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USE OF DEAD AND LIVING FUNGAL BIOMASS FOR REMOVAL OF HEXAVALENT CHROMIUM

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Abstract: The removal of hexavalent chromium from aqueous solution was carried out in batch experiments using dead and living biomass of *Aspergillus niger*. The effects of the operating parameters such as influent Cr(VI) concentration, influent pH and biomass concentration on the Cr(VI) reduction were investigated. The results indicates that the removal rate of Cr(VI) increased with a decrease in pH or with increase of Cr(VI) and biomass concentrations. For chromium bioaccumulation along with nutrients the process is the most intensive within the first 5 days of mycelium formation. For biosorption, the greatest binding of this metal is achieved within the first 4 days of the process.

Keywords: *hexavalent chromium, Aspergillus niger, biosorption, bioaccumulation*

Introduction

Chromium is one of the most prevalent elements in nature. It is a natural component of rocks, minerals, soil and water. Its content in the environment is significantly increased due to anthropogenic activity. It is estimated that chromium quantity introduced into the environment by human constitutes 150% of its emission from natural sources. It may be washed out of chromium waste and soil by rainwater, melt water and surface waters. Moreover, chromium compounds in surface waters frequently come from industrial waste and various other sources associated with anthropic activity (Badura, 1993; Barnhart, 1997; Costa, 2003; Slowik et al., 2011).

Major producers of waste and wastewater containing chromium compounds include tanneries, electroplating plants, metallurgic industry and chemical plants. Furthermore a considerable quantity of chromium compounds is also emitted to atmosphere at treatment and processing of minerals (Badura, 1993; Barnhart, 1997; Costa, 2003). In this case we have to deal with a paradox related to this element. It is important from the world economy point of view, but its production and use contribute

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to degradation of the natural environment (Holda et al., 2009; Kowalski, 2002; Wolak et al., 1995).

Toxicity of chromium-containing waste results from specific properties of this compound. It plays a role both as the essential nutrient, and carcinogenic chemical compound. Its toxicity is determined by oxidation degree and solubility. Chromium(VI) compounds are more hazardous than chromium(III) compounds, due to their greater oxidation strength and permeability through cellular membranes. This all makes chromium waste and wastewater treatment so important (Holda et al., 2009; Kabata- Pendias, 1993; Kowalski, 2002).

There are various methods of chromium-containing wastewater and industrial waste treatment. However, traditional methods such as precipitation, ion exchange, adsorption, crystallization, liquid extraction, etc., are frequently inefficient, and besides they can make a source of secondary waste. Therefore, more effective and safe methods for wastewater purification of hazardous heavy metals are searched for. One of them may be the application of inexpensive and environmentally friendly biological methods, specifically adsorption properties of fungal mass. The use of selectively selected microorganisms considerably limits the quantity of chromium introduced to the environment (Bai et al., 2003; Chen et al., 1997, Singh et al., 1997, Nourbakhsh et al., 1994; Prakasham et al., 1999).

Previous studies describe the use of growing and dead microorganism cells for Cr(VI) removal from aqueous solutions using biosorption (Aksu et al., 2007; Deepa et al., 2006; Park et al., 2005; Kapoor et al., 1995; Kumar et al., 2008; Morales-Barrera et al., 2006; Srivastavaa et al., 2006) and bioaccumulation methods (Donmez et al., 2005, 2007; Dursan et al., 2003). Each of these methods has its advantages and disadvantages. Application of dead biomass eliminates the problems related to toxic metal concentration in test solution, as well as requirements concerning growth medium. Moreover, adsorbed metal can be easily removed, and the remaining biomass can be reused after regeneration (Gupta et al., 2008; Bai et al., 2003). Unfortunately, a limitation of this method is that no biochemical reactions are continued in dried cells.

Application of living biomass makes it possible to remove metal during its growth, thus enabling omission of, among others, growth, drying and storage process. Unfortunately in this case metal concentration in the environment is of great importance since if it is too high it is toxic for growing biomass. The problem can be avoided by using microorganisms showing great tolerance to high concentrations of Cr(VI) (Holda et al., 2011; 2013).

The paper presents studies concerning the effect of pH, contact time, biosorbent quantity and initial concentration of chromium(VI) on chromium(VI) ion biosorption process using *Aspergillus niger* fungus. Furthermore, comparison between biosorption process using dead biomass and bioaccumulation using growing biomass has been carried out as regards the usefulness thereof in the process of biological elimination of Cr(VI) ions from aqueous solutions.

Biosorption kinetics

Metal ion adsorption on the surface of dead biomass is affected by numerous factors, such as pH, initial concentration of metal ions, contact time between biosorbent and solution containing metal ion to be removed and biosorbent content (Religa et al., 2016; Wionczyk, 2013). During the studies temporary concentrations of chromium(VI) ions were determined, and then based on the obtained results two values were calculated: quantity of metal ions adsorbed by biomass (q) and the rate of removal of metal ions from the solution (R). Quantity of metal adsorbed by biomass was calculated according to the following formula:

$$q = \frac{(C_0 - C_e)V}{W} \tag{1}$$

where q is the quantity of Cr(VI) ions adsorbed by biomass (mg/g), C_0 initial concentration of chromium(VI) ions in mg/dm^3, C_e temporary concentration of chromium(VI) ions in mg/dm^3, V solution volume in dm^3, and W biosorbent mass in g.

The rate of removal of metal ions from solution (R) was calculated according to the following formula:

$$R = \frac{C_0 - C_e}{C_0} \cdot 100\% \tag{2}$$

where R is the rate of removal of chromium (VI) ions from the solution (%), C_0 initial concentration of chromium(VI) ions (mg/dm^3), and C_e temporary concentration of chromium(VI) ions (mg/dm^3).

The equilibria of biosorption of heavy metals and organic compounds follow an adsorption-type isotherm (the single-solute adsorption isotherm models of Langmuir and Freundlich). The degree of biosorption of a metal ion on a biosorbent has been found to be a function of the equilibrium metal-ion concentration in solution at constant pH and temperature conditions.

The Langmuir model can be described as (Kumar et al., 2008):

$$q_e = \frac{Q_0 b C_e}{1 + b C_e} \tag{3}$$

where q_e is the uptake of metal per unit weight of the adsorbent (mg/g), Q_0 moles of solute sorbed per unit weight of adsorbent (mg/g), b constant related to affinity between the biosorbents and biosorbate (dm^3/mg), and C_e equilibrium (residual) concentration of ions (mg/dm^3). The Langmuir model is based on the assumption that maximum adsorption occurs when a saturated monolayer of solute molecule is present on the adsorption surface, and the energy of adsorption is constant and that there is no migration of adsorbate molecule in the surface plane. The Freundlich isotherm has the form:

$$q = K_f C_e^{\,1/n}. \tag{4}$$

The logarithmic form of the equation is:

$$\log q_e = \log K_f + \frac{1}{n}\log Ce \tag{5}$$

where q_e is the uptake of metal per unit weight of biosorbent (mg/g), C_e the equilibrium concentration of metal ions in solution (mg/dm^3), K_f the Freundlich constants denoting adsorption capacity (mg/g), n the empirical constant, indicating of adsorption intensity (dm^3/mg).

The adsorption models described above were developed for gas adsorption on surfaces. The application of these models to complex biological system may not be able to explain the biosorption behavior. To define biosorption process mechanism and to determine factors that limit its rate two kinetic models are used most frequently: first-order model defined by the Lagergren equation and second-order model (Table 1) (Ayanda et al., 2012).

Table 1. Pseudo first-order and pseudo second-order models of kinetics

Model	Equation	Linearization	Figure
Pseudo first-order	$\frac{dq}{dt} = k_1(q_e - q_t)$	$ln(q_e - q_t) = lnq_e - k_1 t$	$(q_e - q_t) = f(t)$
Pseudo second-order	$\frac{dq}{dt} = k(q_e - q_t)^2$	$\frac{t}{q_t} = \frac{1}{k \cdot (q_e)^2} - \frac{t}{q_e}$	$\frac{t}{q_t} = f(t)$

Materials and methods

Microorganisms and growth conditions

In the studies mouldy fungus *Aspergillus niger* CIM number 43 was used. It was obtained from the Collection of Pure Cultures of the Institute of Agricultural and Food Technology in Warsaw (IBPRS). The culture was grown on Czapek-Dox agar for 21 days at 21 ^{o}C. Following growth period, biomass and medium were separated. Then biomass was washed few times with deionised water in order to remove medium residue from its surface.

Preparation of dead biomass

Living biomass was autoclaved for 15 minutes at 121^{o}C, and then boiled for 15 minutes in a mixture of 0.5M NaOH and 10% acetic acid solutions in the proportion of 1:1. Then biomass was filtered off and washed with deionised water until neutral pH in filtrate was obtained. The obtained preparation was placed in a dryer at 60^{o}C for 8 hours. After this time dead biomass was ground in a mortar into powder and stored in a desiccator.

Biosorption process

Cr(VI) removal of aqueous solutions using dead biomass of mouldy fungi was tested by measuring Cr(VI) concentration in test samples as a function of time. Experiments were carried out in 250 cm^3 Erlenmeyer flasks containing 100 cm^3 of Cr(VI) solution of a given concentration and biosorbent sample of given mass placed on an orbital shaker in order to provide optimal conditions (pH, contact time and initial concentration of Cr(VI)). The effect of reaction on Cr(VI) biosorption rate was tested within pH range of 1-5 in a solution containing 1 g of biosorbent (biomass concentration 10 mg/dm^3) and 50 mg/dm^3 of Cr(VI) ions. Predefined reaction was obtained by adding 0.5 M H_2SO_4 or 0.1 M NaOH solution. Relation between Cr(VI) concentration and contact time was tested at optimum pH in a solution containing 25-200 mg/dm^3 of Cr(VI) ions and 1g of biosorbent. The effect of biosorbent quantity on the rate of Cr(VI) removal from the solution was tested at optimum pH in a solution containing 50 mg/dm^3 of Cr(VI) ions and 5-25 g of biosorbent. Temporary chromium(VI) concentrations in aqueous solutions under tests were determined using the spectrophotometric method.

Bioaccumulation process

Cr(VI) removal from aqueous solutions using living biomass of mouldy fungi was tested by measuring Cr(VI) concentration in test samples as a function of time.

The effect of reaction on Cr(VI) removal rate was tested within pH range of 4.0-6.5. To this end, after the predefined pH had been achieved, pure mould culture was inoculated onto a medium containing 50 mg of Cr^{6+} ions/dm^3. Then 2.5 cm^3 of sample from each flask was drawn every day at predefined time and chromium(VI) content determination was carried out using the spectrophotometric method.

Relation between Cr(VI) concentration and time was tested at optimum pH in a solution containing 10-125 mg/dm^3 of Cr(VI) ions. To this end pure mould culture was inoculated onto a medium containing predefined quantity of Cr^{6+} ions/ dm^3. Then 2.5 cm^3 of sample from each flask was drawn every day at predefined time and chromium(VI) content determination was carried out using the spectrophotometric method.

Results

The effect of pH on chromium(VI) biosorption

For 130 h the effect of reaction on chromium(VI) ion sorption was tested within pH range of 1 to 5 for initial chromium concentration amounting to 50 mg/dm^3. Based on the obtained results figures were drawn to demonstrate the relation between the rate of removal and time.

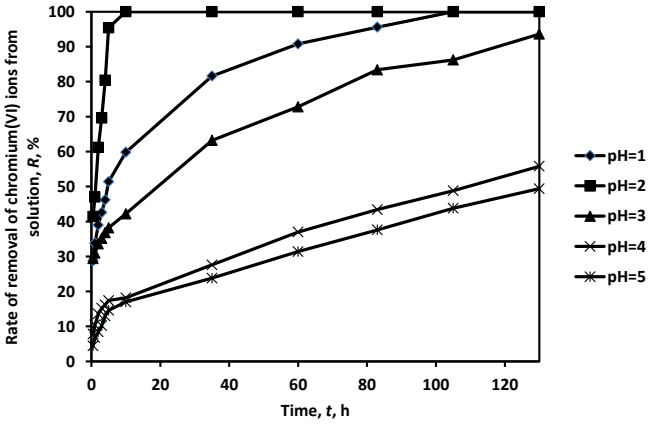

Fig. 1. Effect of pH on Cr(VI) removal by dead fungal biomass; initial Cr(VI) concentration C_0 = 50 mg/dm^3, biosorbent content C_b = 10 g/dm^3

The pH of the solution strongly affected the degree of biosorption of chromium on biomass. Based on the analysis of the obtained results shown in Figure 1 it may be concluded that the rate of removal of chromium(VI) ions from the solution decreases with the increase of pH. At pH equal to 1 and 2 complete removal of chromium(VI) ions from the solution was observed. Besides the maximum percent removal of chromium(VI) at the lowest contact time was observed at pH 2.0. These results are in accordance with earlier observations for different fungal biomass (Kumar et al., 2008; Park et al., 2005; Bai and Abraham, 2001; Nourbakhsh et al.,1994; Sag and Kutsal, 1996). The reason why the complete removal of Cr(VI) was only observed at highly acidic pH is likely because of too short contact time at higher pH values. An increase in Cr(VI) removal with the decreasing pH of the solution can be explained by two factors. First as the pH decreases, the overall fungal surface charge will become positive and the anionic chromate ion binds to the positively charged groups such as amines. As the pH increases, the overall surface charge on the biomass will become negative, resulting in a decrease of anionic Cr(VI) biosorption (Park et al,. 2005). Second the solution chemistry of Cr(VI) ions can affect the biosorption process. Kumar et al. (2008) have noted that in the pH range 2.0–6.0, $HCrO_4^-$ and $Cr_2O_7^{2-}$ ions are in equilibrium whereas, at lower pH (pH < 2.0), there is formation of more polymerized chromium oxide species such as $Cr_3O_{10}^{2-}$ and $Cr_4O_{13}^{2-}$, which results in decrease in Cr(VI) removal.

The effect of initial concentration of Cr(VI) ions on biosorption

The effect of initial concentration of chromium(VI) ions C_0 on biosorption process was tested for 130 h under the following conditions: pH = 2, C_b = 10g/dm^3. Based on the obtained results a figure was drawn, showing the effect of initial chromium(VI) concentration on the removal of these ions by dead fungal biomass (Figure 2).

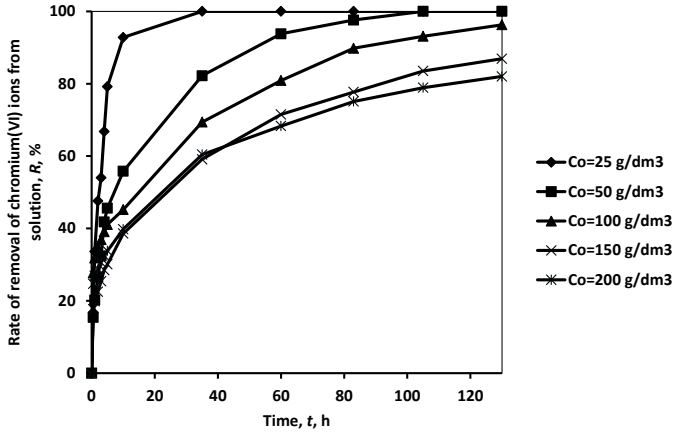

Fig. 2. Effect of initial chromium(VI) concentration on the removal of Cr(VI) ions by dead fungal biomass; C_0 = 25 – 200 mg/dm^3 pH = 2, biosorbent content C_b = 10 g/dm^3

Based on the analysis of the obtained results shown in Figure 2, it may be concluded that the rate of removal of this metal by dead biomass decreases with the increase of initial concentration of Cr(VI). Complete removal of chromium(VI) ions was achieved only at initial concentration amounting to 25 mg/dm^3 and 50 mg/dm^3, while at the concentration of 25 mg/dm^3 the process progressed very rapidly. This may be due to the increase in the number of Cr(VI) ions competing for the available binding sites in the biomass and due to the lack of binding sites for complexation of Cr(VI) ions at higher concentration levels. These results have been observed by other researchers for different fungal biomass. Park et al. (2005) have reported a similar trend for a Cr(VI) concentration of 25 mg/dm^3, Cr(VI) was completely removed in the solution in 30 h, whereas the complete removal of 200 mg/dm^3 of Cr(VI) required about 400 h of contact time. Kumar et al. (2008) have observed a maximum percent removal of Cr(VI) at 30 mg/dm^3: 90.88±2.9%, 87.28±1.48% and 86.61±2.46% with *A. niger*, *A. sydoni* and *P. janthinellum*, respectively. Due to the fact that in the process we studied the most important is to remove the greatest possible quantity of Cr(VI) ions, for further studies on the effect of biomass quantity on biosorption we assumed initial concentration at the level of 50 mg/dm^3.

The effect of biosorbent concentration on chromium(VI) biosorption process

For 130 h the effect of biosorbent concentration (C_b) on chromium(VI) sorption was tested for initial chromium concentration amounting to 50 mg/dm^3 and pH amounting to 2. Based on the obtained results a figure was drawn, showing concentration of chromium(VI) ions as a function of time for various biosorbent concentrations (Fig. 3).

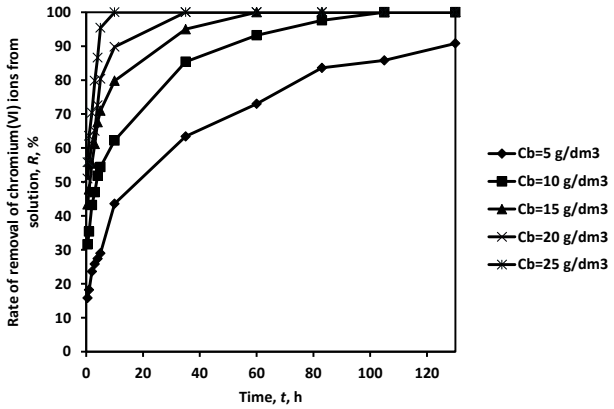

Fig. 3. Effect of biosorbent concentration on Cr(VI) ion removal by dead biomass: C_b = 5 – 25 g/dm^3, pH = 2, initial concentration Cr(VI) C_0 = 50 mg/dm^3

Based on the analysis of the obtained results shown in Fig. 3 it may be concluded that the lower biosorbent concentration, the lower rate of Cr(VI) ion removal. For biosorbent concentrations from 10 to 25 g/dm^3 complete removal of chromium(VI) ions was observed. On the other hand, for biosorbent concentration of 5 g/dm^3, 90% of chromium(VI) ions were removed from the solution. For concentrations between 25 and 15 g/dm^3 chromium adsorption process occurred rapidly compared to concentrations of 10 and 5 g/dm^3.

Biosorption kinetics

For the compilation of results, the second-order kinetic model for predefined process parameters was applied. Based on the obtained results figures were drawn showing the quantity of Cr(VI) ions adsorbed by biomass as a function of time in relation to pH, initial concentration of Cr(VI) ions and biosorbent concentration (Fig. 4).

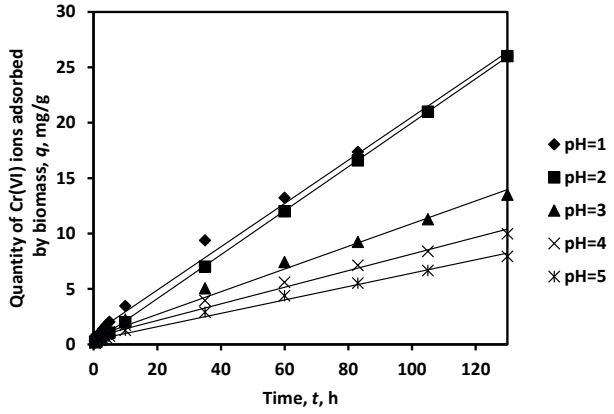

Fig. 4. Quantity of Cr(VI) ions adsorbed by biomass (q) as a function of time (t) in relation to pH

Table 2. Linear regression coefficients read from Figure 4

Coefficient	pH				
	pH = 1	pH = 2	pH = 3	pH = 4	pH = 5
Biosorption process rate constant *k*	0.195	0.198	0.102	0.075	0.060
Biosorption capacity q_{eq},	0.994	1.153	0.659	0.647	0.387
Coefficient of determination	0.995	0.999	0.991	0.989	0.992

Based on the obtained results shown in Fig. 4 it may be concluded that the greatest biosorption capacity and process rate constant *k* was obtained at pH amounting to 2. It can be observed that with the increase of reaction the quantity of the adsorbed ions decreases.

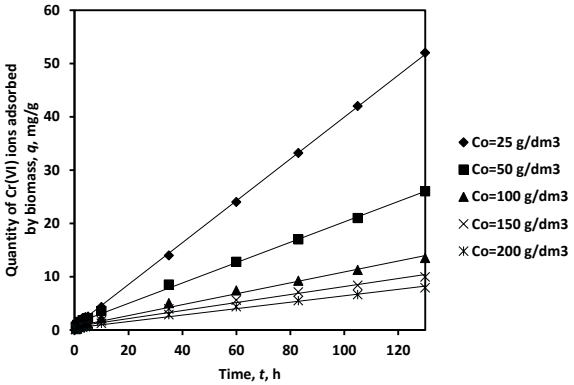

Fig. 5. Quantity of Cr(VI) ions adsorbed by biomass (q) as a function of time (t) in relation to initial concentration of chromium(VI) ions

Table 3. Linear regression coefficients read from Fig. 5

Coefficient	Initial concentration of chromium(VI) ions				
	C_0=25 g/dm^3	C_0 =50 g/dm^3	C_0=100 g/dm^3	C_0=150 g/dm^3	C_0=200 g/dm^3
Biosorption process rate constant *k*	0.393	0.192	0.103	0.076	0.061
Biosorption capacity q_{eq}	0.63	1.035	0.578	0.567	0.339
Coefficient of determination	0.999	0.997	0.990	0.987	0.991

Based on the obtained results shown in Fig. 5 it may be concluded that the greatest biosorption capacity was obtained for initial concentration of chromium(VI) ions amounting to 50 g/dm^3, while rate constant *k* takes the greatest value for the initial concentration of 25 g/dm^3. It can also be observed that with the increase of initial concentration of chromium(VI) ions *k* rate constant value decreases.

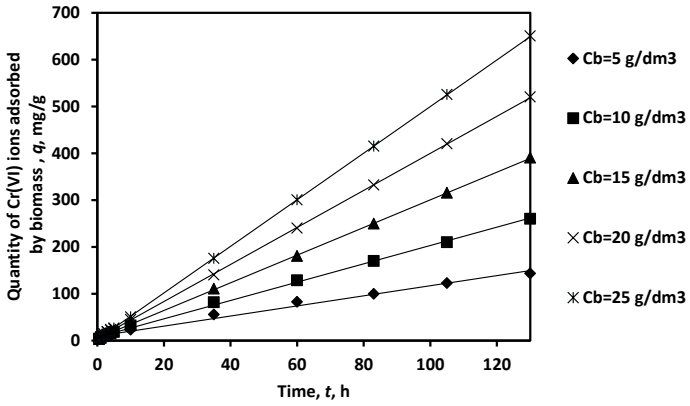

Fig. 6. Quantity of Cr(VI) ions adsorbed by biomass (q) as a function of time (t) in relation to biosorbent concentration

Table 4. Linear regression coefficients read from Fig. 6

Coefficient	Biosorbent concentration				
	C_b= 5 g/dm^3	C_b =10 g/dm^3	C_b =15 g/dm^3	C_b =20 g/dm^3	C_b =25 g/dm^3
Biosorption process rate constant k	1.076	1.955	2.955	3.956	4.975
Biosorption capacity q_{eq},	9.469	7.528	5.111	4.245	2.317
Coefficient of determination	0.990	0.998	0.999	0.999	1

Based on the obtained results shown in Fig. 6 it may be concluded that the greatest biosorption capacity was obtained for biosorbent concentration amounting to 5 g/dm^3. On the other hand, the greatest rate constant k is obtained for the concentration amounting to 25 g/dm^3. It can also be observed that rate constant k increases with the increase of biosorbent concentration, while biosorption capacity reduces.

Bioaccumulation

Test strain of *Aspergillus niger* type fungus was also used in bioaccumulation process (Holda et al., 2011). The obtained results are presented in Figs. 7 and 8.

Based on the obtained results it was concluded that the most intensive process of intracellular absorption of chromium and nutrients is observed within the first five days of mycelium formation. Furthermore, chromium(VI) bioaccumulation depends on the environmental pH and shows the greatest effectiveness at pH amounting to 4.0. It can also be seen that the greater chromium(VI) concentration, the lower bioaccumulation of this element from the environment and the slower mycelium growth.

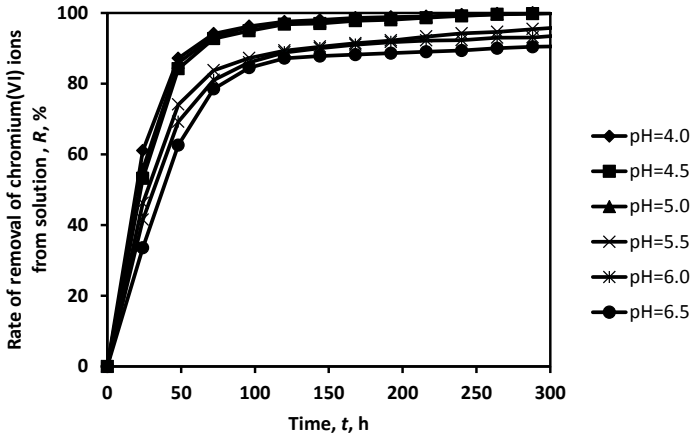

Fig. 7. Effect of pH on Cr(VI) removal by living fungal biomass: initial Cr(VI) concentration C_0 = 50 mg/dm^3

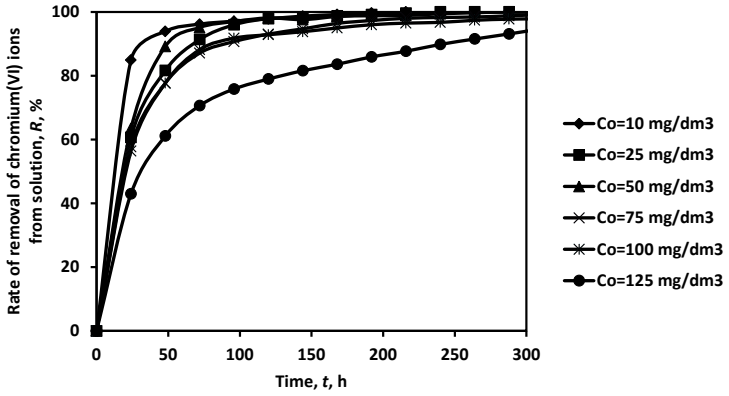

Fig. 8. Effect of initial chromium(VI) concentration on the removal of Cr(VI) ions by living fungal biomass: C_0 = 10 – 125 mg/dm^3, pH = 4

Conclusions

The removal of Cr(VI) ions from aqueous solution by dead and living biomass of *Aspergillus niger* was studied in a batch system. The results showed that the removal rate of Cr(VI) increased with a decrease in pH or with increases in Cr(VI) and biomass concentrations. Particularly, the initial Cr(VI) removal rate exhibited pseudo first-order dependence with respect to both initial Cr(VI) and biomass concentrations. Based on the analysis of biosorption kinetics it was shown that the greatest biosorption capacity and process rate constant *k* was obtained at pH amounting to 2, for initial concentration of chromium(VI) ions equal to 50 g/dm^3 and biosorbent concentration amounting to 5 g/dm^3. On the other hand, the greatest rate constant *k* for the process

was obtained at pH amounting to 1, for the initial concentration of chromium(VI) ions amounting to 25 g/dm^3 and biosorbent concentration amounting to 25 g/dm^3.

After the studies were carried out biosorption and bioaccumulation compared it can be concluded that both processes are effective in the removal of Cr(VI) ions from the solution and can be an excellent alternative for expensive chemical methods. The best choice seems to be biosorption process, which makes a rapid, not expensive, effective and environmentally friendly method of elimination of Cr(VI) ions from aqueous solutions. Its further advantage is the lack of secondary waste generation and the possibility to recover the adsorbed metal.

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