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Chemical Engineering Journal 136 (2008) 151–155

Chemical Engineering Journal

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Chromium(III) removal by *Spirulina platensis* biomass

A. Lodi [*], D. Soletto, C. Solisio, A. Converti

Department of Chemical and Process Engineering "G.B. Bonino", Genoa University, via Opera Pia 15, I-16145 Genoa, Italy

Received 2 August 2006; received in revised form 27 February 2007; accepted 21 March 2007

Abstract

Dried and 48 h re-hydrated biomass of *Spirulina platensis* was employed as a biosorbent in tests of chromium(III) removal from water. Various concentrations of biomass (from 1 to 3 g l^{-1}) and metal (from 25 to 200 mg l^{-1}) were tested. Increasing and re-hydrating biomass allowed removing almost entirely up to $Cr_0 = 100$ mg l^{-1} of Cr^{3+} (95% of removal with $X_0 = 3$ g l^{-1} of re-hydrated biomass), whereas, lower percentages were obtained at higher concentrations of pollutant (56% of removal at $Cr_0 = 200$ mg l^{-1}). Kinetics of the biosorption was generally better at low Cr(III) concentrations ($k_{ads} = 1.41$ and 1.44 h^{-1} at $Cr_0 = 35$ mg l^{-1} and $X_0 = 1$ g l^{-1} of dry and re-hydrated biomass, respectively). The kinetics of the process and the adsorption capacity of biomass were finally put into relationship, highlighting that, at low concentrations of pollutant ($Cr_0 = 25$, 35 and 50 mg l^{-1}), re-hydrated biomass did not lead to noticeable improvement, whereas, as the concentration of Cr(III) was increased from 75 to 200 mg l^{-1}, re-hydratated biomass ensured remarkably higher removal.

Keywords: Chromium; Removal; Biosorption; *Spirulina platensis*; Dry biomass; Re-hydrated biomass

1. Introduction

Various industries, such as electroplating, leather tanning, mining, steel and pigment making are responsible for the release of chromium, which, as is well known, can induce a significant impact on humans and other living organisms [1]. This element exists as Cr(III) or Cr(VI) in the environment. The chromium in aqueous solution may be present mainly as Cr(III) at pH 2 and becomes 62% $Cr(OH)^{2+}$ and 38% $Cr(OH)_2{}^{+}$ when the pH solution increases to about 7 [2]. For chromate, the hydrochromate anion ($HCrO_4{}^{-}$) is known to be predominant at pH of about 4, whilst $CrO_4{}^{2-}$ becomes the main species in solution at pH 7.0 and above [3,4]. The positive charged species can be adsorbed onto the negatively charged soil particles. Moreover chromate can be reduced to the less toxic Cr(III) [5], which can be precipitated by addition of hydroxide. An alternative method can be the employment of a specific low cost adsorbent [6,7].

From this point of view, the biosorbent properties of bacteria and algae have been largely studied [8]. In particular, the microalga *Spirulina platensis*, which is abundantly produced for several commercially uses [9,10], can be alternatively considered a resource for heavy metal removal; it did in fact show excellent capacity of removing lead [11], cadmium [12,13] and copper [14]. Previous work [15] suggested that dry biomass of *S. platensis* re-hydrated for 48 h is the best option for copper removal, as it is able shortening the adsorption time, increasing the percentages of metal removed if compared with dry biomass: the re-hydration promotes the biomass swelling, probably increasing the number of dissociable and polar reactive sites of the cell wall available for the metal attraction. Therefore dry and re-hydrated biomass has been employed in this study to remove Cr(III) from water. In view of possible future application of this system, the removal ability of *S. platensis* has been investigated at variable starting Cr(III) and biomass concentrations.

2. Materials and methods

2.1. *S. platensis* cultivation

S. platensis (UTEX 1926) was obtained from the University of Texas Culture Collection. Cells were grown batch-wise in four outdoor cultivation ponds filled with the medium of Schlösser [16]. Each pond, having surface area of 0.15 m^2 and depth of about 6–7 cm, was kept at 30 °C and continuously illuminated by two fluorescent lamps (40 W), furnishing 8.0 klux

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[*] Corresponding author. Tel.: +39 10 353 2583; fax: +39 10 353 2586.
E-mail address: lodi@unige.it (A. Lodi).

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doi:10.1016/j.cej.2007.03.032

light intensity, located at about 40 cm over its surface. After 1 month cultivation, a layer of microalga formed on the surface of the tanks; it was collected by centrifugation, dried in oven at 50 °C and stored in dessicator at room temperature (20 ± 1 °C).

2.2. Biosorption and analytical procedures

Before using, dry biomass was rinsed by deionised water up to pH 7.5, in order to remove the residual alkalinity, dried at room temperature for 24 h and subsequently at 80 °C in oven for 12 h. It was then ground and passed through a sieve of 60–100 meshes and stored in dessicator at room temperature for adsorption tests. Re-hydrated biomass was prepared by suspending dry biomass in deionised water in 250-ml Erlenmeyer flasks. After agitation in a rotary shaker (150 rpm) at room temperature for 48 h, biomass was recovered by filtration through 0.45 mμ membrane filters (Millipore, Vimodrone, Italy) and then used in adsorption tests.

Two parallel series of tests were carried out with dry biomass or biomass re-hydratred for 48 h at initial concentration of 1, 2 and 3 g l^{-1} dry weight. The fixed amount of biosorbent was put in contact with 100 ml, chromium sulphate solution in distilled water with Cr(III) concentration in the range 25–200 mg l^{-1}. Table 1 illustrates the experimental plan.

Each test was carried out in 250-ml Erlenmeyer flasks agitated on a rotary shaker (150 rpm), at room temperature (20 ± 1 °C). Samples (1.0 ml) were withdrawn every 20 min during the first hour of contact time and every hour successively; biomass was removed by filtration through membrane filters (Millipore, Vimodrone, Italy) with 0.45 μm pore diameter and the filtrate was analysed for metal content using atomic absorption spectroscopy, (Perkin-Elmer, Monza, Italy, Model 5000). According to Deng and Bai [17], chromium adsorption tests were performed at starting pH of 6.0. No significant pH changes were observed during the experiments, so that they were considered to be performed at constant pH level. All tests were carried out in quadruplicate and the experimental results were presented as mean values. Errors between experimental data and mean values were presented as standard deviations.

Table 1
Experimental schedule followed for the removal of Cr(III), at variable initial concentration of biosorbent: dry (D) and re-hydrated (R) biomass of *Spirulina platensis*

Dry biomass						
D^1_{25}	D^1_{35}	D^1_{50}	D^1_{75}			
D^2_{25}	D^2_{35}	D^2_{50}	D^2_{75}	D^2_{100}	D^2_{150}	
		D^3_{50}	D^3_{75}	D^3_{100}	D^3_{150}	D^3_{200}
Re-hydrated biomass						
R^1_{25}	R^1_{35}	R^1_{50}	R^1_{75}			
R^2_{25}	R^2_{35}	R^2_{50}	R^2_{75}	R^2_{100}	R^2_{150}	
		R^3_{50}	R^3_{75}	R^3_{100}	R^3_{150}	R^3_{200}

Superscript and subscript symbols refer to biomass concentration (g l^{-1}) and Cr(III) concentration (mg l^{-1}), respectively.

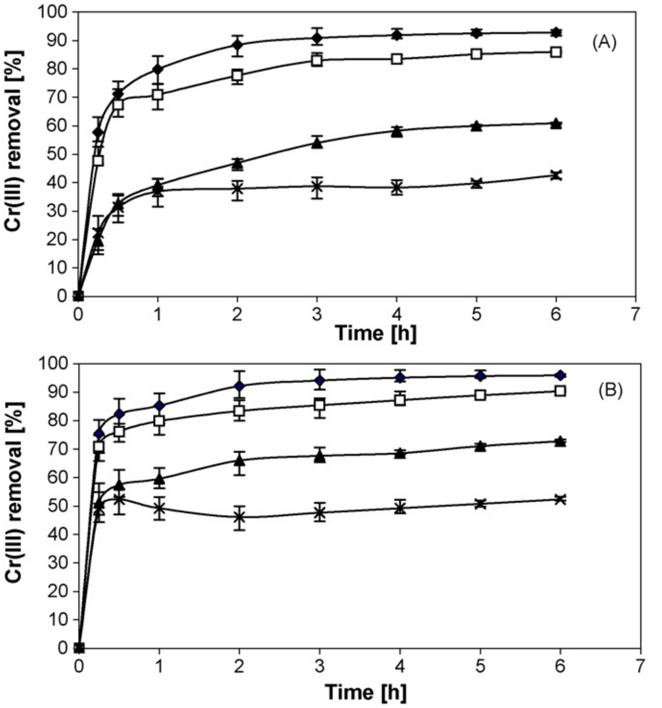

Fig. 1. Percentage of Cr(III) removal at $X_0 = 1$ g l^{-1}. Cr_0 (mg l^{-1}): 25 (♦); 35 (□); 50 (▲); 75 (×). (A) Dry biomass; (B) re-hydrated biomass.

3. Results and discussion

3.1. Adsorption test at variable biomass and chromium levels

To evaluate the behaviour of dry biomass of *S. platensis* in Cr(III) removal, a first set of experiments was carried out with dry biomass concentration (X_0) of 1 g l^{-1} and increasing the initial chromium(III) concentration (Cr_0) from 25 to 75 mg l^{-1} (Table 1, set $D^1_{25–75}$). The equilibrium curves (Fig. 1, panel A) showed a good removal only at $Cr_0 = 25$ and 35 mg l^{-1} (93 and 86%, respectively), whereas, at higher Cr_0 concentration, the removal was remarkably lower (61 and 43% at $Cr_0 = 50$ and 75 g l^{-1}, respectively).

As already observed by other authors [17,18] most of metal was removed within the first hour, then the removal efficiency approached the equilibrium. The first rapid phase of adsorption can be ascribed to electric attractive interactions between the positive chromium ions $Cr(OH)^{2+}$, $Cr(OH)_2{}^+$ and Cr(III) and algal cell wall, containing carboxylic, amino, thio, hydroxo and hydroxy–carboxylic groups [19]. Additional mechanisms, such as entrapment of metal both in the form of insoluble microdeposits in the polysaccharidic reticular region and binding to other biopolymers (ribonucleic acid, polyphosphates, etc.), can contribute to further biosorption of the metal [20]. This first set of tests with dry biomass evidenced the cells tendency to agglomerate, due to its powdered state, thus reducing the contact surface for the binding.

An effective improvement in metal removal was ensured by a re-hydration pretreatment of biomass [14,21]. This treatment contributed to biomass particles dispersion and their swelling, preventing their agglomeration; thus, it was possible to reach two simultaneous aims: an increase in the specific surface of the adsorbing particles and a more effective removal of metal ions by both electrostatic and polar attractions. Fig. 1, panel B, shows the results obtained with re-hydrated biomass (Table 1, set R^1_{25-75}). For the lowest chromium concentration (25 and 35 mg l^{-1}), the removed percentage (93–96%) was comparable to the one obtained with dry biomass (86–90%) but, at higher metal concentration (50 and 75 mg l^{-1}), the re-hydration led to an appreciable yield improvement (9–12%) with respect to the corresponding test with dry biomass.

In order to evaluate the potential of this removal process, further experiments were carried out at increasing dry and re-hydrated biomass and metal concentrations, (Table 1, sets D^2_{25-200} and R^2_{25-200}). Also in this case, at low metal concentration (25, 35 and 50 mg l^{-1}) the use of re-hydrated biomass did not lead to noticeable improvement of metal removal with respect to dry biomass (Fig. 2). On the other hand, the effect of re-hydration became more and more significant as Cr_0 concentration increased, resulting 6% higher at $Cr_0 = 75\ \text{mg l}^{-1}$ and 19% higher at $Cr_0 = 150\ \text{mg l}^{-1}$ with respect to dry biomass performance. Also the experiments carried out with 3 g l^{-1} biomass at chromium levels from 50 to 200 mg l^{-1}(Table 1, sets D^3_{50-200} and R^3_{50-200}), reported in Fig. 3, confirmed this behaviour.

In conclusion, the chromium removal by *S. platensis* biomass can be performed with dry biomass if its level is sufficiently high with respect to the metal one. The re-hydration treatment was shown to enhance the removal as the difference between biomass and metal levels increased.

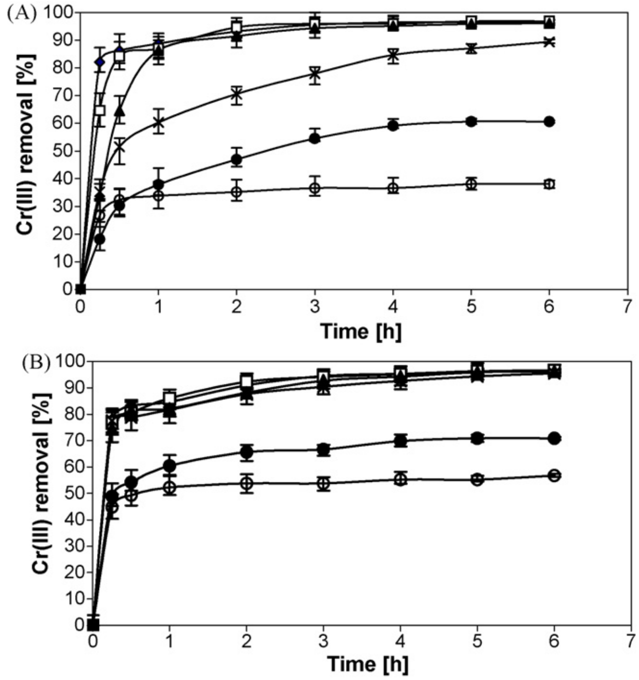

Fig. 2. Percentage of Cr(III) removal at $X_0 = 2\ \text{g l}^{-1}$. Cr_0 (mg l^{-1}): 25 (♦); 35 (□); 50 (▲); 75 (×); 100 (●); 150 (○). (A) Dry biomass; (B) re-hydrated biomass.

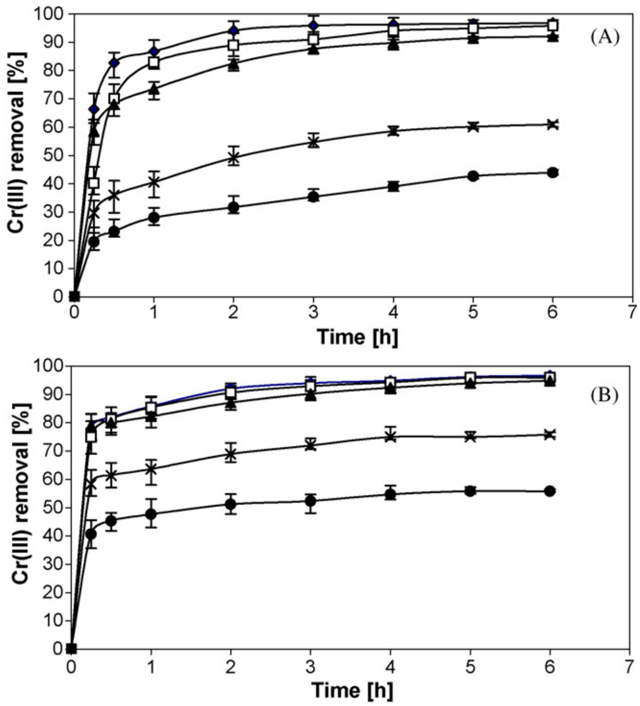

Fig. 3. Percentage of Cr(III) removal at $X_0 = 3\ \text{g l}^{-1}$. Cr_0 (mg l^{-1}): 50 (♦); 75 (□); 100 (▲); 150 (×); 200 (●). (A) Dry biomass; (B) re-hydrated biomass.

3.2. Kinetic and equilibrium study

The adsorption rate constant (k_{ads}, h^{-1}) was estimated from the experimental data of each test by the Lagergren's equation [22]:

$$\log(q_e - q) = \log q_e - \frac{k_{\text{ads}}}{2.303} t \qquad (1)$$

where q_e and q (both in mg l^{-1}) are the amounts of adsorbed metal at equilibrium and at time t(h), respectively. Table 2 reports the values of k_{ads} calculated from the slopes of the straight-line obtained plotting $\log(q_e - q)$ versus t.

Table 2
Influence of variable concentrations of sorbent (*S. platensis*) and pollutant Cr(III) on the adsorption rate constant

Cr_0[a] (mg l^{-1})	k_{ads}[b] (h^{-1})					
	X_0[c] = 1 g l^{-1}		X_0[c] = 2 g l^{-1}		X_0[c] = 3 g l^{-1}	
	D[d]	R[e]	D[d]	R[e]	D[d]	R[e]
25	1.12	1.10	1.25	1.27		
35	0.78	0.76	1.41	1.44		
50	0.73	0.75	1.11	1.15	1.13	1.00
75	0.55	0.67	0.66	0.86	0.89	1.00
100			0.83	0.94	0.86	0.90
150			0.70	0.82	0.78	0.87
200					0.60	0.83

[a] Cr_0: initial concentration of Cr(III).
[b] k_{ads}: adsorption rate constant.
[c] X_0: initial concentration of biomass.
[d] D: dry biomass.
[e] R: re-hydrated biomass.

At low levels of pollutant (25, 35 and 50 mg l^{-1}), under the same adsorbent concentration, the re-hydration treatment did not seem to influence significantly the removal kinetics. This means that, under these conditions, chromium concentration is the limiting factor of the adsorption process; therefore, even the less efficient biosorbent (not re-hydrated biomass), being used in excess with respect to the metal, ensured maximum removal efficiency. No relevant variations of k_{ads} can in fact be observed by comparing the tests carried out with dry and re-hydrated biomass in the metal concentration range 25–50 mg l^{-1}. On the contrary, in the range of chromium level from 75 to 200 mg l^{-1} the adsorbent amount seemed to play a leading role, which became more significant as the pollutant/biomass ratio increased. In particular, the re-hydration allowed obtaining an increase in the adsorption rate constant from 12–22% at $\text{Cr}_0 = 75$ mg l^{-1} to 38% at $\text{Cr}_0 = 200$ mg l^{-1}. As previously mentioned, this confirms that re-hydrated biomass made a higher number of sites available for adsorption with respect to dry biomass.

Taking in mind that the adsorption material was not biologically active because of preliminary drying, the metal uptake can be regarded as a passive adsorption process and, thus, it can be modelled with Langmuir and Freundlich equations.

The Langmuir [23] model assumes that solid surface has a finite number of identical sites which are energetically uniform. According to this hypothesis, there is no interaction between adsorbed species, which means that the amount adsorbed has no influence on the rate of adsorption; a monolayer is formed when the solid surface reaches saturation. The empirical Freundlich [24] nonlinear model is based upon the assumption of a monolayer adsorption with a heterogeneous energetic distribution of active sites, accompanied by interactions among adsorbed molecules.

These equations describe the experimental data in a wide range of concentrations and can be easily transformed into linear ones.

The linear form of Langmuir model is:

$$\frac{C_{\text{e}}}{q_{\text{e}}} = -\frac{1}{q_{\max} b} + \frac{C_{\text{e}}}{q_{\max}} \tag{2}$$

where C_{e} is the equilibrium concentration of chromium (mg l^{-1}), $q_{\max}$ (mg g^{-1}) the overall adsorption capacity of the system and b (mg^{-1}) a parameter related to the energy of adsorption, respectively.

The values of $q_{\max}$ (Table 3) were about 20% higher for re-hydrated than for dry biomass, while, as expected, there was no relevant dependence of adsorption performance on the amount of sorbent. This was probably the result of two opposite effects. On the one hand, the raised biomass level was responsible for an increase in the number of binding site and then of k_{ads}. On the other hand, it could have induced stronger repulsion among the cells, which are notoriously covered by a large number of negative charges. The values of the parameter b, representing the affinity of the binding sites to the adsorption, confirm a good ability by *S. platensis* biomass in Cr(III) removal, especially at 1 g l^{-1} of sorbent (1.18 and 1.43 mg^{-1} for dry and re-hydrated biomass, respectively). Increasing the biomass level to 2–3 g l^{-1}, the parameter b decreased for both dry ($0.69 \leq b \leq 0.80$ mg^{-1}) and re-hydrated biomass ($0.46 \leq b \leq 0.52$ mg^{-1}). This trend may be explained by looking at b as the ratio of the adsorption to the desorption rate: the metal at low concentrations likely bound preferentially to sites with higher affinity whilst an increase in the metal level involved the sites with lower affinity as well [25]. At high concentration of biomass, the increased repulsion among cells could have increased the desorption rate of ions physically bound to the sites by means of weaker bonds if compared to the ionic ones.

Table 3

Parameters of Langmuir and Freundlich model for the adsorption of Cr(III) at variable concentrations of sorbent and pollutant

Set (mg l^{-1})	Langmuir			Freundlich		
	$q_{\max}$ (mg g^{-1})	b (mg^{-1})	r^2	K_{f} (mg g^{-1})	n (g l^{-1})	r^2
$\text{D}^1_{25\text{–}100}$ [a]	30.1	1.18	0.93	N[b]	N	0.64
$\text{R}^1_{25\text{–}100}$ [c]	36.2	1.43	1.00	3.91	6.57	0.82
$\text{D}^2_{25\text{–}150}$	30.4	0.80	0.88	N	N	0.60
$\text{R}^2_{25\text{–}150}$	35.7	0.52	0.87	N	N	0.66
$\text{D}^3_{50\text{–}200}$	30.7	0.69	0.91	N	N	0.54
$\text{R}^3_{50\text{–}200}$	36.8	0.46	0.96	3.53	5.61	0.77

[a] D: dry biomass.

[b] N: not significant.

[c] R: re-hydrated biomass.

The linear form of Freundlich model is:

$$\log q_{\text{e}} = \log K_{\text{f}} + \frac{1}{n} \log C_{\text{e}} \tag{3}$$

where K_{f} (mg g^{-1}) is a constant related to the adsorption capacity and ($1/n$) to the adsorption intensity. From the data reported right

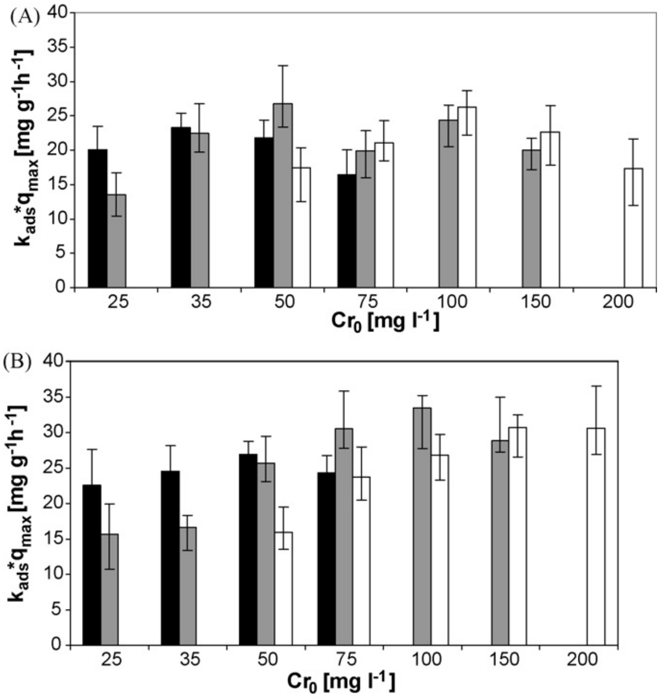

Fig. 4. Amount of Cr(III) removed at equilibrium per gram of biomass per hour at different biosorbent levels. X_0 (g l^{-1}): 1 (■); 2 (▨); 3 (□). (A) Dry biomass; (B) re-hydrated biomass.

hand of Table 3, it can be highlighted that the fit of the isotherms was totally unsatisfactory. Therefore, it was considered that the Langmuir model described better the biosorption process under consideration.

Fig. 4 describes the product of removed chromium at equilibrium (q_{max}) by the adsorption rate constant (k_{ads}) versus Cr_0 concentration and put in relation the kinetics of the process with the adsorption capacity of biomass. At low concentrations of pollutant ($Cr_0 = 25$, 35 and $50\,mg\,l^{-1}$), re-hydrated biomass did not lead to noticeable improvement, whereas, as the concentration of Cr(III) was increased from 75 to $200\,mg\,l^{-1}$, re-hydratated biomass ensured remarkably higher removal.

The highest values of the parameter $q_{max}{\cdot}k_{ads}$ were in fact obtained at $Cr_0 = 150$ and $200\,mg\,l^{-1}$ and $3\,g\,l^{-1}$ (30.7 and $30.6\,mg\,g^{-1}\,h^{-1}$, respectively), at $Cr_0 = 100$ and $2\,g\,l^{-1}$ ($33.4\,mg\,g^{-1}\,h^{-1}$) and at $Cr_0 = 75\,g\,l^{-1}$ with $2\,g\,l^{-1}$ of pre-hydrated biomass ($30.6\,mg\,g^{-1}\,h^{-1}$); anyway, the removal of chromium was not complete in all cases except for the last one, which can be hence considered, in our opinion, the optimum choice from both viewpoints of process performance and global amount of adsorbed Cr(III) (95%).

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