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Biosorption potential of dead and living *Arthrobacter viscosus* biomass in the removal of Cr(VI): Batch and column studies

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ABSTRACT

Batch experiments were conducted with dead and living *Arthrobacter viscosus* biomass for Cr(VI) removal from aqueous solution. Both dead and living cells successfully reduced Cr(VI) to Cr(III) from aqueous solution in highly acidic pH (pH 1 and 2) with an efficiency of 100% for aqueous solutions having the initial concentrations of Cr(VI) lower than 100 mg/L. Langmuir isotherm and kinetic models based on reduction could simulate chromium removal at 5 and 8 g/L biosorbent dosages and in highly acidic pH conditions (pH 1–2). Further, the potential use of the *A. viscosus* biomass was examined in an open system, where Cr(VI) removal from aqueous solution was performed by a bacterial biofilm supported on a new type of polyethylene supports. The experiment showed a favorable uptake of chromium ions bound to the biomass, of 20.37 mg/g, with high potential for scaling up. This study showed that the reduction of toxic Cr(VI) to the less toxic Cr(III) by *A. viscosus*, in batch and continuous modes is an efficient and promising technique for wastewaters polluted with chromium.

1. Introduction

Chromium can be found in natural deposits as ores and also in several other natural materials in its compound forms. A variety of anthropogenic sources release chromium in the environment (plating industry, textile dyeing, cement, leather tanning, wood preservation etc.). These sources could generate severe environmental and public health threats. In the natural environment only hexavalent (Cr(VI)) and trivalent (Cr(III)) chromium are stable forms, although chromium may occur in several different oxidation states ranging from −2 to +6. The two stable oxidation states of chromium may present different behaviors in terms of toxicity and mobility. Cr(III) is relatively insoluble in aqueous systems and exhibits little or no toxicity, being an essential trace nutrient for humans. In contrast, Cr(VI) usually occurs as highly soluble and highly toxic chromate anions (CrO_4^{2-} and $Cr_2O_7^{2-}$), which are suspected as carcinogens and mutagens (Park et al., 2004; Prabhakaran et al., 2009). The aqueous effluents may contain various concentrations of Cr(VI), depending on their source. For example, the concentration of Cr(VI) in chromium plating effluents ranges between 15 mg/L and 300 mg/L, occasionally exceeding 960 mg/L. At an extreme level, effluents from tannery factories have been reported to contain 1300–2500 mg/L of Cr(VI) (Liu et al., 2006). USEPA and the European Union regulated the discharge of chromium(VI) to surface water to

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below 0.05 mg/L, while total chromium, including Cr(III), Cr(VI) and the other forms, is regulated to below 2 mg/L (Baral and Engelken, 2002; Park et al., 2008).

The removal of chromium from contaminated effluents by physical, chemical and electrochemical methods generally involves high energy inputs and costs, large quantities of chemical reagents or difficulties in removing the by-products or secondary waste generated during the process. As a part of environmental biotechnology, biosorption process has been extensively studied for the removal of heavy metals using various biomass (microbial, algae, agricultural or industrial waste) (Altaher et al., 2015; Flouty, 2015; Ghosh et al., 2015; Hlihor et al., 2015; Jaafarzadeh et al., 2014; Liu et al., 2016; Murugavelh and Mohanty, 2014; Murphy et al., 2008; Paduraru et al., 2015; Parvathi and Nagendran, 2007; Ungureanu et al., 2015). It has been demonstrated that these biosorbents can be used successfully for metal removal and wastewater detoxification in a very competitive and cost efficient manner (Chojnacka, 2010; Ebrahimi et al., 2015; Gavrilescu et al., 2015; Hlihor et al., 2013, 2014; Liu et al., 2011; Lopez-Nuñez et al., 2014; Rosca et al., 2015; Vijayaraghavan and Yun, 2008).

In this work the non-pathogenic *Arthrobacter viscosus*, a gram-positive aerobic bacterium from the family of *Micrococcaceae*, order of *Actinomycetales*, which is a good exopolysaccharide producer was chosen as biosorbent due to its high potential in bioremediation (Figueiredo et al., 2010; Fonseca et al., 2012; Quintelas et al., 2009). Up to now, the bacterial biomass was used in the form of biofilms only supported on granular activated carbon or zeolites for the removal of different heavy metals from aqueous solutions (Figueiredo et al., 2010; Fonseca et al., 2012; Quintelas et al., 2008a, 2009). There is only one study addressing Cr(VI) reduction and removal from aqueous solutions by *A. viscosus* biomass itself, but it is limited to the effect of pH on metal removal (Silva et al., 2009).

Given this context, the objectives of the present work are to evaluate and discuss: (i) the effects of various factors on Cr(VI) removal efficiency by dead and living *A. viscosus* in batch operating mode, (ii) the potential of an up-flow bacterial biofilm for Cr(VI) removal in an open system column, (iii) the mechanism that governs the removal of Cr(VI) by dead and living biomass of *A. viscosus*.

2. Materials and methods

2.1. Culture and growth conditions of Arthrobacter viscosus

The *A. viscosus* bacterium strain was obtained from the Spanish Type Culture Collection of the University of Valência. For the growth of the microorganism, a medium containing peptone (5 g/L), malt extract (3 g/L), yeast extract (3 g/L) and glucose (10 g/L) was used. The pH of the medium was adjusted to 7 by using concentrated NaOH. Further, the medium was sterilized at 120 °C for 20 min, inoculated with bacteria and kept at 28 °C and 150 rpm for 72 h. For the experiments involving dead *A. viscosus*, the bacterial biomass was centrifuged at 7000 rpm for 10 min and deactivated by drying in an oven at 55 °C for 72 h. The dried biomass of *A. viscosus* was crushed and sieved to 125–250 μm particle size and stored in a desiccator until further use. For the experiments with living *A. viscosus* biomass, after inoculation and incubation, the liquid containing *A. viscosus* biomass was centrifuged at 7000 rpm for 10 min. Afterwards, the biomass was resuspended in distilled water and kept at 4 °C until different sets of experiments were developed.

2.2. Reagents and equipments

All chemicals used in this investigation were of analytical grade and no further purification was necessary. A stock solution of 1000 mg/L Cr(VI) was prepared by dissolving $K_2Cr_2O_7$ (Riedel) in distilled water. The solution was diluted for different Cr(VI) concentrations using distilled water as required by the working procedure. The concentration of total Cr in liquid samples was determined by an Atomic Absorption Spectrophotometer (Varian Spectra AA-400 type). In parallel, samples of Cr(VI) were analyzed spectrophotometrically by measuring the absorbance of the pink colored complex of Cr(VI) with 1,5-diphenylcarbazide in acidic solution at 540 nm (T60 UV-Visible Spectrophotometer) as described in the Standard Methods (Clesceri et al., 2005). The concentrations of Cr(III) were obtained by the difference between total Cr and Cr(VI) concentrations.

2.3. Batch experimental procedure

Experiments regarding the biosorption of Cr(VI) by both dead and living biomass categories were carried out in batch mode at selected pH values, at various contact times and biomass dosages. Erlenmeyer flasks of 250 mL were used for batch experiments with 100 mL of working volume containing Cr(VI) solution of known concentrations together with biomass and agitated in an orbital incubator at 150 rpm. The effect of pH on Cr(VI) removal efficiency was investigated by varying the solution pH from 1 to 4, while biomass dosages of 1–8 g/L were used. In experiments developed to investigate the effect of initial Cr(VI) concentration, concentrations of 25–250 mg/L were used, while in experiments performed to evaluate the contact time dependence on removal efficiency, concentrations of 25, 50 and 100 mg/L were used.

Thermodynamic studies were also conducted for the biosorption of Cr(VI) by dead *A. viscosus* biomass by establishing a temperature interval of 26–50 °C. The initial pH of working solutions was adjusted by addition of 0.1 M H_2SO_4 and 0.1 M NaOH solutions. The change in the working volume due to the addition of H_2SO_4 and NaOH was negligible. Control experiments (without heavy metal) were also conducted for each investigation by considering the same procedure stated above. After sampling, the solutions were centrifuged at 13,000 rpm for 5 min, then the Cr(VI) and total Cr concentrations in the supernatant were measured. The total chromium uptake ($q_{Cr_{tot}}$) was calculated using the mass balance equation (Eq. (1)):

$$q_{Cr_{tot}} = \frac{(C_i - C_f) \cdot V}{m} \quad (1)$$

where C_i and C_f are the initial and final total chromium concentrations (mg/L), respectively, V is the solution volume (L), and m is the mass of biomass used in experiments (g).

The removal efficiency (%) was calculated using Eq. (2):

$$\text{Removal efficiency (\%)} = \frac{C_i - C_f}{C_i} \cdot 100 \quad (2)$$

All experiments were carried out in duplicate and the mean average values were used in further analysis. The experimental error was less than 5%.

2.4. Column biosorption experiments

The removal of Cr(VI) was investigated using *A. viscosus* biofilm supported on a new type of polyethylene, developed by researchers at University of Minho and consisting of hollow, star-shaped carriers with 17 mm external diameter and a height of 10 mm (Nogueira et al., 2009). The supports (38.36 g) were initially placed in an acrylic column (25 cm × 3.2 cm) and washed for 24 h with hypochlorite solution for sterilization. Afterwards, the supports were washed with distilled water. The microorganism culture was previously grown for 72 h in an orbital incubator as explained in Section 2.1 and was pumped upwards at a flow rate of 19 mL/min. This high flow rate allows optimal formation and adhesion of a compact biofilm, resistant to erosion stress resulting from the hydrodynamic forces (Quintelas et al., 2008a). The culture medium was used to grow the microorganism on the support for 120 h. After this time period, the biofilm formation could be observed by naked eye. Next, the Cr(VI) solution (25 mg/L, pH 2, room temperature) was passed through the column at a flow rate of 10 mL/min to avoid breaking of the formed *A. viscosus* biofilm. Samples of 5 mL were withdrawn from the effluent, centrifuged and analyzed for chromium content. The metal solution continued to pass until reaching the influent–effluent Cr(VI) concentration equilibrium. This indicated that no further metal reduction/sorption was occurring.

The total Cr mass biosorbed on the column bed (m_{ad}) is calculated from the area above the breakthrough curve (effluent metal concentration versus time) multiplied by flow rate. Dividing this mass (m_{ad}) by the biosorbent mass (M) leads to the uptake capacity (q) of the biomass (Vijayaraghavan et al., 2005).

2.5. Modeling of Cr(VI) biosorption

Authors have reported that the biosorption mechanism of Cr(VI) by biomaterials is not an "anionic adsorption" but "adsorption-coupled reduction" process (Park et al., 2005, 2006, 2007, 2008; Wu et al., 2010). Therefore, classical kinetic models based on reduction and adsorption were applied to fit the experimental data as follows (Eqs. (3)–(6)) (Ho, 2006; Wu et al., 2010):

Pseudo-first order reduction:

$$\frac{dC}{dt} = -k_1 C, \quad \ln C = \ln C_0 - k_1 t \tag{3}$$

Pseudo-second order reduction:

$$\frac{dC}{dt} = -k_2 C^2, \quad \frac{1}{C} = k_2 t + \frac{1}{C_0} \tag{4}$$

Pseudo-first order adsorption:

$$\frac{dq}{dt} = -k_3(q_e - q), \quad \ln(q_e - q) = \ln q_e - k_3 t \tag{5}$$

Pseudo-second order adsorption:

$$\frac{dq}{dt} = -k_4(q_e - q)^2, \quad \frac{1}{q_e - q} = \frac{1}{q_e} + k_4 t \tag{6}$$

where C_0 and C are Cr(VI) concentrations in solution (mg/L) at time 0 and t respectively, q and q_e are the amount of Cr(VI) adsorbed at time t and at equilibrium per gram of sorbent (mg/g), and k_1, k_2, k_3, k_4 are the apparent rate constants.

With respect to isotherm modeling, Langmuir model was applied (Eq. (7)):

$$q_{Cr_{tot}} = \frac{q_{Cr_{tot}}^{max} b[Cr_{tot}]}{1 + b[Cr_{tot}]} \text{ (mg/g)} \tag{7}$$

where $q_{Cr_{tot}}$ is the amount of total Cr bound to the biomass (mg/g), $q_{Cr_{tot}}^{max}$ is the maximum amount of total Cr bound at high [Cr_{tot}] (mg/g) and b is a constant related to the affinity of the binding sites (mg/L).

Thermodynamic parameters are calculated by using the Eq. (8):

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{8}$$

where ΔH°, ΔS° and T are the enthalpy, entropy, and temperature, respectively, and R is the gas constant. The values of enthalpy (ΔH°) and entropy (ΔS°) are obtained from the slope and intercept of $\ln K_d$ vs. $1/T$ plots.

The distribution coefficient (K_d) is calculated from the concentration of total chromium in suspension (C_0) and that of total chromium in supernatant (C_e) after centrifugation according to Eq. (9):

$$K_d = \frac{C_0 - C_e}{C_e} \frac{V}{m} \tag{9}$$

where V is the volume of the solution (L) and m is the mass of dead biomass (g) (Hlihor et al., 2015).

The change of Gibbs free energy (ΔG°) was calculated from Eq. (10):

$$\Delta G^\circ = \Delta H^\circ - T\,\Delta S^\circ \tag{10}$$

Different models parameters were evaluated using OriginPro 8 software.

2.6. FTIR analysis

Infrared spectra of dead and living *A. viscosus* biomass, with and without metal ion were acquired by using a BOMEN MB 104 spectrometer. The dried samples were prepared with KBr at a proportion of 1 mg sample per 100 mg of KBr and analyzed in the range 4000–500 cm^{-1} with a resolution of 8 cm^{-1}.

3. Results and discussion

3.1. Removal of Cr(VI) ions: reduction to Cr(III) and biosorption by dead biomass of A. viscosus

3.1.1. Effect of pH on Cr(VI) reduction and total Cr removal

Solution pH was found to be one of the most important parameters in sorption processes, since it affects not only the speciation of metal ions but also the availability of sorption sites (Hlihor et al., 2015; Park et al., 2007; Wang et al., 2008). In order to study the effect of initial pH on Cr(VI) removal by dead *A. viscosus* biomass, experiments were conducted for pH values ranging from 1 to 4 with an initial Cr(VI) concentration of 100 mg/L at 26 °C (Fig. 1). Results revealed that the removal

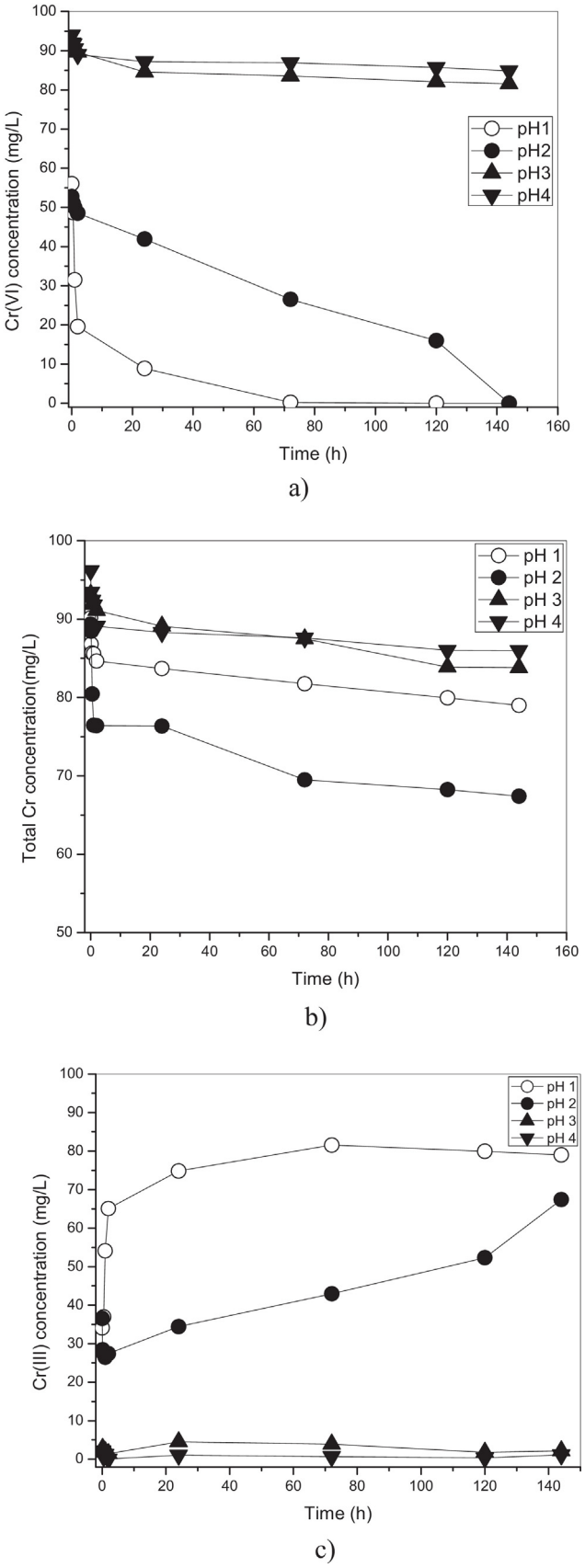


Fig. 1 – Effect of solution pH on chromium reduction and biosorption from aqueous solution using dead *A. viscosus*: (a) Cr(VI) concentration vs. time, (b) Total Cr concentration vs. time, (c) Cr(III) concentration vs. time (biomass dosage: 5 g/L; initial Cr(VI) concentration: 100 mg/L; temperature: 26 °C; contact time: 144 h).

efficiency was 100% at pH 1–2, for 5 g/L of dead *A. viscosus*. The necessary time for a complete removal of Cr(VI) at pH 1 was 72 h, while at pH 2 it was double, of 144 h (Fig. 1a). For the initial Cr(VI) solution of pH 3 or 4, the removal efficiency reached only 15.76% and 13.18% respectively, after 144 h. Several studies discuss the dynamics of Cr(VI) removal rate as increasing with decreasing the pH for various biomass types (Bai and Abraham, 2001; Nourbakhsh et al., 1994; Park et al., 2005; Zhang et al., 2015).

The removal efficiency of total Cr was also found to be dependent on pH values. At pH 2, the removal efficiency was of 31%, while at pH 1, the removal efficiency was of 17.9%. Therefore, pH 2 seems to be the optimal value for total Cr removal (Fig. 1b). The appearance of Cr(III) in solution is a clear evidence of the reduction of Cr(VI) to Cr(III) (Fig. 1c).

Considering the above information, we observed that the removal efficiency of Cr(VI) ions tends to decrease with any increase in pH. The results obtained indicate that Cr(VI) removal is highly pH dependent as also suggested by several researchers (Hlihor et al., 2013; Park et al., 2005; Samuel et al., 2015; Silva et al., 2009; Wang et al., 2008). The same trend of pH influence on Cr(VI) reduction and removal by biomaterials was reported by other authors (Cabatingan et al., 2001; Kumar et al., 2008; Silva et al., 2009; Wu et al., 2010). The observed behavior of Cr(VI) sorption at various pH values is a consequence of various mechanisms which are responsible for adsorption on surface (electrostatic attraction/repulsion, chemical interactions etc.) (Baral et al., 2006).

Donmez et al. (1999) revealed that the most prevalent forms of Cr(VI) in solution seems to be acid chromate ($HCrO_4^-$), chromate (CrO_4^{2-}), dichromate ($Cr_2O_7^{2-}$) and other Cr oxyanions. At low pH, $HCrO_4^-$ species are dominant and enter in reactions when Cr(VI) is reduced to Cr(III).

The reactions leading to reduction of Cr(VI) to Cr(III) can be summarized as follows (Eqs. (11) and (12)):

$$HCrO_4^- + 7H^+ + 3e^- = Cr^{3+} + 4H_2O \quad (11)$$

$$Cr_2O_7^{2-} + 14H^+ + 6e^- = 2Cr^{3+} + 7H_2O \quad (12)$$

Both pH 1 and pH 2 are favorable for the reduction of Cr(VI) to Cr(III), but at pH 1 biomass is most likely fully protonated and will limit the affinity for Cr(III) because of the charge repulsion between the cation and surface. At pH 2, the biomass protonation may occur to a lesser degree and the surface will have enough negative charges (or negative functional groups) to attract the Cr(III) cations. At higher hydrogen ion concentrations, the negative charges at the surface of the biomass are neutralized, so that new adsorption sites may be available, providing a positive charge for the adsorption of chromium ions (Silva et al., 2009; Singh et al., 2005).

Taking into consideration Cr(VI) reduction and total chromium sorption, pH 2 was selected in further experiments.

3.1.2. *Effect of biomass dosage on Cr(VI) reduction and total Cr removal*

A series of experiments addressing the effect of biomass dosage on Cr(VI) removal efficiency were performed at different initial dosages of sorbent, in the range 1–8 g/L, while working at pH 2 and 26 °C (Fig. 2). The results revealed that the removal of Cr(VI) is enhanced with increasing of biomass dosage (Fig. 2a), i.e. the removal efficiency varies from 26.9% (for 1 g/L sorbent) to 100% (for 5 g/L and 8 g/L biomass) for a contact time of 144 h, the duration of the experiment. Therefore,

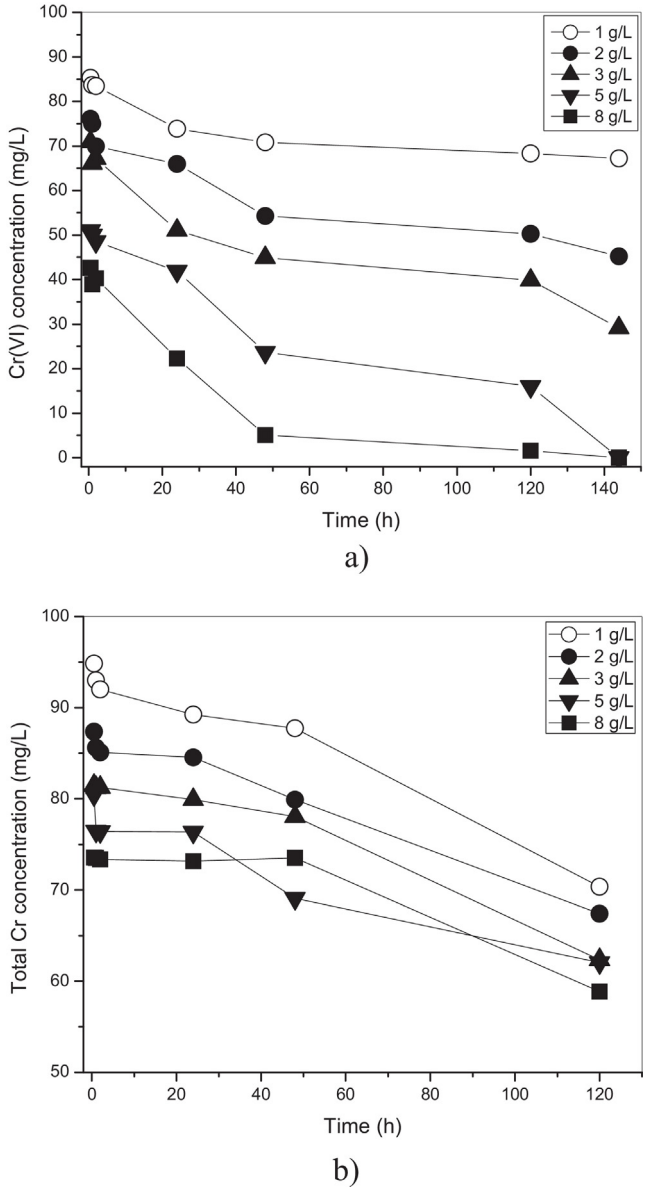


Fig. 2 – Effect of biomass dosage on chromium reduction and biosorption from aqueous solution using dead *A. viscosus*: (a) Cr(VI) concentration vs. time, (b) total Cr concentration vs. time (initial Cr(VI) concentration: 100 mg/L; temperature: 26 °C; contact time: 144 h; pH 2).

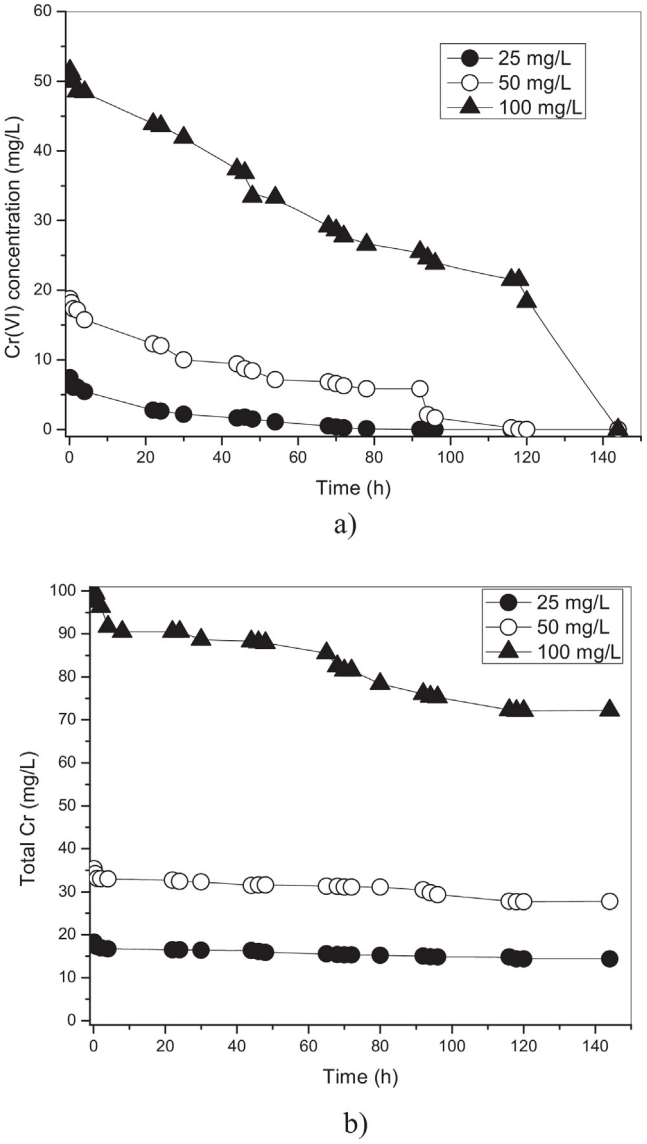


Fig. 3 – (a) The effect of contact time on Cr(VI) reduction by dead *A. viscosus*; (b) The effect of contact time on total Cr removal by dead *A. viscosus* (temperature: 26 °C; contact time: 144 h; pH 2).

the Cr(VI) removal rate was enhanced as biomass dosage was increased. The extent of reduction/sorption increases rapidly in the first 40–50 h, but becomes slower in the later stages.

Also the removal efficiency of total Cr increased from 32.2 to 43.5% in 120 h, with increasing the biomass dosage (Fig. 2b). Lower chromium concentrations and high biomass dosages lead to a shorter reduction time, enhancing the removal ratio. For further studies 5 g/L of dead *A. viscosus* biomass was selected as biosorbent dosage, as it showed good reduction and removal of Cr(VI) and total Cr, respectively.

3.1.3. *Effect of contact time on Cr(VI) reduction and total Cr removal*

Fig. 3 shows the time-dependency curves of Cr(VI) reduction and total Cr removal by dead *A. viscosus* biomass. The concentration changes of Cr(VI) along time were followed for Cr(VI) initial concentrations of 25 mg/L, 50 mg/L and 100 mg/L, while working at pH 2 with 5 g/L dead *A. viscosus* biomass and at 26 °C. For Cr(VI) initial concentration of 25 mg/L, it was observed that Cr(VI) was completely reduced to Cr(III) in 92 h, for 50 mg/L initial concentration, Cr(VI) was completely reduced in 116 h, while the complete removal of 100 mg/L of Cr(VI) required about 144 h of contact time (Fig. 3a). When the removal of total Cr was evaluated (Fig. 3b), we could observe a removal efficiency of 43.5% for 100 mg/L initial Cr(VI) concentration, of 42.6% for 50 mg/L initial Cr(VI) concentration and 42.3% for 25 mg/L initial Cr(VI) concentration, again in 144 h.

3.1.4. *Sorption kinetics*

In order to develop the kinetic models of Cr(VI) removal by *A. viscosus*, reduction kinetics and adsorption kinetic models (Eqs. (3)–(6)) were applied to the experimental data. The effects of the initial Cr(VI) concentration, pH and biomass dosage were investigated to find the best kinetic model, for a better understanding of a possible mechanism of Cr(VI) removal by *A. viscosus*. The kinetic constants and correlation coefficients are given in Table 1.

Kinetic models based on reduction reaction, either pseudo-first or pseudo-second order, described the data with the

Table 1 – Regression parameters of the kinetic models applied for Cr(VI) removal by dead *A. viscosus* biomass.

Kinetic models	Parameters	Value	Pseudo-first order		Pseudo-second order	
			k	R^2	k	R^2
Reduction kinetics	Cr(VI) concentration	25 mg/L	0.0308	0.9607	0.0101	0.9876
		50 mg/L	0.0156	0.9746	0.0012	0.9821
		100 mg/L	0.0071	0.9267	0.0001	0.9165
	pH	1	0.0728	0.9684	0.0631	0.88763
		2	0.0071	0.9267	0.0001	0.9165
		3	7.34E−4	0.8284	8.58E−6	0.8360
		4	5.23E−4	0.68724	5.91E−6	0.6995
	Biomass dosage	1 g/L	0.0015	0.7593	2.04E−5	0.7811
		2 g/L	0.0033	0.8943	5.69E−5	0.9196
		3 g/L	0.0052	0.8891	1.15E−4	0.8927
		5 g/L	0.0071	0.9267	0.0001	0.9165
		8 g/L	0.0285	0.9305	0.0051	0.9589
Adsorption kinetics	Cr(VI) concentration	25 mg/L	0.0308	0.9677	0.0507	0.9876
		50 mg/L	0.0156	0.9746	0.0063	0.9821
		100 mg/L	0.0127	0.9180	0.0027	0.8780
	pH	1	0.0728	0.9684	9.56E−6	0.5851
		2	0.0127	0.9180	0.0027	0.8780
		3	0.0230	0.9540	1.40E−6	0.8235
		4	0.0170	0.8387	9.91E−7	0.6793
	Biomass dosage	1 g/L	0.0232	0.9455	0.0069	0.9733
		2 g/L	0.0152	0.9093	2.26E−6	0.8715
		3 g/L	0.0111	0.8539	0.0017	0.9616
		5 g/L	0.0127	0.9180	0.0027	0.8780
		8 g/L	0.0287	0.9317	0.0424	0.9575

highest correlation coefficients, $R^2 > 0.91$. Pseudo-first order equation described well the batch experimental data at pHs 1 and 2, only for biomass dosages of 5 and 8 g/L respectively, indicating possible differences under different pH conditions and at higher biomass dosages.

3.1.5. *Biosorption isotherms and thermodynamic parameters*

One of the most important aspects of biosorption seen as a mass transfer unit operation is the equilibrium. The equilibrium data allow the development of equations useful for comparison of various biosorbents, under different operational conditions, as well as for optimization and operating purposes (Khambhaty et al., 2009; Yang et al., 2016). As seen from the experimental data, some of the total Cr, i.e. the reduced Cr(III), was retained by the biomass during Cr(VI) biosorption process. It might be assumed that the adsorption rate of the reduced Cr(III) might be faster than the reduction rate of Cr(VI) and that Cr(III) remains in equilibrium (Park et al., 2007). Fig. 4 shows the equilibrium isotherm of total Cr at pH 2, while working at different temperatures ranging from 26 °C to 50 °C. In order to analyze the differences between sorption and aqueous concentrations of chromium at equilibrium, some isotherm models are available for fitting the data. In the present study, a two-parameter model, i.e. Langmuir isotherm was used to describe the equilibrium of the sorption system. By using Eq. (7), a non-linear regression fitting gave the values of the Langmuir isotherm parameters as follows: for experiments performed at 26 °C, $q^{max}_{Cr_{tot}} = 14.44$ mg/g and $b = 0.0019$ mg/L; for experiments performed at 40 °C, $q^{max}_{Crtot} = 17.32$ mg/g and $b = 5.39E{-}4$ mg/L; and for experiments performed at 50 °C, $q^{max}_{Crtot} = 1089.20$ mg/g and $b = 1.43$ mg/L. These results show that the maximum uptake of total Cr occurs at 50 °C. The experimental data show that the equilibrium was attained only when considering working at 26 and 40 °C, while for 50 °C, the *A. viscosus* seems to be able to remove higher

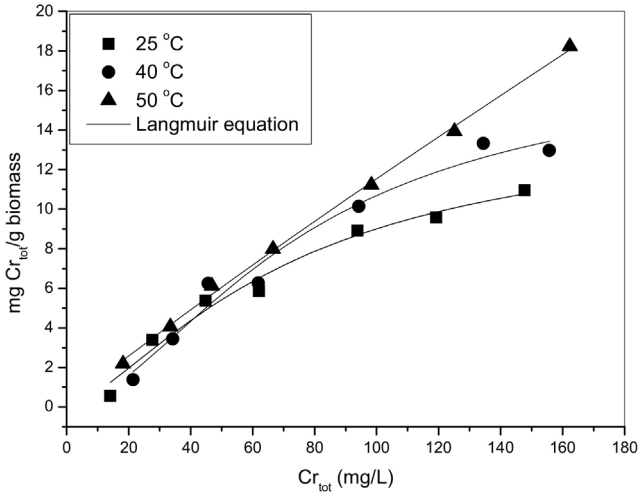


Fig. 4 – Isotherm plot of total Cr retention at different temperatures (dead biomass dosage, 5 g/L).

concentrations than the ones used in our experiments. In this case, the heavy metal ions are not in equilibrium with the biomass up to a concentration of 250 mg/L Cr(VI), so higher concentrations of heavy metal should be considered to attain equilibrium. A similar behavior was reported by Khambhaty et al. (2009), which consider that the enhancement of sorption capacity is the result of an increasing in collision frequency between sorbent and heavy metal. The resulting data was well fitted for the studied temperatures (26 °C, 40 °C and 50 °C), the correlation coefficient being greater than 0.96 in all three cases. This means that the Langmuir model can represent this process very well, possibly due to a homogeneous distribution of active sites available for sorption on the biomass surface (Baral et al., 2006; Park et al., 2005).

Sorption isotherm data obtained at different temperatures were used to calculate the thermodynamic parameters using Eqs. (8)–(10). The calculated values are listed in Table 2.

Table 2 – The thermodynamic data of total chromium biosorption on dead *A. viscosus* biomass at different initial chromium concentrations.

C_i (mol/L)	ΔH° (kJ/mol)	ΔS° (J/mol K)	ΔG° (kJ/mol)		
			299.15 K	313.15 K	323.15 K
4.86×10^{-4}	34.35	87.98	8.03	6.79	5.91
19.23×10^{-4}	7.26	4.60	5.88	5.81	5.77
28.84×10^{-4}	5.90	0.26	5.82	5.81	5.81
38.46×10^{-4}	10.50	14.23	6.24	6.04	5.90
48.08×10^{-4}	12.58	20.20	6.53	6.25	6.05

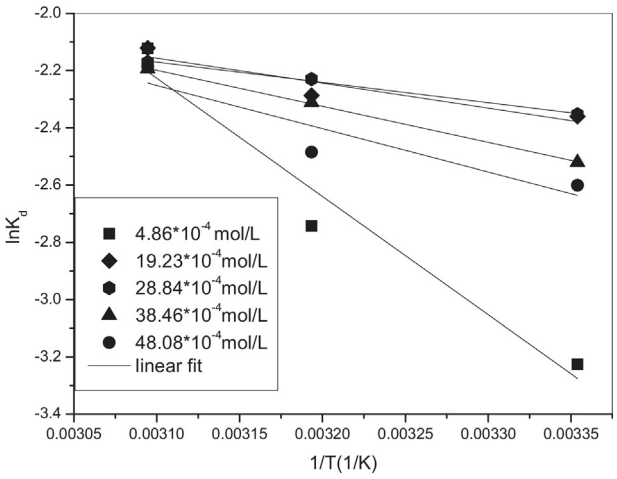


Fig. 5 – Effect of temperature on the distribution coefficient (K_d) of total chromium biosorption on dead *A. viscosus* biomass at different Cr(VI) concentrations.

The thermodynamic parameters resulted from the slope and intercept of the plot $\ln K_d$ vs. $1/T$ (Fig. 5). As it can be seen from Table 2, the positive enthalpy change (ΔH°) in the temperature interval 299.15–323.15 K means that the process of chromium removal from solution is endothermic. The positive values of entropy (ΔS°) reflect the affinity of dead *A. viscosus* biomass toward chromium ions in aqueous solution and may suggest some structural changes in the biosorbent. In a similar context, Loukidou et al. (2004) considered that at higher temperatures, the energy of the system can facilitate the attachment of chromium ions onto cell surface. The positive values of ΔG° indicate a non-spontaneous process for total Cr biosorption by *A. viscosus* biomass, while the positive ΔS° and ΔH° indicate that the process is spontaneous at high temperatures (Fan et al., 2009).

3.2. *Removal of Cr(VI) ions: reduction to Cr(III) and biosorption by living biomass of A. viscosus*

3.2.1. *Effect of pH on Cr(VI) reduction and total Cr removal*

Fig. 6 shows the time profiles of Cr(VI) (Fig. 6a), total Cr (Fig. 6b) and Cr(III) (Fig. 6c) removal by living *A. viscosus* at various solution pH values. As indicated in the experiments performed up to now, total Cr was also analyzed to see if the reduction of Cr(VI) to Cr(III) is possible as well for the living bacteria as in the case of dead biomass. As seen from Fig. 6, the results also suggest that some of the Cr(VI) was reduced to Cr(III) when brought into contact with the living biomass of *A. viscosus*. Results revealed that pH 1 was the optimum pH for 100% removal efficiency of Cr(VI), starting from a solution of 100 mg/L Cr(VI) and working with 5 g/L living *A. viscosus* biomass, at a contact time of 48 h. For pH 2, pH 3 and pH 4, in 96 h, we could observe a removal efficiency of 74.8%, 55.1% and 33.1%, respectively. Compared to pH 1, pHs 2–4 have a relatively slow reduction rate, a longer contact period being required for Cr(VI) removal from aqueous media. The removal rate of Cr(VI) increased with decreasing the pH value. Additionally, for total Cr removal, pH 2 seems to be the optimum value. As pH of the system increases, the number of negatively charged sites increases. Due to the electrostatic repulsion, a negatively charged surface site does not favor the adsorption of anions (Kumar et al., 2008). Bacterial reduction of Cr(VI) under low pH conditions and with no addition of nutrients can be considered as a mechanism of resistance to Cr(VI), including periplasmatic biosorption, intracellular biotransformation either via direct enzymatic reaction or indirectly, via metabolites (Pei et al., 2009). It is also possible that some of the reduced Cr(III) is being accumulated by the living *A. viscosus*. The reduction of Cr(VI) to Cr(III) has also been reported by some bacterial (Abskharon et al., 2009; Silva et al., 2009; Xu et al., 2011) and fungal strains (Acevedo-Aguilar et al., 2006).

3.2.2. *Effect of biomass dosage on Cr(VI) reduction and total Cr removal*

The effect of living *A. viscosus* biomass dosage in the range of 1 to 8 g/L on Cr(VI) reduction and total Cr removal at initial pH 1 is shown in Fig. 7. Results showed that the removal of Cr(VI) (Fig. 7a) reached 100% and increased with increasing the biomass dosage, from 3 g/L to 8 g/L. Biomass maximum efficiency was achieved in 48 h for 5 and 8 g/L and in 144 h for 3 g/L. Also, the removal of total Cr increased from 18% to 34% in 144 h with an increase of biomass dosage (Fig. 7b). High reduction and removal capacity of Cr(VI) could be observed at low pH values (1–2), and higher biomass dosages. The reason could be attributed to the large number of H^+ ions, which neutralize the negatively charged adsorbent surface and to more adsorption sites available at a higher quantity of biosorbent (Ertugay and Bayhan, 2008; Kumar et al., 2008). Hence, 5 g/L of living *A. viscosus* showed good reduction and removal of Cr(VI) in a short time period and it was selected as optimum biosorbent dosage.

3.2.3. *Effect of contact time and kinetics of Cr(VI) reduction and total Cr removal*

Fig. 8 shows the effect of contact time on Cr(VI) reduction and total Cr removal by living *A. viscosus*. 25 mg/L, 50 mg/L and 100 mg/L Cr(VI) solutions were evaluated along time for 48 h, the necessary time for 100% removal, at pH 1 and 26 °C. For 25 mg/L and 50 mg/L of initial Cr(VI) concentration, total removal was achieved in 4 h and 20 h respectively, while the complete removal in the case of 100 mg/L of Cr(VI) required 48 h of contact time (Fig. 8a). In the case of total Cr removal (Fig. 8b), an efficiency of 51%, 40% and 34% was noticed in the first 30 min for Cr(VI) concentrations of 25 mg/L, 50 mg/L

Table 3 – Regression parameters of the kinetic models applied for Cr(VI) removal by living *A. viscosus*.

Kinetic models	Parameters	Value	Pseudo-first order		Pseudo-second order	
			k	R^2	k	R^2
Reduction kinetics	Cr(VI) concentration	25 mg/L	0.7942	0.8124	0.8217	0.9966
		50 mg/L	0.3653	0.7456	0.0399	0.9215
		100 mg/L	0.04212	0.9777	0.0025	0.9094
	pH	1	0.06673	0.9339	0.0047	0.9951
		2	0.04212	0.9777	0.0025	0.9094
		3	0.0063	0.8750	1.00E−4	0.8175
		4	0.0029	0.9562	3.76E−4	0.9506
	Biomass dosage	1 g/L	0.0075	0.9990	2.50E−4	0.9660
		2 g/L	0.0182	0.9955	0.0022	0.8409
		3 g/L	0.0362	0.9923	0.01	0.7570
		5 g/L	0.0421	0.9777	0.0025	0.9094
		8 g/L	0.0863	0.9990	0.0181	0.9990
Adsorption kinetics	Cr(VI) concentration	25 mg/L	0.7942	0.8124	0.4741	0.9914
		50 mg/L	0.3653	0.7456	0.1997	0.9215
		100 mg/L	0.7942	0.8124	0.4108	0.9966
	pH	1	0.0667	0.9339	0.0237	0.9951
		2	0.7942	0.81243	0.4108	0.9966
		3	0.0124	0.7895	0.1004	0.6909
		4	0.0200	0.8268	0.0109	0.6933
	Biomass dosage	1 g/L	0.0161	0.9783	0.0010	0.8817
		2 g/L	0.0139	0.9985	0.0038	0.9070
		3 g/L	0.0362	0.9923	0.03	0.7570
		5 g/L	0.7942	0.8124	0.4108	0.9966
		8 g/L	0.0863	0.99	0.1211	0.99

and 100 mg/L respectively, and after that, it was kept constant until 48 h. In Table 3 the regression parameters of the kinetic models applied for Cr(VI) removal by living *A. viscosus* are presented. Pseudo-first order reduction kinetics described better the experimental data than adsorption kinetics, with a high correlation coefficient for pHs 1, 2 and 4; $R^2 > 0.93$ and $R^2 > 0.97$ were achieved in the case of all kinetics regarding the biomass dosage experiments.

3.2.4. *Biosorption isotherms*

Fig. 9 shows the isotherm plot of total Cr retention. The model was able to predict the total Cr biosorption with a correlation coefficient of 0.96. The Langmuir model parameters with the assumption that the reduced Cr(III) remains in an equilibrium state between the biomass and aqueous solution were estimated as $q^{max}_{Cr_{tot}} = 1161.3$ mg/g and $b = 8.38E{-}5$ mg/L. In addition, the predicted value of $q^{max}_{Cr_{tot}}$ by Langmuir equation for living biomass was much higher than the experimental one ($q^{max}_{Cr_{tot}} = 12.4$ mg/g). This fact can lead to the conclusion that the biosorption of living biosorbent might follow a heterogeneous model and other mechanisms such as intracellular bioaccumulation would contribute to the uptake of total Cr except for surface binding (Li et al., 2010).

3.3. *Column study*

For the evaluation of the characteristics of Cr(VI) removal by *A. viscosus* biofilm supported on polyethylene, the effluent profiles of Cr(VI) and total Cr concentrations were monitored. The column biosorption process required prediction of concentration time profile or breakthrough curve (Fig. 10). Based on the batch studies, the pH of influent was set at 2. It can be seen from Fig. 10 that for a short period of time (first 5 min) the concentration of Cr(VI) in the column effluent remained zero and then increased reaching the influent level after 350 min. This is due to the formation of the mass transfer zone in the column. When a fresh layer of the biomass is exposed to a solution that contains a metal, the metal ions are sequestered by the biomass until the retained amount is in equilibrium with the influent concentration (Quintelas et al., 2008b). The amount of biofilm produced on supports could be quantified as 5.75 g biomass/L of solution. The difference between the total Cr and Cr(VI) concentrations was identified as Cr(III), indicating the reduction of Cr(VI) by the *A. viscosus* biofilm. As the operation in the column proceeded, the amount of total Cr bound to the biomass increased to 20.37 mg/g at the end of contact time required for establishment of the equilibrium. Previous studies employing biomaterials showed that the chromium bound onto biomass was not in the hexavalent, but in the trivalent form (Park et al., 2006). Our study showed that *A. viscosus* biofilm has good potential as Cr(VI) reducing agent with unlimited potential in bioremediation.

3.4. *FTIR analysis*

The FTIR (Fourier Transform Infrared) spectra of unloaded and chromium loaded *A. viscosus* biomass in the range of 500–4000 cm^{-1} were analyzed to investigate the functional groups involved in the biosorption process and the possible mechanism that may be involved in the reduction/removal of Cr(VI). The infrared spectrum of the *A. viscosus* bacterium (Fig. 11) is typical for bacterial extracellular polymeric substances with a complex mixture of macromolecular polyelectrolytes including polysacharides, proteins, nucleic acids and lipids or humic substances (Figueiredo et al., 2010). As seen in Fig. 11, the unloaded and metal loaded biomass displays a number of absorption peaks, reflecting the complex nature of the biomass. FTIR spectrum of *A. viscosus* shows one broad band at 3409.81 cm^{-1} due to the vibrations of hydroxyl (OH stretching) and amino (NH stretching) groups; the small bands in the range between 2975 and 2840 cm^{-1} are attributed to C–H stretching of the groups CH_2 and CH_3; the

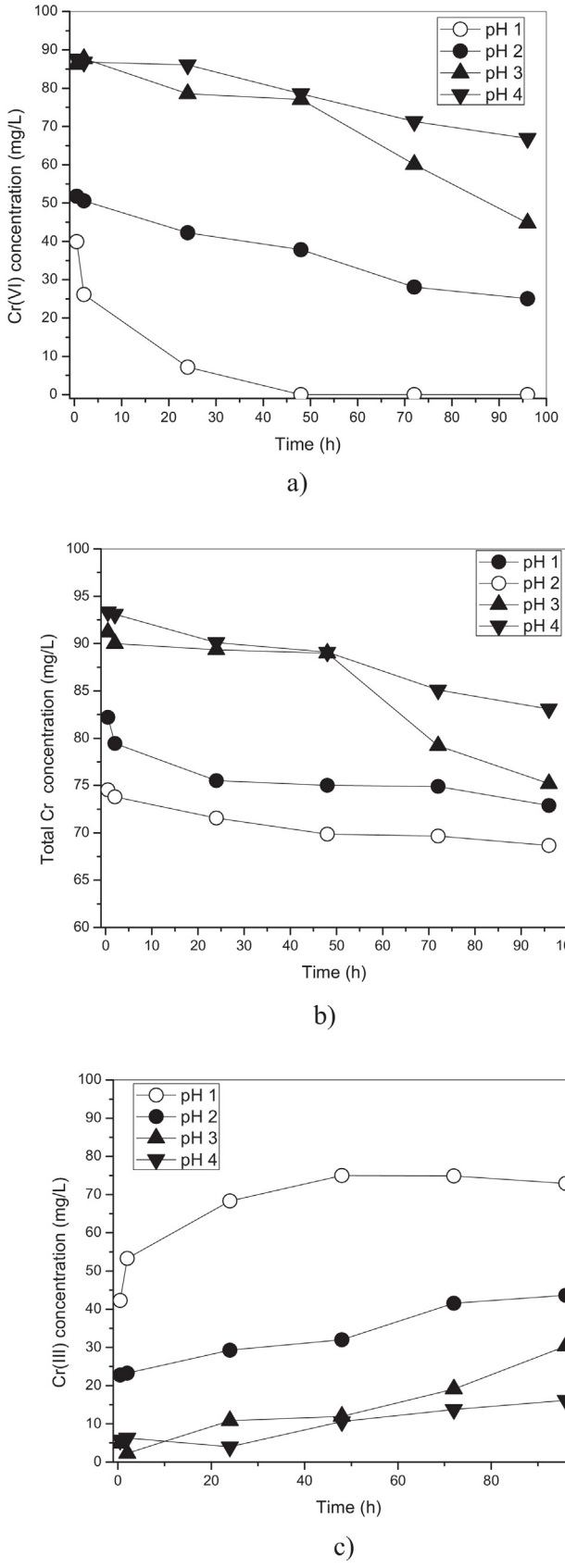


Fig. 6 – Effect of solution pH on the chromium reduction and biosorption from aqueous solution using living *A. viscosus*: (a) Cr(VI) concentration vs. time, (b) total Cr concentration vs. time, c) Cr(III) concentration vs. time (biomass dosage: 5 g/L; initial Cr(VI) concentration: 100 mg/L; temperature: 26 °C; contact time: 96 h).

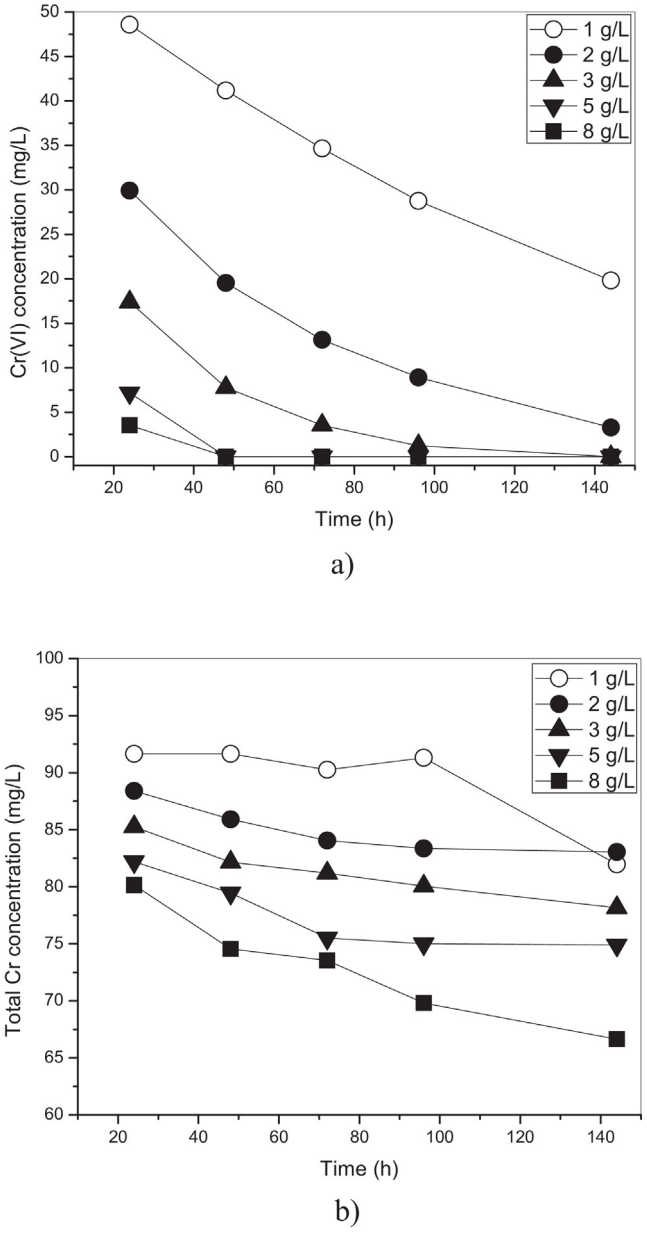
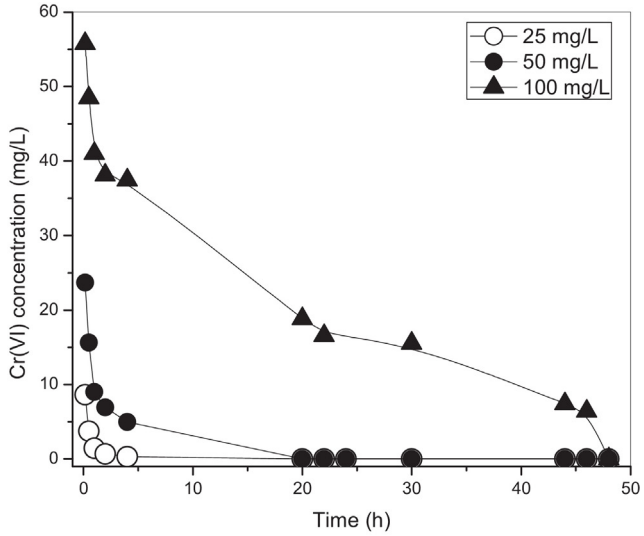


Fig. 7 – Effect of biomass dosage on chromium reduction and biosorption from aqueous solution using living *A. viscosus*: (a) Cr(VI) concentration vs. time, (b) total Cr concentration vs. time (initial Cr(VI) concentration: 100 mg/L; temperature: 26 °C; contact time: 144 h; pH 1).

band at 1539.08 cm^{-1} is indicative for C–N stretching and N–H deformation; the characteristic region of the bands between 1660 and 1400 cm^{-1} are attributed to the vibrations of the functional groups such as carboxyl, phosphoric, amine and the bands in the frequency range of 1250–900 cm^{-1} result from vibrations of the polysaccharides from the bacterium. The spectrum pattern of the unloaded *A. viscosus* biomass showed changes of certain bands when compared to Cr-loaded biomass. When considering the reduction/removal of Cr(VI) by the dead *A. viscosus* biomass, the changes in bands were seen for hydroxyl (OH stretching) and amino (NH stretching) groups, C–H stretching of the groups CH_2 and CH_3, C–N stretching and N–H deformation and for the functional groups such as carboxyl, phosphoric or amine. In the case of the living biomass, C–N stretching, N–H deformation and functional groups such as carboxyl, phosphoric or amine are indicative for the reduction/removal of Cr(VI).



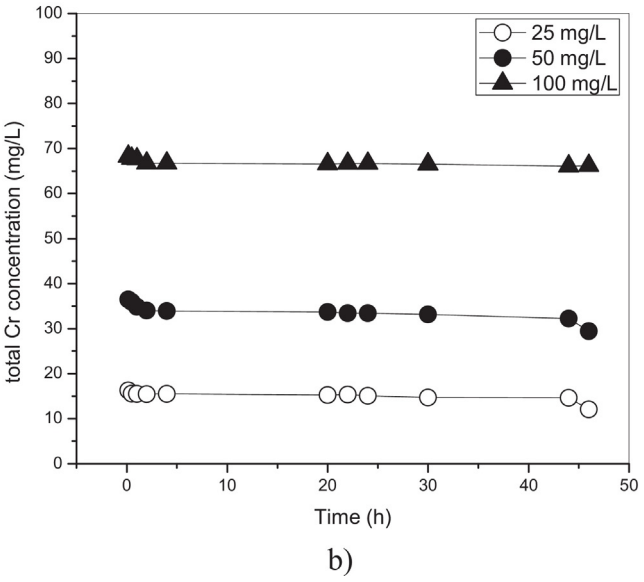


Fig. 8 – (a) The effect of contact time on Cr(VI) reduction by living *A. viscosus*; (b) The effect of contact time on total Cr removal by living *A. viscosus*.

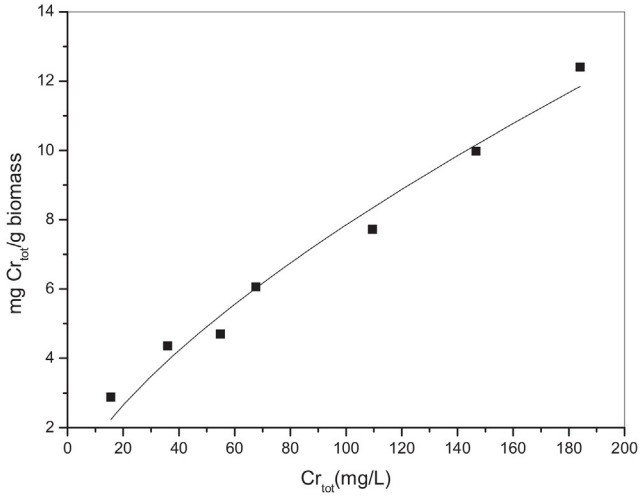


Fig. 9 – Isotherm plot of total Cr retention – Langmuir equation (living biomass dosage, 5 g/L).

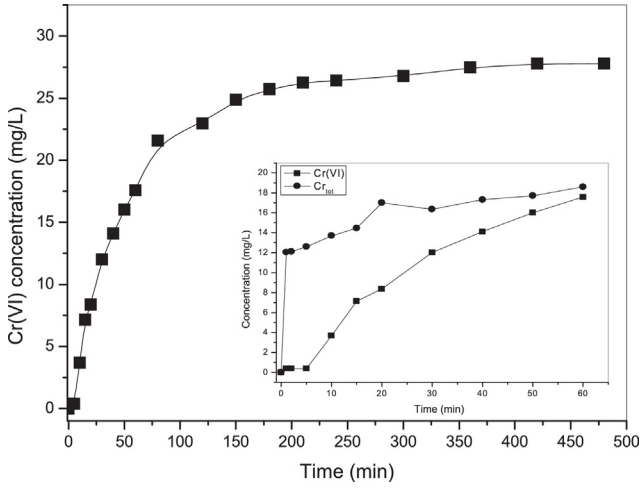


Fig. 10 – Breakthrough curves for Cr(VI) removal by *A. viscosus* biofilm (initial Cr(VI) concentration: 25 mg/L; pH 2; flow rate: 10 mL/min; temperature: 26 °C).

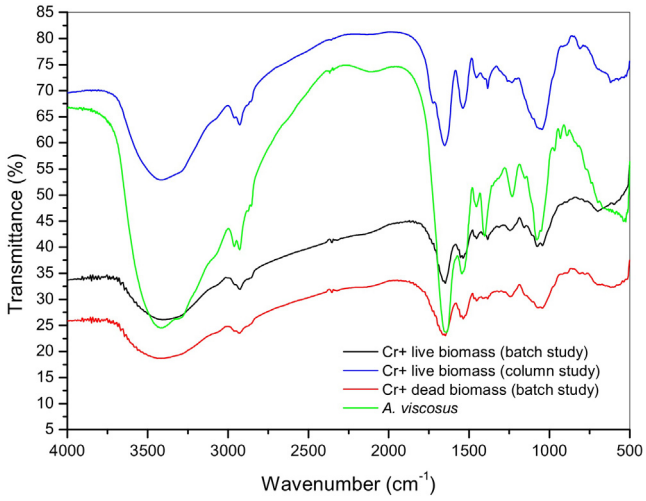


Fig. 11 – FTIR spectra of *A. viscosus* before and after chromium(VI) loading.

Cr(VI) removal is a complex phenomenon due to reduction of Cr(VI) to Cr(III). From the experimental results and FTIR analysis we can conclude that Cr(VI) can be directly reduced to Cr(III) in aqueous phase by contact with the electron-donor groups from the biomass. Electronic repulsion between positively charged functional groups and Cr(III) ions, release the Cr(III) in aqueous solution. The released Cr(III) in aqueous phase is bonded predominantly by the functional groups through an ion-exchange mechanism. Langmuir model fitting suggested the monolayer sorption of total Cr bound to the biomass.

3.5. *Comparison of dead and living A. viscosus in chromium removal*

The removal of Cr(VI) from aqueous solutions by dead and living biomass of *A. viscosus* is a complex phenomenon based on reduction and adsorption mechanisms. Both living and dead cells of *A. viscosus* removed Cr(VI) under highly acidic pH. These pH values represent an advantage due to the acidic nature of chromate – containing wastewaters. The work with dead biomass proved to be more suitable at high temperature. In the case of dead biomass, the process is endothermic, meaning that at high temperatures, high uptake values could

be obtained (at 50 °C, $q_{Cr_{tot}}^{max} = 1089.20$ mg/g), similar to those from living biomass analysis at 26 °C ($q_{Cr_{tot}}^{max} = 1161.3$ mg/g) according to Langmuir isotherm modeling. Also, the positive thermodynamic parameters ΔS° and ΔH° indicated the process spontaneity at high temperatures for dead biomass. The uptake capacity of living and dead *A. viscosus* appears to be similar under optimum conditions established in the experiments, although the living biomass is able to completely reduce Cr(VI) to Cr(III) in fewer hours than the dead biomass (e.g. for 25 mg/L and 50 mg/L of initial Cr(VI) concentration, a complete reduction by living biomass was seen in 4 h and 20 h respectively, while 100% reduction in the case of 100 mg/L Cr(VI) required 48 h of contact time; in the case of dead biomass, for an initial concentration of 25 mg/L Cr(VI), it was observed that Cr(VI) was completely reduced to Cr(III) in 92 h, for 50 mg/L initial concentration, Cr(VI) was completely reduced in 116 h, while the complete removal of 100 mg/L of Cr(VI) required about 144 h of contact time). Meanwhile, experiments focusing on Cr(VI) removal by *A. viscosus* biofilm supported on polyethylene were also analyzed and showed a good uptake of chromium ions bound to the biomass ($q_{Cr_{tot}} = 20.37$ mg/g). The uptake capacity of the biofilm is higher than the uptake capacity obtained under optimum conditions in batch experiments ($q_{Cr_{tot}} = 12.4$ mg/g). Taking into consideration the present findings, we can consider that both dead and living *A. viscosus* are effective biosorbents for removal and reduction of Cr(VI) from wastewaters under optimum conditions established in the experimental procedures.

4. Conclusions

Dead biomass as well as living biomass of *A. viscosus* proved to be promising biosorbents and may be used for Cr(VI) reduction to the less toxic Cr(III) from aqueous solution in highly acidic conditions. The solution pH has a strong influence on chromium biosorption and reduction. Both living and dead cells could successfully remove Cr(VI) from aqueous solution in highly acidic pH (pH 1 and 2) with an efficiency of 100% for 100 mg/L initial Cr(VI) concentration. The living *A. viscosus* proved its efficiency as biosorbent with respect to uptake values of total Cr, as predicted by Langmuir model 1161.3 mg/g compared to 14.4 mg/g in the case of dead biomass, at 26 °C. The uptake values of living biomass obtained at room temperature (26 °C) were similar to the uptake values obtained in the case of dead biomass under high temperature conditions (50 °C). In addition to batch mode experiments, a column experiment was performed with the aim of removing Cr(VI) by an *A. viscosus* biofilm supported on a new type of polyethylene. The results obtained in this case showed a good uptake of chromium ions bound to the biomass, of 20.37 mg/g.

In conclusion, *A. viscosus* biomass can be used to convert Cr(VI) to Cr(III) in batch and continuous modes with good results. Furthermore, the availability, low cost and low environmental impact makes this biomass an attractive option in treating wastewater polluted with chromium.

Conflict of interest

We declare no conflict of interest.

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