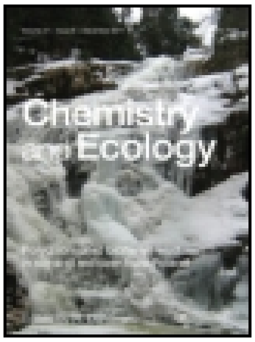

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Removal of metals from synthetic and real galvanic nickel-containing effluents by *Saccharomyces cerevisiae*

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ABSTRACT
The efficiency of *Saccharomyces cerevisiae* in the removal of heavy metals from effluents was tested using one real and four synthetics nickel-containing effluents. The removal of metal ions from synthetic effluents was studied as a function of pH, interaction time, nickel concentration and temperature. Characterisation of biosorption equilibrium was evaluated employing the Langmuir, Freundlich and Temkin models. The maximum sorption capacity of biomass for Ni(II) was 8.9 mg/g in Ni(II) system, 8.3 mg/g in Ni(II)–Cr(VI)–Fe(III), 11.9 mg/g in Ni(II)–Zn(II)–Sr(II)–Cu(II) and 7.3 in Ni(II)–Zn(II)–Cu(II)–Mo(VI) systems. The kinetics of the biosorption was described using pseudo-first order, pseudo-second order, Elovich model and the intra-particle Weber and Morris diffusion models. According to the thermodynamic parameters the biosorption can be described as a spontaneous process. Fourier-transform infrared analysis was carried out to identify the role of functional groups on metal ions binding. To determine the main metal species present in the solution at different pH values, thermodynamic calculations were performed. The effect of pH and sorbent dosage on metal removal from real industrial effluent was investigated. The two-stage sequential scheme of Ni(II) removal from effluent by the addition of different dosage of new biomass sorbent was proposed.

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KEYWORDS
Saccharomyces cerevisiae; metal ions; industrial effluent; neutron activation analysis; FTIR; thermodynamic calculations

Introduction

Effluents from the mining operations, metal plating facilities, paper industries, power generation facilities, electronic device manufacturing units, tanneries, iron-sheet cleaning, metal processing, automobile parts manufacturing, dyeing, textile, fertiliser and petroleum industries release heavy metals in the environment in concentrations exceeding the permissible levels [1–3]. Raw industrial effluents are characterised by complex chemical

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composition and presence of metal ions in a wide range of concentrations. Thus, the effluent collected from an electroplating unit from the Metropolitan Area of Oporto, Portugal, contained Cu (8 mg/L), Ni (17.8 mg/L), Zn (12 mg/L), Cr (23 mg//L) [4]. Industrial effluents collected from an electroplating industry in Dubna, Russia were used in several studies and contained metal ions in a wide range of concentrations: Cr from 9.4 to 74 mg/L [5–7], Ni from 4.3 to 117 mg/L [5,6,8], Zn from 18.3 to 45 mg/L [5,9], Cu from 12.2 to 54.8 mg/L and iron from 4.2 to 18.7 mg/L [5]. Wastewater taken from electroplating unit in Balti, Moldova contained zinc in concentration 95 mg/L, along with Fe, As, Sb and W ions [10]. In this context, metal-bearing effluents require an extensive purification before being discharged in a water body or used for irrigation.

Conventional technologies, coagulation/flocculation, precipitation, filtration, ion exchange, nanofiltration, solid-phase extraction, adsorption and electrokinetic remediation have been commonly used for the removal of heavy metals from wastewaters [1,11,12]. However, all these techniques suffer from high costs of capital and operations as well as the generation of hazardous sludge [12,13]. Often they are unsuitable for wastewater containing relative low metal concentrations, since in this case it is difficult to achieve complete metal ion removal [11]. Thus, in China the concentration of Cr, Pb and Ni in water discharged by urban wastewater treatment plants received wastewater from electroplate plants exceeded the national standards [14]. Cu, Zn and tin in water discharged by urban wastewater treatment plants in Ireland exceeded environmental quality standards [15]. Therefore, there is a need for the development of low-cost, eco-friendly processes of metal removal [1]. Biosorption is a cost-effective and simple technique for removing heavy metals from effluent, based on the ability of living and/or non-living biomass to rapidly adsorb and concentrate heavy metal ions from even dilute aqueous solution [13,17]. Cyanobacterium *Arthrospira platensis* was used for metal removal from the complex industrial effluents of an engineering company. The preference of spirulina biomass for metal ions was observed as follows: Ba > Fe > Sr > Al > Zn > Cr [16]. Waste-activated sludge from a municipal wastewater treatment plant was used as an adsorbent to remove zinc ions from aqueous solutions. The adsorption capacity of biosorbent for zinc(II) was found to be 17.86 mg/g at pH of 5 and 25°C [18]. A dried biomass wasted from biotrickling filters showed to be efficient for removing lead ions from aqueous solutions. The maximum Pb(II) biosorption capacity of dried biomass was 160.0 mg/g at 25°C [19]. A mixture of three non-living algal biomasses, belonging to classes Chrysophyta, Cyanophyta and Chlorophyte was tested as biosorbents for nickel ion removal from the aqueous medium. The maximum uptake of Ni(II) was 9.848 mg/g and it was found that Temkin model best fitted the isotherm biosorption data [20].

Among the wide variety of biomass available, yeast *Saccharomyces cerevisiae* (*S. cerevisiae*) is considered as a good candidate for wastewater treatment. Since *S. cerevisiae* is widely used in food and beverage manufacturing, it can be obtained in large quantities as a waste of the fermentation processes at very low cost. *S. cerevisiae* is generally recognised as a safe micro-organism and can be used without public concern [2,4,21]. The yeast biosorption largely depends on parameters such as pH, the ratio of the initial metal ion and initial biomass concentration, culture conditions, presence of various ligands and competitive metal ions in solution and to a limited extent on temperature [22].

Several studies have shown the ability of *S. cerevisiae* to remove toxic metals, from aqueous solutions, including industrial effluent [1,4,23,24]. *S. cerevisiae* was used in the bioremediation, in a batch mode, of a real electroplating effluent containing Cu, Ni and Cr ions. Cr(VI) was selectively removed (98%) by yeast biomass at pH 2.3, while pH 6.0 was found to be optimal for the removal of Cu(II) and Ni (II) [4]. The commercial biomass of the yeast *S. cerevisiae* Perlage® BB was used as a biosorbent for Cu (II). The best fit of the data was obtained with the Langmuir model, detecting the maximum biosorption capacity of 4.73 mg/g [25]. The performance of the yeast *S. cerevisiae* to remove Pb, Cd, Cr, Cu, Co and Zn ion from aqueous solutions was evaluated by Farhan and Khadom [26]. The order of accumulated metal ions was Pb > Zn > Cr > Co > Cd > Cu. The biosorption process obeys Freundlich and the Langmuir adsorption isotherms.

Regarding real effluents, it should be mentioned that the main part of studies is carried out with single-element synthetic solutions. At the same time, treatment of real effluents, especially nickel containing one is a major challenge due to the low affinity of nickel to biomass [5,6,11].

The present work is focussed on the application of yeast *Saccharomyces cerevisiae* for metal removal from four synthetic effluents with different chemical composition and one real nickel-containing industrial effluent. For synthetic effluents the effect of contact time, initial nickel concentration, temperature, pH, on sorption process was investigated. The kinetic data were fitted to pseudo-first order, pseudo-second order (PSO), Elovich model (EM) and the intra-particle Weber and Morris diffusion models and the isotherm equilibrium data were described by Langmuir, Freundlich and Temkin models. Thermodynamic parameters were evaluated from biosorption data. For real effluent the effect of pH and sorbent dosage on metal removal was investigated.

Materials and methods

Preparation of biosorbent

As the biosorbent the yeast *Saccharomyces cerevisiae* obtained from company Efes Vitanta Moldova Brewery (Chisinau, Republic of Moldova) were used. Yeast were dried in an oven at 105°C for 48 h, then the biomass was homogenised at 400 rpm for 10 min using Planetary Mono Mill PULVERISETTE 6 (Fritsch, Germany) and afterwards used in the experiments.

Preparation of synthetic effluents

Four synthetic effluents with the following composition Ni(II), Ni(II)–Sr(II)–Cu(II)–Zn(II), Ni (II)–Cr(VI)–Fe(III), Ni(II)–Zn(II)–Mo(VI)–Cu(II) were prepared from metal salt stock solutions of $Ni(NO_3)_2{\cdot}6H_2O$, $Cu(NO_3)_2{\cdot}2.5H_2O$, $Zn(NO_3)_2{\cdot}6H_2O$, $Sr(NO_3)_2$, $Na_2MoO4{\cdot}2H_2O$, CrO_3. All chemicals were of analytical grade purchased from Sigma-Aldrich company. The concentration of Ni(II) in all systems was 10 mg/L, of Cr(VI), Sr(II) and Fe(III) – 5 mg/L, of Mo(VI) – 0.5 mg/L, and of Zn(II) – 2 mg/L. Cu(II) was 1 mg/L in Ni(II)–Cu(II)–Sr(II)-Zn(II) system and 5 mg/L in Ni(II)–Zn(II)–Mo(VI)–Cu(II) system. The literature review showed that chemical composition of nickel-containing effluents as well as nickel concentration in them can vary significantly and depends on the process, which generates wastewater. Thus, in the present study metal concentration in analysed systems was chosen randomly. The chemical composition of modelled systems is presented in Table 1.

Table 1. Chemical composition of the effluent.

Element	Sr	Mo	Cr	Ni	Cu	Zn	Fe	pH
Concentration, [µg/l]	311	2.3	4.6	143155	31	500	690	7.0

Industrial effluent characterisation

The real nickel-containing effluent was obtained from the electroplating company in Dubna (Russia). The chemical composition of the effluent and the initial pH are given in Table 1.

Biosorption experiments with synthetic effluents

In experiments with synthetic effluents the effect of time (5–120 min), concentration (10–100 mg/L), pH (2.0–6.0) and temperature (20–50°C) on yeast sorption capacity was investigated. 50 mL of synthetic effluents was added in 100 mL flasks containing 10 g/L of dried biomass. Samples were placed on the shaker and continuously agitated during 60 min.

Biosorption experiments with real effluent

In experiment with real effluent the effect of pH and sorbent dosage on metal removal efficiency was studied. To assess the effect of pH on biomass sorption capacity 10 g/L g of dry biomass was added to 50 mL of effluent in 100 mL flask and continuously stirred for 60 min. The pH of the effluent varied from 2.0 to 7.0.

Experiment on the effect of dosage of sorbent on metal removal was performed in two stages. On the first stage sorbent in the dosages ranging from 20 to 40 g/L was added to 100 mL of effluent at initial effluent pH. The suspension was shaken at 200 rpm for 60 min, then sorbent was removed by filtration. Supernatant obtained for each sorbent dosage was divided into three parts. One part was used for ICP-MS analysis, while two others were used for the second stage of the experiment. On the second stage 1 g/L or 10 g/L of new biomass was added to supernatant, obtained after the first stage and shacked during 60 min. Then, biomass was again separated from supernatant by filtration.

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:

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

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

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

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

Methods

To assess metal sorption from synthetic effluents neutron activation analysis at the pulsed fast reactor IBR-2 (Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research, Dubna, Russia) was used. Samples were irradiated for 3 days 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 1099.25 keV of isotope ^{59}Fe, nickel by a γ-line with the energy of 810.57 keV of isotope ^{58}Co, zinc by a γ-line with the energy of 1115.54 keV of isotope ^{65}Zn, chromium by a γ-line with the energy of 320 keV of isotope ^{51}Cr, molybdenum by a γ-line with the energy of 140.5 keV of isotope ^{99}Mo and strontium by a γ-line with the energy of 514 keV of isotope ^{85}Sr. Copper concentration in solution was determined by applying atomic absorption spectrometry (Thermo Scientific iCE 3400, USA) with electrothermal atomisation. The calibration solutions were prepared from 1 g/L stock solution (AAS standard solution; Merck, Germany).

Chemical composition of the effluent and metal concentration in solution after experiments with real effluents were determined by means of Element 2™ High-Resolution ICP-MS systems (The Thermo Scientific, Germany). 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 4000–400 cm^{-1} using a Nicolet 6700 spectrometer (Thermo Scientific, USA). PHREEQC 2.18 computer code was used for thermodynamic calculations, which were performed in frames of computational methodology DESTRUCT development for the evaluation of engineering barrier system property evolution.

Results and discussion

Metal removal from synthetic effluents

Electroplating industries generate large amounts of effluents containing heavy metals, such as Cu, Cr, Ni, Fe and Zn [4]. In the present study, the chemical composition of the synthetic effluent was modelled based on our previous results obtained for nickel-containing effluents [5].

Effect of pH on metal removal

The pH is considered to be one of the most important factors in biosorption process, since it influences the competition of metallic ions and the activity of the biomass functional groups [2].

Since at pH > 6.0 metal ions are present in studied systems form hydroxides, the effect of pH on metal ions sorption was studied at pH range 2.0–6.0. According to the data presented in Figure 1 with the increase of pH from 2.0 to 6.0 Ni(II) removal efficiency increased from 5 to 61% in the system containing only Ni(II), from 5 to 53% in Ni(II)–Cu(II)–Sr(II)–Zn(II) system, from 5 to 62% in Ni(II)–Cr(VI)–Fe(III) system and from 1.2 to 59% in Ni(II)–Zn(II)–Mo(VI)–Cu(II) system. Low removal of Ni(II) and other cations present in the analysed systems at pH 2.0 is attributed to the presence of a large number of H^+ molecules in the solution, which easily occupies the binding sites [2]. With increasing pH, the total surface area of the adsorbent becomes negative leading to an enhanced biosorption of metal ions present in solution in cationic forms [13]. It should be mentioned that Ni(II) removal efficiency was almost on the same level at the pH range 3.0–6.0 in all analysed systems. Özer and Özer [24] showed maximum Ni(II) removal by *S. cerevisiae* at pH 5.0.

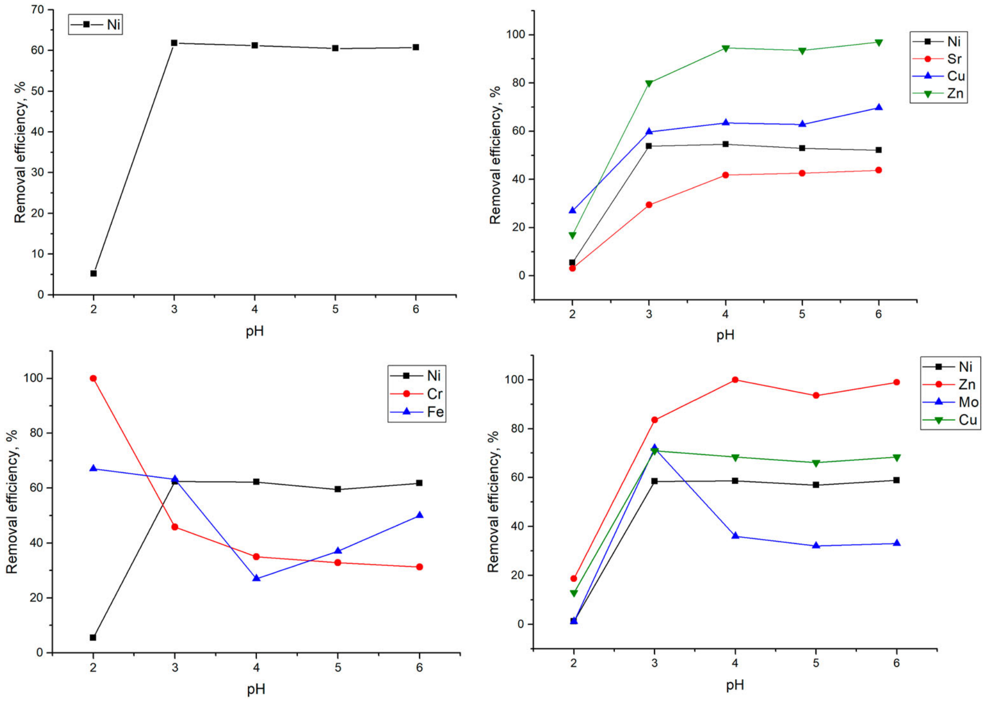

Figure 1. Removal of metal ions at different initial pH (at T 20°C; sorbent dosage 10 g/L; adsorption time 1 h).

According to thermodynamic calculations performed using the database of thermodynamic data llnl.dat of calculation code PhreeqC 2.18 in analysed systems nickel is present in solution in the dissolved form, while at $pH > 8.2$ low-soluble $Ni(OH)_2$ is formed, transforming nickel in the solid state (Figures 1–4S).

Reduction of Ni(II) removal efficiency in Ni(II)–Cu(II)–Sr(II)–Zn(II) can be associated with the presence of another metal cations in the system. For Zn(II), Sr(II) and Cu(II) the maximum removal was achieved at pH 6.0 and constituted 44% for Sr(II), 98% for Zn(II) and 70% for Cu(II). In Ni(II)–Cu(II)–Sr(II)–Zn(II) system metal ions start to from solid hydroxide mineral phases with the pH increase: for Zn(II) at pH 8.8, for Ni(II) at pH 8.4 and for Cu(II) at pH 6.5 (Figure 2S). In multi-element systems metal ions compete for binding sites; as a consequence, displacement of one metal species by another, which has higher affinity for biomass binding sites, can occur [14]. In the Ni(II)–Cr(VI)–Fe(III) system Ni(II) removal was not affected by the presence of Cr(VI) and Fe(III) ions in the system. Cr(VI) was completely removed (100%) at pH 2.0 and with the pH increase the removal efficiency of Cr(VI) decreased up to 31%. The distribution of Cr(VI) as a function of pH is as follows: hydrochromate ion $HCrO_4^-$ shows a dominant role in the solution to the dissociated form, CrO_4^{2-} start to dominate at pH>6.2. The input of dichromate form in such low-mineralised solution is near zero (Figure 3S). Machado et al. [11], Goyal et al. [1] and Zinicovscaia et al. [23] showed maximum removal of Cr(VI) by *S. cerevisiae* at pH 2.0. High efficiency of Cr(VI) removal can be explained by the protonation of functional groups on the yeast surface and presence of chromium in solution in anionic form [23]. Iron(III) ions were also more effectively adsorbed at low pH values, thus maximum Fe(III) removal (67%) was achieved at pH 2.0

and then it decreased up to 27% at pH 4.0. Iron(III) starts to form solid mineral phase at pH>4.2 (Figure 3S). The increase of the Fe(III) removal at pH >5 up to 50% can be explained by the formation of $Fe(OH)_3$ and its co-deposition on the metal ions already sorbed on the surface of yeast cells [27] or formation of a hydrated, iron oxide-coated biosorbent capable of removing the iron as well as other metal ions [28].

In Ni(II)–Zn(II)–Mo(VI)–Cu(II) system Ni(II) removal was almost on the level of Ni(II) system. The maximum removal of Zn(II) was achieved at pH 4 (100%), of Cu(II) and of Mo(VI) at pH 3.0 (71 and 72%, respectively). In Ni(II)–Zn(II)–Mo(VI)–Cu(II) system Zn(II) is presented in solution in dissolved form until pH 8.3 and then zinc hydroxide is formed (Figure 4S). In this system, Cu(II) at the pH range 2–7.8 is partly presented in dissolved form and partly in precipitated form as molybdate, $CuMoO_4$. Starting from pH 6.6, the copper hydroxide is formed, becoming the dominant form at pH>7.3. Ni is present in solution in the dissolved form till pH 7.3. With the pH increase the solid mineral forms are formed – firstly molybdate and then hydroxide, which at pH >9.5 become the main nickel form in solution. Molybdenum in analysed complex system in the dissolved form is present in solution at pH 2–3 and pH .9.4. In the pH range 3–9.4 molybdenum is firstly present in the form of copper molybdate up to pH 7.3 and later in the form of zinc and nickel molybdates. Pennesi et al. [29] showed maximum removal of Mo by seagrass *Posidonia oceanica* at pH 3.0.

In both systems containing Zn(II), Ni(II) and Cu(II) biomass showed the highest affinity for Zn(II) followed by Cu(II) and Ni(II). Volesky and May-Phillips [30] showed pH 4–5 to be optimum for uranium, zinc and copper biosorption by *S. cerevisiae* and the biomass preference for metal ions changed in the following order Zn > U > Cu. In Farhan and Khadom [26] study metal uptake by *S. cerevisiae* was maximum at pH values (5.0–6.0), and the order of accumulated metal ions was Pb > Zn > Cr > Co > Cd > Cu. Machado et al. [4] showed that metal sorption *by dried S. cerevisiae* biomass decreased in the following order: Cu^{2+}>> Zn^{2+} and Ni^{2+}.

Since nickel was the main element of interest further, experiments were performed at pH 6.0. At pH 6.0, the main chemical groups of biomass surface that are able to participate in the removal of metal cations are already totally or partially deprotonated [13]. The interaction of metal ions with yeast biomass was also investigated by the FTIR technique. FTIR spectrum of native *S. cerevisiae* biomass (Figure 5S) shows strong absorption bands in the regions 1020 cm^{-1} due to strong C–O stretching (primary alcohol) [31]. Peaks at 1510 cm^{-1} may correspond to N–O asymmetric stretching, C = C stretching (in-ring) and C–H asymmetric deformation vibration of CH_3. The peaks at 1225 cm^{-1} are related to the stretching vibration of the S = O groups [32], whereas the peaks at 1400 and 2800 cm^{-1} represent the stretching vibration of alkyl groups ($-CH_3$ or CH_2). The peak at 1730 cm^{-1} is related to the vibration of C=H groups of alkene or may be attributed by the presence of C = O from the acetyl groups. The strong boarded peak at wavenumber area 3600–3200 cm^{-1} could be attributed to hydroxyl (–OH) and amine (–NH) functional groups [32,33]. The presence of asymmetric CH_2 stretch vibrations could be confirmed by the adsorption peak at wavenumbers region 2950–2800 cm^{-1} [31]. The band at 3230 cm^{-1} is relevant to standard absorption band of amido group (HN = O). In addition, CH_2 bending vibration, COO–, –C–O, –C–C and –C–OH stretching vibrations could be found at the adsorption peaks of the 1650–1200 cm^{-1} region or the strong bands in this area could also correspond bands of polypeptide/proteins [31,33].

In the Ni-loaded biomass a slight shift, by 2–5 cm^{-1}, of bands 1025, 1230, 1400, 1512, 1732, 2800, 3235 cm^{-1} was noticed indicating involvement of OH, $\mathrm{CH{=}CH}$, $\mathrm{C{=}O}$ and $\mathrm{N = O}$ groups in Ni(II) binding. In Ni(II)–Cr(II)–Fe(II) system OH, $\mathrm{CH{=}CH}$, $\mathrm{C{=}O}$ and $\mathrm{HN = O}$ were involved in metal binding. The peaks of these groups were shifted by 2–7 cm^{-1}. The same pattern was observed in Ni(II)–Cu(II)–Sr(II)–Zn(II) system. In Ni(II)–Zn(II)–Mo(VI)–Cu(II) system the shift of bands 1025, 1225, 1400, 1513, 1735, 2800, 3240 by 2–10 cm^{-1} shows that OH, $\mathrm{CH{=}CH}$ and $\mathrm{HN = O}$ groups participate in metal binding. The absorption bands corresponding to $\mathrm{CH{=}CH}$ and $\mathrm{C = O}$ remained unchanged.

Machado et al. [11] suggested 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 in Ni, Cu and Zn sorption. Positively charged groups, mainly amine groups, are usually involved in Mo and Cr ion removal [29,34].

Effect of time and kinetics of the sorption

Time is an important parameter in the biosorption process. According to the data presented in Figures 2–5, experimental values are presented together with data described by kinetic models, the adsorption of metal ions in all analysed systems was very rapid at the first stage of sorbent sorbate interaction that can be explained by the availability of the large amount of binding sites, then the sorption slows down and the equilibrium was achieved. For the main part of metal ions, the adsorption equilibrium occurs within 60 min. In the system containing only Ni(II) during 60 min 53% of ions were removed from solution. In Ni(II)–Cr(VI)–Fe(III) system during 1 h 51% of Ni(II), 48% of Cr(VI) and 25% of Fe(III) were removed from solution. In Ni(II)–Cu(II)–Sr(II)–Zn(II) system after 60 min 52% of Ni(II), 46% of Sr(II) and 98% of Zn(II) were removed from solution. Cu(II) maximum removal (74%) was achieved after 120 min of interaction. Almost the same amount of Ni(II), Zn(II) and Cu(II) was removed from Ni(II)–Zn(II)–Mo(VI)–Cu(II) 53, 99 and 79%, respectively. For Mo(VI) maximum removal (56%) was achieved in 120 min.

The adsorption kinetic data were analysed using the four most common models: pseudo-first order (PFO), PSO, EM and the intra-particle Weber and Morris diffusion model (IPM). The models are expressed by the following formulas (3–6):

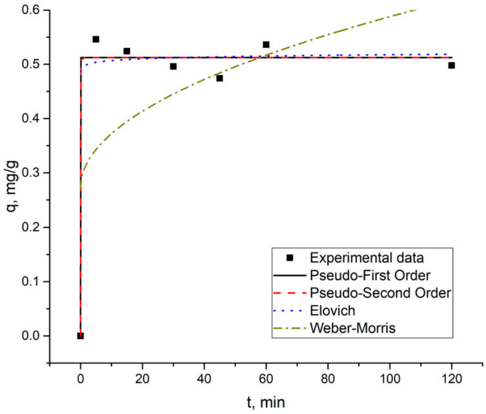

Figure 2. Kinetics of the metal adsorption using *S. cerevisiae* in Ni(II) system.

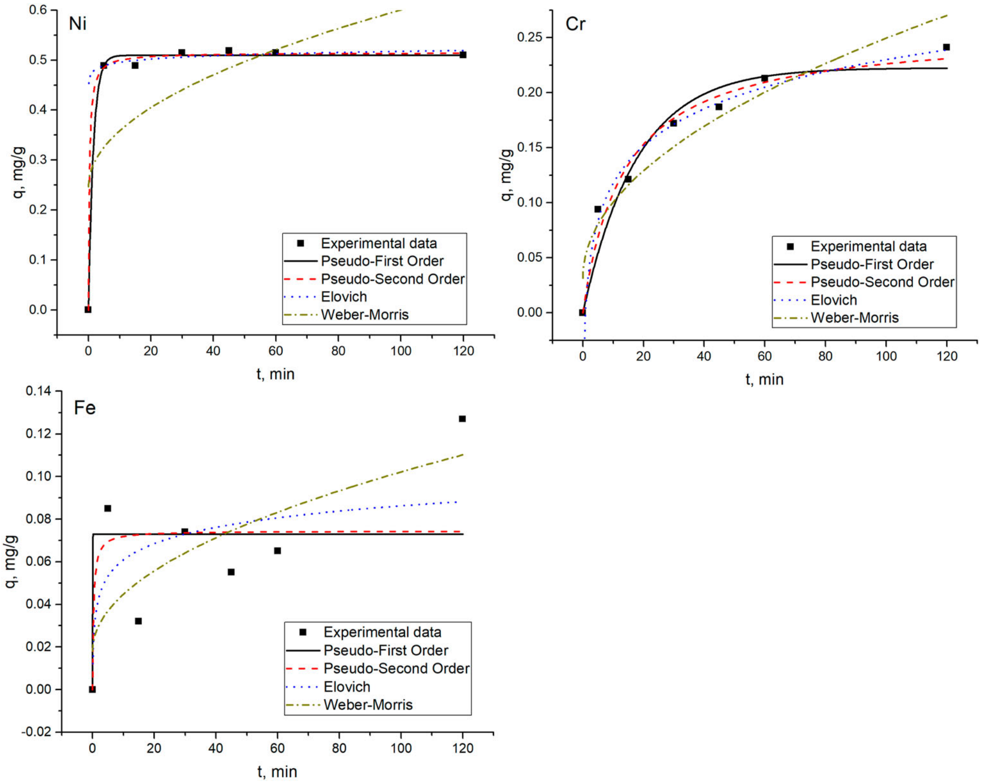

Figure 3. Kinetics of the metal adsorption using *S. cerevisiae* in Ni(II)–Cr(VI)–Fe(III) system.

Pseudo-first order model:

$$q = q_e\left(1 - e^{-k_1 t}\right) \tag{3}$$

where q (mg/g) is the amount of adsorbate absorbed at time t, q_e (mg/g) the adsorption capacity in equilibrium and k_1 (1/min) is the rate constant of pseudo-first order and t (min) is the time.

Pseudo-second order model:

$$q = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \tag{4}$$

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

Elovich model:

$$q_t = \frac{1}{\beta}\ln(1 + \alpha\beta t) \tag{5}$$

where α (g/mg·min) and β(g/mg) are the Elovich equation constants.

Weber and Morris intra-particle diffusion model:

$$q = k_{\text{diff}} \cdot t^{0.5} + C_i \tag{6}$$

where k_{diff} is the rate parameter (mg/g·min$^{1/2}$), C_i is the intercept, giving an idea about the

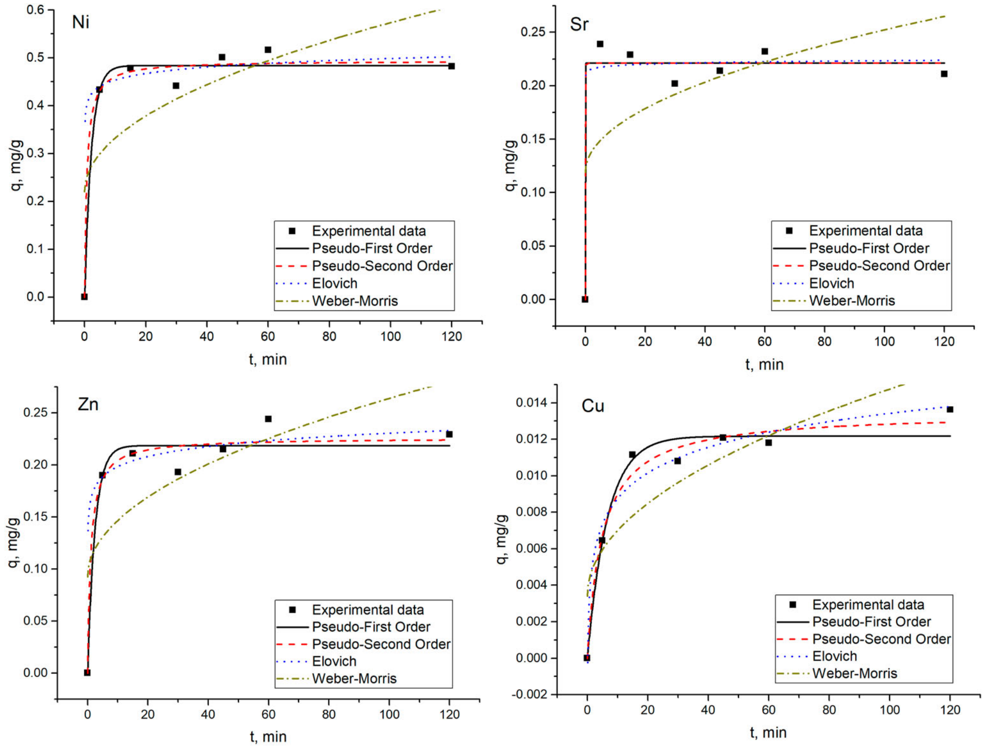

Figure 4. Kinetics of the metal adsorption using *S. cerevisiae* in Ni(II)–Sr(II)–Zn(II)–Cu(II) system.

thickness of the boundary layer. The calculated parameters and the coefficients of determination are given in Table 2.

Ni(II) sorption in all systems fitted well PFO and PSO models, with coefficients of determination values ranging from 0.97 to 0.99. In both models, the calculated $q_{e,\mathrm{cal}}$ were very close to experimentally obtained values $q_{e,\mathrm{exp}}$. Applicability of PFO model indicates that sorption is occurring exclusively onto one site per ion, while satisfiability of PSO model shows that Ni(II) sorption is controlled by chemical processes, through sharing of electrons between biosorbent and sorbate, or covalent forces, through the exchange of electrons between the particles involved [35]. In Ni(II)–Cr(VI)–Fe(III) system EM was suitable to describe biosorption of Cr(VI). EM gives good correlation for adsorption on highly heterogeneous surfaces and shows that chemisorption is one of the main mechanisms of metal biosorption [36]. In the case of Fe(III) coefficients of determination for all models were very low. This is explained by the fact that for Fe(III) equilibrium was not attained. In Ni(II)–Zn(II)–Sr(II)–Cu(II) system according to the coefficient of determination values, the EM fits well the data for Zn (II). It should be mentioned that coefficients of determination of PFO and PSO models were also high and experimentally obtained values of adsorption capacity were in good agreement with calculated values. PFO was suitable to describe the data obtained for Sr(II), while PSO was more applicable to describe Cu(II) sorption. In Ni(II)–Zn(II)–Cu(II)–Mo(VI) system sorption of Zn(II) and Cu(II) was described by PFO and PSO models, while EM was more suitable for illustration of Mo(VI) sorption. The R^2 values obtained for IPM were significantly lower.

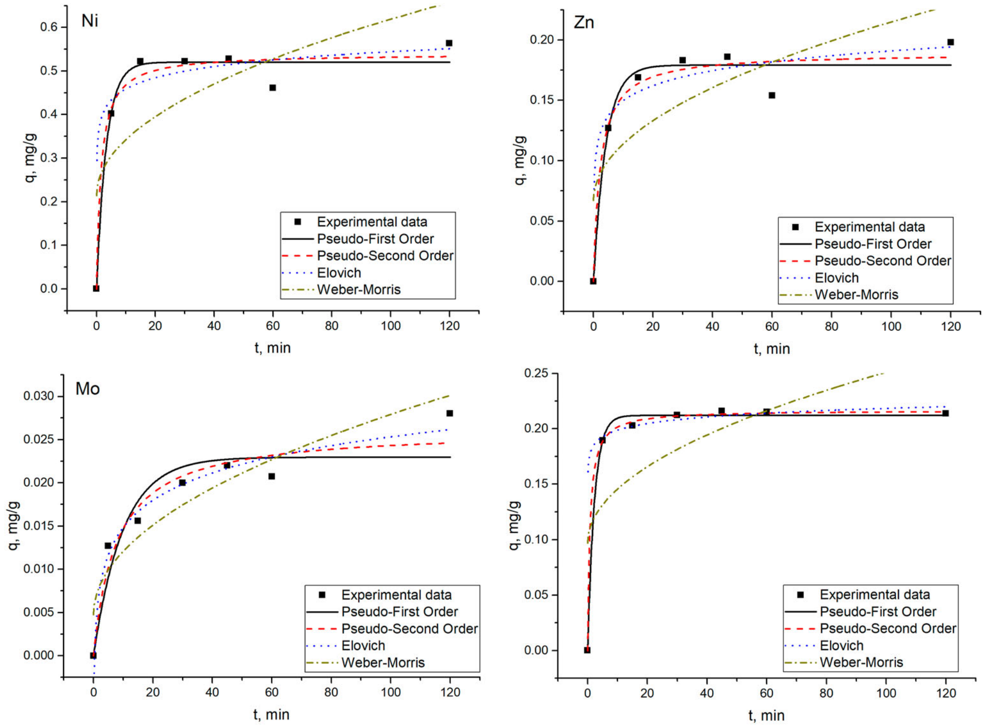

Figure 5. Kinetics of the metal adsorption using *S. cerevisiae* in Ni(II)–Cu(II)–Zn(II)–Mo(VI) system.

Effect of initial concentration of heavy metals and isotherm studies

Increase of the Ni(II) concentration from 10 to 100 mg/L resulted in raising of its sorption on yeast biomass from 0.6 to 3.95 mg/g in Ni(II) system, from 0.7 to 4.77 mg/g in Ni(II)–Sr (II)–Zn(II)–Cu(II) system, from 0.71 to 4.12 mg/g in Ni(II)–Cr(VI)–Fe(III) system and from 0.58 to 3.5 mg/g in Ni(II)–Cu(II)–Zn(II)–Mo(VI) system. It should be mentioned that the concentration of other metal ions present in the systems was maintained constant. Mixtures of Ni (II) with (Sr(II), Zn(II) and Cu(II)) and (Cr(VI) and Fe(III)) increased yeast biosorption capacity towards Ni(II) by 20.7 and 4.3%, respectively. Increase of Ni(II) adsorption by 20.7% can be associated with desorption of Zn(II) and Sr(II) and the appearance of new binding sites for Ni(II) binding [37]. The decrease of Zn(II) and Sr(II) removal by approximately 20% with the increase of Ni(II) concentration in solution supports this suggestion. On the other side, such metal ion behaviour can be explained by the preference of Ni(II), Zn(II) and Sr(II) for the same binding sites. At lower concentrations of metal ions in solution high metal biosorption is associated with the large number of the available sorption sites. At higher concentrations, the available sites of biosorption became fewer and saturation of the sorption sites is observed, resulting in the decrease of metal ion removal [38]. Cu(II) removal remained on the same level at all Ni(II) concentrations in both systems containing copper ions. It is suggested that most divalent metal ions, with the exception of Cu(II), bind to sorbent surface mainly as hydrated ions (outer sphere complexes), whereas copper binding appears to involve the exchange of one or two aquo ligands by carboxylate oxygens [37].

Table 2. The constants and determination coefficients (R^2) of the kinetic models.

				Model											
				PFO			PSO			EM			IPM		
		Metal	q_{exp}, mg/g	q_e, mg/g	k_1, min^{-1}	R^2	q_e, mg/g	k_2, g/mg·min	R^2	α, mg/g·min	β, g/min	R^2	k_{diff}	C_i	R^2
Systems	Ni(II)	Ni	0.52	0.51	0.89	**0.98**	0.51	2.3	**0.98**	n.a.	n.a.	n.a.	0.03	0.3	0.21
	Ni(II)–Cr(VI)–Fe(III)	Ni	0.52	0.51	0.64	**0.99**	0.51	6.4	**0.99**	n.a.	n.a.	n.a.	0.03	0.3	0.34
		Cr	0.22	0.22	0.05	0.93	0.26	0.28	0.97	0.05	20.4	**0.99**	0.03	0.03	0.91
		Fe	–	0.07	29.2	0.36	0.07	3.7	0.37	0.2	90.7	0.46	0.008	0.02	0.5
	Ni(II)–Zn(II)–Sr(II)–Cu(II)	Ni	0.5	0.48	0.45	**0.98**	0.49	2.8	**0.98**	n.a.	n.a.	n.a.	0.03	0.2	0.38
		Zn	0.22	0.23	0.4	0.96	0.22	4.2	0.96	216	72	**0.97**	0.02	0.09	0.48
		Sr	0.22	0.22	45.4	**0.97**	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	0.02	0.1	0.19
		Cu	0.01	0.01	0.15	0.96	0.01	1.5	**0.98**	n.a.	n.a.	n.a.	0.001	0.003	0.72
	Ni(II)–Zn(II)–Cu(II)–Mo(VI)	Ni	0.52	0.52	0.3	**0.97**	0.54	1.2	**0.97**	881	23	0.96	0.04	0.2	0.48
		Zn	0.19	0.18	0.24	**0.95**	0.19	2.3	**0.95**	7.8	55	0.94	0.01	0.07	0.54
		Mo	0.02	0.02	0.1	0.87	0.02	4.9	0.93	0.01	218	**0.97**	0.002	0.006	0.87
		Cu	0.2	0.2	0.44	**0.99**	0.2	6.1	**0.99**	n.a.	n.a.	n.a.	0.01	0.1	0.4

In Ni(II)–Cr(VI)–Fe(III) system with the increase of Ni(II) concentration in solution the increase of Fe(III) and Cr(VI) removal efficiency takes place. Ni(II) mixture with Cu(II), Zn (II) and Mo(VI) leads to the reduction of Ni(II) biosorption by 11% in comparison with Ni (II) system. In Ni(II)–Cu(II)–Zn(II)–Mo(VI) system the behaviour of Zn(II) and Cu(II) was similar to Ni(II)–Sr(II)–Zn(II)–Cu(II) system, while Mo(VI) content increased almost twice at the increase of Ni(II) concentration up to 100 mg/L. Continuous sorption of Mo(VI) indicates the yeast high affinity for molybdate ions and their competition with Ni(II) for binding sites.

The equilibrium data obtained for Ni(II) were described using Langmiur, Freundlich and Temkin equilibrium models (Figure 6). The Langmuir model suggests a monolayer adsorption and is expressed by the formula (7):

$$q_e = \frac{q_m\, bC_e}{1 + bC_e} \tag{7}$$

where C_e is the metal ion concentration at equilibrium (mg/L), q_e is the amount of metal adsorbed at equilibrium (mg/g), $q_{\max}$ is the maximum adsorption capacity of the sorbent (mg/g) and b is the Langmuir adsorption constant (L/mg).

The mathematical expression of Freundlich isotherm model is presented by formula (8):

$$q_e = K_F C^{\frac{1}{n}} \tag{8}$$

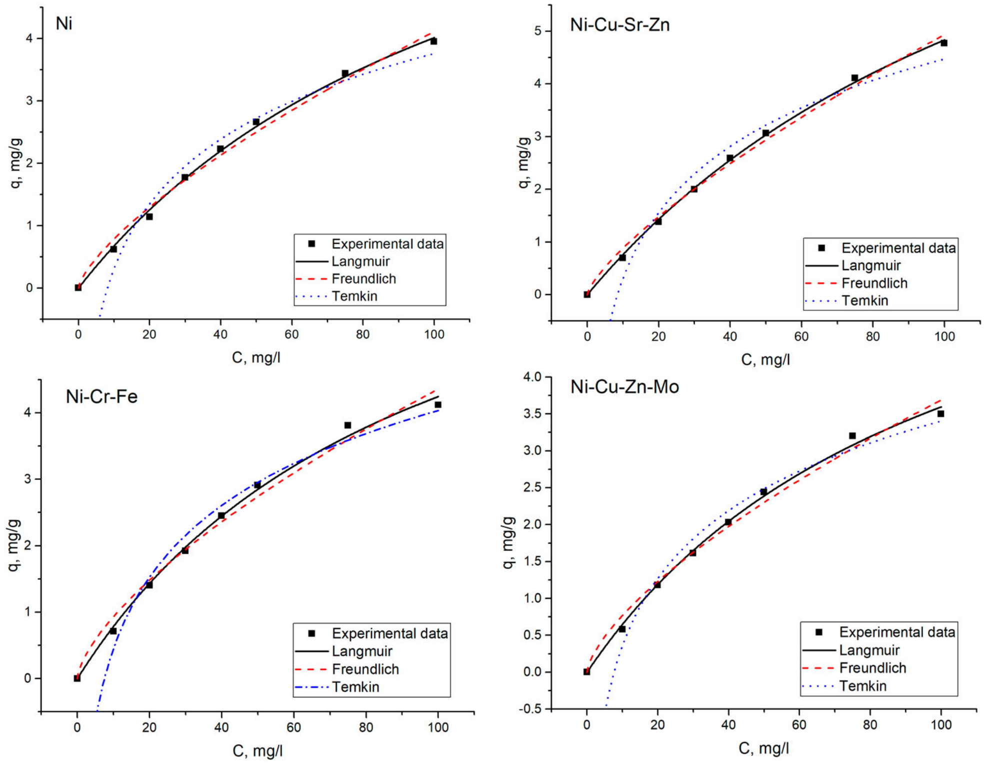

Figure 6. The adsorption isotherms for Ni(II) ions removal on *S. cerevisiae*.

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

The Temkin isotherm model is given below:

$$q_e = \frac{RT}{b_T} \ln(a_T C_e) \tag{9}$$

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

The parameters of each model as well as the coefficient of determination values are grouped in Table 3. The coefficients of determination for all three models were sufficiently high (0.98–0.99). However, the highest values were obtained for Langmiur model, suggesting a homogeneous adsorption within the biosorbent and formation of monolayer [26]. The maximum sorption capacity of *S. cerevisiae* towards Ni(II) constituted 8.9 mg/g in Ni(II) system, 8.3 mg/g in Ni(II)–Cr(VI)–Fe(III), 11.9 mg/g in Ni(II)–Zn(II)–Sr(II)–Cu(II) and 7.3 in Ni(II)–Zn(II)–Cu(II)–Mo(VI) systems. The obtained data also follow Freundlich isotherm model, which assumes a heterogeneous energetic distribution of the active binding sites on the biomass as well as interactions between the adsorbed molecules [26]. Biosorption can be considered favourable since $1/n$ lies between 0 and 1. Applicability of Langmiur model describes Ni uptake was also shown in [24]. For Temkin isotherm R^2 values were slightly lower and the constant (B) values related to the heat of adsorption were in the range 11.2–15.0 kJ/mol. It has been reported by Ho et al. [39] that the typical range of bonding energy for ion-exchange mechanism is 8–16 kJ/mol. Thus, ion-exchange can be one of the mechanisms of Ni(II) removal.

Effect of initial temperature and thermodynamic studies

Temperature has an influence on the biosorption of metal ions; however, usually biosorption process is not operated at high temperatures because it will increase the operational cost [40]. In all analysed systems removal of Ni(II) slightly decreased with the rise of the temperature up to 50 °C (not more than 5%) (Figure 7). Increase of the temperature did not influence significantly Sr(II) and Cu(II) removal in Ni(II)–Zn(II)–Sr(II)–Cu(II) system. At the same time Zn(II) removal increased approximately by 20%. Increase of temperature also expanded Cr(VI) removal efficiency. The results are in agreement with [1], who found that biosorption of Cr(VI) on *S. cerevisiae* increases with increasing temperature in the range of 25–45 °C. In our previous study [10] it was shown that Cr(VI) removal from

Table 3. The parameters and determination coefficients (R^2) of the adsorption isotherms.

Model	Parameters	System			
		Ni(II)	Ni(II)–Cr(VI)–Fe(III)	Ni(II)–Zn(II)–Sr(II)–Cu(II)	Ni(II)–Zn(II)–Cu(II)–Mo(VI)
Langmiur	q_m, mg/g	8.9	8.3	11.9	7.3
	b, L/mg	0.008	0.01	0.007	0.01
	R^2	0.99	0.99	0.99	0.99
Freundlich	K_F, mg/g	0.15	0.2	0.15	0.16
	$1/n$	0.71	0.67	0.77	0.67
	R^2	0.988	0.98	0.99	0.99
Temkin	a_T, L/g	0.12	0.13	0.12	0.13
	B, J/mol	13.5	13	11.2	15
	R^2	0.98	0.98	0.97	0.98

multi-elements systems was not affected or decreased with the rise of the temperature. Increase of the temperature led to the drastic decrease of Fe(III) removal from 46 to 9%. Temperature is a critical parameter for Fe(III) removal, since its increase led to iron precipitation and consequently reduction of its removal [41]. In Ni(II)–Zn(II)–Cu(II)–Mo(VI) system increase of the temperature up to 50°C resulted in the increase of Zn(II) removal (by 13%), decrease in the Mo(VI) removal (by 6%) and did not affect the Cu(II) sorption.

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 formulas (10–12) presented below:

$$\ln K_d = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \tag{10}$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \tag{11}$$

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

$$K_d = \frac{(C_0 - C_e)V}{mC_e} \tag{12}$$

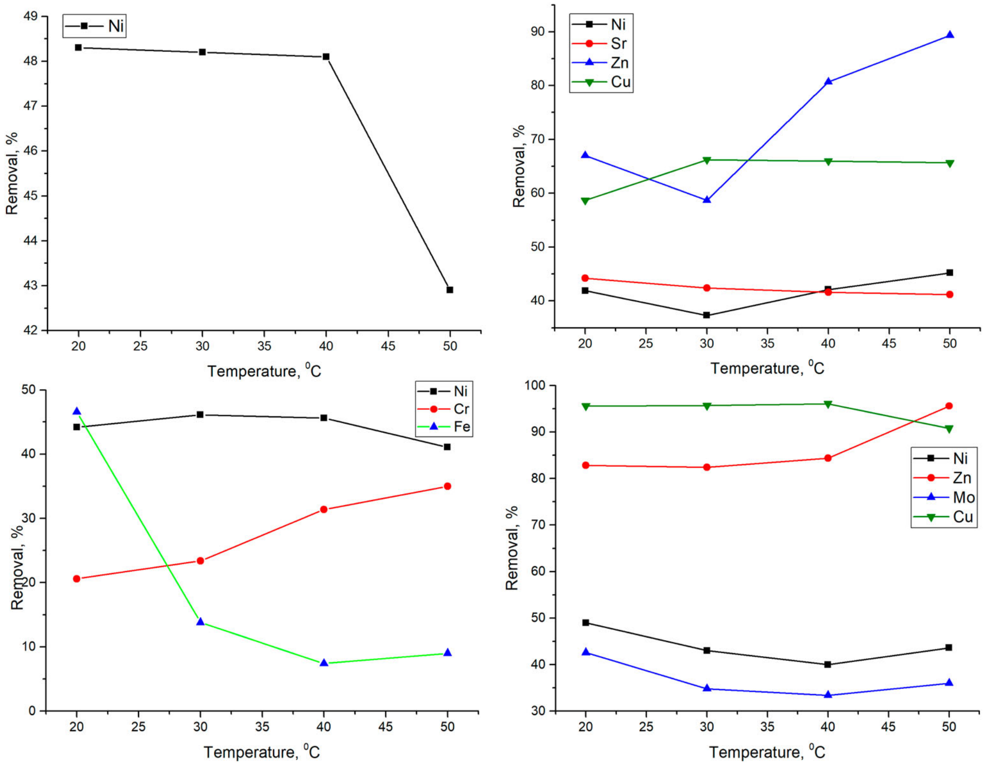

Figure 7. Effect of temperature on the sorption of metal ions by *S. cerevisiae* biomass (at T 20°C; sorbent dosage 10 g/L; adsorption time 1 h).

where C_0 is the initial concentration of metal, (mg/L), C_e is the metal concentration in aqueous solution at equilibrium, (mg/L), V is the volume of aqueous solution (L) and m is the sorbent mass (g).

A linear van't Hoff plot (Figure 6S) of $\ln K_d$ versus $1/T$ gives slope and intercept to determine the value of ΔH° and ΔS°, respectively. The obtained results are listed in Table 4.

The negative values of $\Delta G°$ obtained for all elements in analysed systems indicate that biosorption is a feasible and spontaneous process.

The endothermic nature of Ni(II) sorption Ni(II)-system, Ni(II) and Cr(III) in Ni(II)–Cr(VI)–Fe(III) system, Sr(II) in Ni(II)–Zn(II)–Sr(II)–Cu(II) and Ni(II) in Ni(II)–Zn(II)–Cu(II)–Mo(VI) was confirmed by the positive value of ΔH°. For the rest of elements in analysed systems it was exothermic. A sorption process is generally considered as physical if ΔH°<25 kJ/mol and as chemical when ΔH° >40 kJ/mol [42]. The positive ΔS° value for all metal ions, except Cr(VI) suggests the increase of the randomness at the solid/liquid interface at metal ions sorption on *S. cerevisiae*. Negative ΔS° values obtained for Cr(VI) indicate the decrease in the degree of freedom of the adsorbed species.

According to functional groups determined by FTIR data the main reactions of metal binding could be described as follows:

Farhan and Khadom [26] showed that when heavy metals become tightly bound to acid groups in the side chains of amino acids on the yeast surface, salt linkages are broken and the proteins are dissolved from the cell wall. Thus, metal ions can bind either to dissolved proteins or to functional groups present on the yeast surface.

Metal removal from real industrial effluent

Efficient removal of metal ions from industrial effluents can be achieved by varying the pH of the effluent and the sorbent dosage. In some cases, when effluent is heavily polluted it can be diluted with tap water before purification.

Effect of pH on metal removal from industrial effluent

As it was shown in the experiments with synthetic solutions pH is an important parameter which allows selective metal removal from effluents. Balintova and Petrilakova [43] studying the effect on pH on metal removal from wastewater showed that iron maximum

Table 4. Thermodynamic parameters for metal biosorption on *S. cerevisiae.*

			ΔG°, kJ/mol					
		Metal	293 K	303 K	313 K	323 K	ΔH°, kJ/mol	ΔS°, J/mol·K
System	NI(II)	Ni	−4.1	−4.3	−4.5	−4.8	2.7	23.3
	Ni(II)–Cr(VI)–Fe(III)	Ni	−5.6	−5.8	−6.1	−6.3	1.7	24.9
		Cr	79	80	81	82	44.4	−116
		Fe	−11.1	−11.3	−11.7	−12	−2.1	30.7
	Ni(II)–Zn(II)–Sr(II)–Cu(II)	Ni	−12.7	−13.1	−13.5	−13.9	−1.1	40
		Zn	−42.5	−43.4	−44.3	−45.1	−16.7	88
		Sr	−5.5	−5.7	−6.0	−6.2	1.8	25
		Cu	−13.4	−13.8	−14.2	−14.6	−1.7	40
	Ni(II)–Zn(II)–Cu(II)–Mo(VI)	Ni	−2.4	−2.6	−2.8	−3.0	3.4	19.9
		Zn	−19.6	−20.1	−20.7	−21.2	−4.5	51.5
		Cu	−40.1	−40.9	−41.7	−42.5	−16.2	81.3
		Mo	−0.10	−0.25	−0.41	−0.56	4.4	15.5

removal was achieved at pH 4.05, of aluminum at 4.5–5, of copper at pH 4.5–6.0, of zinc at pH 5.5–7.2 and of manganese at pH 5.5–9.98. The process of Zn(II), Ni(II) and Cu(II) removal by *Shewanella xiamenensis* biofilm supported on zeolite showed to be pH dependent. The maximum removal of Ni(II) was achieved at pH 5.0–6.0, of Zn(II) at pH 5.0 and of Cu(II) at pH 3.0 [27].

In experiments with real effluent the pH varied from 2.0 to 7.0. As it can be seen from Figure 8 maximum removal of metals presented in anionic forms Mo(VI) and Cr(VI) was achieved at pH 3.0 55 and 75%, respectively. pH 3.0 was also found to be optimum for Fe(III) and Cu(II) removal.

The greatest amount of Ni(II) and Sr(II) 42% and 10%, respectively, was removed at pH 6.0, while of Zn(II) ions at pH 7.0 (87%). Varying the pH of the solution it is possible to treat chemically complex effluents. According to the FTIR analysis (data not shown) the main groups, which participated in metal binding at studied pH range were OH, C=O and HN–C=O. The pH 6.0 was shown as optimum for Ni(II) ion removal from effluents in Machado et al. [11] study, while in Zinicovscaia et al. [6, 8] studies it lies in the range 4.0–5.0.

Effect of sorbent dosage on Ni(II) ion removal from industrial effluent

The treatment of effluents containing multi-elements is more complex because metal ions compete for binding sites; as a consequence, displacement of one metal species by another, which has higher affinity for biomass binding sites, can occur [5]. For an efficient bioremediation process, besides optimal pH value, it is important to use an

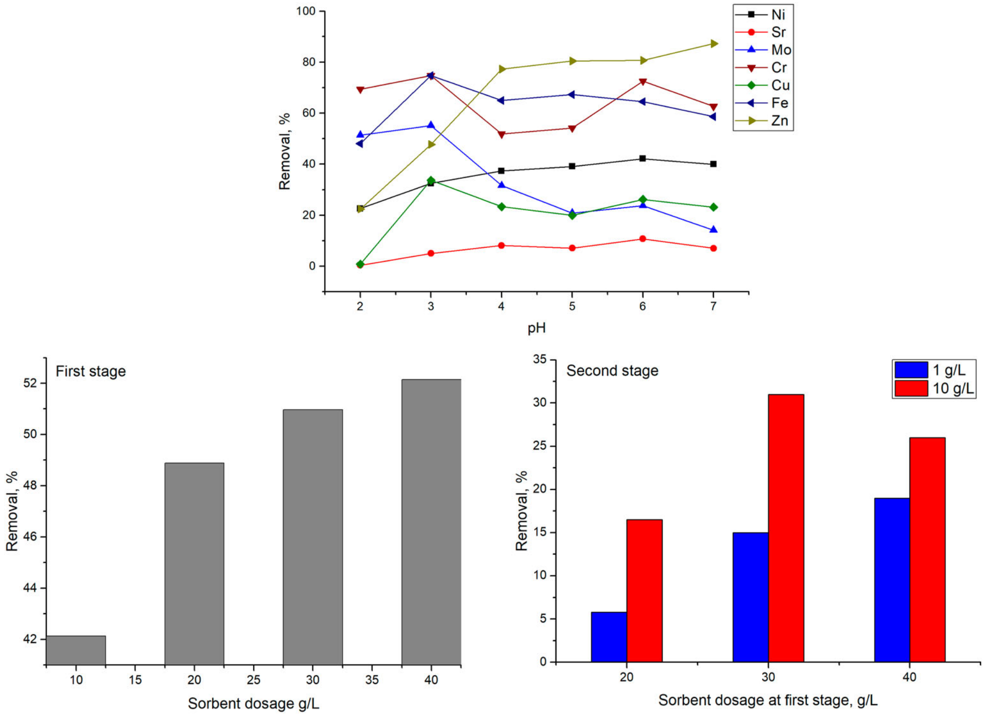

Figure 8. Removal of metal ions from nickel containing effluent at different initial pH and effluent at different sorbent dosage (at T 20°C; sorbent dosage 10 g/L; adsorption time 1 h).

excess of the amount of sorbent which will ensure removal of all metals ions from effluent. In our previous experiments it was shown that at the increase of the sorbent dosage from 6 to 40 g/L nickel removal efficiency by *Spirulina platensis* increased from 42 to 68% [8]. In order to determine the dosage of sorbent required for effective Ni(II) removal the experiments were performed in two stages using new yeast biomass on each stage (Figure 8). It should be noted that in this experiment only Ni(II) removal efficiency was assessed since other metal ions are presented in effluent in significantly lower concentrations than nickel. At the first stage the amount of biomass varied from 10 to 40 g/L that lead to the rise of Ni (II) removal from 42 to 52%. On the second stage to supernatants obtained after first stage were divided into two parts and 1 or 10 g/L of new sorbent was added. On addition of 1 g/L of new yeast biomass Ni(II) removal was 5.7% (first stage 20 g/L), 15% (first stage 30 g/L) and 18% (first stage 40 g/L), thus, the total cumulative removals constituted 54.5%, 66% and 71%, respectively. Addition of 10 g/L of new biomass led to the removal of 16% (first stage 20 g/L), 31% (first stage 30 g/L) and 26% (first stage 40 g/L) of Ni(II) ions. In this case, cumulative removals constituted 65%, 82% and 78%, respectively. Thus, optimal scheme for maximum Ni(II) removal is as follows: 30 g/L of sorbent on the first stage and 10 g/L on the second stage of effluent treatment.

Mahado et al. [5] used 12 g/L of yeast cells to remove nickel from the effluents in a batch mode. After the third batch, the removal of Ni(II) constituted 89%. However, it should be mentioned that initial Ni(II) concentration in effluent was 17.8 mg/L and in our study it is significantly higher 143 mg/L.

Conclusions

Saccharomyces cerevisiae showed to be an efficient sorbent for metal removals from complex nickel-containing effluents. The process of metal removal showed to be pH dependent, maximum Ni(II) removal from synthetic and real effluent was achieved at pH 6.0. For Cr (VI), Mo(VI), Fe(III) and Cu(II) optimal pH values were 2.0–3.0, while for Zn(II) and Sr(II) 6.0–7.0. The OH, $CH{=}CH$, $C{=}O$ and $N = O$ groups were mainly involved in metal ion binding. Biosorption equilibrium data fit well the Langmuir and Freundlich models, with maximum biomass sorption capacity 8.9 mg/g in Ni(II), 8.3 mg/g in Ni(II)–Cr(VI)–Fe(III), 11.9 mg/g in Ni(II)–Zn(II)–Sr(II)–Cu(II) and 7.3 in Ni(II)–Zn(II)–Cu(II)–Mo(VI) systems. Kinetic studies reveal that nickel biosorption by Saccharomyces cerevisiae could be described more favourably by the pseudo-first and pseudo-second-order kinetic models. Sorption of other metal ions present in the effluents was represented by pseudo-first, pseudo-second-order and Elovich kinetic models. The process of metal ion biosorption was visible and spontaneous, while the nature of metal ions sorption was dependent on the effluent composition. Application of two-stage process with 30 g/L of biomass on the first stage and 10 g/L of biomass on the second stage allowed to remove up to 82% of Ni(II) ions from industrial effluent. *Saccharomyces cerevisiae* can be considered as cheap and efficient sorbent for complex effluents treatment and especially Ni(II) ion removal.

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