Fe(III)-Ni(II)-Zn(II)-Cu(II) system at 20°C. With temperature increase, up to 50°C Cu(II) ions removal decreased from 37% to 16%.

The optimum Cr(VI) removal by *S. cerevisiae* occurred at temperatures 25°C–35°C [36]. Brady and Duncan [31] reported maximum uptake of Cu(II) ions by *S. cerevisiae* at temperature 25°C–30°C. The optimum temperature for Zn(II) removal by yeast biofilm biomass was found to be 28°C [12].

3.4. Thermodynamic parameters of adsorption

Thermodynamics of metal ions removal by *S. cerevisiae* was evaluated using the standard thermodynamic variables: Gibbs free energy change ($\Delta G°$), enthalpy change ($\Delta H°$), and entropy change ($\Delta S°$). The values were calculated according to Eqs. (3)–(5) presented below:

$$\ln K_d = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \tag{3}$$

$$\Delta G° = \Delta H° - T\Delta S° \tag{4}$$

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

$$K_d = \frac{(C_0 - C_e)V}{mC_e} \tag{5}$$

where C_0 is an initial concentration of vanadium, (mg L^{-1}), C_e is vanadium concentration in aqueous solution at equilibrium, (mg L^{-1}), V is the volume of aqueous solution (L), and m is sorbent mass (g).

A linear van't Hoff plot (Fig. 7) of $\ln K_d$ vs. $1/T$ gives slope and intercept to determine the value of $\Delta H°$ and $\Delta S°$, respectively. The obtained results are listed in Table 2.

The negative values of $\Delta G°$ obtained for Cr(VI), Fe(III), Zn(II), Ni(II) and Cu(II) in all studied systems indicate on feasible and spontaneous biosorption process. With the increase of temperature, the $\Delta G°$ value decreased for all elements, except Ni(II) and Zn(II) (in Cr(VI)-Fe(III)-Ni(II)-Zn(II)-Cu(II) system), which point out at the fact that the increase of temperature is favorable to the adsorption process [38,39].

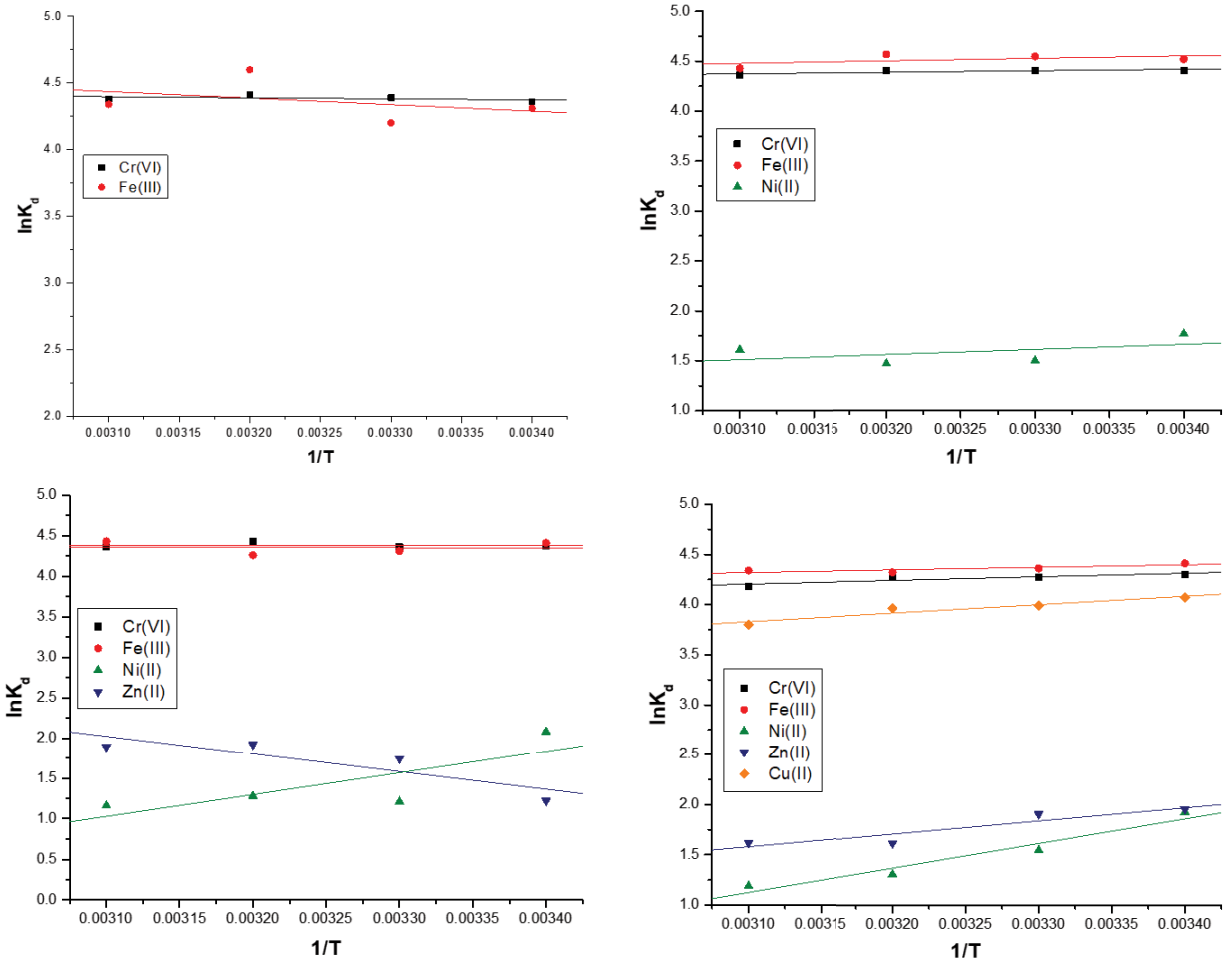

Fig. 7. $\ln K_d$ vs. $1/T$.

The values of energy $\Delta G°$ between 0 and 20 kJ mol^{-1} indicate that the adsorption process is physisorption, while the values between 80 and 400 kJ mol^{-1} correspond to chemisorption [40]. The positive value of $\Delta H°$ indicates the endothermic nature of metal ions sorption, while negative on the exothermic one [41]. In Cr(VI)-Fe(III) system positive $\Delta H°$ values were obtained for Cr(VI) and Fe(III) ions, while in Cr(VI)-Fe(III)-Ni(II) system the character of metal biosorption was exothermic. In Cr(VI)-Fe(III)-Ni(II)-Zn(II) system $\Delta H°$ values for Cr(VI) and Zn(II) ions were positive and negative for Fe(III) and Ni(II) ions.

In the system containing five components, $\Delta H°$ values were negative for all elements, indicating on exothermic character of biosorption. A sorption process is generally considered as physical if $\Delta H° < 25$ kJ mol^{-1} and as chemical when $\Delta H° > 40$ kJ mol^{-1} [42]. According to the scale proposed by Xu et al. [39], the main mechanism of metal interaction for present systems include the adsorption heat for van Edward force, hydrogen bond, and dipole interaction.

The positive $\Delta S°$ value suggests increasing randomness due to metal ions sorption on *S. cerevisiae*. Negative $\Delta S°$ values were obtained only for Ni(II) and Zn(II) (in Cr(VI)-Fe(III)-Ni(II)-Zn(II)-Cu(II) system) and indicate the decrease in the degree of freedom of the adsorbed species. Thus, it can be concluded that metal removal from studied systems is primarily controlled by the physisorption process.

3.5. Effect of contact time on metal biosorption

The effect of contact time on the adsorption of metal ions onto *S. cerevisiae* was carried out at 20°C and pH 2.0 and shown in Fig. 8.

In Cr(VI)-Fe(III) system the high rate of both metals removal: 91% for Cr(VI) ions and 94% for Fe(III) ions was achieved in the first 45 min of biomass interaction with a solution and then the equilibrium was attained. At the addition of Ni(II) ions in the system Cr(VI) ions were almost completely removed from solution (99.8%), while Fe(III) removal was significantly reduced (by 28%), that can be explained by Fe(III) and Ni(II) ions competition for the binding sites on the yeast surface. In Cr(VI)-Fe(III)-Ni(II)-Zn(II) system metal maximum removal changed in the following order: Cr(VI) (95%) > Fe(III) (79%) > Ni(II) (9.9%) > Zn(II) (6%). In Cr(VI)-Fe(III)-Ni(II) and Cr(VI)-Fe(III)-Ni(II)-Zn(II) systems equilibrium for all elements was achieved in 30 min of sorbate-sorbent interaction. Addition of Cu(II) ions in the system affected mainly Cr(VI) biosorption, the sorption of other elements was on the level of two, three and four-component systems. Equilibrium for Cr(VI) and Fe(III) ions was attained in 60 min, while for Zn(II) and Cu(II) in 30 min of sorbate-sorbent interaction. It was interesting to notice that Ni(II) removal in all systems went down with time and the maximum removal was achieved in the first 5 min of sorbent-sorbate interaction.

3.6. Adsorption kinetic models

Kinetic models are generally used to understand sorbent–sorbate interactions. Four models, namely pseudo-first-order (PFO), pseudo-second-order (PSO), Elovich model (EM) and the intra-particle Weber and Morris diffusion model (IPM), were applied in the present study to describe experimental data. The models are expressed by Eqs. (6)–(9):

Pseudo-first-order model:

$$q = q_e\left(1 - e^{-k_1 t}\right) \tag{6}$$

where q_e and q_t are the amounts of metal (mg g^{-1}) adsorbed at equilibrium and at t (min) time, respectively, and k_1 (min^{-1}) is the rate constant of PFO.

Pseudo-second-order model:

$$q = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \tag{7}$$

Table 2
Thermodynamics parameters for metal biosorption on *Saccharomyces cerevisiae*

		Metal	$\Delta G°$, kJ mol^{-1}				$\Delta H°$, kJ mol^{-1}	$\Delta S°$, J mol^{-1} K^{-1}
			293 K	303 K	313 K	323 K		
System	Cr(VI)-Fe(III)	Cr	–10.5	–10.9	–11.3	–11.7	0.6	38.2
		Fe	–10.3	–10.8	–11.3	–11.8	4.1	49
	Cr(VI)-Fe(III)-Ni(II)	Cr	–17.8	–18.4	–18.9	–19.5	–1.2	56.5
		Fe	–11.1	–11.4	–11.7	–12	–2.1	30.7
		Ni	–4.09	–4.09	–4.08	–4.08	–4.2	–0.5
	Cr(VI)-Fe(III)-Ni(II)-Zn(II)	Cr	–10.6	–11	–11.3	–11.7	–0.8	36.5
		Fe	–10.4	–10.7	–11.1	–11.4	–0.8	35.7
		Ni	–4.7	–4.1	–3.5	–2.9	–22.3	–60.3
		Zn	–3.2	–4	–4.7	–5.4	18.2	73.2
	Cr(VI)-Fe(III)-Ni(II)-Zn(II)-Cu(II)	Cr	–10.5	–10.8	–11	–11.3	–2.9	25.9
		Fe	–10.6	–10.9	–11.2	–11.5	–2.1	29.1
		Ni	–4.6	–4.1	–3.6	–3	–20.4	–54
		Zn	–5.1	–4.9	–4.7	–4.5	–10.9	–19.9
		Cu	–9.9	–10	–10.1	–10.2	–6.9	9.9

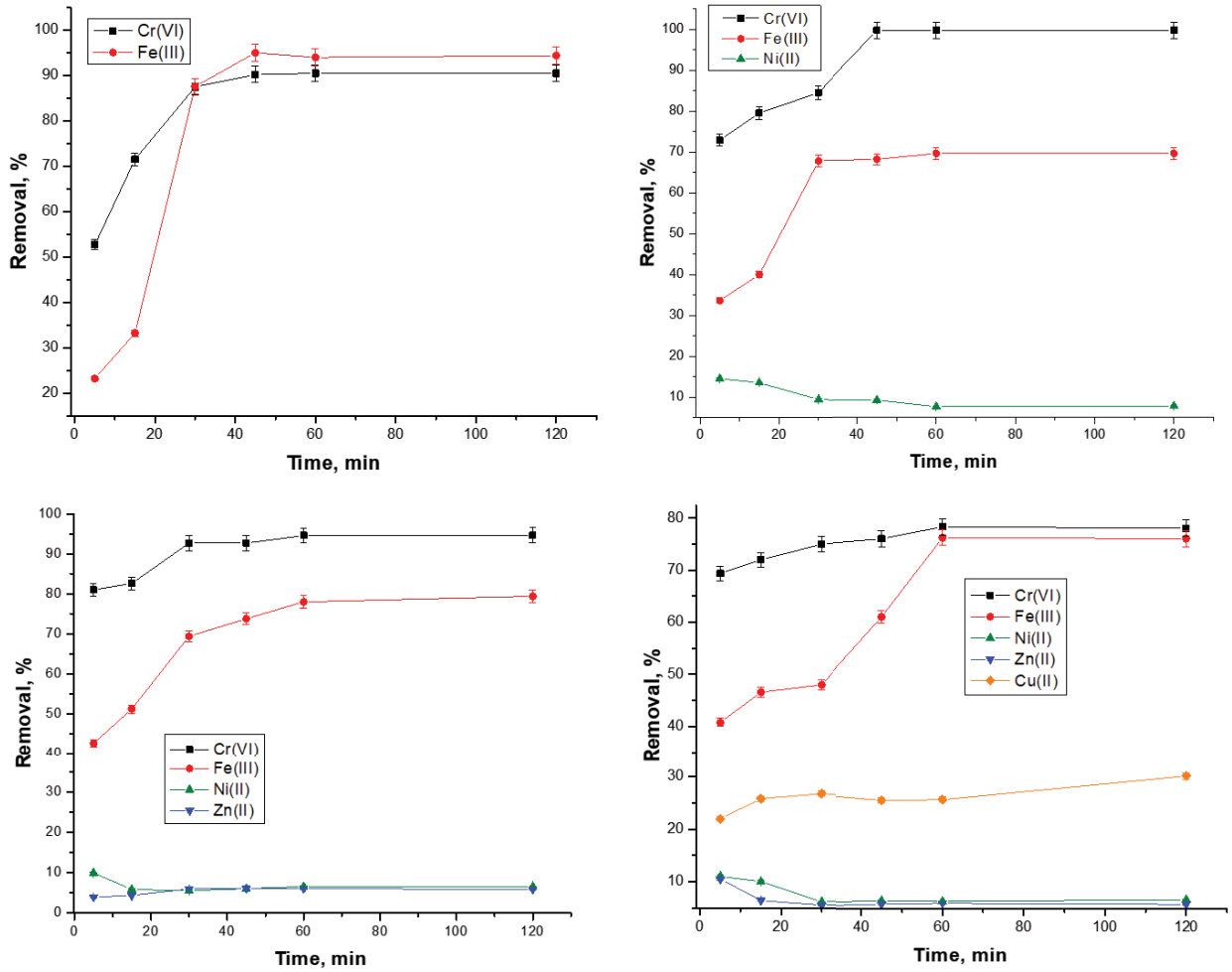

Fig. 8. Adsorption of metal ions on *Saccharomyces cerevisiae* as the function of time (at *T*: 20°C and sorbent dosage: 0.5 g L^{-1}).

where k_2 (g mg^{-1} min^{-1}) is the rate constant of second-order.

Elovich model:

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln(t) \quad (8)$$

where α and β are the Elovich equation constants.

Weber and Morris intra-particle diffusion model:

$$q = k_{diff} \times t^{0.5} + C_i \quad (9)$$

where k_{diff} is the rate parameter of *i* step (mg g^{-1} $min^{-1/2}$), 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 abovementioned models (Figs. 9–12) and the coefficients of correlation as well as the kinetic parameters are given in Table 3. Since Ni(II) and Zn(II) (in Cr(VI)-Fe(III)-Ni(II)-Zn(II)-Cu(II) system) adsorption decreased with the increase of time of contact it was not possible to describe obtained experimental data by kinetic models.

In Cr(VI)-Fe(III) and Cr(VI)-Fe(III)-Ni(II) systems, the PSO model fits well the experimental values obtained for Cr(VI), while both, PFO and PSO model were suitable for description of Fe(III) biosorption. According to Ho and McKay [43] PSO model is based on the assumption that in sorption the rate-limiting step can be chemical sorption or chemisorption involving valency forces through sharing or exchange of electrons between sorbent and sorbate. The PFO Lagergren model is obtained under the ideal assumption of a homogenous adsorption surface [44]. In Cr(VI)-Fe(III)-Ni(II)-Zn(II) system according to the coefficient of determination (R^2) values, the PSO model fit well the data for Cr(VI) ions, PSO and EM are applicable for description of Fe(III) and Zn(II) ions sorption. The Elovich equation is used to describe the chemical adsorption processes and is suitable for systems with heterogeneous adsorbing surfaces [44]. In Cr(VI)-Fe(III)-Ni(II)-Zn(II)-Cu(II) system R^2 value 0.9 indicates that the adsorption of Cr(VI) on *S. cerevisiae* follows EM, while IPM was more applicable for description of Fe(III) and Cu(II) biosorption. Determination coefficients determined for the intra-particle diffusion model were in the range 0.49–0.81.

It should be mentioned that in Cr(VI)-Fe(III) and Cr(VI)-Fe(III)-Ni(II) systems Cr(VI) and Fe(III) ions sorption was

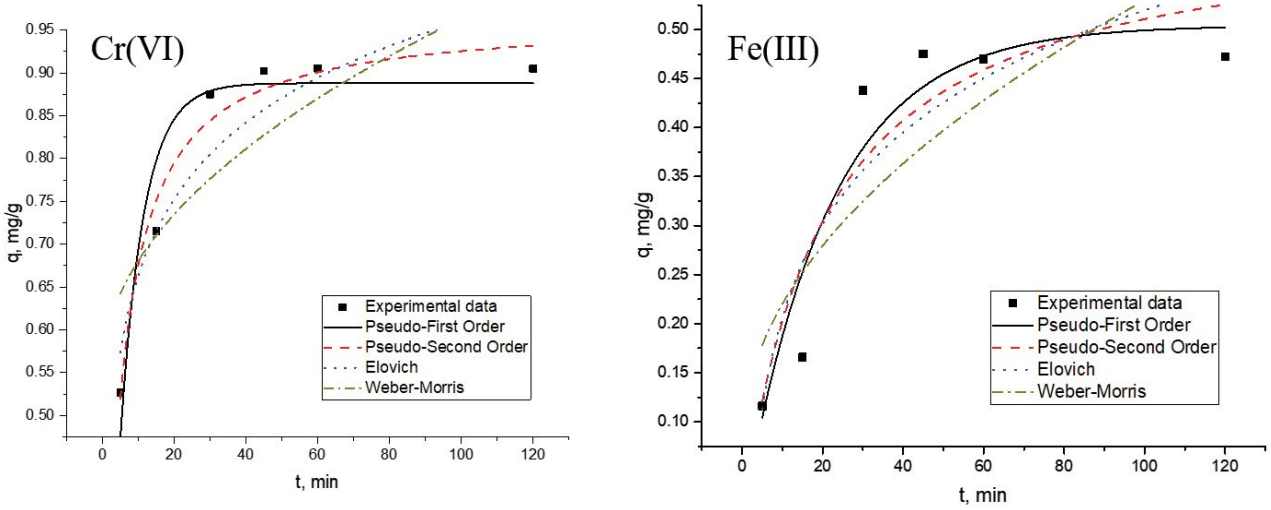

Fig. 9. Kinetics of the metal adsorption using *Saccharomyces cerevisiae* in Cr(VI)-Fe(III) system.

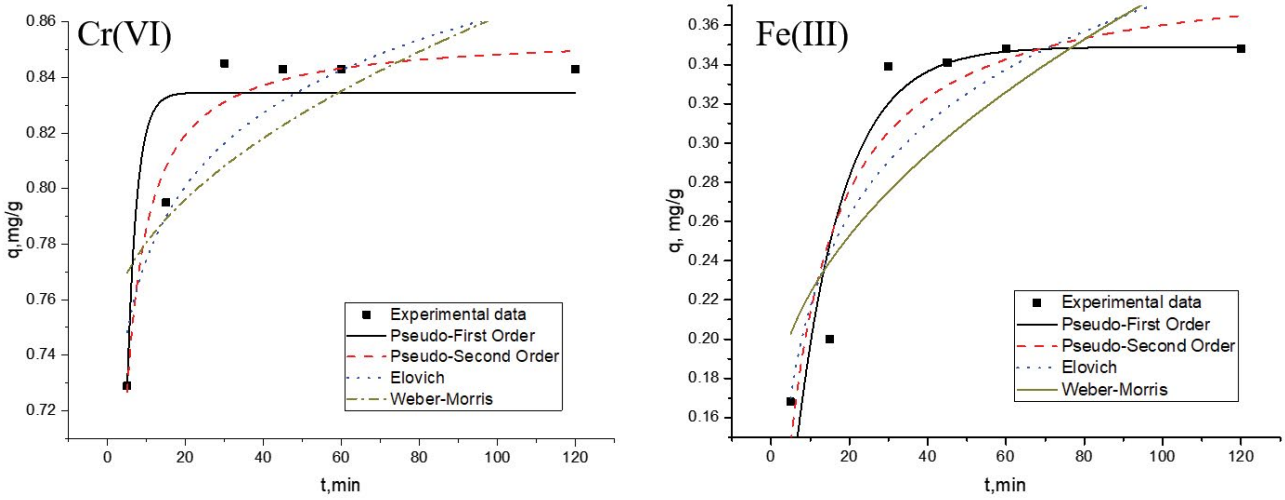

Fig. 10. Kinetics of the metal adsorption using *Saccharomyces cerevisiae* in Cr(VI)-Fe(III)-Ni(II) system.

described by the same models. At the addition of Zn(II) ions in the system data obtained for Cr(VI) and Fe(III) ions were better described by EM, while at addition of Cu(II) ions by EM and IPM. Applicability of different models to describe metal biosorption in multi-metal systems indicates a complex mechanism of metal ions interaction with biosorbent. However, since PSO and EM described better the sorption of ions present in the studied systems it can be suggested that chemisorption plays an important role in the adsorption of metal ions onto *S. cerevisiae*.

3.7. Effect of chromium ions concentration on metals adsorption

The effect of initial Cr(VI)concentration on metal biosorption was studied by maintaining a constant concentration of interfering metals (Fe, Zn, Ni, and Cu) and varying Cr(VI) concentration from 10 and 100 mg L^{-1}. Data presented in Fig. 13 show that adsorption of Cr(VI) ions on *S. cerevisiae* increased with increasing Cu(VI) ion concentrations up to 100 mg L^{-1} in all studied systems. Zinc removal efficiency by yeast biofilm increased with an increase in initial Zn(II) concentration ranging from 10 to 90 mg L^{-1} [36]. The maximum Cr(VI) adsorption was found to be 8.3 mg g^{-1} in Cr(VI)-Fe(III) system, 7.9 mg g^{-1} in Cr(VI)-Fe(III)-Ni(II) system, 7.9 mg g^{-1} in Cr(VI)-Fe(III)-Ni(II)-Zn(II) system and 6.9 mg g^{-1} in Cr(VI)-Fe(III)-Ni(II)-Zn(II)-Cu(II) system. The decrease of Cr(VI) sorption in three, four and five components systems can be explained by the increase of the number of metal ions in the system and their competition for the same binding sites on the cell surface. Brady et al [45] showed that granular biosorbent biomass produced by treating yeast with hot alkali was effective for simultaneous uptake of Zn(II), Cr(VI) and Cu(II) ions from electroplating wastewater. The sorbent showed a high affinity toward Cu(II) ions.

In Han et al [46] it was shown that at the simultaneous presence of lead and copper ions in solution biosorption

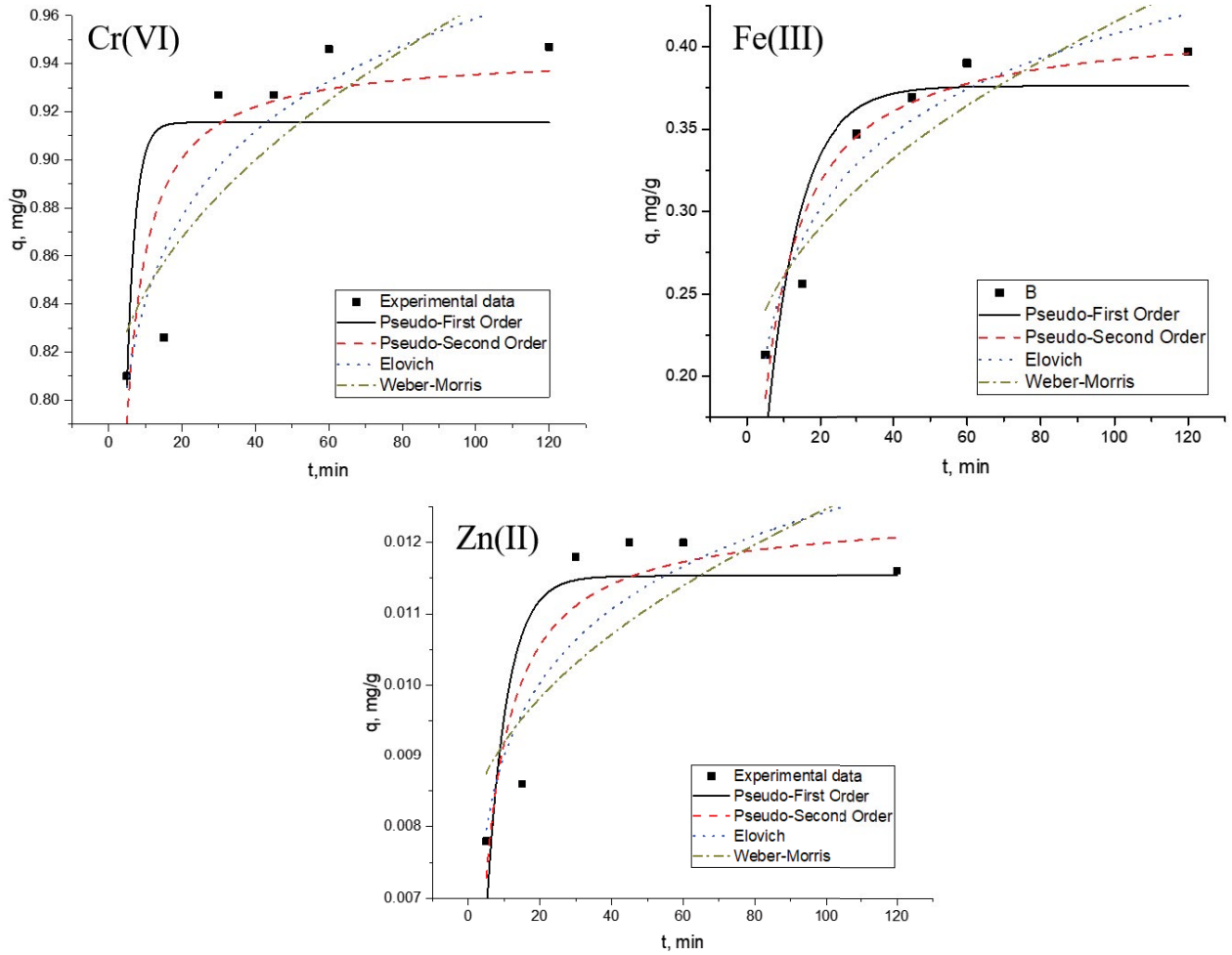

Fig. 11. Kinetics of the metal adsorption using *Saccharomyces cerevisiae* in Cr(VI)-Fe(III)-Ni(II)-Zn(II) system.

capacity of waste beer yeast biomass decreased with increasing competing for metal ion concentration.

Increase of Cr(VI) concentration did not affect iron sorption in Cr(VI)-Fe(III) and Cr(VI)-Fe(III)-Ni(II) systems, but it was slightly reduced at the addition of Zn(II) and Cu(II) ions in the systems. Due to acidic pH of studied multi-component systems, Zn(II) and Ni(II) sorption by *S. cerevisiae* were very low and it was not affected by the increase of Cr(VI) concentration in solution. At the same time, Cu(II) sorption significantly increased from 15 to 50% with an increase of Cr(VI) concentration from 10 to 100 mg L^{-1}, leading to a decrease of Cr(VI) sorption.

3.8. Biosorption isotherms

The equilibrium data obtained for Cr(VI) removal by *S. cerevisiae* were described using Langmuir, Freundlich, Temkin and DR equilibrium models. The Langmuir model suggests a monolayer adsorption and is expressed by Eq. (10):

$$q_e = \frac{q_m b C_e}{1 + b C_e} \tag{10}$$

where C_e is metal ions concentration at equilibrium (mg L^{-1}), q_e is the amount of metal adsorbed at equilibrium (mg g^{-1}), q_{max} is maximum adsorption capacity of the sorbent (mg g^{-1}) and b is Langmuir adsorption constant (L mg^{-1}).

The mathematical expression of the Freundlich isotherm model is presented by Eq. (11):

$$q_e = K_F C^{\frac{1}{n}} \tag{11}$$

where q_e is the amount of metal adsorbed at equilibrium (mg g^{-1}), C_e is a concentration of metal ions in aqueous solution at equilibrium (mg L^{-1}); K_F and n are Freundlich constants that include factors that affect adsorption capacity and adsorption intensity, respectively.

The DR isotherm mode is expressed by Eq. (12):

$$q_e = q_m \exp\left(-K_{DR}\varepsilon^2\right) \tag{12}$$

where K_{DR} is a constant related to adsorption energy (mol^2/kJ^2), q_m is a constant that indicates the sorption capacity of sorbent (mg g^{-1}).

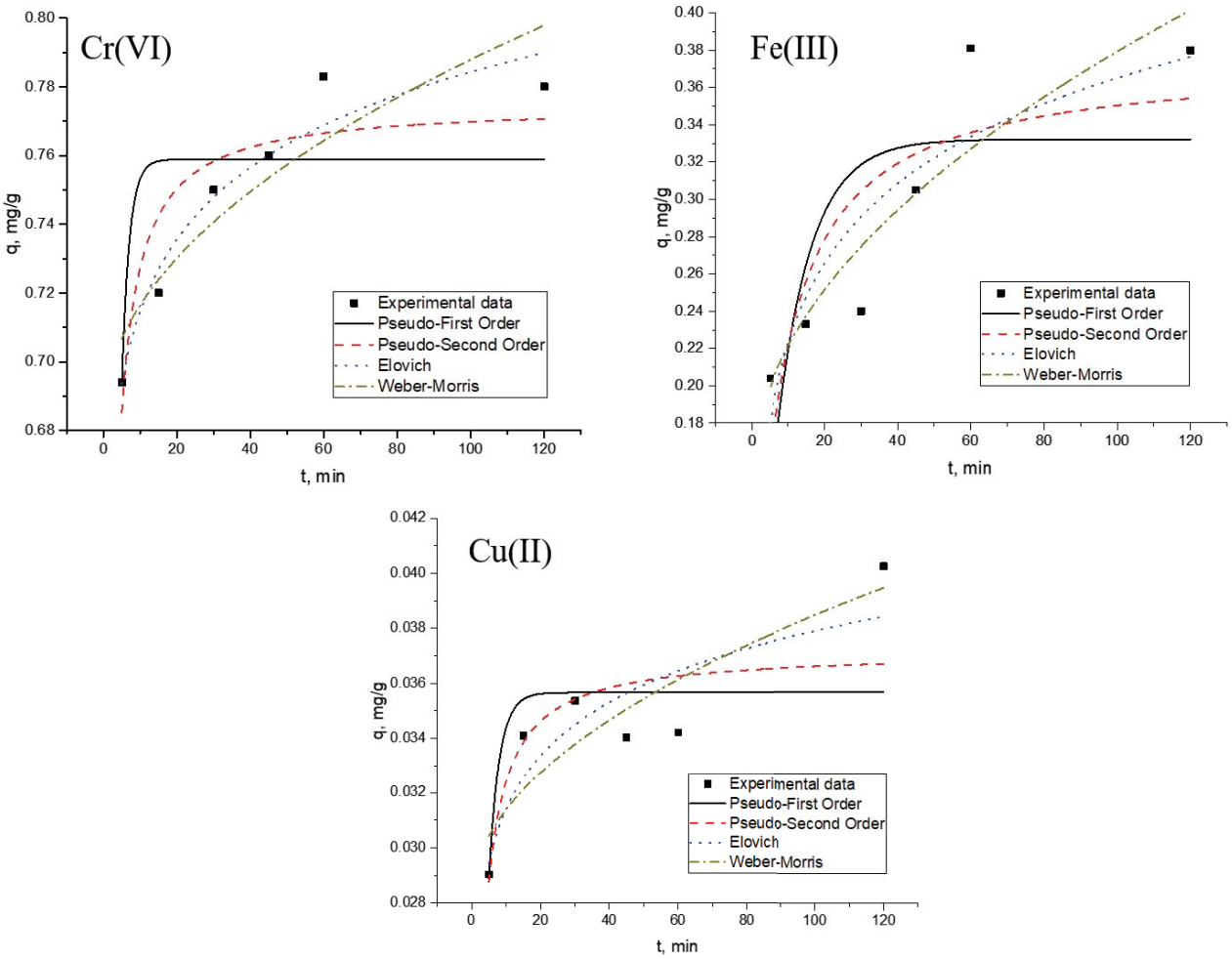

Fig. 12. Kinetics of the metal adsorption using *Saccharomyces cerevisiae* in Cr(VI)-Fe(III)-Ni(II)-Zn(II)-Cu(II) system.

Table 3
Constants and determination coefficients (R^2) of the kinetics models

			Model												
				PFO			PSO			EM			IPM		
		Metal	q_{exp}, mg g^{-1}	q_e, mg g^{-1}	k_1, min^{-1}	R^2	q_e, mg g^{-1}	k_2, g mg^{-1} min^{-1}	R^2	α, mg g^{-1} min^{-1}	β, g min^{-1}	R^2	k_{diff}	C_i	R^2
Systems	Cr(VI)-Fe(III)	Cr	0.91	0.88	0.15	0.89	0.96	0.2	0.96	2.2	7.7	0.83	0.04	0.5	0.59
		Fe	0.47	0.5	0.05	0.88	0.6	0.08	0.82	0.06	7.3	0.77	0.04	0.08	0.6
	Cr(VI)-Fe(III)-	Cr	0.84	0.83	0.4	0.8	0.86	1.32	0.95	2.7	26.3	0.77	0.01	0.7	0.5
	Ni(II)	Fe	0.34	0.35	0.08	0.81	0.39	0.03	0.83	0.17	14.8	0.77	0.02	0.15	0.5
	Cr(VI)-Fe(III)-	Cr	0.95	0.91	0.42	0.35	0.94	1.1	0.7	6.9	19.5	0.81	0.01	0.79	0.67
	Ni(II)-Zn(II)	Fe	0.39	0.38	0.11	0.74	0.4	0.39	0.9	0.33	15.2	0.91	0.02	0.19	0.77
		Zn	0.012	0.01	0.17	0.58	0.012	2.3	0.77	0.06	670	0.71	0.0004	0.008	0.49
	Cr(VI)-Fe(III)-	Cr	0.78	0.76	0.48	0.47	0.77	1.97	0.78	5.35	32.9	0.93	0.01	0.7	80
	Ni(II)-	Fe	0.38	0.33	0.11	0.29	0.39	0.3	0.58	0.22	16.1	0.76	0.02	0.15	0.81
	Zn(II)-Cu(II)	Cu	0.034	0.04	0.33	0.46	0.037	1.85	0.6	1.921	354	0.72	0.001	0.03	0.74

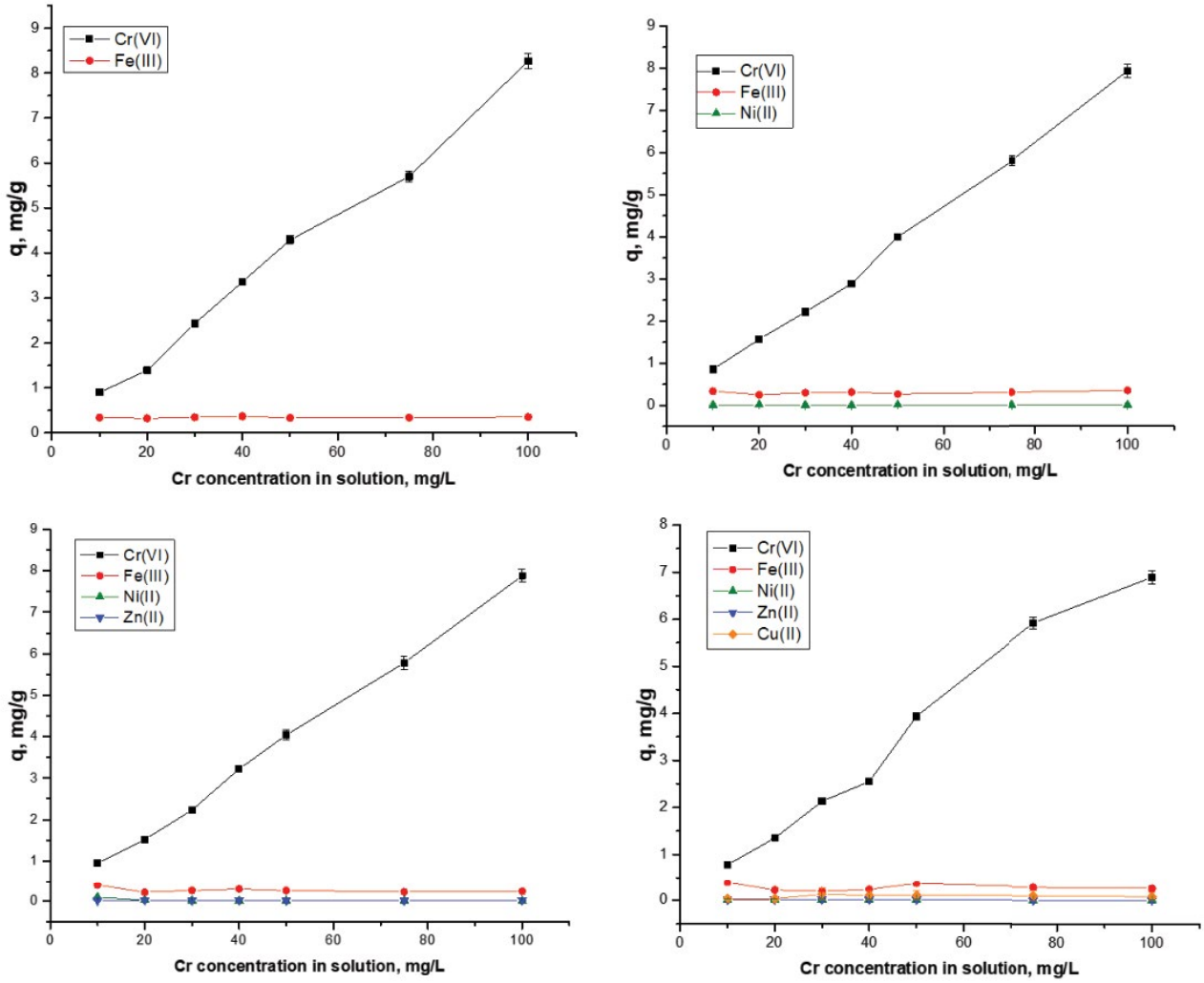

Fig. 13. Removal of metal ions at different chromium concentration in solution (at T: 20°C; sorbent dosage: 0.5 g L^{-1}; and adsorption time: 1 h).

Polanyi potential, ε, was calculated with Eq. (13):

$$\varepsilon = RT\ln\left(1+\frac{1}{C_e}\right) \tag{13}$$

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

$$E_s = \left(-2K_{\mathrm{DR}}\right)^{\frac{-1}{2}} \tag{14}$$

The Temkin isotherm model is given below:

$$q_e = \frac{RT}{b}\ln\left(a_T C_e\right) \tag{15}$$

$1/b_T$ indicates the sorption potential of the sorbent, and a_T is Temkin constant.

The Freundlich, Temkin and DR constants were calculated from by nonlinear regression (Fig. 14), while Langmuir model constants were calculated from the approximation of linearized experimental plot data (Fig. 15). The values of the parameters calculated from the used models are shown in Table 4.

The adsorption capacity of Cr(VI) ions on species on *S. cerevisiae* were calculated from the Langmuir adsorption isotherm and it varied from 17.4 mg g^{-1} (Cr(VI)-Fe(III)-Ni(II)-Zn(II) system) to 31.7 mg g^{-1} (Cr(VI)-Fe(III)-Ni(II)-Zn(II)-Cu(II) system). The high values of determination coefficients indicate the applicability of Langmuir isotherm for a description of experimental. Langmuir model that assumes a monolayer coverage and uniform activity distribution on the sorbent surface [24,29]. Cr(VI) biosorption onto *S. cerevisiae* also fits well Freundlich isotherm. The $1/n$ values calculated from the Freundlich model for all elements were near 1.0, which shows that the biosorption of Cr(VI) ions onto *S. cerevisiae* biomass is favorable.

The values of determination coefficients obtained for the DR isotherm indicated model fit to the sorption process.

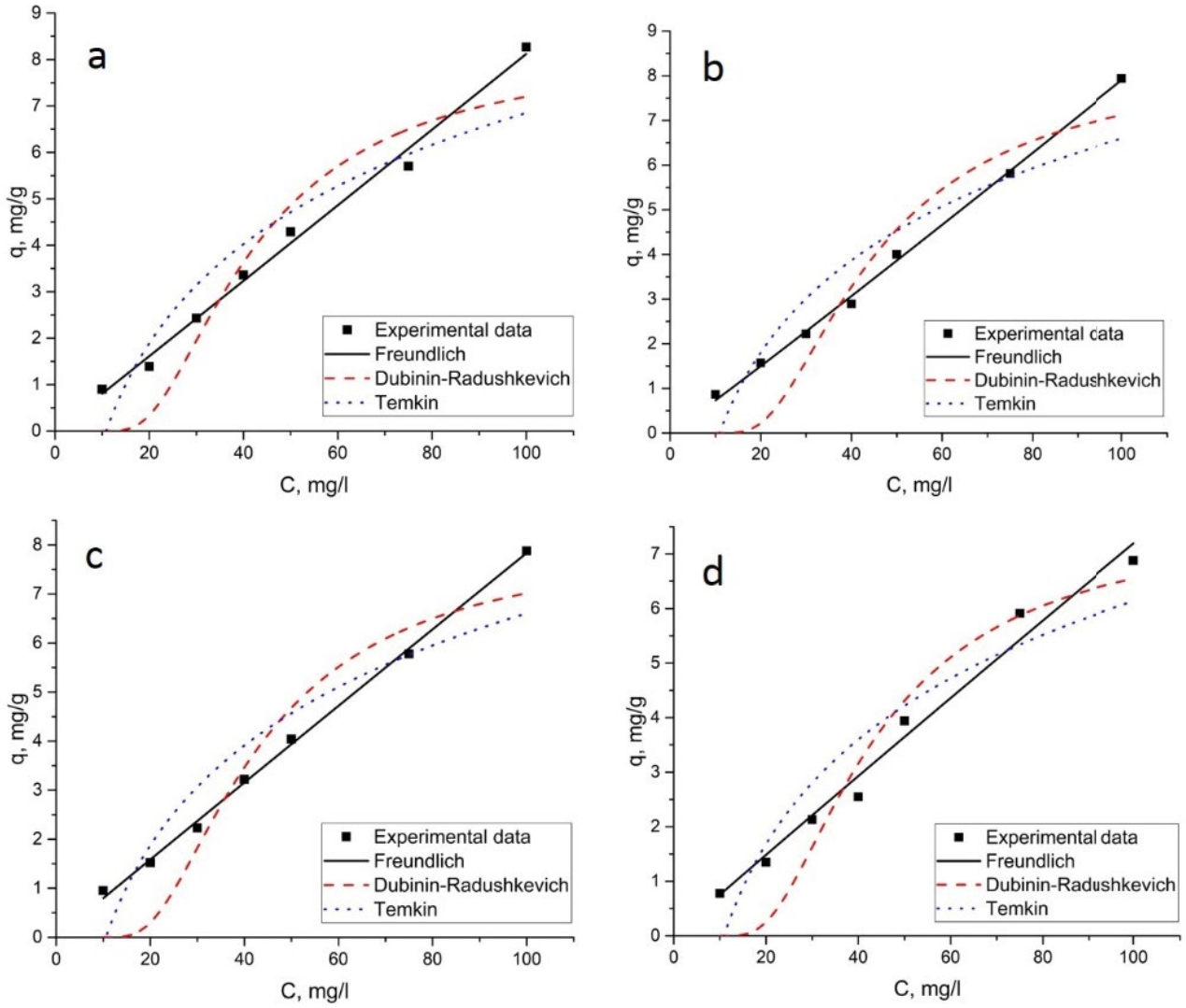

Fig. 14. Adsorption isotherms: (a) Cr(VI)-Fe(III), (b) Cr(VI)-Fe(III)-Ni(II), (c) Cr(VI)-Fe(III)-Ni(II)-Zn(II), and (d) Cr(VI)-Fe(III)-Ni(II)-Zn(II)-Cu(II) systems.

A sorption process is considered as physical if free energy (E) is less than <8 kJ mol^{-1} and as chemical when the E value is between 8 and 16 kJ mol^{-1} [30]. Calculated E values (Table 3), indicated on physisorption process in all studied systems. The lowest coefficient of determination values were obtained for Temkin isotherm. In all studied systems the constant b_T, related to the heat of adsorption, has positive values, indicating the endothermic character of the sorption process [47].

Langmuir model was suitable to describe Cr(VI) and Fe(II) removal by *Rhizopus arrhizus* from single and binary systems [2]. Chromium (VI) biosorption using untreated *S. cerevisiae* was better described by the Freundlich model [7].

Langmuir model fitted well Zn(II), Ni(II) and Cu(II) uptake by live and heat-inactivated biomass of *S. cerevisiae* [33]. Biosorption of Ni(II) ions by deactivated protonated yeast was described better by the Langmuir isotherm model [30]. Copper and lead removal by waste beer yeast fit well Langmuir model [46].

4. Conclusions

The results of the present study showed that *S. cerevisiae* can be applied for chromium-containing effluent treatment. Maximum Cr(VI) and Fe(III) removal was achieved at pH 2.0, while for Zn(II), Cu(II) and Ni(II) ions optimal pH values were in the range 3.0–5.0. Different optimal pH values determined for metal present in studied systems indicate the possibility of selective metal biosorption from complex systems The experimental data of Cr(VI) sorption were better described by Langmuir and Freundlich models. The maximum adsorptive capacity of *S. cerevisiae* for Cr(VI) was 26.8 mg g^{-1} in Cr(VI)-Fe(III) system, 27.3 mg g^{-1} in Cr(VI)-Fe(III)-Ni(II) system, 17.4 mg g^{-1} in Cr(VI)-Fe(III)-Ni(II)-Zn(II) system and 31.8 mg g^{-1} in Cr(VI)-Fe(III)-Ni(II)-Zn(II)-Cu(II) system. Different kinetics model showed to be suitable to describe metal biosorption in studied systems, indicating a complex character of metal interaction with biomass in

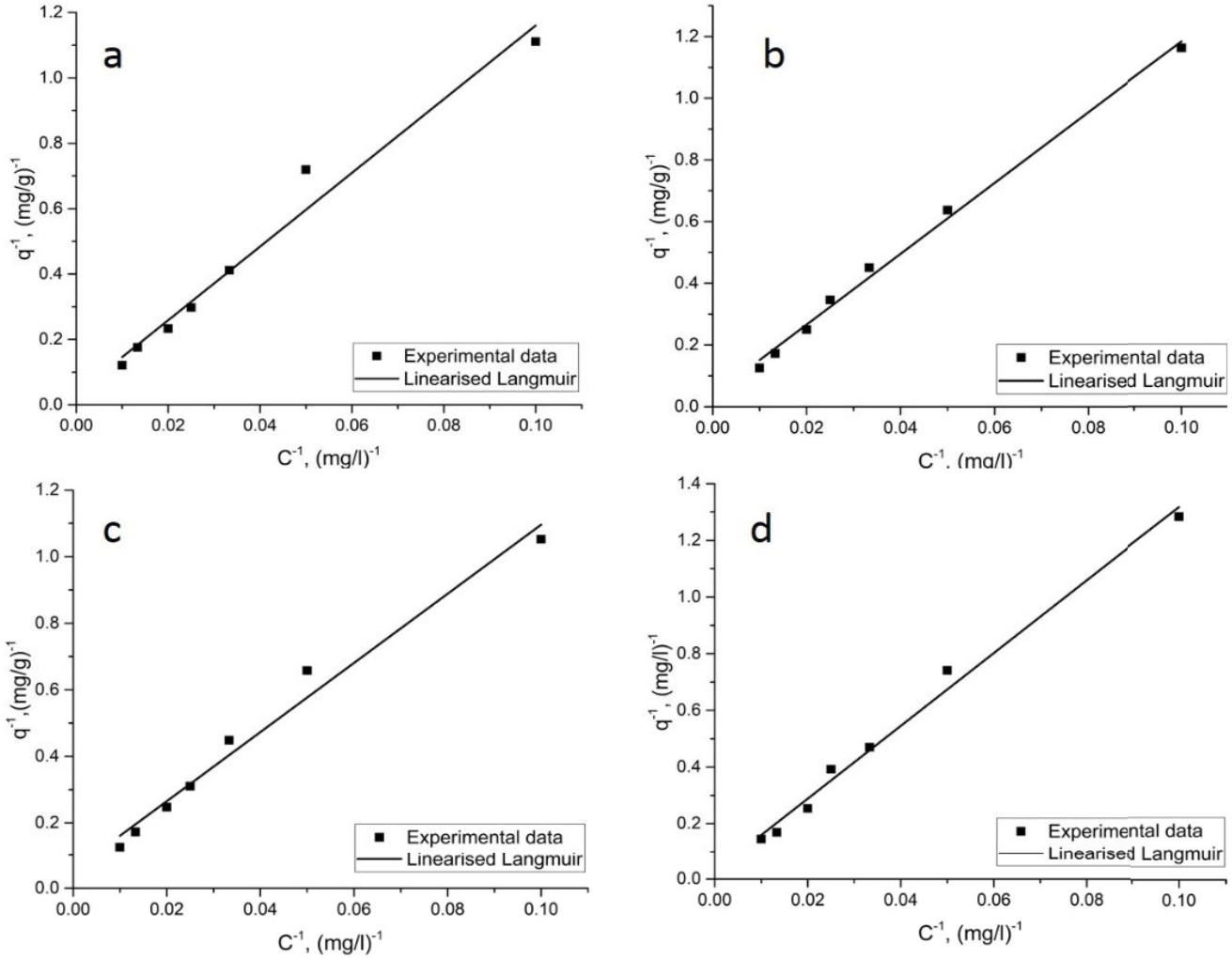

Fig. 15. Langmuir adsorption isotherm: (a) Cr(VI)-Fe(III), (b) Cr(VI)-Fe(III)-Ni(II), (c) Cr(VI)-Fe(III)-Ni(II)-Zn(II), and (d) Cr(VI)-Fe(III)-Ni(II)-Zn(II)-Cu(II) systems.

Table 4
Parameters and determination coefficients (R^2) of the adsorption isotherms

Model	Parameters	System			
		Cr(VI)-Fe(III)	Cr(VI)-Fe(III)-Ni(II)	Cr(VI)-Fe(III)-Ni(II)-Zn(II)	Cr(VI)-Fe(III)-Ni(II)-Zn(II)-Cu(II)
Langmuir	q_m, mg g^{-1}	26.8	27.3	17.40	31.8
	b, L mg^{-1}	0.003	0.003	0.006	0.002
	R^2	0.97	0.99	0.98	0.99
Freundlich	K_F, mg g^{-1}	0.08	0.07	0.08	0.08
	$1/n$	0.99	0.97	1.0	1.0
	R^2	0.99	0.99	0.99	0.98
Temkin	a_T, L g^{-1}	0.09	0.09	0.09	0.09
	B, J mol^{-1}	3,045	3,045	3,045	3,045
	R^2	0.86	0.84	0.85	0.86
Dubinin–Radushkevich	q_{DR}, mg g^{-1}	8.2	8.3	8.0	7.5
	β, mol^2/kJ^2	225	256	233	240
	R^2	0.87	0.86	0.87	0.9
	E, kJ mol^{-1}	0.05	0.04	0.05	0.05

multi-metal systems. The biosorption process for Cr(VI), Fe(III), Ni(II), Zn(II) and Cu(II) ions was feasible and spontaneous, while the nature of metal ions was dependent on the composition of the effluent.

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