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JSCS–3987 *Original scientific paper*

Hexavalent chromium removal by waste mycelium of *Aspergillus awamori*

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Abstract: In this study, the Cr(VI) removal potential of waste mycelium from the industrial xylanase-producing strain *Aspergillus awamori* was evaluated. It was determined by FTIR analysis that amino groups from the major fungal wall constituents, chitin and chitosan, played a key role in the metal binding process. The effect of pH, initial ion concentration, temperature and amount of biomass on the removal was also studied. The removal efficiency increased with decreasing pH and increasing temperature and amount of biomass. The mechanism of Cr(VI) removal by *A. awamori* can be explained by a two-stage process involving an initial adsorption stage followed by a reducing stage. The removal process was described by a second-order polynomial and the optimal process parameters for attaining R_{max} 94.4 % in 48 h were predicted, *i.e.*, pH 1.5 and t = 40 °C. From both economic and ecological points of view, a promising possibility for the utilization of waste industrial mycelium of *A. awamori* as a low-cost Cr(VI) removal agent was proposed.

Keywords: *Aspergillus awamori*; Cr(VI) removal; waste fungal mycelium.

INTRODUCTION

Due to the accelerated development of various industries, constantly increasing amounts of pollutants are annually discharged into ecosystems. Environmental pollution with industrial wastewaters contaminated with heavy metals has become one of the major ecological problems. One such heavy metal is Cr(VI). Due to its carcinogenic, mutagenic, teratogenic and tissue damaging potential, Cr(VI) is known to be very toxic to both plants and animals and has been classified in Group A of human carcinogens.[1–4] The high risk of Cr(VI) bioaccumulation through the food chain and the disadvantages of traditional chemical

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methods for metal removal have led scientific attention to be focused on non--conventional, biological methods for Cr(VI) removal by various biomaterials, such as bacteria, yeast, algae, seaweed, filamentous fungi and agricultural waste biomass.[5–20] On the one hand, compared to living and resting cells, non-living cells possess higher metal removal capacities.[11,21–23] On the other hand, from both economic and ecological points of view, it is very important to utilize inexpensive and waste biomaterials as metal removal agents. Many of the cited studies for Cr(VI) removal were not realized with waste fungal biomasses, but with especially cultivated fungal strains that were then killed. Filamentous fungi belonging to genera *Aspergillus*, *Penicillium* and *Rhizopus* are intensively used in fermentation industries for producing enzymes, antibiotics and other bioproducts, which means large amounts of waste fungal mycelium are produced annually. Only Fourest and Roux[24] and Gulati *et al.*[25] have studied the biosorption of Cu, Ni, Zn, Cd and Pb by waste fungal mycelium of *A. terreus* and *R. arrhizus* obtained as by-products from industrial fermentation processes. To the best of our knowledge, no articles considering Cr(VI) removal using waste fungal mycelium from industrial fermentations exist in the literature.

The aim of this study was to evaluate for the first time the potential of waste mycelium of the industrial xylanase-producing strain *A. awamori* for Cr(VI) removal from aqueous solutions. The cell surface binding groups before and after Cr(VI) removal were detected. The effects of pH, initial Cr(VI) concentration, amount of biomass and temperature on metal removal from aqueous solutions were studied in a batch system. The activation energy of the process was calculated and Cr(VI) removal was explained by a pseudo-first order kinetic model.

EXPERIMENTAL

Preparation of the biosorbent

Waste mycelium of the industrial strain *A. awamori* was harvested by filtration at the end of the fermentation process for the industrial production of a complex enzyme preparation with a leading xylanase activity.[26,27] The waste mycelium was killed by autoclaving at 121 °C for 20 min, washed thoroughly with deionized water and dried in an oven at 80 °C for 10 h. Then it was powdered to particles of uniform size of about 100 µm. This powdered biomass was used in the further biosorption experiments.

Chemical modification of the amino groups

Formaldehyde and sodium iodoacetate treatment were performed as described by Park *et al.*[28] Acetic anhydride treatment was performed as described by Bai *et al.*[11] At the end of the treatment procedures, biosorbent was separated, washed with deionized water and dried in an oven at 80 °C for 10 h.

Preparation of the Cr(VI) solution

A stock solution (1000 mg L^{-1}) of Cr(VI) was prepared by dissolving the adequate amount of $K_2Cr_2O_7$ (Merck, Darmstadt, Germany) in deionized water. For metal biosorption experiments, Cr solutions of different concentrations (25, 50 and 100 mg L^{-1}) were prepared by appropriate dilution of the stock solution with deionized water.

Analysis of the Cr concentration

The residual Cr(VI) concentration after biosorption was determined spectrophotometrically (Camspec, UK) at 540 nm using 1,5-diphenylcarbazide as the complexing agent in acidic solution.[29] To estimate the total chromium concentration, Cr(III) was first converted to Cr(VI) at 130–140 °C by the addition of excess of $KMnO_4$ prior to the 1,5-diphenylcarbazide reaction. The Cr(III) concentration was calculated from the difference between the total chromium and the Cr(VI) concentration. The detection limit was 0.03 mg L^{-1}.

Biosorption studies

In order to evaluate the effect of pH, initial Cr(VI) concentration, amount of biosorbent and temperature, a series of biosorbtion experiments were performed in a batch system. The pH of the metal solution was adjusted to values between 1.5 and 4.0 using 1.0 M HCl or 1.0 M NaOH. Biosorption of Cr was realized at temperatures ranging from 20 to 40 °C. The effect of the quantity of biosorbent was studied at concentrations ranging from 1 to 20 g L^{-1}. A known amount of biosorbent was added to 100 mL Cr(VI) solution of the desired concentration and pH in 250 mL Erlenmeyer flasks. The flasks were placed on a rotary shaker at the desired temperature and 150 rpm for 48 h. At the end of the biosorption process, the biosorbent was separated from the solution by filtration and residual Cr(VI) concentration was measured as given above. To eliminate the probable influence of glassware and filter papers on the metal sorption capacity, the Cr(VI) concentration was measured under the same batch experimental conditions (pH, temperature, duration and agitation) without using biosorbent.

All experiments were performed in triplicate. For all graphical representation, the mean values of three independent experiments were considered and standard deviations within the triplicates were too small to be plotted as error bars (< 1 %).

Removal efficiency of Cr(VI)

The removal efficiency was calculated as:

$$R = 100\frac{c_i - c_f}{c_i} \quad (1)$$

where: c_i and c_f denote respectively the initial concentration of Cr(VI) and final residual concentration of Cr(VI) at the moment *t*, in mg L^{-1}.

Fourier transform infrared spectroscopy

The chemical characteristics of the biosorbent surface before and after Cr(VI) adsorption were analyzed and interpreted by FTIR spectroscopy of the biomass in KBr pellets using a Perkin–Elmer Spectrum One, FT-IR spectrometer equipped with software Spectrum, v. 5.0.2, for interactive interpretation of possible structure units.

RESULTS AND DISCUSSION

FTIR Analysis of the biosorbent

Biosorption is defined as the property of microorganisms to accumulate metal ions by adsorption on the cell surface. The major constituents of fungal cell wall are carbohydrates chitin (3–39 %) and chitosan (5–33 %), polyuronide and polyphosphates (2–12 %), lipids (2–7 %) and proteins (0.5–2.5 %) and there are marked variations in the wall composition between different fungal taxonomic groups.[23,24] For this reason, to study the mechanism of Cr(VI) removal by waste mycelium of xylanase-producing *A. awamori*, the active chemical groups on the cell surface before and after Cr(VI) removal were evaluated by FTIR spectrescopy. The obtained results are shown in Fig. 1.

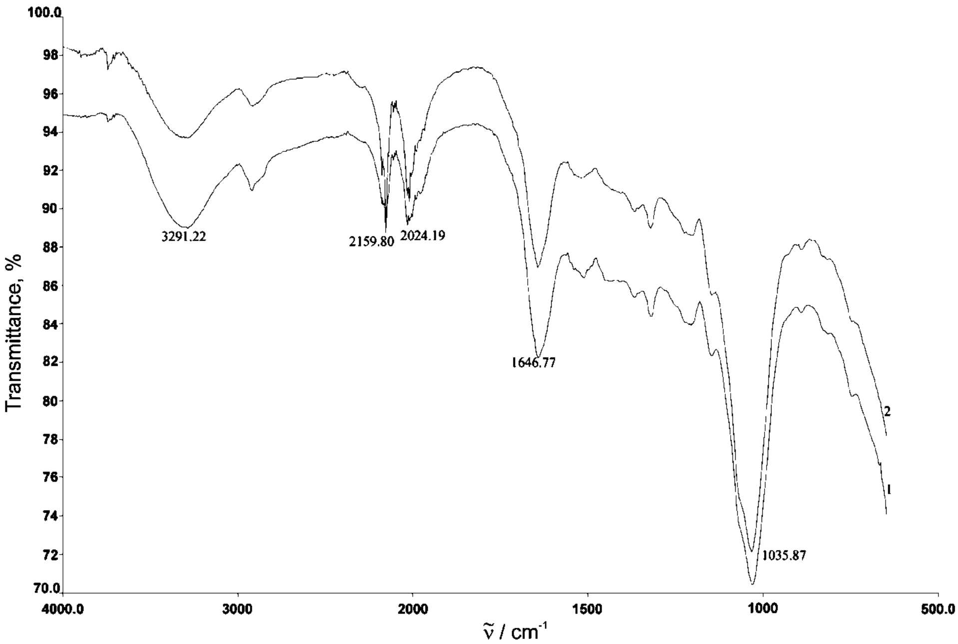

Fig. 1. FTIR Spectra of waste *A. awamori* biomass before (1) and after (2) Cr(IV) adsorption.

The FTIR spectroscopic analysis indicated broad absorption bands at 3291 cm^{-1}, representing the –OH groups of glucose and the –NH stretching of the proteins and the acetamido group of chitin. The absorption bands at 2159 and 2024 cm^{-1} can be assigned to C=O and C=N groups. The absorption band at 1646 cm^{-1} can be attributed to the amide bond in the *N*-acetyl glucosamine polymer of the protein peptide bond. The strong absorption band at 1035 cm^{-1} could be assigned to the –CN stretching vibrations of the chitin–chitosan and protein fractions. The spectral analysis before and after Cr(VI) binding indicated that –NH group were involved in the binding process because there were substantial changes in the absorption intensity of the –NH bending (1646 cm^{-1}) and –NH stretching (3291 cm^{-1}) bands after Cr(VI) adsorption. As chitin and chitosan are the major constituents of the fungal cell wall and major donors of –NH groups, their key role in the Cr(VI) removal process can be assumed. The results obtained were in accordance with published FTIR spectra of untreated *Rhizopus nigricans* biomass before and after Cr(VI) adsorption and the active groups involved in the metal binding process and major fungal cell wall constituents.[11,23,24]

Chemical modification of amino groups

To elucidate the role of amino groups in Cr(VI) removal, they were modified by chemical treatment with a mixture of formaldehyde and formic acid, acetic anhydride and sodium iodoacetate. The chromium removal capacity of the chemically treated biosorbent was compared to that of untreated biosorbent. The results are shown in Fig. 2.

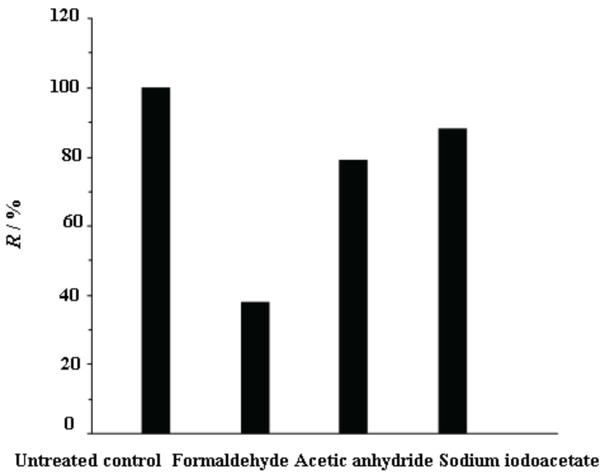

Fig. 2. Effect of chemical modification of the amino groups on the Cr(VI) removal capacity of waste *A. awamori* biomass.

As shown, Cr(VI) removal from the aqueous solution was dependent on the chemical treatment of the biosorbent. Formaldehyde treatment caused methylation of the amino groups and reduced the number of positively charged sides on the biosorbent surface, which significantly reduced Cr(VI) removal by about 42 % compared to untreated biosorbent. An about 21 % reduction in Cr(VI) removal by the acetic anhydride-treated biosorbent in comparison to the untreated was determined. Acetic anhydride caused acetylation of the amino groups and in this way also reduced the number of positively charged groups on the surface of the biosorbent.[11] Treatment of the biosorbent with sodium iodacetate caused a 12 % reduction in Cr(VI) removal compared to that of the native biosorbent. Sodium iodacetate attaches to and neutralizes amino groups at low pH values by introducing carboxyl groups.[28] The obtained results confirmed our assumption that positively charged amino groups play a key role in Cr(VI) removal from aqueous solutions by waste mycelium of *A. awamori*. Among the tested treatment procedures, replacement of amino groups with carboxyl groups demonstrated the smallest negative effect on the removal process, which means that carboxyl groups may also participate in the Cr(VI) removal process. The results obtained are in accordance with data published by other authors.[11,28]

Effect of pH

The pH of the metal solution is one of the major factors affecting the Cr(VI) removal process.[10,22] The effect of the initial pH on Cr(VI) removal by waste *A. awamori* biomass was evaluated in the range from 1.5 to 4. The results are shown in Fig. 3.

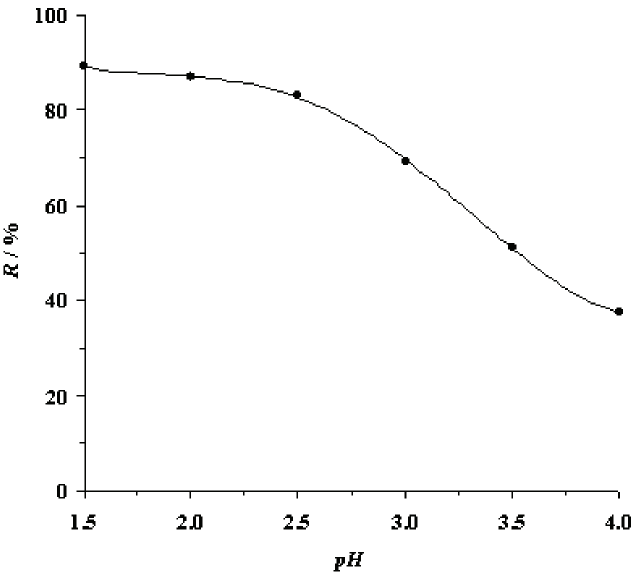

Fig. 3. Effect of pH on Cr(VI) removal by waste *A. awamori* biomass (c_0 = 25 mg L^{-1}, V = 100 mL, W = = 1 g L^{-1}, τ = 48 h).

Increasing the initial pH of the solution from 1.5 to 4 decreased Cr(VI) removal by *A. awamori* from 89.26 to 27.50 %. The effect of pH can be explained by its influence on the protonation of the functional groups on the cell surface.[11,29] At the pH values 1.5 and 2, functional groups such as amino groups are protonated (NH_3^+) and chromate ions are in the forms $Cr_2O_7^-$ and $HCr_2O_4^-$. The negatively charged dichromate ions are electrostatically attracted by the positively charged amino groups but at these pH values, Cr(VI) is also rapidly reduce to Cr(III).[10,31–33] During and after the Cr(VI) removal process, the pH was almost constant and varied in a very narrow interval between 2.00–2.12, which means that the removal mechanism is not ion exchange. The removal of Cr(VI) from aqueous solution by waste mycelium of *A. awamori* is probably due to a combination of two processes: Cr(VI) adsorption by the biomass and its reduction to the less toxic Cr(III). Park *et al.* published that the contact time for Cr(VI) removal is a pH dependent process and at pH 2.0 and an initial concentration of 25 mg L^{-1}, Cr(VI) was removed completely by dead *Aspergillus niger* biomass in about 30 h.[31] In the present study, a Cr(VI) removal of 89.26 % was reached at pH 2.0 after 48 h. Based on the performed experiments, pH 2.0 was selected as the most appropriate pH value for Cr(VI) removal by waste mycelium of *A. awamori* and all of the following experiments were performed at pH 2.0.

Effect of the initial Cr(VI) concentration and the amount of biomass

The effect of the initial Cr(VI) concentration on the effectiveness of the removal process was studied at three concentrations: 25, 50 and 100 mg L^{-1} and the results are shown in Fig. 4.

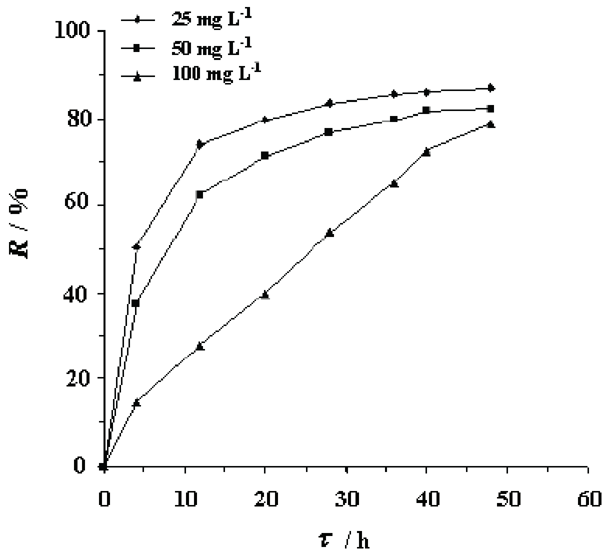

Fig. 4. Effect of initial Cr(VI) concentration on the removal efficiency of waste *A. awamori* biomass (V = 100 mL, W = 1 g L^{-1}, τ = 48 h).

As shown, after a 48-h contact time, 87.0, 82.4 and 78.6 % removal was attained for initial Cr(VI) concentrations of 25, 50 and 100 mg L^{-1}, respectively. Thus, lowering the initial Cr(VI) concentration increased the % metal removed for a 48-h contact time. According to Park *et al.*, increasing the initial metal ion concentration prolonged the process for complete Cr(VI) removal.[10,31]

To evaluate the effect of the biomass concentration, experiments were performed in which the biomass concentration was varied from 0.5 to 2 g/100 mL and the results are shown in Fig. 5.

The obtained results indicate that increasing the biomass concentration increased the Cr(VI) removal. This fact may be attributed to the higher number of active groups available for Cr(VI) adsorption and reduction because of the increased amount of *A. awamori* biomass.

Effect of temperature

Another major factor affecting both processes the adsorption and reduction processes is temperature. The effect of temperature on the Cr(VI) removal process by waste biomass of *A. awamori* at three temperatures: 20, 30 and 40 °C was studied and the results are shown in Fig. 6.

Increasing of temperature increased the Cr(VI) removal. According to Wittbrodt and Palmer, increased temperature induces and accelerates the rate of redox reactions.[34]

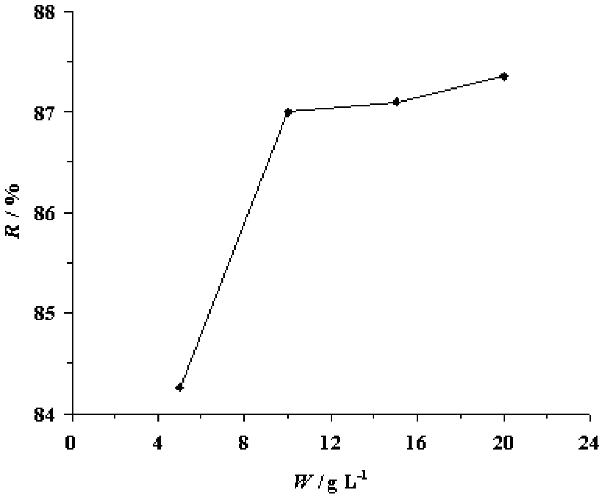

Fig. 5. Effect of biomass concentration on Cr(VI) removal by waste *A. awamori* biomass (c_0 = 25 mg L^{-1}, V = 100 mL, τ = 48 h).

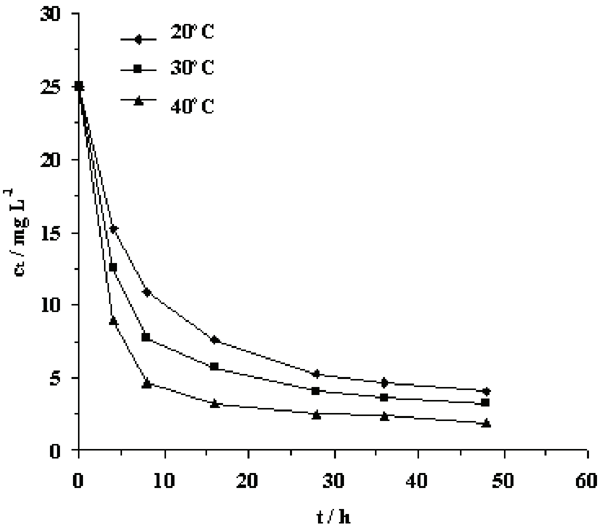

Fig. 6. Effect of temperature on Cr(VI) removal by waste *A. awamori* biomass (c_0 = 25 mg L^{-1}, V = 100 mL, τ = 48 h).

A pseudo-first order equation with respect to the Cr(VI) concentration was used:

$$\log(c_\tau - c_f) = -\frac{kt}{2.303} + \log c_0 \quad (2)$$

where c_τ, c_f and c_0 are the concentration of Cr(VI) at the moment *t*, and the final and the initial Cr(VI) concentrations, respectively, and *k* is the rate constant.

In order to determine the reaction rate constants, log $(c_\tau - c_f)$ was plotted *vs*. time (Fig. 7). The calculated rate constants and the correlation coefficients are shown in Table I.

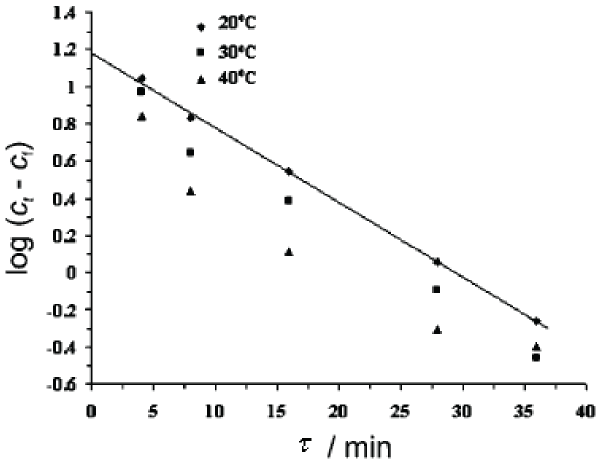

Fig. 7. Pseudo-first kinetic model for Cr(VI) removal by waste *A. awamori* biomass (c_0 = 25 mg L^{-1}, *V* = 100 mL, *W* = 1 g.L^{-1}, τ = 48 h).

TABLE I. Reaction rate constants and correlation coefficients for Cr(VI) removal at different temperatures

t / °C	*k* / h^{-1}	*R*
20	0.0949	0.998
30	0.0956	0.992
37	0.1075	0.987

The activation energy for the Cr(VI) removal process was determined by the Arrhenius Equation. The activation energy of Cr(VI) removal by waste biomass of *A. awamori* was calculated to be 5.15 kJ mol^{-1}. Park *et al*. reported an activation energy of 7.8 kJ mol^{-1} for the same temperature interval for Cr(VI) removal by dead biomass of *A. niger*, which means that the removal process realized with *A. awamori* will be faster.[31]

Mechanism of Cr(VI) removal

In an attempt to explain the mechanism of Cr(VI) removal by waste biomass of *A. awamori*, decreasing Cr(VI) concentrations and increasing Cr(III) concentrations in time were studied. The results are shown in Fig. 8.

As can be seen, the Cr(VI) concentration decreased with time. Cr(III) was not observed in the solution at the beginning of the removal process but it appeared with time. Probably during the first stage, when Cr(III) was absent (first 8 hours), Cr(VI) adsorbed to protonated active groups on the biomass surface. Then, during the second stage, some of the Cr(VI) was easily or spontaneously reduced to Cr(III), as reported by Lytle *et al.*[31]. After 48 h, the concentration of Cr(III) reached 7.25 mg L^{-1}. The results obtained demonstrated that both processes, adsorption and reduction, were involved in the removal process and were described well by the two stage Cr(VI) removal mechanism proposed by Park *et al.*[10,31] Taking into consideration the previously obtained experimental data, a model based on a second degree polynomial was chosen to describe the dependences between $R = f(\text{pH})$ and $R = f(T)$, *i.e.*:

$$z = a + bx + cy + dy^2 \quad (3)$$

where z is the removal efficiency, x is the pH of the solution and y is the temperature.

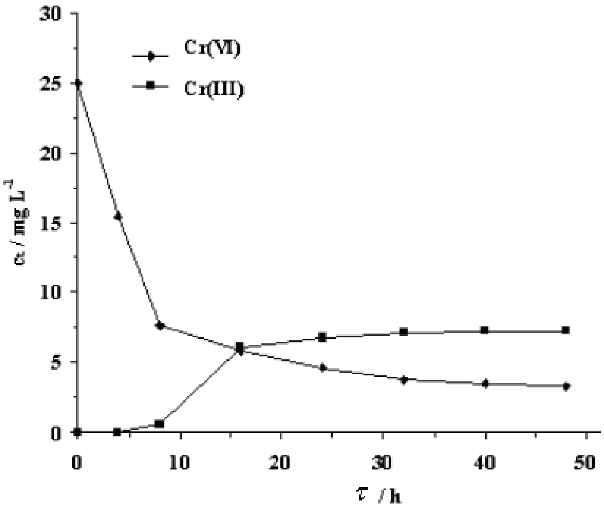

Fig. 8. Time curves of Cr(VI) and Cr(III) concentrations (pH 2.0, c_0 = 25 mg L^{-1}, V = 100 mL, W = 1 g L^{-1}).

The inputs of the model were the temperature and pH, and the output was the removal efficiency. The coefficients a, b, c and d of the postulated polynomial model were determined by means of the D-optimum composition plan.[35] The independent factors were varied as follow: 1.5 < pH < 4.0 and 20 °C < t < 40 °C. The experimental matrix of the DOE, applied for the modelling and optimisation of the R of Cr(VI) by waste *A. awamori* biomass is shown in Table II.

The mathematical analysis of the results led to a suitable response model according to the following equation:

$$(z / \%) = 59.547 + 23.468\text{pH}^2 + 0.461(t / °\text{C}) \quad (6)$$

The values of statistics r^2 and $r^2_{adjusted}$ were 0.989 1 and 0. 9874, respectively. The model is shown in graphical form in Fig. 9.

Maximization of the model allowed the optimal set of parameters for reaching maximum removal to be predicted, *i.e.*, R_{max} = 94.4 %, pH 1.5 and t = 40 °C.

TABLE II. Experimental matrix of DOE applied for the modelling and optimisation of the removal of Cr(VI) from aqueous solutions by waste *A. awamori* biomass (V = 100 mL, c_0 = 25 mg L^{-1}, τ = 48 h, W = 1 g.L^{-1})

No.	pH	t / °C	R / %	No.	pH	t / °C	R / %	No.	pH	t / °C	R / %
1	1.5	20	84.79	11	3.5	25	49.68	21	2.5	35	85.84
2	2	20	83.64	12	4	25	35.88	22	3	35	72.04
3	2.5	20	79.72	13	1.5	30	89.26	23	3.5	35	54.04
4	3	20	65.92	14	2	30	87	24	4	35	40.24
5	3.5	20	47.92	15	2.5	30	83.10	25	1.5	40	94.38
6	4	20	34.12	16	3	30	66.26	26	2	40	92.32
7	1.5	25	86.76	17	3.5	30	51.25	27	2.5	40	88.40
8	2	25	85.40	18	4	30	37.50	28	3	40	74.60
9	2.5	25	81.48	19	1.5	35	91.84	29	3.5	40	59.28
10	3	25	67.68	20	2	35	89.76	30	4	40	42.80

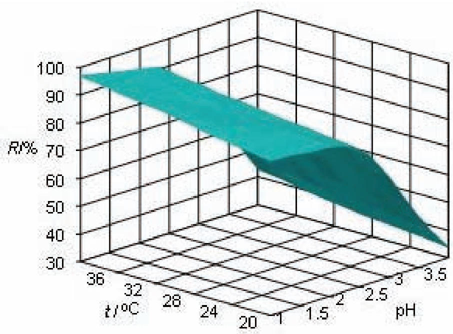

Fig. 9. Removal efficiency of Cr(VI) by waste *A. awamori* biomass as a function of pH and temperature (c_0 = 25 mg L^{-1}, τ = 48 h).

Usually for comparing the biosorption potential of various biosorbents, the sorption capacity of the biomaterial, expressed as mg or mol metal ion adsorbed per gram of biomass, is used. The results obtained in the present study and those published by Park *et al.*[10,31]. and Lytle *et al.*[32]. unambiguously proved that Cr(VI) removal from aqueous solutions is not pure biosorption, but rather a combination of biosorption and reduction. For this reason, it was decided to compare the studied biosorbent with other Cr(VI) biosorbents based on removal capacity not on specific sorption capacity (Table III). As can be seen, waste mycelium of *A. awamori* is competitive with other fungal biosorbents, because using an about five times shorter contact time, relatively high Cr(VI) removal was reached. For the same contact time, only the removal capacity of the biosorbent from *Rhizopus oryzae* exceeded the removal capacity of waste mycelium of *A. awamori*. The major advantage of *A. awamori* mycelium over other fungal biosorbents is not only the high Cr(VI) removal capacity and relatively short contact time, but also its low cost, because it is a waste product from enzyme production. Most of the other published Cr(VI) fungal biosorbents were specially cultivated and then killed for preparation of the biosorbent, which inevitably increases the total costs of the removal process, especially if large amounts of polluted solutions are to be treated. Real industrial wastewaters are multicomponent systems containing various organic and inorganic compounds that can negatively influence the metal removal process.[36] According to Gadd, one of the major disadvantages of the currently published research in the sphere of biosorption is the lack of information concerning the applicability of the results in real industrial effluents and scale-up of the removal process to the industrial scale.[37] For these reasons, the present results for the removal of Cr(VI) from aqueous solutions by waste mycelium of *A. awamori* cannot be applied directly to real wastewaters and additional experiments are a necessity.

TABLE III. Cr(VI) removal capacity of various fungal biosorbents (pH 2.0, $W = 5$ g L^{-1})

Biosorbent	c_0 / mg L^{-1}	τ / h	Cr(VI) Removal, %	Reference
Aspergillus awamori	50	48	85.46	Current study
Rhizopus oryzae	50	48	100	22
Aspergillus niger	50	218	100	22
Penicillium chryzogenum	50	218	100	22
Saccharomyces cerevisiae	50	254	100	22
Aspergillus sp.	500	24	36	30

CONCLUSIONS

It was demonstrated by FTIR analysis and chemical treatment of the biosorbent that amino groups from the major fungal wall constituents, chitin and chitosan, played a key role in the Cr(VI) removal process. The effectiveness of the removal process depended mainly on pH followed by temperature, amount of biomass and initial Cr(VI) concentration. The process can be explained by an indirect two-stage mechanism involving first an adsorption stage and then a reducing stage. The activation energy of Cr(VI) removal by waste biomass of *A. awamori* was lower than that of the same process based using dead biomass from *A. niger*. The removal process could be described by a second-degree polynomial and the optimal process parameters for attaining an R_{max} of 94.4 % in 48 h were predicted (pH 1.5 and $t = 40$ °C). Based on the performed experiments and the obtained results, it can be summarized that waste mycelium from the industrial xylanase-producing strain *A. awamori* is a prospective, competitive and low-cost biomaterial with possible application in Cr(VI) removal. Further experiments for application of the current results and waste mycelium of *A. awamori* for Cr(VI) removal from real industrial wastewaters and a study of the process in a column bioreactor are in progress.

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ИЗВОД

УКЛАЊАЊЕ ШЕСТОВАЛНЕТНОГ ХРОМА ОТПАДНИМ МИЦЕЛИЈУМОМ ГЉИВЕ *Aspergillus awamori*

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У овом раду је процењен потенцијал уклањања Cr(VI) отпадним мицелијумом индустријског соја *Aspergillus awamori* који се користи за производњу ксиланазе. FTIR Анализом је одређено да су амино групе основних састојака ћелијског зида гљиве, цитина и цитозана, играле кључну улогу у процесу везивања метала. Такође је испитиван и утицај pH, почетне концентрације јона, температуре и количине биомасе на процес уклањања. Механизам уклањања Cr(VI) гљивом *A. awamori* може бити објашњен процесом у два ступња, који се састоји од почетног адсорпционог ступања за којим следи ступањ редукције. Процес уклањања описан је полиномом другог реда, а утврђени су и оптимални параметри за постизање R_{max} од 94,4 % за 48 h , тј. pH 1,5 и t = 40 °C. Предложена је обећавајућа могућност употребе отпадног индустријског мицелијума гљиве *A. awamori* као јефтиног агенса за уклањање Cr(VI) са економског и еколошког гледишта.

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