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Modelling Cr(VI) removal by a combined carbon-activated sludge system

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Abstract

The combined carbon-activated sludge process has been proposed as an alternative to protect the biomass against toxic substances in wastewaters; however, the information about the effect of powdered-activated carbon (PAC) addition in activated sludge reactors for the treatment of wastewaters containing Cr(VI) is limited. The objectives of the present study were: (a) to evaluate the removal of hexavalent chromium by (i) activated sludge microorganisms in aerobic batch reactors, (ii) powdered-activated carbon, and (iii) the combined action of powdered-activated carbon and biomass; (b) to propose mathematical models that interpret the experimental results.

Different Cr(VI) removal systems were tested: (S1) biomass (activated sludge), (S2) PAC, and (S3) the combined activated carbon–biomass system. A Monod-based mathematical model was used to describe the kinetics of Cr(VI) removal in the system S1. A first-order kinetics with respect to Cr(VI) and PAC respectively, was proposed to model the removal of Cr(VI) in the system S2. Cr(VI) removal in the combined carbon–biomass system (S3) was faster than both Cr(VI) removal using PAC or activated sludge individually. Results showed that the removal of Cr(VI) using the activated carbon–biomass system (S3) was adequately described by combining the kinetic equations proposed for the systems S1 and S2.

Keywords: Chromium removal; Activated sludge; Activated carbon; Combined activated carbon–biomass system

1. Introduction

Heavy metal residues in contaminated habitats may accumulate in microorganisms, aquatic flora and fauna, which in turn, may enter into the human food chain and result in health problems. For instance, chromium-poisoning causes skin disorders and liver damages. Chromium is usually encountered in the environment in the oxidation states of (III) and (VI). Each of the above oxidation states has very different biological and chemical properties. Cr(III) is considered to be a non-labile, inert element in the environment and essential for mammals in trace amounts, whereas Cr(VI) is much more labile, toxic and carcinogenic for a variety of organisms [1]. Due to its common presence in effluent discharge from steelworks, chromium electroplating, leather tanning and chemical manufacturing, chromium is often detected in sewage plants that combine industrial and municipal wastewater for treatment.

Besides, many heavy metals that have inhibitory or toxic effects on activated sludge microorganisms can upset the operation of the activated sludge process. Literature data on toxicity effects of Cr(VI) on activated sludge process are contradictory. Stasinakis et al. [2] reported that Cr(VI) concentrations equal or greater than 10 mg L^{-1} inhibit the growth of unacclimatized activated sludge. Chromium at a sub-toxic level of 0.05 mg L^{-1} affected the sequencing batch reactor performance to different extents depending on the hydraulic retention time [3]. Yetis et al. [4] reported stimulatory effects on biomass yield in the presence of 25 mg L^{-1} Cr(VI).

The most commonly used technology for treatment of heavy metals in wastewaters is chemical precipitation. In the case of chromium, Cr(III) but not Cr(VI) may be removed from water as an insoluble chromium hydroxide. Recently, several Cr(VI) reducing bacterial species have been identified; these bacteria reduce the toxic hexavalent chromium to the less toxic and less mobile state Cr(III) utilizing a wide range of substrate at near neutral pH [5]. In addition, the reduction of Cr(VI) to Cr(III) using activated sludges under aerobic conditions has also been reported [6].

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Adsorption with activated carbon is a widely used method to eliminate organic and inorganic contaminants in industrial wastewaters. The performance of the process is influenced by different parameters including the operating conditions, type of activated carbon and physicochemical characteristics of the wastewater. Several researchers [7,8] have studied the incorporation of powdered-activated carbon (PAC) in activated sludge systems for the treatment of complex liquid waste containing non biodegradable compounds and toxic or inhibitory substances to improve the performance treatment. However, information about the effect of PAC addition in activated sludge reactors for the treatment of wastewaters containing heavy metals is limited.

The objectives of the present study were: (a) to evaluate the removal of hexavalent chromium by (i) activated sludge microorganisms in aerobic batch reactors, (ii) powdered-activated carbon, and (iii) the combined action of powdered-activated carbon and biomass; (b) to propose mathematical models that interpret the experimental results.

2. Materials and methods

2.1. Biological and chemical materials

The biomass used in this work was cultured in a laboratory scale (4.5 L) activated sludge aerobic reactor. The plant was fed with synthetic wastewater containing dehydrated cheese whey: 1500 mg, $SO_4(NH_4)_2$: 94 mg and $NaHCO_3$: 1030 mg dissolved in 1 L of tap water. Hydraulic retention time was two days; sludge age was maintained at 45 days by daily wasting of the mixed liquor directly from the reactor. During the experiments the reactor temperature was kept at $20 \pm 2\,^{\circ}C$; under steady state conditions dissolved oxygen concentration was above 5 mg L^{-1}, pH was 7.5 ± 0.4, and soluble chemical oxygen demand (COD) ranged between 30 and 80 mg L^{-1}.

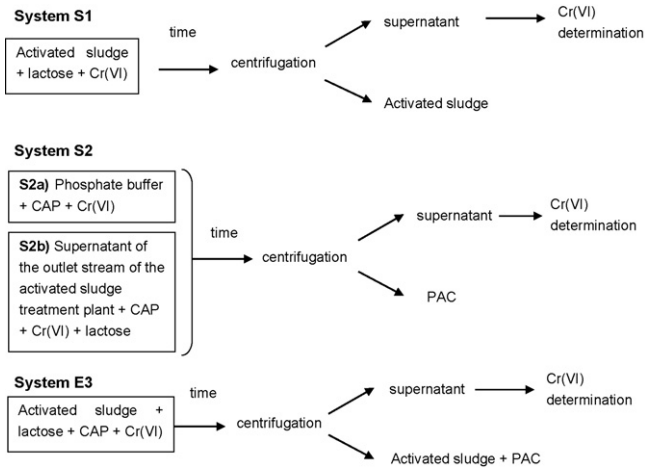
Cr(VI) stock solutions were freshly prepared using analytical grade $K_2Cr_2O_7$; tested Cr(VI) concentrations ranged between 10 and 100 mg L^{-1}. Powdered-activated carbon (PAC) concentrations between 0.5 and 8 g L^{-1} (Clarimex S.A., type 061) were tested. Table 1 shows the characteristics of the activated carbon used.

2.2. Chromium removal kinetics

Cr(VI) batch removal assays were performed in 0.5 L aerated vessels at constant temperature ($20 \pm 2\,^{\circ}C$) and initial pH 7.0 ± 0.1; this pH was selected because it is the optimum value for the metabolic activity of most of the microorganisms that are present in a typical activated sludge. The initial Cr(VI) concentration ranged between 10 and 100 mg L^{-1}. Cr(VI) removal experiments were performed using different systems: (S1) activated sludge (biomass), (S2) PAC, (S3) biomass with the addition of activated carbon. Scheme 1 shows a representation of the performed experiments.

Table 1
Characteristics of the powdered-activated carbon (PAC) used

Properties	Value
Surface area, BET (N_2/77 K)	889 $m^2\,g^{-1}$
Methylene blue adsorption	260 mg g^{-1}
Iodine adsorption	800 mg g^{-1}
Bulk density	0.29 g cm^{-3}
Moisture	12%
pH (1% suspension)	6.0–8.0
Screen analysis, passes mesh #325	60–80 wt%



Scheme 1. Scheme of the tested Cr(VI) removal systems.

In systems S1 and S3, where biomass was present, lactose was added as the carbon source in a concentration of 5 gCOD L^{-1}. This sugar was chosen as the electron donor because it was the main component of the cheese whey used to feed the activated sludge reactor. Previous works [9] showed that the presence of lactose was necessary for the biomass to remove Cr(VI). In systems S1 and S3, the biomass concentration was 2000 ± 300 mgCOD L^{-1}. In system S3 the PAC concentration used was 4 g L^{-1}, based on the reports of Lee et al. [10]. Experiment S2 was performed using two different media:

S2a phosphate buffer (NaH_2PO_4, 1 g L^{-1}; K_2HPO_4, 0.25 g L^{-1}) pH 7.0 ± 0.1 with PAC concentration ranging between 0.5 and 8 g L^{-1}.

S2b the supernatant of the centrifuged (13,000 rpm, 5 min Eppendorf centrifuge 5415C, Hamburg, Germany) and filtered (Cellulosic membranes, 0.45 μm OSMONICS INC.) outlet stream of the activated sludge treatment plant. In this case, lactose (5 gCOD L^{-1}) was added in order to have the same conditions than those found in the systems with biomass (S1 and S3); tested PAC concentrations ranged between 2 and 8 g L^{-1}.

At different time intervals samples were taken and were centrifuged to eliminate the biomass and/or PAC; then, the Cr(VI) concentration in the supernatant was determined. Hexavalent chromium was measured colorimetrically by reaction with diphenylcarbazide in acid solutions [11]. The absorbance was measured at 540 nm with a Hach spectrophotometer. Biomass concentration was measured as chemical oxygen demand [12] using a commercial kit (Hach). All assays were performed at room temperature ($20 \pm 2\,^{\circ}C$).

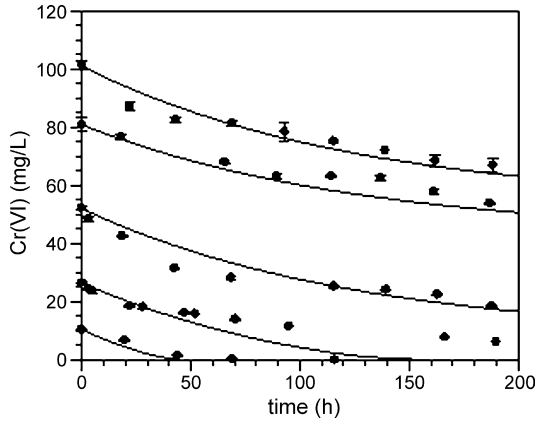


Fig. 1. Hexavalent chromium removal using activated sludge as a function of time for different initial Cr(VI) concentrations (experiment S1). Solid lines indicate the calculated values using the proposed model (Eq. (3), Table 2).

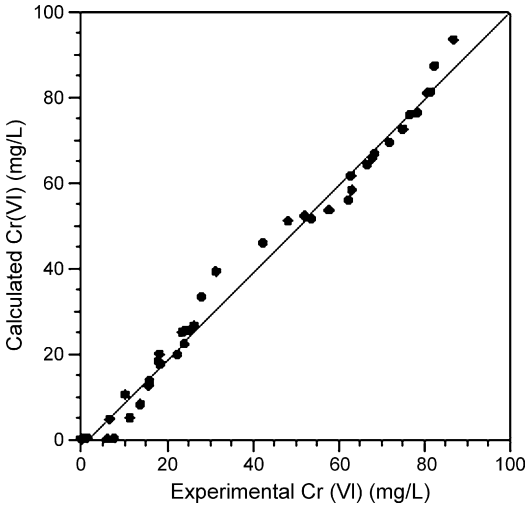


Fig. 2. Experimental vs. calculated values of Cr(VI) concentration based on Eq. (3) for all the tested initial Cr(VI) concentrations corresponding to the hexavalent chromium removal using activated sludge (experiment S1).

3. Results and discussion

3.1. Cr(VI) removal using biomass (activated sludge)

The reduction of Cr(VI) to Cr(III) using both pure and mixed cultures under aerobic conditions was previously reported by different authors [5,13,14]. The Cr(VI) reductase activity of the microorganisms is generally dependent on the presence of a suitable electron donor [5,15–19]. Fig. 1 shows the removal of Cr(VI) by activated sludge (System 1) as a function of time for different initial Cr(VI) concentrations in the mixed liquor. In these experiments biomass concentration was $2000 \pm 300\,\mathrm{mgCOD\,L^{-1}}$ and lactose was utilized as electron donor in a concentration of $5\,\mathrm{gCOD\,L^{-1}}$. Control experiments using lactose, phosphate buffer (pH 7), Cr(VI) without activated sludge and without PAC addition showed that the Cr(VI) removal in these cases was negligible.

Wang and Shen [5] demonstrated that for pure cultures the rate of Cr(VI) reduction can be expressed as a Monod-type equation:

$$-\frac{dA}{dt} = \frac{k_m A}{K_C + A} X \quad (1)$$

where A ($\mathrm{mg\,L^{-1}}$) is the concentration of Cr(VI) at time t (h); X ($\mathrm{gCOD\,L^{-1}}$) is the active biomass concentration at time t; k_m ($\mathrm{mgCr(VI)\,gCOD^{-1}\,h^{-1}}$) is the maximum specific rate of Cr(VI) reduction and K_C ($\mathrm{mgCr(VI)\,L^{-1}}$) is the half-velocity constant. In addition, the active biomass concentration may be assumed to decrease proportionally to the amount of Cr(VI) reduced due to the toxicity of Cr(VI) as follows:

$$-\frac{dX}{dt} = \frac{1}{R_C}\frac{k_m A}{K_C + A} X \quad (2)$$

where R_C ($\mathrm{mgCr(VI)\,gCOD^{-1}}$) is the maximum specific Cr(VI) reduction capacity of the active biomass [5]. Combining Eqs. (1) and (2) and integrating, the following equation was obtained:

$$t = \frac{K_C}{k_m(A_0/R_C - X_0)} \ln\left[\frac{AX_0}{A_0(X_0 - A_0 - A/R_C)}\right] + \frac{R_C}{k_m} \ln\left[\frac{X_0}{X_0 - A_0 - A/R_C}\right] \quad (3)$$

Table 2
Comparison of the kinetic parameters (Eq. (3)) for Cr(VI) removal using activated sludge in batch systems (present work) and literature data using different microorganisms

Type of culture	k_m mgCr(VI) ($\mathrm{g\,COD^{-1}\,h^{-1}}$)	K_C ($\mathrm{mgCr(VI)\,L^{-1}}$)	R_C $\mathrm{mgCr(VI)\,g^{-1}COD}$	Reference
Activated sludge	0.15 ± 0.02	1.1 ± 0.4	18.8 ± 1.6	This work
Bacillus sp.[a]	0.26	5.4	5.2	[b]
D. vulgaris ATCC 29579[a]	1.60	19.2	–	[b]
E. coli ATCC 33456[a]	1.20	8.6	17.8	[b]
P. fluorescens LB300[a]	0.21	5.6	7.8	[b]
Surface soil mixed culture[a]	0.73 ± 0.33	1.48 ± 0.11	–	[c]
Subsurface soil mixed culture[a]	2.43 ± 0.64	0.39 ± 0.51	–	[c]
River sediment mixed culture[a]	0.96 ± 0.13	0.19 ± 0.17	–	[c]
E. cloacae HO1[a]	1.04 ± 0.21	1.56 ± 0.57	–	[c]

[a] Assuming that the dry weight of one cell corresponds to 3×10^{-13} g [30], a cell volatile fraction of 0.95, and standard biomass composition ($C_5H_7O_2N$).
[b] Wang and Shen [5].
[c] Schmieman et al. [20].

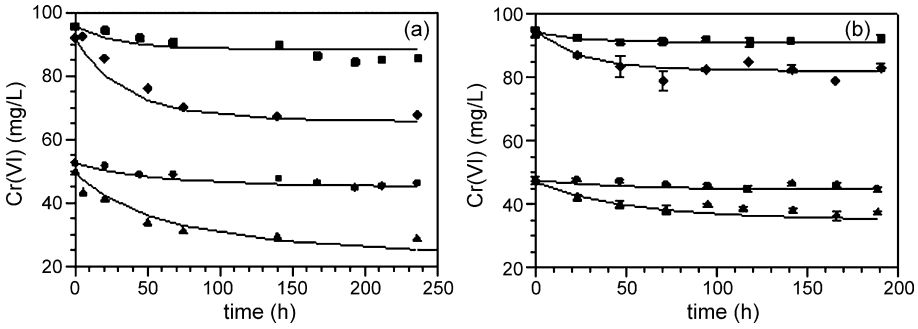


Fig. 3. Cr(VI) removal using powdered-activated carbon (PAC) in: (a) phosphate buffer pH 7.0 ± 0.1 (system S2a), (b) supernatant of the centrifuged and filtered outlet stream of the activated sludge treatment plant with lactose addition (system S2b). Symbols correspond to the following PAC and Cr(VI) initial concentrations: (●) 2 gPAC L^{-1}, 50 mgCr L^{-1}; (▲) 8 gPAC L^{-1}, 50 mgCr L^{-1}; (■) 2 gPAC L^{-1}, 95 mgCr L^{-1}; (♦) 8 gPAC L^{-1}, 95 mgCr L^{-1}. Lines represent the values predicted using the Eq. (6) with the kinetic constants shown in Table 3.

where A_0 (mg L^{-1}) is the initial Cr(VI) concentration and X_0 (gCOD L^{-1}) is the initial active biomass concentration. Eq. (3) was fitted to the experimental data of Cr(VI) concentrations versus time in order to obtain the parameters k_m, K_C, and R_C. Satisfactory agreement between model and experimental data were obtained for all the tested initial Cr(VI) concentrations (Figs. 1 and 2). Table 2 shows that the obtained coefficients were in the range of those reported by other authors. Schmieman et al. [20] studied the Cr(VI) removal kinetics of enriched mixed cultures from soil; the enrichment medium contained 10 mgCr(VI) L^{-1} and sucrose as the carbon source. Thus, the maximum specific rates of Cr(VI) reduction (k_m) reported by Schmieman et al. [20] were higher than those corresponding to non-acclimated cultures such as the activated sludge samples used in the present work. However, the half-velocity constant (K_C) corresponding to both types of mixed cultures (soil samples and the activated sludge used in our work) was lower than for pure cultures.

3.2. Cr(VI) removal using powdered-activated carbon

Fig. 3 shows the decay of Cr(VI) as a function of time for two different activated carbon concentrations in both experiments S2a (Fig. 3a) and S2b (Fig. 3b). The rate of chromium removal was higher as the concentration of activated carbon increased; the obtained results agree with those of Lalvani et al. [21] and Selvi et al. [22]. The results reported by Lee et al. [23] and Selvi et al. [22] suggested that the removal of Cr(VI) by activated carbon is a complex process that cannot only be explained on the basis of a physical adsorption or ions interchange; in addition, they pointed out that the main mechanism for Cr(VI) elimination may be the reduction to Cr(III) by the activated carbon. Selomulya et al. [24] analyzed Cr(VI) removal using different activated carbons from different precursors; these authors reported the presence of Cr(III) indicating that the tested carbons could reduce Cr(VI). The presence of Cr(III) in Cr(VI) removal assays using activated carbons had been reported by other authors [25]. Based on these works a kinetic model was proposed considering that the reaction between Cr(VI) and PAC follows a first-order kinetics with respect to each reactant (global second-order):

$$\frac{dA}{dt} = -k_A A B \tag{4}$$

$$\frac{dB}{dt} = -k_B A B \tag{5}$$

where A and B represent the concentrations of Cr(VI) (mg L^{-1}) and PAC (g L^{-1}), respectively, as a function of time (t) and k_A, k_B are second-order kinetic constants. The following expression was obtained when solving the equation system:

$$A = \frac{(k_B A_0 - k_A B_0) A_0 \exp^{(k_B A_0 - k_A B_0)t}}{(k_B A_0 - k_A B_0) - A_0 k_B (1 - \exp^{(k_B A_0 - k_A B_0)t})} \tag{6}$$

where A_0 and B_0 are the initial concentrations of Cr(VI) and PAC respectively. Values of k_A and k_B were determined by fitting Eq. (6) to the experimental data by non-linear regressions (Sigma Plot 2.0); the obtained coefficients are shown in Table 3. Fig. 3 shows that the proposed model was very effective in describing the experimental data. The experiments S2b were performed with initial Cr(VI) concentrations higher than 50 mg L^{-1}; when lower Cr(VI) concentrations were used, microbial growth was observed. Fig. 4 shows the results; when the initial Cr(VI) concentration was 50 mg L^{-1} the values of COD and pH remained approximately constant during the whole experiment, whereas when initial Cr(VI) concentration was 25 mg L^{-1}, COD and pH values began to diminish after 48 h.

Table 3
Kinetic constants of the proposed model (Eq. (6)) for Cr(VI) removal using powdered-activated carbon corresponding to systems S2a and S2b

	pH	k_A (gCarbon^{-1} L h^{-1})	k_B (mg Cr^{-1} L h^{-1})	k_A/k_B (mgCr gCarbon^{-1})	r^2
S2a	7	$1.27 \pm 0.05 \times 10^{-3}$	$3.48 \pm 0.21 \times 10^{-4}$	3.65 ± 0.27	0.9958
S2b	7	$6.60 \pm 0.85 \times 10^{-4}$	$4.38 \pm 0.69 \times 10^{-4}$	1.50 ± 0.31	0.9929

(2a) Phosphate buffer pH 7.0 ± 0.1 and (2b) Supernatant of the centrifuged and filtered outlet stream of the activated sludge treatment plant; with addition of lactose (5 g L^{-1}).

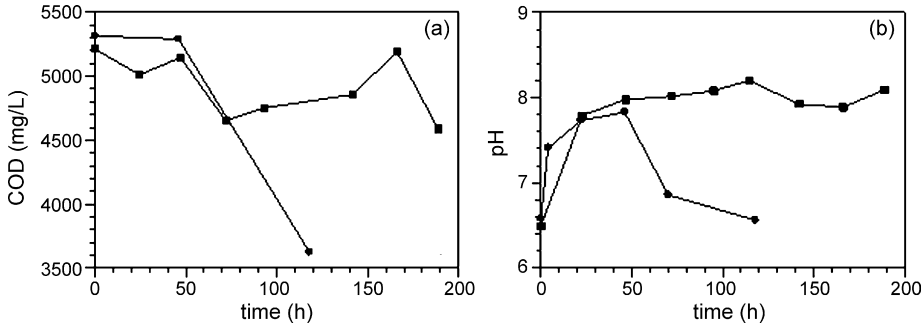


Fig. 4. Effect of the initial Cr(VI) concentration (●, 25 mg L^{-1}; ■, 50 mg L^{-1}) on (a) the soluble COD and (b) pH as a function of time using powdered-activated carbon (PAC) in the supernatant of the centrifuged and filtered outlet stream of the activated sludge treatment plant with lactose addition (system S2b).

The experiments S2a and S2b were performed to study the capacity of PAC to remove Cr(VI) taking into account the composition of the media. In experiment S2b the medium was the same as in experiments S1 and S3 where biomass was present. Fig. 3 shows that the medium strongly affects the kinetics of Cr(VI) removal with PAC. In addition, the chromium removal capacity of PAC in phosphate buffer (S2a) was higher than in the supernatant of the outlet stream of the activated sludge treatment plant (S2b). This difference can be attributed to the fact that the substances present in S2b, mostly metabolic products of the activated sludge and the lactose added, could interfere with the reduction of Cr(VI) to Cr(III) by the activated carbon. Using the proposed model the maximum specific capacity of the carbon to remove Cr(VI) can be calculated as $q_m = k_A/k_B$. When phosphate buffer was used (S2a) the value of q_m obtained in the present work (3.65 mgCr gCarbon^{-1}, Table 3) was similar to that reported by other authors. Riviera–Utrilla et al. [26] obtained values ranging between 3.3 and 3.9 mgCr gCarbon^{-1}; Selomulya et al. [24] reported maximum specific capacities ranging between 1.7 and 5.3 mgCr gCarbon^{-1} depending on pH, type of activated carbon and initial Cr(VI) concentration; Selvi et al. [22] reported a value of 3.46 mgCr gCarbon^{-1}. Nevertheless, the value of q_m obtained in the experiments using the medium 2b was lower (1.5 mgCr gCarbon^{-1}, Table 3). The difference in the obtained q_m values was determined mainly by k_A values, while k_B was similar for the two tested media (Table 3). The k_A value obtained in S2a was higher than in S2b, indicating that the Cr(VI) reduction in phosphate buffer (medium 2a) was faster than in the supernatant of the outlet stream of the activated sludge treatment plant (medium 2b). Thus, the added lactose and the metabolic products modified not only the stoichiometry (q_m) but also the kinetics (k_A) of the reduction of Cr(VI) to Cr(III) by the activated carbon decreasing both coefficients q_m and k_A.

3.3. Cr(VI) removal using the combined activated carbon–biomass system

Fig. 5 shows an example of chromium removal using powdered-activated carbon (4 gCarbon L^{-1}), biomass (2000 ± 300 mgCOD L^{-1}) and the combined activated carbon–biomass system. Chromium removal using biomass in the presence of lactose was faster than using PAC alone. In addition, Cr(VI) removal using the combined method (activated carbon–biomass system) was faster than both Cr(VI) removal using PAC or activated sludge individually.

The obtained experimental results for Cr(VI) removal using the combined activated carbon–biomass system (S3) were modeled by combining the kinetic equations corresponding to the tested systems S1 and S2:

$$\frac{dX}{dt} = -\frac{k_m A}{K_C + A}\frac{X}{R_C} \quad (2)$$

$$\frac{dA}{dt} = -\frac{k_m A}{K_C + A}X - k_A A B \quad (7)$$

$$\frac{dB}{dt} = -k_B A B \quad (5)$$

In Eq. (7) the first term of the right member represents the Cr(VI) removal by the biomass; the second term takes into account the removal of Cr(VI) using PAC. Eqs. (2), (7) and (5) were solved numerically using a fourth-order Runge–Kutta method (Sigma Plot 2.0) to calculate the Cr(VI) concentration as a function of time (Fig. 6); the coefficients used in the calculations are shown in Tables 2 and 3 corresponding to the individually performed experiments. Figs. 6 and 7 show that the simultaneous solution of Eqs. (2), (7) and (5) agreed with the experimental results.

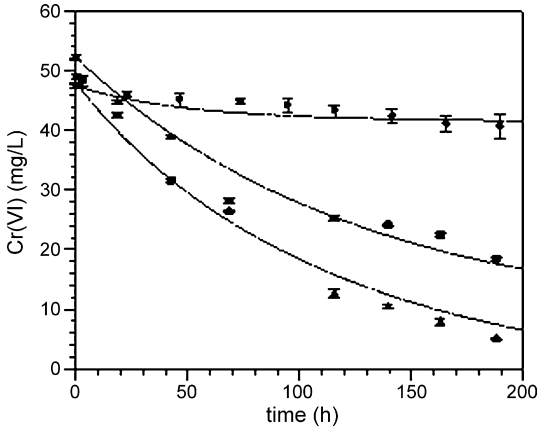


Fig. 5. Chromium removal as a function of time using activated carbon (4 gCarbon L^{-1}) (●), activated sludge (2.5 gCOD L^{-1}) (■) and the combined activated carbon (4 gCarbon L^{-1}) + biomass (2.5 gCOD L^{-1}) system (▲). Lines represent the proposed model.

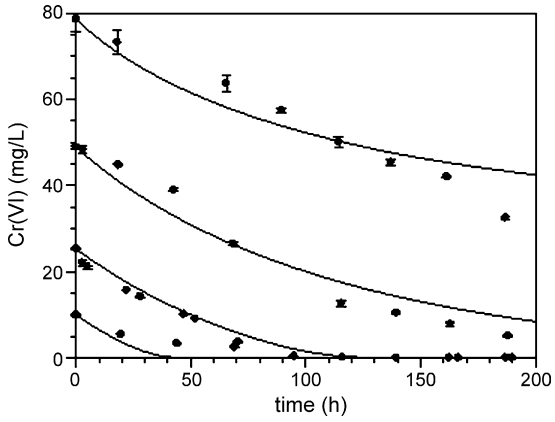


Fig. 6. Chromium removal as a function of time for different initial Cr(VI) concentrations using the combined activated carbon–biomass system (S3). In all cases the PAC concentration was 4 gCarbon L^{-1}. Lines represent the predicted curves using the proposed model (solution of Eqs. (2), (7), and (5)).

Several authors reported a stimulative or protective effect of PAC on the metabolic activity of different microorganisms or activated sludge against toxic organic substances. Taniguchi et al. [27] and Orshansky and Narkis [7] reported that the biodegradation rate of phenol and mixtures of phenol with *m*-aminobenzoic acid increased by the addition of PAC. Okada et al. [28] showed that the growth yield of *E. coli* K-12 increased in systems with PAC. Morinaga et al. [29] demonstrated that the cell adhesion on PAC enhanced the denitrification activity of *E. coli* K-12. There is not information about this enhancement or protective effect of PAC when bacteria are exposed to heavy metals. The obtained results in this work showed that the Cr(VI) removal in the combined activated carbon–biomass system can be adequately described by combining the kinetic equations proposed for the individual systems (S1 and S2) within the ranged of the tested hexavalent chromium and PAC concentrations. However, such a stimulative or protective (synergistic) effect of PAC on the metabolic activity of activated sludge against Cr(VI) cannot be discarded for higher PAC and hexavalent chromium concentrations. Thus, the model could be improved in the future including the effect of pH, temperature, dissolved oxygen and higher PAC and hexavalent chromium concentrations.

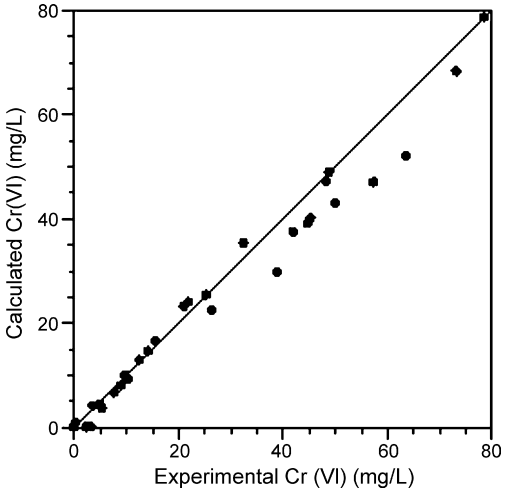


Fig. 7. Experimental vs. calculated values of Cr(VI) concentration in solution based on the simultaneous solution of Eqs. (2), (7) and (5) for all the initial Cr(VI) concentrations corresponding to the combined activated carbon–biomass system (S3).

4. Conclusions

The kinetics of Cr(VI) removal in batch cultures of activated sludge was adequately described by a Monod-type equation with respect to the chromium concentration. A satisfactory agreement between the model and experimental data was observed for all the tested initial Cr(VI) concentrations.

A first-order kinetics with respect to Cr(VI) and PAC respectively, (second global order) was proposed to model the removal of Cr(VI) when activated carbon was used individually. The proposed model was very effective in describing the experimental data for both tested media (phosphate buffer and the supernatant of the outlet stream of the activated sludge treatment plant with lactose). The amount of Cr(VI) reduced per gram of PAC (q_m) measured in phosphate buffer (S2a) was higher than the value obtained in the experiments using the supernatant of the outlet stream of the activated sludge treatment plant with lactose (S2b). In addition, the kinetic coefficient k_A obtained in S2a was higher than in S2b. Thus, the added lactose and the metabolic products modified not only the stoichiometry (q_m) but also the kinetics (k_A) of Cr(VI) to Cr(III) reduction by the activated carbon decreasing both coefficients q_m and k_A.

Cr(VI) removal in the combined activated carbon–biomass system was faster than Cr(VI) removal using PAC or activated sludge individually. Experimental results were adequately described by combining the kinetic equations proposed for the individual experiments.

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