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Effects of combining biological treatment and activated carbon on hexavalent chromium reduction

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ABSTRACT

The objectives of the present work were: (a) to analyze the Cr(VI) removal by combining activated sludge (AS) with powdered activated carbon (PAC), (b) to analyze the effect of PAC and Cr(VI) on the growth kinetics of activated sludge, and (c) to determine if the combined method (AS-PAC) for Cr(VI) removal can be considered additive or synergistic with respect to the individual processes. Chromate removal was improved by increasing PAC concentrations in both PAC and AS-PAC systems. Cr(VI) removal using the AS-PAC system was higher than using AS or PAC. The increase of Cr(VI) caused longer lag phase and lower observed specific growth rate (μ_{obs}), biomass yield ($Y_{X/S}$), and specific growth substrate consumption rate (q_S) of activated sludge; additionally, PAC did not enhance the growth kinetic parameters (μ_{obs}, $Y_{X/S}$, q_S). Cr(VI) reduction in AS-PAC system was the result of the additive effect of each individual Cr(VI) removal process.

1. Introduction

The widespread use of chromate in industries such as leather tanning, metallurgy, electroplating, petroleum refining, textile manufacturing, and pulp production has resulted in large quantities of chromium discharged into the environment (Barnhart, 1997). Chromium is usually found in trivalent (Cr(III)) and hexavalent (Cr(VI)) forms. Hexavalent chromium has high water solubility, is the most toxic among chromium species, and it is also a known carcinogen. On the other hand, trivalent chromium is less soluble in water, and it is an essential dietary element. At neutral pH, hydrolysis of Cr(III) produces insoluble chromium hydroxides that can be easily removed from wastewaters. Therefore, reducing Cr(VI) to Cr(III) constitutes the principal mechanism to decrease the Cr(VI) toxicity before being discharged into the environment.

During the last decade interest in the biological Cr(VI) removal process has greatly increased. The biological reduction of Cr(VI) to Cr(III) using both pure and mixed cultures under aerobic conditions was previously reported by many authors (Dermou and Vayenas, 2008; Asatiani et al., 2004; Stasinakis et al., 2004; Mondaca et al., 2002; Myers et al., 2000; Wang and Shen, 1997; Imai and Gloyna, 1990). Factors that affect the microbial Cr(VI) reduction have been also studied. Considering the nutritional requirements of the cells, it was demonstrated that the microbial Cr(VI) reduction occurs only if a suitable carbon source is available (Ferro Orozco et al., 2007; Stasinakis et al., 2003, 2004; Philip et al., 1998). On the other hand, Ferro Orozco et al. (2010a) concluded that the biological Cr(VI) reduction is associated to the cell multiplication phase, when there is no limitation in carbon or nitrogen sources.

The potential for biotransformation of Cr(VI) to Cr(III) can differ between microorganisms; in addition, different bacteria are able to tolerate different chromium concentrations. Therefore, another challenge to be overcome before the application of a Cr(VI) biological treatment is the chromate toxicity, which may lead to cell inactivation, causing a negatively effect on the removal process. Literature provides many reports describing Cr(VI) toxicity effects on activated sludge process and specifically, on respiration rate and bacterial growth. Vankova et al. (1999) reported that the Cr(VI) concentration that inhibited 50% of the respiration rate of activated sludge in 1 h exposure was in the range of 40–90 mgCr L^{-1}. Madoni et al. (1999) found that 1 h exposure of activated sludge to 100 mgCr L^{-1} reduced the oxygen uptake rate (OUR) by 21.5%. Maziersky (1995) observed a continuous decrease of the maximum specific growth rate (μ_m) in the presence of 2–11 mgCr L^{-1}. Stasinakis et al. (2002) reported the inhibition of the activated sludge growth exposed to chromate concentrations higher than 10 mg L^{-1}.

The addition of powdered activated carbon (PAC) into the activated sludge (AS) reactor is known for its ability to improve biological treatment efficiency, to remove refractory organic compounds, and to enhance nitrification (Çeçen and Aktas (2001). The combined activated sludge-powdered activated carbon (AS-PAC)

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system has been mostly studied for organic pollutants-containing wastewaters (Papadimitriou et al., 2009; Aktas and Çeçen, 2001; Çeçen and Aktas, 2001; Orshansky and Narkis, 1997; Jonge et al., 1991, 1996). The presence of PAC enhances the performance of the system due to the biological removal and adsorption of pollutants simultaneously. In addition, it has been reported that the biological inhibition caused by some organic compounds decreases due to the presence of PAC (Papadimitriou et al., 2009; Sher et al., 2000).

The removal of Cr(VI) using AS or PAC individually and the combined AS-PAC processes has been studied in previous works (Ferro Orozco et al., 2007, 2008). In the AS system the microbial metabolism was responsible for Cr(VI) reduction. Considering the hexavalent chromium removal by PAC alone, it was demonstrated that the main mechanism was the Cr(VI) reduction by oxidation of the carbon surface (Ferro Orozco et al., 2008). With regard to the combined system (AS-PAC), the removal of chromate was improved due to the presence of activated carbon. However, it must be considered that in those works a high ratio between biomass concentration and initial substrate concentration (X_0/S_0) was used; in those conditions the growth of the biomass was negligible. Thus, even if PAC would protect the activated sludge against Cr(VI) toxicity, such protective effect could not be measured because the high X_0/S_0 conditions using in the previous works (Ferro Orozco et al., 2007, 2008). Conversely, when the ratio X_0/S_0 is low, a significant increase of the biomass concentration is expected. In this case, the protective effect of PAC against Cr(VI) could be assessed via its effect on the growth kinetics of activated sludge, for example. Additionally, previous works demonstrated that biological Cr(VI) reduction is mostly associated to the cell multiplication phase and the maximum chromate removal rate occurs when there is no limitation on carbon or nitrogen sources. Therefore, low X_0/S_0 conditions favor the biological removal of Cr(VI) (Ferro Orozco et al., 2010a).

Among other factors, the amount of adsorbed substrates is a function of the added PAC concentration. When high PAC concentrations are used, a substantial amount of substrate may be adsorbed, leading to a potential limitation of the chromate removal rate. Ferro Orozco et al. (2010b) analyzed the adsorption of cheese whey (carbon source) onto PAC, and the effect of different PAC concentrations on the growth kinetics of activated sludge in the absence of Cr(VI). These authors found that by increasing PAC concentrations lower initial soluble COD values were obtained. Thus, although the presence of high PAC concentrations enhances the removal of Cr(VI) by oxidation of the carbon surface (Ferro Orozco et al., 2008), PAC also decreases the growth substrate bioavailability. Therefore, the actual substrate concentration in solution is lower leading to high X_0/S_0 ratios that could hamper the biological reduction of Cr(VI).

In order to improve the knowledge concerning the combined activated sludge-powdered activated carbon process for Cr(VI) removal, the present work analyze the Cr(VI) removal by combining activated sludge with powdered activated carbon in the presence of growing biomass, the effect of PAC concentration on the growth kinetics of activated sludge in the presence of Cr(VI) and if the application of the combined method (AS-PAC) for Cr(VI) removal can be considered additive or synergistic with respect to the use of the individual processes.

2. Methods

2.1. Biological and chemical materials

Dehydrated cheese whey was obtained from Food S.A. (Villa Maipú, Argentina). Powdered activated carbon (PAC) type 061 was from Clarimex S.A. (Mexico). The biomass used in all the experiments was harvested from an aerobic laboratory scale (4.5 L) activated sludge reactor with partial biomass recycle. The reactor was fed with a synthetic wastewater with the following composition: dehydrated cheese whey 1.5 g, $(NH_4)_2SO_4$ 0.94 g, and $NaHCO_3$ 1.03 g dissolved in 1 L of tap water. The soluble chemical oxygen demand (COD_S) of the synthetic wastewater was 1500 mg L^{-1}. The hydraulic retention time was 2 d; the sludge age was maintained at 45d by daily wasting of mixed liquor directly from the reactor. During the experiments the temperature of the reactor was 20 ± 2 °C. Under steady-state conditions dissolved oxygen (DO) concentration was above 4 mg L^{-1}, pH was 7.5 ± 0.4, COD_S of the effluent ranged between 30 and 80 mg L^{-1}, and total suspended solid (TSS) concentration ranged between 2600 and 2900 mgTSS L^{-1}.

2.2. Cr(VI) reduction assays in batch reactors using activated sludge (AS)

In order to study the biological Cr(VI) reduction and the effect of the initial Cr(VI) concentration on the growth kinetics of activated sludge (AS), batch assays were performed in 250 mL aerated vessels. Inoculum was obtained from the activated sludge reactor described previously (Section 2.1); the biomass was washed three times with phosphate buffer (KH_2PO_4 2 g L^{-1}, K_2HPO_4 0.5 g L^{-1}, pH = 7) before performing the assays. The medium composition was the following: organic substrate 5 gCOD L^{-1} (cheese whey), ammonium sulfate 212 mgN L^{-1}, and micronutrient solutions M1 and M2 (1 mL L^{-1}). The composition of M1 was (expressed as g/100 ml): $FeSO_4.7H_2O$ 1.5, $ZnSO_4.7H_2O$ 0.5, $MnSO_4.H_2O$ 0.3, $CuSO_4.5H_2O$ 0.075, $CoCl_2.6H_2O$ 0.015, and citric acid 0.6. M2 solution contained the following (g/100 ml): $(NH_4)_6Mo_7O_{24}.4H_2O$ 0.05, BO_3H_3 0.01, KI 0.01. All inorganic salts used in the present work were commercial products of reagent grade from Anedra (San Fernando, Argentina). In all the experiments the initial biomass concentration (X) was 700 ± 50 mgTSS L^{-1}; the initial X_0/S_0 ratio was 0.14 mgTSS $mgCOD^{-1}$, which allowed observing an exponential growth phase. The initial N:COD ratio of the culture medium was 42.4 mgN $gCOD^{-1}$; thus, the nitrogen source was in excess with respect to the carbon source, which was the growth limiting substrate (Ferro Orozco et al., 2010a). Tested Cr(VI) concentrations were 25, 50, 100 and 300 mgCr L^{-1}. Control experiments without Cr(VI) were also performed. At predetermined time intervals samples were taken to determine soluble Cr(VI), total suspended solids (TSS), soluble COD (COD_S), and pH. All the assays were performed at a temperature of 20 ± 2 °C.

For each experiment, the observed specific growth rate (μ_{obs}, h^{-1}) was calculated from the slope of the linear part of the plot of ln(X) as a function of time. The biomass yield ($Y_{X/S}$, mgTSS $mgCOD_S^{-1}$) was obtained from the slope of X as a function of the COD_S concentration. The specific growth substrate consumption rate (q_S, mgCOD $mgTSS^{-1}$ h^{-1}) was calculated as follows:

$$q_S = \mu_{obs}/Y_{X/S} \quad (1)$$

2.3. Cr(VI) reduction assays in batch reactors using powdered activated carbon (PAC)

Cr(VI) removal batch assays were carried out as it was described in the previous section, but without the addition of biomass. Initial Cr(VI) concentration ranged between 25 and 100 mgCr L^{-1} and tested PAC concentrations were 2, 4 and 8 g L^{-1}. At predetermined time intervals, samples were taken and centrifuged to eliminate the PAC; then, Cr(VI) concentration in the supernatant was measured.

2.4. Cr(VI) reduction assays in batch reactors using the combined activated sludge - powdered activated carbon system (AS-PAC)

These experiments were performed as it was described in Section 2.2. Tested PAC concentrations were 2, 4, and 8 g L^{-1}. The initial Cr(VI) concentrations were 0, 25, 50, 100 and 300 mgCr L^{-1}. At predetermined time intervals samples were taken to determine soluble Cr(VI), total suspended solids (TSS), soluble COD (COD_S), and pH. From these data μ_{obs}, $Y_{X/S}$, and q_S were calculated as it was described previously in Section 2.2.

2.5. Determination of the type of interaction between the individual Cr(VI) removal processes (AS or PAC) in the combined AS-PAC system

The type of interaction between the individual Cr(VI) removal processes (AS or PAC) in the combined AS-PAC system was determined as follows. Removals of Cr(VI) obtained by each individual system were calculated: ΔCr_{AS} represented the reduction of Cr(VI) by activated sludge; ΔCr_{PAC} corresponded to the Cr(VI) removal by PAC. The experimental Cr(VI) removal by the combined AS-PAC system ($\Delta Cr_{AS\text{-}PAC}$) was compared to the sum of the Cr(VI) removal by PAC in the absence of biomass (ΔCr_{PAC}), and by activated sludge in the absence of PAC (ΔCr_{AS}). Then, the type of interaction between the individual Cr(VI) removal systems (AS or PAC) in the combined AS-PAC system was defined as follows:

$$\text{Synergism}: \quad \Delta Cr_{AS\text{-}PAC} > \Delta Cr_{AS} + \Delta Cr_{PAC} \tag{2a}$$

$$\text{No interactions}: \quad \Delta Cr_{AS\text{-}PAC} = \Delta Cr_{AS} + \Delta Cr_{PAC} \tag{2b}$$

$$\text{Antagonism}: \quad \Delta Cr_{AS\text{-}PAC} < \Delta Cr_{AS} + \Delta Cr_{PAC} \tag{2c}$$

2.6. Analytical methods

Total suspended solids (TSS) were used to measure the biomass concentration (X, mgTSS L^{-1}). Known sample volumes (8 mL in this work) were poured into pre-weighted centrifuge tubes, centrifuged and washed twice with distilled water, and placed at 105 °C for 24 h; TSS of each sample was calculated as the difference between the final weight (dry sample + tube) and the initial weight (tube alone) divided by the sample volume. When PAC was present, the biomass concentration was calculated as the difference between TSS and the added PAC concentration (Ferro Orozco et al., 2010b).

Growth substrate (S) expressed as soluble COD (COD_S) was determined as follows: 3-mL of culture samples were centrifuged for 5 min at 16110g using an Eppendorf 5415C centrifuge. Because a proportion of the PAC particles could not be removed using this procedure, the supernatant was filtered through 0.45 μm cellulosic membranes (Osmonics Inc.). Then, soluble COD of the filtrate was determined using commercial reagents (Hach Company, Loveland, CO).

Cr(VI) of the filtrate was determined colorimetrically using a spectrophotometer (Hach DR 2000) at 540 nm by reaction with 1,5-diphenylcarbazide in acid solution (APHA, 1989).All the results presented in this work are average values of at least two experiments.

3. Results and discussion

3.1. Cr(VI) removal by AS, PAC, and the combined AS-PAC system

Fig. 1 shows the removal of Cr(VI) as a function of time by the individual systems activated sludge (AS, Fig. 1a,c,e), and powdered activated carbon (PAC, Fig. 1b,d,f), and by the combined activated sludge-powdered activated carbon system (AS-PAC, Fig. 1a,c,e). Within the tested conditions, AS could remove about 11–16 mgCr L^{-1}, regardless the initial Cr(VI) concentration (Fig. 1a,c,e). Ferro Orozco et al. (2010b) demonstrated that in the cases when the nitrogen source is in excess with respect to the carbon source (as it was in the present work), the amount of Cr(VI) reduced by AS is proportional to the initial COD concentration, being about 2.9 mgCr $gCOD^{-1}$ the reported proportionality constant. Taking into account that in the present work the initial COD concentration was 5 g L^{-1}, the Cr(VI) reduction calculated using the above mentioned constant is about 14.5 mgCr L^{-1}, which is in agreement with the obtained Cr(VI) removal by AS.

With regard to the reduction of Cr(VI) by PAC, Fig. 1b,d,f shows that the increase of the initial PAC concentration improved the chromate removal. However, in most cases this reduction was close to the obtained by AS (Fig. 1a,c,e); PAC was slightly better than AS to reduce Cr(VI) only when the initial Cr(VI) was 100 mg L^{-1} and using 4 or 8 gPAC L^{-1} (Fig. 1f). Early reports by Lee et al. (1995) and Selvi et al. (2001) suggested that the removal of Cr(VI) by PAC is a complex process that cannot only be explained on the basis of a physical adsorption or ions interchange. Those authors pointed out that the main mechanism for Cr(VI) elimination may be its reduction to Cr(III) by the PAC surface. Selomulya et al. (1999) analyzed Cr(VI) removal using different activated carbons from different precursors; those authors reported the presence of Cr(III), indicating that the tested carbons could reduce Cr(VI). The formation of Cr(III) during Cr(VI) removal assays using activated carbons had been reported by other authors (Ferro Orozco et al., 2007; Perez-Candela et al., 1995).

Fig. 1a,c,e shows that chromate removal by the combined AS-PAC system was enhanced by increasing the added PAC concentration. In addition, for all the initial PAC concentrations tested Cr(VI) reduction using the combined AS-PAC system was higher than the obtained using each individual AS or PAC systems. For example, for an initial Cr(VI) concentration of 25 mgCr L^{-1}, when the combined AS-PAC system was tested using the lower PAC concentration (2 g L^{-1}), the final Cr(VI) concentration was 13 mgCr L^{-1} (Fig. 1a). This final Cr(VI) concentration was lower than the obtained by using AS (16 mgCr L^{-1}) or PAC alone (19 mgCr L^{-1}). Even more, using 8 g L^{-1} of PAC alone (the highest tested PAC concentration) the final Cr(VI) concentration was about 15 mgCr L^{-1} (Fig. 1b). Therefore, the removal of Cr(VI) by PAC using the highest tested concentration (8 g L^{-1}) was lower than the combined AS-PAC with the lower tested PAC concentration (2 g L^{-1}).

As it was mentioned previously, different authors suggested that the inhibition caused by toxic compounds on microbial metabolism decreases due to the presence of PAC (Papadimitriou et al., 2009; Sher et al., 2000). The improvement of the chromate removal in the AS-PAC system in comparison with the individual systems (AS or PAC alone) could be attributed to the additive effects of both individual Cr(VI) removal systems. Moreover, an enhancement of the microbial metabolism caused by the presence of PAC may also be considered. If this is the case, the removal of chromate in the combined AS-PAC system should be higher than the sum of the individual processes due to the favorable interaction between them (synergism).

3.2. Effect of PAC and initial Cr(VI) concentrations on the biomass growth kinetics

Batch growth experiments were performed using Cr(VI) concentration ranging from 0 to 300 mgCr L^{-1} and PAC concentrations 0 to 8 gPAC L^{-1}. Fig. 2 shows examples of the growth substrate (S) and the observed biomass (X) concentrations as a function of time in the absence of PAC (open symbols) and in the presence of 4 g L^{-1} (grey symbols). Considering that similar trends for 2, 4, and

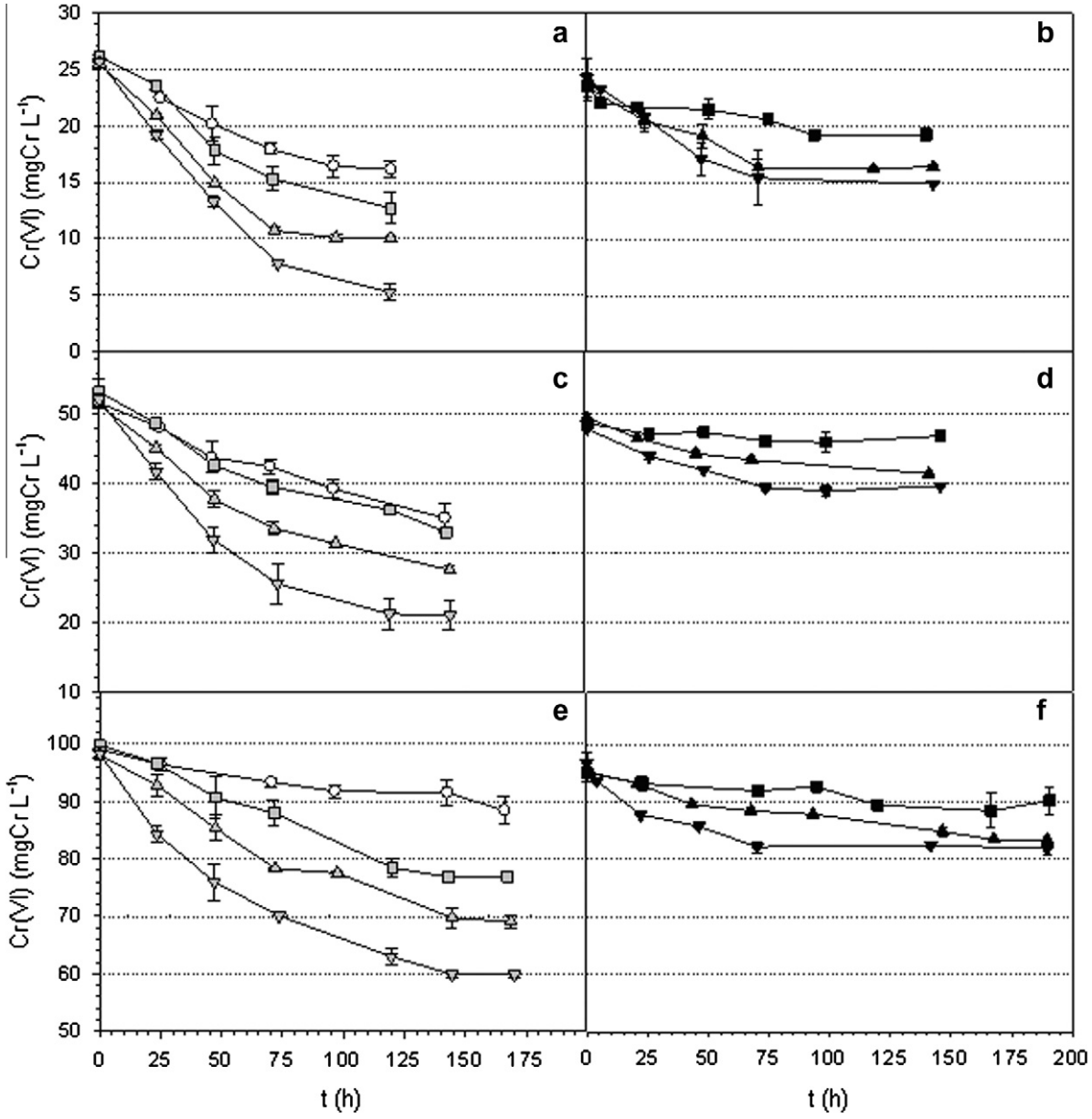

Fig. 1. Cr(VI) concentration as a function of time corresponding to the following Cr(VI) removal systems: AS (open symbols), PAC alone (black symbols), AS-PAC (grey symbols). Initial Cr(VI) concentrations were: 25 (a, b), 50 (c, d), and 100 (e, f) mgCr L^{-1}. Tested PAC concentrations: 0 g L^{-1} (circle), 2 g L^{-1} (square), 4 g L^{-1} (triangle up), and 8 g L^{-1} (triangle down). For AS and AS-PAC systems, initial biomass and soluble COD concentrations were 700 ± 50 mgTSS L^{-1} and 5 gCOD L^{-1}, respectively. Bars indicate one standard deviation.

8 gPAC L^{-1} were observed, only the results corresponding to the addition of 4 gPAC L^{-1} are shown in Fig. 2.

Control experiments without the addition of Cr(VI) showed a lag phase of 8 h; during this period the growth substrate and the biomass concentrations remained constant. After the lag phase, an increase of the biomass concentration and a decrease of the soluble COD were observed in both systems (with and without PAC). Finally, a decrease of X was observed as a result of the growth substrate depletion (Fig. 2a,b). In the experiments carried out with 25 mgCr L^{-1} (Fig. 2c,d) the same qualitative behavior was observed; however, the lag phase increased from 8 to 25 h, regardless of the presence of PAC. This increment of the lag phase due to the presence of Cr(VI) was observed for both the substrate consumption (Fig. 2c) and biomass growth (Fig. 2d). A similar trend was observed when the experiments were performed with 50 mgCr L^{-1} (Fig. 2e,f) and 100 mgCr L^{-1} (Fig. 2g,h). The increase of the lag phase as a function of the initial Cr(VI) concentration was also reported by other authors (Elangovan and Philip, 2009; Li et al., 2007; Bae et al., 2000).

Fig. 2 shows that in comparison with the control experiment without Cr(VI), the observed maximum biomass concentration decreased due to the presence of 25 mgCr L^{-1}. However, the increase of the chromate concentration from 25 to 100 mgCr L^{-1} did not produce further reductions in the maximum biomass concentration. The time required to deplete the growth substrate increased by increasing the initial chromate concentration. For Cr(VI) concentrations of 25, 50, and 100 mgCr L^{-1} the time required to consume the growth substrate was 70, 97, and 167 h, respectively (Fig. 2c,e,g). Experiments performed with 300 mgCr L^{-1} (Fig. 2i,j) did not show an increment of the biomass or substrate consumption during 300 h, suggesting a loss of metabolic activity due to chromium toxicity. This result indicates that the threshold

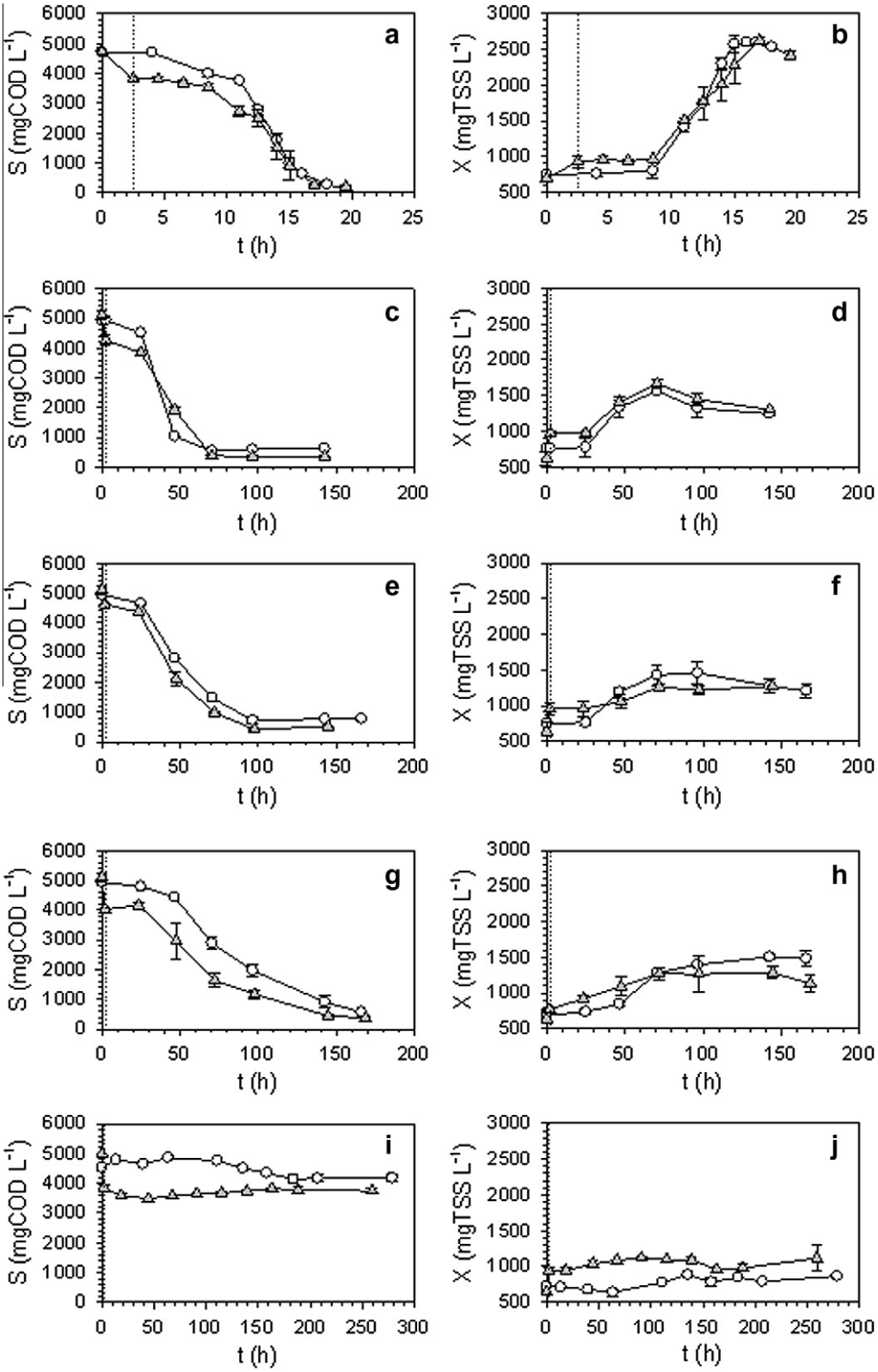

Fig. 2. Effect of Cr(VI) on biomass (X) growth and substrate (S) consumption corresponding to the following Cr(VI) removal systems: AS (open circles), AS-PAC (grey triangles). In these examples 4 g L^{-1} of PAC was added to the AS-PAC system. Tested initial Cr(VI) concentrations were 0 (a, b), 25 (c, d), 50 (e, f), 100 (g, h), and 300 (i, j) mgCr L^{-1}. In all cases, initial biomass and soluble COD concentrations were 700 ± 50 mgTSS L^{-1} and 5 gCOD L^{-1}, respectively. Bars indicate one standard deviation.

inhibitory concentration of Cr(VI) is within the range of 100 to 300 mg L^{-1}. Fig. 2 also shows that the presence of PAC did not have effect on the obtained maximum biomass concentration or on the time required to deplete the growth substrate (COD_S). It is important to point out that in all the experiments with the addition of PAC, a fast decrease of COD_S and an increase of TSS was observed within the first 2.5 h (Fig. 2, vertical dotted lines). Besides, by increasing PAC concentrations (from 2 to 8 g L^{-1}) lower initial

COD_S values were obtained. For example, COD_S decreased from 5100 mg L^{-1} in the case without PAC to 3400 ± 200 and 4200 ± 200 mg L^{-1} when PAC concentrations were 4 and 8 g L^{-1}, respectively. This phenomenon was independent of the presence of chromate, it was attributed to the adsorption of the growth substrate onto the carbon surface (Ferro Orozco et al., 2010b).

Based on the obtained time profiles of the growth substrate (S) and the observed biomass (X), the effects of PAC and the initial Cr(VI) concentration on the observed specific growth rate (μ_{obs}), biomass yield ($Y_{X/S}$), and specific growth substrate consumption rate (q_S) were evaluated.

Fig. 3 shows that for all the tested PAC concentrations, the addition of 25 mgCr L^{-1} produced a marked decrease on μ_{obs} with respect to the experiment without chromium. However, further increments from 25 to 100 mgCr L^{-1} caused only a minor decrease in μ_{obs} (inset in Fig. 3). Similar results were reported by other authors. Maziersky (1995) studied the growth of activated sludge in a chemostat; the author found a continuous reduction of μ_{max} for inlet Cr(VI) concentrations ranging between 0.1 and 11 mgCr L^{-1}. Bae et al. (2000) studied the Cr(VI) removal using batch cultures of *E. coli* ATCC 33456; those authors reported that the addition of increasing Cr(VI) concentrations from 5 to 50 mgCr L^{-1} generated a gradual decrease on the specific growth rate. The effect of the addition of Cr(VI) on the values of μ_{max} corresponding to activated sludge was studied by Stasinakis et al. (2002); those authors also reported a decrease of the maximum specific growth rate as a function of Cr(VI). Gikas and Romanos (2006) reported a decrease of μ_{max} with increasing Cr(VI) concentrations up to 10 mg L^{-1} in activated sludge batch reactors; those authors reported that μ_{max} values were almost zero for concentrations higher than 160 mgCr L^{-1}, which is within the range reported in the present work.

With regard to the effect of PAC on μ_{obs}, Fig. 3 shows that a gradual decrease on μ_{obs} was obtained by increasing PAC concentration. This effect was evident in the case without Cr(VI) and also for all the tested initial Cr(VI) concentrations (inset in Fig. 3). Similar findings in the absence of Cr(VI) were reported by Ferro Orozco et al. (2010b).

Fig. 4 shows the effects of Cr(VI) and PAC on the biomass yield ($Y_{X/S}$). The value of $Y_{X/S}$ decrease from 0.47 ± 0.03 mgTSS $mgCOD^{-1}$ in the experiment without Cr(VI) to 0.19 ± 0.03 mgTSS $mgCOD^{-1}$ in the presence of 25 mgCr L^{-1}. Then, considering the experimental errors, $Y_{X/S}$ remained about 0.19 ± 0.01 mgTSS $mgCOD^{-1}$ for chromate concentrations higher than 25 mgCr L^{-1}. Besides, Fig. 4 shows that $Y_{X/S}$ values were not affected by the presence of PAC for all the tested initial Cr(VI) concentrations.

The effects of Cr(VI) and PAC on the specific growth substrate consumption rate (q_S) (Fig. 5) were similar to those corresponding to the observed specific growth rate (μ_{obs}) (Fig. 3). For all the tested PAC concentrations, 25 mgCr L^{-1} caused a marked decrease of q_S with respect to the control experiment (without chromium); the effect of further incrementing Cr(VI) concentrations beyond 25 mgCr L^{-1} on q_S was less marked (inset in Fig. 5). Coefficients q_S and μ_{obs} are related by Eq. (1); thus, because $Y_{X/S}$ values were not affected by PAC (Fig. 4), both q_S and μ_{obs} showed a similar trend with respect to the presence of different PAC concentrations.

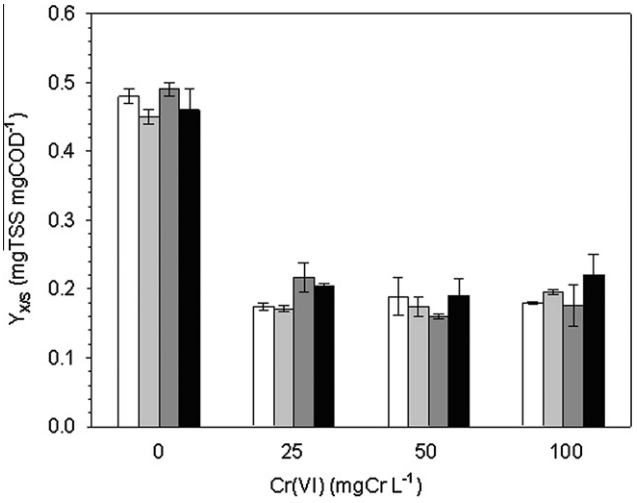

Fig. 4. Effect of PAC and Cr(VI) concentrations on the biomass yield ($Y_{X/S}$, mgTSS mg COD^{-1}) of activated sludge in batch reactors. PAC concentrations: (□) 0 g L^{-1}, (■) 2 g L^{-1}, (■) 4 g L^{-1}, (■) 8 g L^{-1} . In all cases, initial biomass and soluble COD concentrations were 700 ± 50 mgTSS L^{-1} and 5 gCOD L^{-1}, respectively. Bars indicate one standard deviation.

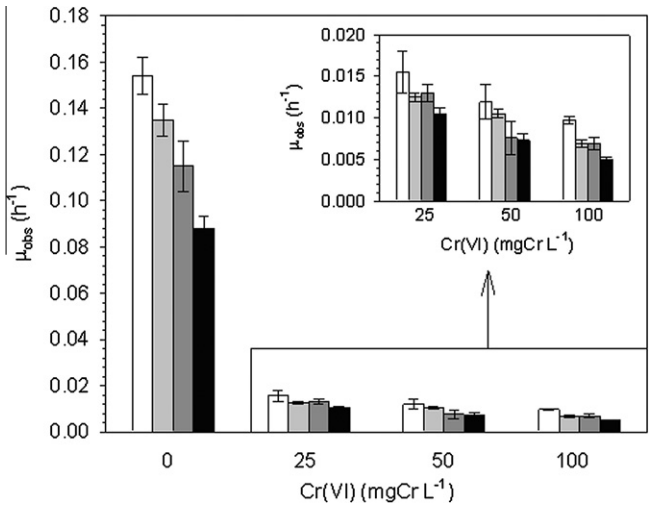

Fig. 3. Effect of PAC and Cr(VI) concentrations on the observed specific growth rate (μ_{obs}, h^{-1}) of activated sludge in batch reactors. PAC concentrations: (□) 0 g L^{-1}, (■) 2 g L^{-1}, (■) 4 g L^{-1}, (■) 8 g L^{-1}. In all cases, initial biomass and soluble COD concentrations were 700 ± 50 mgTSS L^{-1} and 5 gCOD L^{-1}, respectively. Bars indicate one standard deviation.

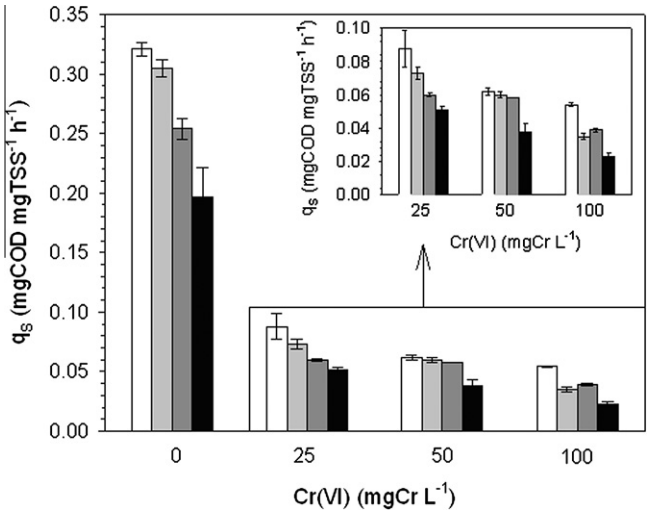

Fig. 5. Effect of PAC and Cr(VI) concentrations on the specific growth substrate consumption rate (q_S, mgCOD $mgTSS^{-1}$ h^{-1}) of activated sludge in batch reactors. PAC concentrations: (□) 0 g L^{-1} , (■) 2 g L^{-1} , (■) 4 g L^{-1}, (■) 8 g L^{-1}. In all cases, initial biomass and soluble COD concentrations were 700 ± 50 mgTSS L^{-1} and 5 gCOD L^{-1}, respectively. Bars indicate one standard deviation.

3.3. Determination of the type of interaction between the individual Cr(VI) removal processes (AS or PAC) in the combined AS-PAC system

From the previous analysis it could be concluded that the addition of PAC into activated sludge reactors for the treatment of Cr(VI)-containing wastewaters did not produce an enhancement of the microbial metabolism. Therefore, the observed improvement on the chromate removal of the combined AS-PAC system in comparison with the individual treating systems (AS or PAC) cannot be explained by this mechanism. Moreover, these findings suggest that the removal of chromate by the combined AS-PAC system could be simply described as the sum of the effects of each individual treatment (AS and PAC), rather than being represented by a synergistic process.

In order to demonstrate if the combined method (AS-PAC) for Cr(VI) removal can be considered additive or synergistic with respect to the use of the individual processes, the removal of Cr(VI) obtained by the individual systems were calculated from the data shown in Fig. 1. Tables 1 and 2 shows the removal of Cr(VI) obtained by the individual systems: ΔCr_{AS} represents the removal of Cr(VI) by activated sludge, and ΔCr_{PAC} corresponds to the removal of Cr(VI) by PAC alone. In Table 3 the experimental Cr(VI) removal obtained by the combined AS-PAC system ($\Delta Cr_{(AS\text{-}PAC)}$) was compared to the sum of the Cr(VI) removal by PAC in the absence of biomass (ΔCr_{PAC}), and by the activated sludge system in the absence of PAC (ΔCr_{AS}). Table 3 shows that in all cases, the removal of Cr(VI) calculated by the sum of the individual process ($\Delta Cr_{AS} + \Delta Cr_{PAC}$) was close to those obtained in the combined AS-PAC system. A t-test (Zar, 1999) showed that there were no significant differences ($p < 0.05$) between calculated and experimental values. Thus, based on the definition of the type of interaction adopted in this work (Eq. (2a), (2b), (2c)), synergism or antagonism between the individual Cr(VI) reduction processes could not be established. Therefore, the observed improvement on the removal of Cr(VI) in the combined AS-PAC system can be adequately described as the sum of the effects of each individual treatment (AS and PAC), rather than being represented by a synergistic process and without a significant interference between each other.

Table 1
Cr(VI) removal by activated sludge (ΔCr_{AS}) as a function of the initial tested chromate concentration.

Cr(VI) (mgCr L^{-1})	ΔCr_{AS} (mgCr L^{-1})
25	13.39 ± 3.51
50	16.15 ± 2.45
100	13.42 ± 2.72

Table 2
Cr(VI) removal by PAC (ΔCr_{PAC}) as a function of the initial tested chromate and PAC concentrations.

PAC (g L^{-1})	Cr(VI) (mgCr L^{-1})	ΔCr_{PAC} (mgCr L^{-1})
2	25	5.56 ± 1.65
	50	4.06 ± 0.92
	100	4.66 ± 2.10
4	25	8.98 ± 0.82
	50	10.20 ± 1.60
	100	11.40 ± 1.96
8	25	12.00 ± 6.35
	50	10.90 ± 1.27
	100	12.39 ± 2.70

Table 3
Comparison between the removal of Cr(VI) by the combined AS-PAC system ($\Delta Cr_{AS\text{-}PAC}$) and the removal calculated from the sum of the individual processes ($\Delta Cr_{AS} + \Delta Cr_{PAC}$, see Tables 1 and 2) as a function of the initial tested chromate and PAC concentrations.

PAC (g L^{-1})	Cr(VI) (mgCr L^{-1})	$\Delta Cr_{AS\text{-}PAC}$ (mgCr L^{-1})	$\Delta Cr_{AS} + \Delta Cr_{PAC}$ (mgCr L^{-1})
2	25	13.40 ± 1.40	18.95 ± 3.88
	50	18.20 ± 1.90	20.21 ± 2.62
	100	22.80 ± 0.82	18.08 ± 3.44
4	25	15.40 ± 0.30	22.37 ± 3.60
	50	23.80 ± 0.60	26.35 ± 2.93
	100	29.00 ± 1.35	24.82 ± 3.36
8	25	20.40 ± 0.70	25.39 ± 7.26
	50	30.90 ± 2.50	27.05 ± 2.76
	100	38.40 ± 1.11	25.82 ± 3.84

4. Conclusions

This work analyzes the removal of Cr(VI) using activated sludge (AS), powdered activated carbon (PAC), and the combined AS-PAC system. Chromate removal was improved by increasing PAC concentrations in both PAC and AS-PAC systems. In addition, Cr(VI) removal using the combined AS-PAC system was higher than using AS or PAC individually. However, the presence of PAC did not enhance the growth kinetic parameters. The observed improvement of the Cr(VI) removal in the combined AS-PAC system in comparison with the individual AS or PAC treatments was the result of the additive effect of each Cr(VI) removal process.

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