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Dynamic response of combined activated sludge-powdered activated carbon batch systems

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ABSTRACT

The objective of this study was to evaluate the effect of powdered activated carbon (PAC) on the growth kinetics of activated sludge; in addition, a kinetic model for this system was developed. Adsorption kinetic experiments of the growth substrate (cheese whey) in the absence of activated sludge were carried out in conical flasks (20 °C, pH 7). Substrate adsorption attained the equilibrium within the first hour. The Langmuir adsorption equation adequately fitted the specific adsorption capacity (q_C) as a function of the soluble COD (COD_S). Activated sludge batch growth experiments in the presence of different PAC concentrations were also performed. Specific growth rate (μ_{obs}) and specific oxygen uptake rate (q_{O_2}) decreased as PAC concentration increased; however, stoichiometric coefficients $Y_{X/S}$ and $Y_{O/S}$ were almost constant. A mathematical model was developed to represent the effect of PAC on the microbial growth kinetics. The model combined biochemical processes (biomass growth, substrate consumption and product generation) with the adsorption kinetics of the substrate onto PAC. A good agreement between the proposed model and the experimental data was obtained. Simulations show that PAC acts as a buffer of substrate, yielding slower responses to changes of the substrate concentration.

1. Introduction

Activated sludge (AS) treatment is a technically and economically feasible option to treat many types of wastewaters containing highly biodegradable organic matter [1]. Many hazardous substances are transformed into less harmful compounds by cometabolism. The term cometabolism can be defined as the transformation of a nongrowth (also called secondary) substrate by growing cells in the presence of a growth (or primary) substrate. Because cometabolic reactions yield no carbon or energy benefits to the transforming cells, a primary substrate must be available to grow new cells, provide an energy source, and induce production of cometabolic enzymes [2]. For this reason, the bioavailability of primary substrates is a key factor for the biodegradation of hazardous compounds.

Refractory organic compounds and heavy metals often can negatively affect the micro-organisms in activated sludge, decreasing the efficiency of the treatment. In these cases, the addition of powdered activated carbon (PAC) into the aeration basin has been proposed as a suitable technique to protect the activated sludge against toxic wastewaters [3,4]. Organic matter removal in AS–PAC systems is the combination of adsorption and biodegradation. Activated carbon in conjunction with activated sludge increases the removal efficiency by adsorbing non-biodegradable, toxic and/or inhibitory organics and some heavy metals [5–7]. However, PAC may also adsorb primary substrates, decreasing the cometabolism of certain hazardous compounds. Therefore, although the overall performance of the combined AS–PAC process are better than the conventional activated sludge system, the removal capacity of hazardous compounds by cometabolism may decrease.

There are many reports concerning the advantages of the combined AS–PAC process over the conventional activated sludge system to remove organic matter. Some authors have reported an apparent synergism in the combined AS–PAC process, e.g., the total effect of adsorption and biological oxidation being greater than the sum of their effects taken independently [3,8,9]. However, there are reports that organic matter removal in these systems is a simple addition of effects from carbon adsorption and biological removal [10–13]. These contradictory reports indicate that mechanisms involved on the combined AS–PAC process are not entirely elucidated. In addition, they reflect the difficulty to clearly define and to quantify the concept of synergism. In order to evaluate the degree of synergism of the AS–PAC process to remove a given hazardous/toxic compound, many researchers often studied its removal by using AS alone, then the efficiency of PAC to remove

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Table 1
Some characteristics of the powdered activated carbon (PAC).

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

such compound, and finally the performance of the combined AS–PAC process. Then, synergism degree can be evaluated comparing the removal efficiency of the hazardous compound for these systems [14]. However, this methodology relies on the assumption that PAC has a negligible effect on microbial growth kinetics.

The removal of Cr(VI) using AS and AS–PAC processes were studied in previous works [6,7]. It was proved that activated sludges are capable of reducing Cr(VI) to Cr(III) if a suitable electron donor is available [6]. In the cases when the biomass growth is negligible (e.g. high initial biomass to substrate ratio), Cr(VI) removal using the combined AS–PAC process can be adequately described by a simple combination of the kinetic expressions proposed for AS and PAC alone, respectively [7]. However, when the initial biomass to substrate ratio is low, a significant increase of the biomass concentration would be expected. In such cases PAC addition may affect the microbial growth kinetics (and Cr(VI) removal, for example) due to the adsorption of the growth substrate.

The objectives of this study were (a) to determine the adsorption kinetic and equilibrium isotherm of the growth substrate (cheese whey) onto PAC in the absence of biomass, (b) to analyze the effect of different PAC concentrations on the growth kinetics of activated sludge, and (c) to propose a kinetic model for the combined AS–PAC process.

2. Materials and methods

2.1. Biological and chemical materials

All inorganic salts used in the present work were commercial products of reagent grade from Anedra (San Fernando, Argentina). Dehydrated cheese whey was from Food S.A. (Villa Maipú, Argentina). Powdered activated carbon (PAC) type 061 was from Clarimex S.A. (Mexico); several characteristics of the used PAC are shown in Table 1.

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 [6,7]: 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 45 d 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 mg L^{-1}.

2.2. Growth substrate adsorption experiments on PAC in the absence of biomass

Growth substrate (cheese whey) adsorption experiments onto PAC were carried out in 200 mL well-agitated conical flasks at a constant temperature (20 ± 2 °C) and pH (7.00 ± 0.05). Adsorption assays were performed in the same media used in the biomass growth tests in order to obtain comparable results. The medium was prepared dissolving in 1 L of distilled water the following [15]: $(NH_4)_2SO_4$ (1 g), KH_2PO_4 (2 g), K_2HPO_4 (0.5 g), micronutrient solutions M1 (1 mL) and M2 (1 mL). The composition of the micronutrient solution M1 was (in g/100 mL): $FeSO_4{\cdot}7H_2O$ 1.5, $ZnSO_4{\cdot}7H_2O$ 0.5, $MnSO_4{\cdot}H_2O$ 0.3, $CuSO_4{\cdot}5H_2O$ 0.075, $CoCl_2{\cdot}6H_2O$ 0.015, and citric acid 0.6. M2 solution contained (in g/100 mL): $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ 0.05, BO_3H_3 0.01, KI 0.01. The initial pH was adjusted to 7.00 ± 0.05 adding a few drops of a concentrated NaOH solution.

2.2.1. Adsorption equilibrium isotherm

To determine the adsorption equilibrium isotherm of the cheese whey onto the used PAC, different initial soluble COD concentrations (COD_{S0} = 1200–10,000 mg L^{-1}) were obtained dissolving appropriate amounts of cheese whey; in these experiments tested PAC concentrations (C_T) ranged from 1 to 16 g L^{-1}. The flasks were agitated 24 h to ensure the equilibrium condition; then, soluble COD (COD_S) was determined. From COD_S equilibrium data, PAC specific adsorption capacity (q_C, mg g^{-1}) was calculated as follows:

$$q_C = \frac{COD_{S0} - COD_S}{C_T} \quad (1)$$

2.2.2. Adsorption kinetics

Adsorption kinetic experiments were performed using different initial soluble COD (COD_{S0}) concentrations dissolving 2500 or 5500 mg L^{-1} of dehydrated cheese whey. In these experiments tested PAC concentrations were 8 and 14 g L^{-1}; at t = 0.5, 1, 2, 3, and 4 h, samples were taken to measure soluble COD.

2.3. Biomass growth experiments with different PAC concentrations

In order to study the effect of PAC on the biomass growth kinetics, batch assays were performed in 250 mL aerated vessels. The tested PAC concentrations were 2, 4, and 8 g L^{-1}; in addition, batch assays without PAC were also carried out. The culture medium used in the batch tests was similar to the one described in the previous section; however, in these experiments the initial dehydrated cheese whey concentration was 5000 mg L^{-1}. In all cases the initial biomass concentration was 700 ± 50 mgTSS L^{-1}. The initial pH was adjusted to 7.00 ± 0.05 adding a few drops of a concentrated NaOH solution; this pH was selected because it is the optimum value for the metabolic activity of most of heterotrophic micro-organisms that are present in a typical activated sludge [16]. All experiments were performed at room temperature (20 ± 2 °C). At predetermined time intervals samples were taken to determine TSS, COD_S, pH and oxygen uptake rate (OUR).

2.4. Analytical methods

To determine TSS, 8-mL of the culture were poured into preweighted centrifuge tubes, centrifuged and washed twice with distilled water, and heated at 105 °C for 24 h; TSS of the sample was calculated as the difference between final (dry sample + tube) and initial (tube alone) weights. The observed biomass concentration (X, mgTSS L^{-1}) was calculated as the difference between TSS and the added PAC concentration. It must be pointed out that this difference was a lumped parameter that included active (growing) biomass (X_G), inert (non-growing) biomass (X_{NG}), and a fraction of the adsorbed substrate that could not be removed from the PAC surface by the washing procedure. In addition, the difference between TSS and the added PAC concentration may also include adsorbed and suspended (non-adsorbed) biomass; how-

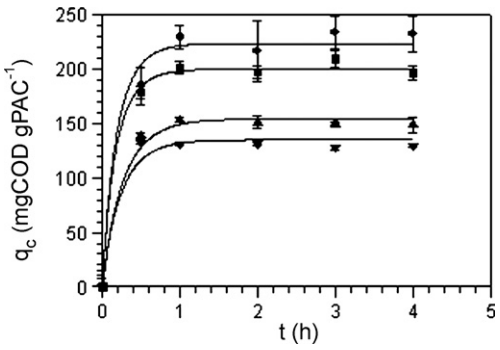

Fig. 1. PAC specific adsorption capacity (q_C) as a function of time (t) corresponding to the following initial conditions: (●) PAC = 8 g L^{-1}, COD_{S0} = 5500 mg L^{-1}; (■) PAC = 14 g L^{-1}, COD_{S0} = 5500 mg L^{-1}; (▲) PAC = 8 g L^{-1}, COD_{S0} = 2500 mg L^{-1}; (▼) PAC = 14 g L^{-1}, COD_{S0} = 2500 mg L^{-1}. Bars indicate the standard deviation. Lines indicate the kinetic expression of the Langmuir adsorption model (Eqs. (4)–(6)) using the coefficients shown in Table 3.

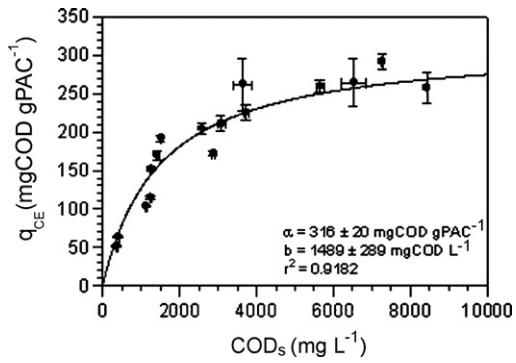

Fig. 2. PAC specific adsorption capacity at the equilibrium condition (q_{CE}) as a function of the cheese whey equilibrium concentration expressed as soluble COD (COD_S). Bars indicate the standard deviation. Line indicates the Langmuir adsorption model at the equilibrium condition (Eq. (2)).

ever, microscopic observations performed at the end of batch tests showed that contact time was not long enough to find significant amounts of biomass attached to PAC particles. In all batch growth experiments, duplicate biomass measurements were performed to reduce experimental errors; obtained mean and maximum errors for the biomass concentration were 4% and 13%, respectively.

Soluble COD of the culture as a function of time was determined as follows [7]: 3-mL of culture samples were centrifuged for 5 min at 13,000 rpm (Eppendorf 5415C). Because some 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). For each sample, COD_S measurements were in duplicates.

Oxygen uptake rate (OUR, mgO_2 L^{-1}) measurements were performed using a closed respirometer consisted in a 30 mL glass vessel maintained at 20 ± 0.5 °C by means of a water bath. The vessel was filled with the tested sample, air was supplied until oxygen saturation level was reached; and then, the vessel was sealed with the insertion of a polarographic oxygen probe (YSI model 5739). The sample was continuously stirred with a magnetic stirring and the decay of the dissolved oxygen (DO) concentration as a function of time was recorded. Data were acquired by a personal computer interfaced to the DO monitor (YSI model 58).

All the results presented in this paper are average values of at least two experiments.

3. Results and discussion

3.1. Growth substrate adsorption on PAC in the absence of biomass

In order to study the effect of PAC on the bioavailability of the growth substrate (cheese whey in this work), the adsorption kinetic was studied. Fig. 1 shows that the specific adsorption capacity (q_C) increased as a function of time, reaching maximum values within the first hour. In addition, Fig. 1 shows that the specific adsorption capacity at the equilibrium condition (q_{CE}) increased with higher initial soluble COD and lower PAC concentrations. Sarkar et al. [17] studied the reuse of wastewater of dairy industries using PAC, among other procedures; those authors found that the equilibrium corresponding to the adsorption of the soluble COD was achieved within the first 2 h.

Fig. 2 shows the specific adsorption capacity of PAC at the equilibrium condition (q_{CE}) as a function of the substrate equilibrium concentration expressed as soluble COD (COD_S). The Langmuir adsorption model was used to represent the equilibrium isotherm data:

$$q_{CE} = \alpha \frac{COD_S}{b + COD_S} \quad (2)$$

where α (mgCOD gPAC^{-1}) is the maximum specific adsorption capacity of the PAC and b (mgCOD L^{-1}) is the concentration at which half saturation of the adsorbent is reached. Eq. (2) was fitted to the experimental data obtaining the following coefficients: $\alpha = 316 \pm 20$ mgCOD gPAC^{-1} and $b = 1489 \pm 289$ mgCOD L^{-1}. Considering that the initial substrate concentration in the batch growth experiments was about 4900 mgCOD L^{-1}, it is clear that coefficient b of the adsorption isotherm (Eq. (2)) was not negligible in comparison with the initial soluble COD; within the tested conditions, less than 76% of the maximum specific adsorption capacity ($q_C/\alpha = 0.76$) could be achieved.

Galiatsatou et al. [18] studied the treatment of olive mill wastewater for COD abatement using activated carbons from agricultural by-products. Those authors found that COD adsorption isotherms were adequately represented by the Langmuir model. In addition, α and b values reported by those authors ranged from 555 to 1667 mgCOD gPAC^{-1} and 5681–12,345 mgCOD L^{-1}, respectively. Although maximum specific adsorption capacity of the PAC used in the present paper was lower than the value corresponding to PAC produced from agricultural by-products, its affinity for the soluble COD (measured as the inverse of b) was higher.

3.2. Effect of PAC on the biomass growth kinetics

Batch growth experiments were performed to evaluate the effect of PAC concentration on the biomass growth kinetics. Fig. 3 a–h shows the soluble COD (COD_S), the observed biomass concentration (X) and the oxygen uptake rate (OUR) as a function of time corresponding to the control experiment (without PAC addition) and the different tested PAC concentrations (2, 4, 8 gPAC L^{-1}). During the first 8 h a lag phase was observed; thus, OUR values remained around 20 mgO_2 L^{-1} h^{-1} and X ranged between 660 and 850 mgTSS L^{-1}. However, in the systems with PAC, a fast decrease of COD_S was observed within this stage due to the substrate adsorption. By increasing PAC concentrations, lower initial soluble COD concentrations were obtained. For example, when PAC concentration was 8 g L^{-1}, soluble COD decreased from 4900 to 3100 mg L^{-1} within the first 2 h due to the adsorption of the substrate onto the used PAC; thus, PAC reduced the growth substrate bioavailability (the actual substrate concentration in solution). After the lag phase, X and OUR increased, and soluble COD decreased; the exponential growth phase ended at t = 15 h. Then, a sharp decrease of OUR was

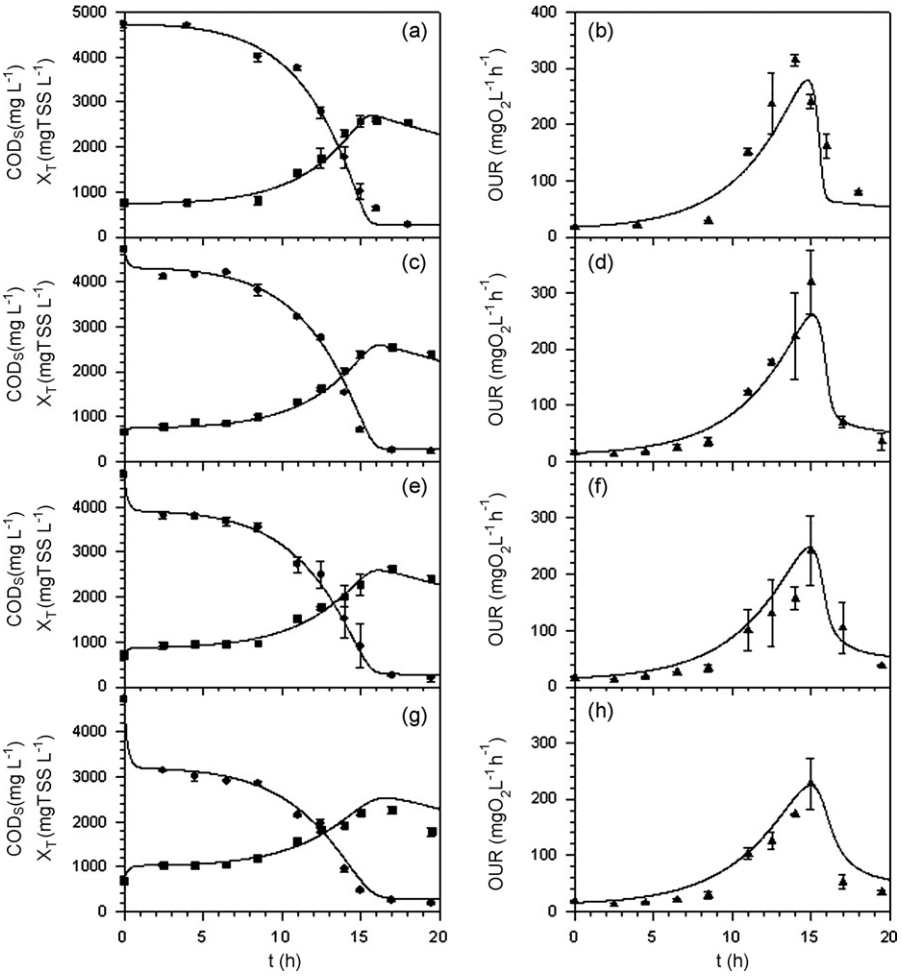

Fig. 3. Observed biomass concentration (X, ■), soluble COD concentration (COD_S, ●), and oxygen uptake rate (OUR, ▲) as a function of time corresponding to the control experiment without PAC (a and b), and to the following initial PAC concentrations: (c and d) 2 g L^{-1}; (e and f) 4 g L^{-1}; (g and h) 8 g L^{-1}. Bars indicate the standard deviation. Lines indicate the proposed model (Eqs. (4)–(12)) using the coefficients shown in Table 3.

observed due to the growth substrate (S) depletion; however, the soluble COD stayed about 260 mgCOD L^{-1}.

For each tested PAC concentration (2–8 gPAC L^{-1}) and for the experiment without PAC, the observed maximum specific growth rate (μ_{obs}) was calculated from the slope of the linear part of the plot of Ln(X) as a function of time. The biomass growth yield ($Y_{X/S}$) and the substrate oxidation coefficient ($Y_{O/S}$) were obtained from the slopes of X and total oxygen consumption (OC) as functions of the soluble COD concentration respectively. The specific oxygen uptake rate (q_{O_2}) was obtained from the slope of OUR as a function of X. Table 2 shows that kinetic coefficients μ_{obs} and q_{O_2} decreased as the initial PAC concentration increased; on the contrary, taking into account the experimental errors, stoichiometric coefficients $Y_{X/S}$ and $Y_{O/S}$ were almost constant. In addition, for all the tested conditions, COD mass balances were close to 100% (Table 2); hence, this provides a powerful validation of the experimental data. Table 2 shows that kinetic coefficients μ_{obs} and q_{O_2} were affected by the presence of PAC due to the adsorption of the growth substrate. On the contrary, because the substrate adsorbed during the first hours of batch tests could be desorbed and becoming bioavailable for growth, the maximum biomass concentration for each tested PAC concentration was almost constant. For this reason, stoichiometric coefficients $Y_{X/S}$ and $Y_{O/S}$ were not affected by the addition of PAC.

Results showed in Table 2 agree with those reported by other authors. Orshansky and Narkis [3] studied some physiological aspects of the simultaneous adsorption and biodegradation of aniline from aqueous solution; these authors found that the presence of PAC decreased the microbial respiration. In addition, a significant amount of aniline remained strongly adsorbed on the PAC and was not available for biodegradation. Specchia and Gianetto [19] determined activated sludge growth coefficients and kinetic constants

Table 2
Effect of PAC concentration on the growth kinetics of activated sludge.

PAC (g L^{-1})	μ_{obs} (h^{-1})	q_{O_2} (mgO_2 gTSS^{-1} h^{-1})	$Y_{X/S}$ (gTSS gCOD^{-1})	$Y_{O/S}$ (gO_2 gCOD^{-1})	COD mass balance[a] (%)
0	0.154 ± 0.008	198 ± 8	0.48 ± 0.01	0.37 ± 0.01	102 ± 2
2	0.135 ± 0.007	189 ± 8	0.45 ± 0.01	0.32 ± 0.03	93 ± 3
4	0.115 ± 0.011	149 ± 10	0.49 ± 0.01	0.30 ± 0.03	97 ± 3
8	0.088 ± 0.005	175 ± 10	0.46 ± 0.03	0.32 ± 0.02	95 ± 4

[a] Assuming a standard biomass composition ($C_5H_7O_2N$) and 96% of volatile compounds of the biomass, the following conversion factor from biomass TSS to COD units was obtained: f_X = 1.36 gCOD/gTSS.

Table 3
Coefficients of the proposed model (Eqs. (4)–(12)).

Coefficient	Value ± SD	Experimental data used to obtain the model coefficients
α (mgCOD gPAC^{-1})	316 ± 20	Equilibrium adsorption isotherm
b (mgCOD L^{-1})	1489 ± 289	
k_{ads} (L mgCOD^{-1} h^{-1})	(7.52 ± 0.64) × 10^{-4}	Adsorption kinetics
$k_{des} = b\, k_{ads}$ (h^{-1})	1.12 ± 0.24	
μ_m (h^{-1})	0.352 ± 0.014	Batch growth kinetics with different initial PAC concentrations
K_S (mgCOD L^{-1})	188 ± 52	
$Y^T_{X/S}$ (gTSS gCOD^{-1})	0.515 ± 0.023	
k_d (h^{-1})	0.055 ± 0.005	
$Y_{P/S}$ (gCOD gCOD^{-1})	0.060 ± 0.007	
$q_{O_2 m}$ (mgO$_2$ gTSS^{-1} h^{-1})	152 ± 17	
q_E (mgO$_2$ gTSS^{-1} h^{-1})	23 ± 6	
β (mgTSS gPAC^{-1})	71.9 ± 6.0	
τ (h)	83.3 ± 6.9	

of biological oxidation with the presence and absence of PAC. Those authors found that the addition of PAC decreased the sludge growth rate suggesting that the lack of substrate due to the adsorption onto PAC probably imposes a limitation on bacterial growth [19].

3.3. Kinetic model for microbial growth with simultaneous substrate adsorption

3.3.1. Model development

In order to develop a simplified model of the effect of PAC on the bioavailability of the growth substrate (S), it was assumed that PAC can adsorb only the growth substrate (cheese whey in this work); in addition, the adsorption of microbial soluble products (P) was neglected. It must be pointed out that a typical batch experiment lasted about 20 h; within this time, microscopic observations showed that the biomass attached to PAC particles was negligible in comparison to the biomass in the liquid phase. For this reason, consideration of adsorbed biomass was not included in the model. The model considers that biomass in the liquid phase was mainly responsible for the soluble COD oxidation, oxygen consumption, and biomass production.

In accordance with the results shown in Fig. 2, it was assumed that the sorption process can be represented by the Langmuir adsorption isotherm model. In the Langmuir model the sorption process is the result of two reactions, the (forward) adsorption of growth substrate (S) onto free carbon (C_F) to yield combined carbon (C_C), and the (reverse) desorption of S from C_C:

$$\alpha S + C_F \underset{k_{des}}{\overset{k_{ads}}{\rightleftarrows}} C_C \tag{3}$$

where k_{ads} (L mgCOD^{-1} h^{-1}) and k_{des} (h^{-1}) are the adsorption and desorption rate constants respectively, and α (mgCOD gPAC^{-1}) is the amount of substrate adsorbed per gram of carbon. Taking into account that the total PAC concentration (C_T) was equal to $C_F + C_C$, the reaction rates corresponding to the species C_F and C_C were the following:

$$\frac{dC_F}{dt} = -k_{ads} S C_F + k_{des} C_C \tag{4}$$

$$\frac{dC_C}{dt} = k_{ads} S C_F - k_{des} C_C \tag{5}$$

Regarding the growth substrate (S), it was assumed that the uptake of S by micro-organisms follows a Monod type kinetics. The lag phase observed during the first hours in batch growth assays (Fig. 3) was modeled assuming that the biomass was composed by growing (X_G) and non-growing (X_{NG}) fractions, and that the activation process from X_{NG} to X_G follows a first order kinetics with a rate constant $1/\tau$ [20]. Thus, growth substrate (S), growing biomass (X_G), and non-growing biomass (X_{NG}) balances were the following:

$$\frac{dS}{dt} = -\alpha(k_{ads} S C_F - k_{des} C_C) - \frac{\mu_m}{Y^T_{X/S}} \left(\frac{S}{K_S + S}\right) X_G \tag{6}$$

$$\frac{dX_G}{dt} = \left[\mu_m \left(\frac{S}{K_S + S}\right) - k_d\right] X_G + \frac{X_{NG}}{\tau} \tag{7}$$

$$\frac{dX_{NG}}{dt} = -\frac{X_{NG}}{\tau} \tag{8}$$

where $Y_{X/S}$ (mgTSS mgCOD^{-1}) is the true biomass growth yield, μ_m (h^{-1}) is the maximum specific growth rate, K_S is the growth substrate saturation constant (mgCOD L^{-1}), and k_d (h^{-1}) is the biomass decay constant.

Fig. 3 shows that COD_S values at the end of the batch tests were about 260 mgCOD L^{-1}; this soluble COD was attributed to the presence of microbial soluble products [21]. Usually these products are divided in two categories: products associated with biomass decay, and products associated with substrate uptake and biomass growth [22]. In the proposed model the presence of a growth-linked microbial soluble product (P) was assumed; thus, the mass balance for P was the following:

$$\frac{dP}{dt} = Y_{P/S} \frac{\mu_m}{Y^T_{X/S}} \left(\frac{S}{K_S + S}\right) X_G \tag{9}$$

where $Y_{P/S}$ (mgCOD mgCOD^{-1}) is the product yield.

Regarding the oxygen uptake rate (OUR), it was assumed that both X_G and X_{NG} had the same endogenous specific oxygen uptake rates (q_E). However, because only X_G was capable of consuming substrate, X_G was responsible for the exogenous respiration:

$$OUR = q_{O_2 m} \left(\frac{S}{K_S + S}\right) X_G + q_E (X_G + X_{NG}) \tag{10}$$

where $q_{O_2 m}$ and q_E (mgO$_2$ gTSS^{-1} h^{-1}) were the maximum exogenous, and endogenous specific oxygen uptake rates, respectively.

The measurable outputs of the proposed model are OUR (Eq. (10)), soluble COD (COD_S), and the observed biomass concentration (X). The soluble COD concentration is:

$$COD_S = S + P \tag{11}$$

Taking into account that X was calculated as the difference between TSS and the added PAC concentration, this difference included growing biomass (X_G), non-growing biomass (X_{NG}), and the amount of the adsorbed substrate that could not be removed from the PAC surface by the used washing procedure; therefore, the observed biomass concentration (X) in terms of the proposed model is:

$$X = X_G + X_{NG} + \beta C_C \tag{12}$$

where β (mgTSS gPAC^{-1}) is the adsorbed substrate after washing the sample per unit of combined carbon. If the washing procedure can remove all the adsorbed substrate, then $\beta = 0$; if the substrate cannot be removed by the washing procedure then $\beta = \alpha$.

3.3.2. Estimation of the model coefficients

The estimation of the coefficients of the model proposed in this paper (Eqs. (4)–(12)) and the dynamic simulations were performed using the software package Gepasi 3 [23]. Gepasi integrates the systems of differential equations with the routine LSODA (Livermore Solver of Ordinary Differential Equations). LSODA algorithm measures the stiffness of the equations and switches the integration method dynamically according to this measure. For non-stiff regions, the Adams integration method with variable step size and variable order up to 12th order is used; for stiff regions the Gear (or BDF) method with variable step size and variable order up to 5th order is used. Among the optimization methods available in Gepasi 3, the Multistart Optimization algorithm (with Levenberg–Marquardt local optimization) was selected. Multistart is a hybrid stochastic–deterministic optimization method. Rather than run a simple local optimization (e.g. gradient descent methods), Multistart runs several of them, each time starting from a different initial guess. The first start takes for initial guess the parameter values entered by the user. The initial guesses for the subsequent starts are generated randomly within the boundaries for the adjustable parameters. The local optimizer used is the Levenberg–Marquardt method as this has proved the most efficient gradient optimizer used in Gepasi 3 [23].

The estimation of the proposed model coefficients was performed in three steps. In a first step the model was used to represent the growth substrate (cheese whey) adsorption equilibrium isotherm onto PAC in the absence of biomass (Fig. 2); therefore, in this case: $X_G = X_{NG} = P = 0$. In addition, the initial conditions ($t = 0$) were the following: $S = S_0$, $C_{C0} = 0$, $C_{F0} = C_T$. In this case, by combining Eqs. (4)–(6) the following was obtained:

$$C_C = \frac{S_0 - S}{\alpha} \tag{13}$$

$$C_F = C_T - \frac{S_0 - S}{\alpha} \tag{14}$$

When the adsorption process reaches the equilibrium, adsorption and desorption rates are equal,

$$k_{ads} S C_F = k_{des} C_C \tag{15}$$

and combining Eqs. (13)–(15) the following was obtained:

$$q_{CE} = \frac{S_0 - S}{C_T} = \alpha \frac{S}{(k_{des}/k_{ads}) + S} \tag{16}$$

By the comparison of Eqs. (2) and (16), it is clear that both coefficients α and $b = (k_{des}/k_{ads})$ can be adopted from the Langmuir adsorption equilibrium isotherm coefficients obtained in the previous section.

In the following calibration step, the software Gepasi 3 was used to fit Eqs. (4)–(6) to the adsorption kinetic data shown in Fig. 1. It must be pointed out that in this condition the model had three adjustable coefficients (α, k_{ads}, and k_{des}); however, taking into account the above mentioned constraint ($b = (k_{des}/k_{ads})$), only a single coefficient (k_{ads} in this work) was necessary to fit the model to the experimental data. This procedure reduces computational efforts and fitting errors. Eqs. (4)–(6) were fitted to the measured values of q_C as a function of time for different initial PAC and COD concentrations. Fig. 1 shows a satisfactory agreement between the Langmuir model (Eqs. (4)–(6)) and the experimental data. Using the above mentioned procedure, the following coefficients values were obtained: $k_{ads} = (7.52 \pm 0.64) \times 10^{-4}$ L mgCOD^{-1} h^{-1}, $k_{des} = 1.12 \pm 0.24$ h^{-1} (Table 3).

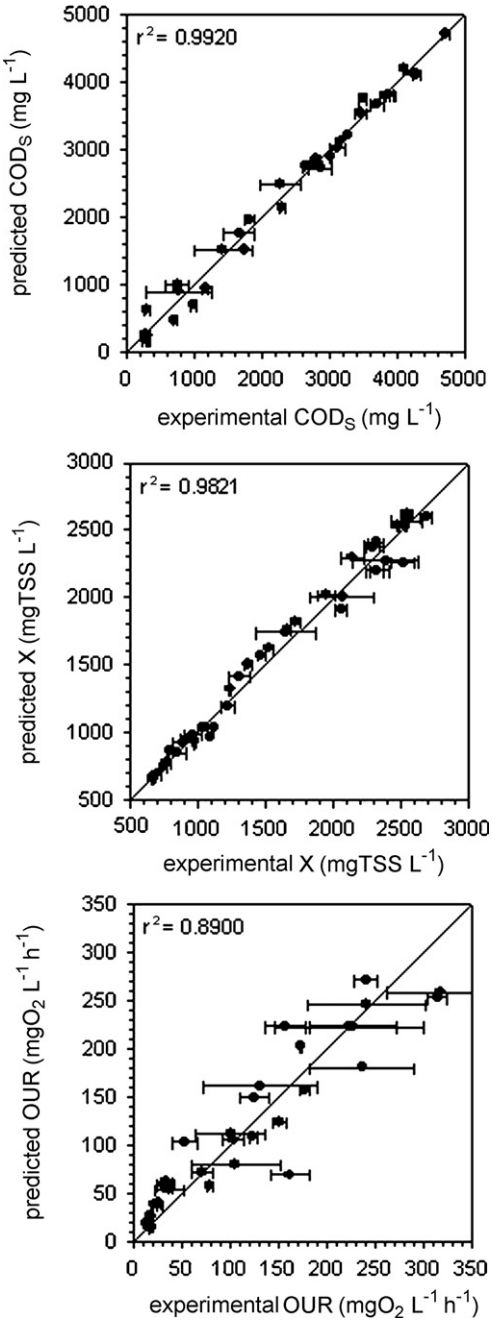

Fig. 4. Proposed model predictions (Eqs. (4)–(12)) as a function of experimental data. Lines indicate the identity line (model = experimental data). Bars indicate the standard deviation.

Once coefficients α, k_{ads}, and k_{des} were obtained, the proposed kinetic model (Eqs. (4)–(12)) was fitted to batch growth experimental data (COD_S, X, and OUR as a function of time) for the different initial PAC concentrations tested (0–8 g L^{-1}) using the software Gepasi 3. Obtained coefficients are shown in Table 3; these values are within the range reported by other authors [24,25]. Figs. 3 and 4 show that in all cases a good agreement between the proposed model and the experimental data was obtained. This result demonstrates that kinetic behavior of the tested AS–PAC system can be represented as a combination of a microbial process that comprises substrate consumption and biomass growth, with the sorption process of substrate onto the added PAC.

The proposed model was used to simulate the effect of the initial substrate and PAC concentrations on COD_S, X, and OUR as a

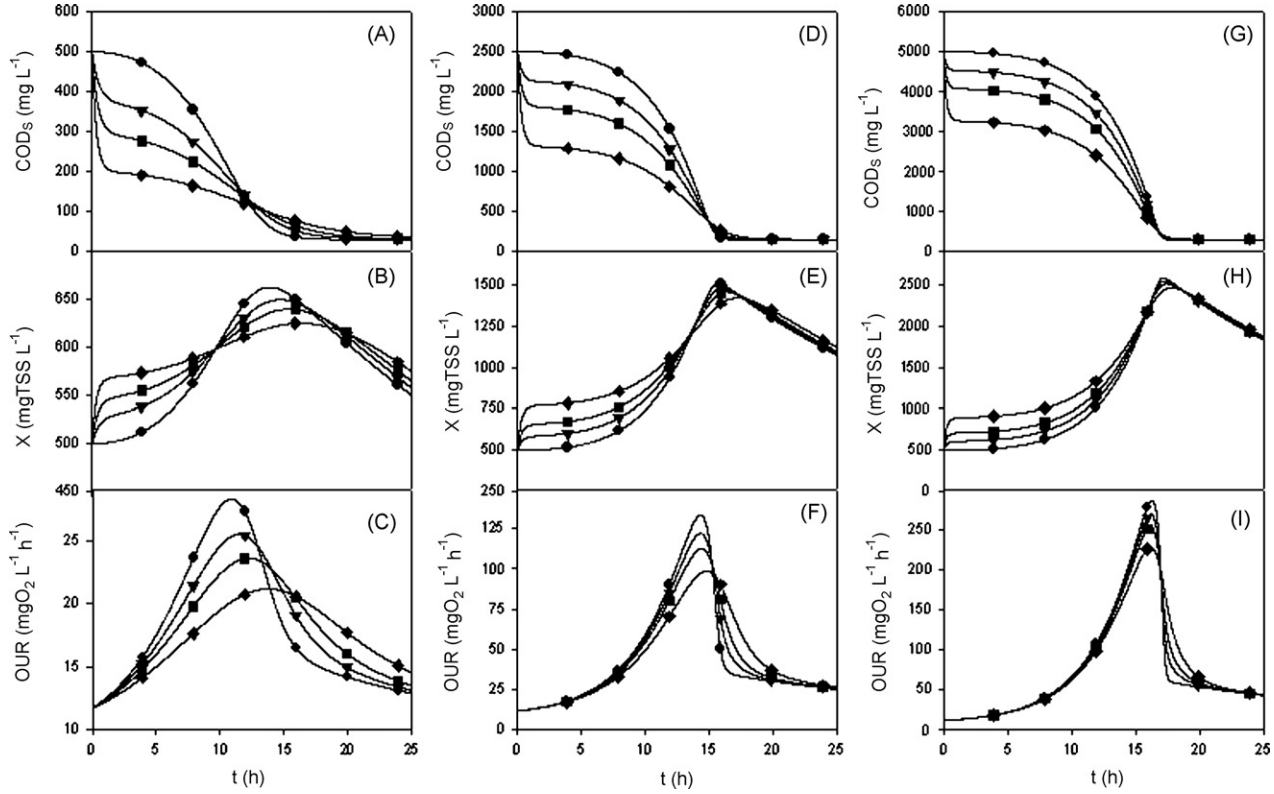

Fig. 5. Soluble COD (COD_S), biomass concentration (X), and oxygen uptake rate (OUR) calculated by the proposed model (Eqs. (4)–(12)) as a function of time. Initial substrate (S_0) and PAC (C_T) concentrations were: S_0 = 500 mgCOD L^{-1} (a–c); S_0 = 2500 mgCOD L^{-1} (d–f); S_0 = 5000 mgCOD L^{-1} (g–i); C_T = 0 gPAC L^{-1} (●); C_T = 2 gPAC L^{-1} (▼); C_T = 4 gPAC L^{-1} (■); C_T = 8 gPAC L^{-1} (♦). In all the simulations the initial biomass concentration was 500 mgTSS L^{-1}. Model coefficients used in all simulations are shown in Table 3.

function of time. Fig. 5 shows that PAC acts as a buffer of substrate concentration changes, yielding slower responses to the changes of substrate concentration due to the microbial consumption. During the first hours of a batch test, when the substrate concentration (S) is higher than the corresponding to the sorption equilibrium concentration (S_E), PAC adsorbs substrate decreasing its concentration to reach the sorption equilibrium. However, after the lag phase, S decreases to a value lower than S_E due to the metabolic activity of micro-organisms. In this case, substrate is desorbed from PAC surface in order to reach a new S_E value. The slower responses of substrate concentration changes in systems with PAC determine also slower responses on X and OUR changes. In addition, Fig. 5 shows that the substrate buffer effect due to the presence of PAC is more evident with higher ratio PAC to initial substrate concentration. It must be pointed out that one of the advantages of the combined AS–PAC process over the conventional AS system would be this substrate buffer function that helps to maintain the stability of AS–PAC combined bioreactors.

4. Conclusions

The adsorption of growth substrate (cheese whey) onto the used PAC attained the equilibrium within the first hour; the Langmuir adsorption model described adequately the specific adsorption capacity (q_C) as a function of the soluble COD (COD_S).

Batch growth experiments showed that microbial kinetic coefficients μ_{obs} and q_{O_2} decreased as the initial PAC concentration increased; however, stoichiometric coefficients $Y_{X/S}$ and $Y_{O/S}$ were constant. Increasing PAC concentrations, lower initial soluble COD concentrations were obtained; thus, PAC reduced the growth substrate (cheese whey) bioavailability, that is, the actual substrate concentration in solution.

Activated sludge batch growth experiments in the presence of PAC could be described adequately by the developed mathematical model. This model was a combination of biochemical processes (biomass growth, substrate consumption and product generation) with the adsorption kinetics of the substrate. The model was fitted to the experimental data; for all the tested conditions, a good agreement between the proposed model and the experimental data was obtained. Therefore, kinetic behavior of the tested AS–PAC system can be represented by a combination of a microbial process with the sorption process of substrate onto the added PAC.

Simulations show that the main effect of PAC on the growth kinetics is to act as a buffer of substrate concentration changes, yielding slower responses to the changes of substrate concentration; the buffer function of substrate due to the presence of PAC helps to maintain stable environmental conditions in combined bioreactors.

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References

[1] S.R. Quasim, W. Chiang, Sanitary Landfill leachate: Generation, Control and Treatment, Technomic Publishing Co., Lancaster, 1994.
[2] L. Alvarez-Cohen, G.E. Speitel Jr., Kinetics of aerobic cometabolism of chlorinated solvents, Biodegradation 12 (2001) 105–126.
[3] F. Orshansky, N. Narkis, Characteristics of organics removal by PACT simultaneous adsorption and biodegradation, Water Res. 31 (1997) 391–398.
[4] C. Costa, M.C. Márquez, Kinetics of the PACT process, Water Res. 32 (1998) 107–114.
[5] F. Çeçen, O. Aktas, Effect of PAC addition in combined treatment of landfill leachate and domestic wastewater in semi-continuously fed batch and continuous-flow reactors, Water SA 24 (2) (2001) 177–188.

[6] A.M. Ferro Orozco, E.M. Contreras, N.E. Zaritzky, Hexavalent chromium removal using aerobic activated sludge batch systems added with powdered activated carbon, Water SA 33 (2) (2007) 239–244.
[7] A.M. Ferro Orozco, E.M. Contreras, N.E. Zaritzky, Modelling Cr(VI) removal by a combined carbon-activated sludge system, J. Hazard. Mater. 150 (1) (2008) 46–52.
[8] M. Okada, H. Morinaga, W. Nishijima, Activated carbon as a better habitat for water and wastewater treatment, Water Sci. Technol. 42 (2000) 149–154.
[9] H. Morinaga, W. Nishijima, M. Okada, Stimulation of bacterial activity by the addition of PACs, Environ. Technol. 24 (2003) 179–186.
[10] K.L. Sublette, E.H. Snider, N.D. Sylvester, A review of the mechanism of powdered activated carbon enhancement of activated sludge treatment, Water Res. 16 (1982) 1075–1082.
[11] Z. Xiaojian, W. Zhansheng, G. Xiasheng, Simple combination of biodegradation and carbon adsorption—the mechanism of the biological activated carbon process, Water Res. 25 (1991) 165–172.
[12] S. Tsuneda, J. Auresenia, Y. Inoue, Y. Hashimoto, A. Hirata, Kinetic model for dynamic response of three-phase fluidized bed biofilm reactor for wastewater treatment, Biochem. Eng. J. 10 (2002) 31–37.
[13] S. Tsuneda, Y. Inoue, J. Auresenia, A. Hirata, Adsorption effect on the dynamic response of a biochemical reaction in a biofilm reactor for wastewater treatment, Eng. Life Sci. 3 (9) (2003) 371–375.
[14] G.M. Walker, L.R. Weatherley, Biological activated carbon treatment of industrial wastewater in stirred tank reactors, Chem. Eng. J. 75 (1999) 201–206.
[15] E.M. Contreras, L. Giannuzzi, N.E. Zaritzky, Growth kinetics of the filamentous microorganism *Sphaerotilus natans* in a model system of a food industry wastewater, Water Res. 34 (2000) 4455–4463.
[16] M. Henze, P. Harremoes, J.L. Jansen, E. Arvin, Wastewater Treatment, 3rd ed., Springer-Verlag, Berlin, Germany, 2002.
[17] B. Sarkar, P.P. Chakrabarti, A. Vijaykumar, V. Kale, Wastewater treatment in dairy industries—possibility of rehuse, Desalination 195 (2006) 141–152.
[18] P. Galiatsatou, M. Metaxas, D. Arapoglou, V. Kasselouri-Rigopoulou, Treatment of olive mill waste water with activated carbons from agricultural by-products, Waste Manage. 22 (2002) 803–812.
[19] V. Specchia, A. Gianetto, Powdered activated carbon in an activated sludge treatment plant, Water Res. 18 (1984) 133–137.
[20] P.A. Vanrolleghem, G. Sin, K.V. Gernaey, Transient response of aerobic and anoxic activated sludge activities to sudden substrate concentration changes, Biotechnol. Bioeng. 86 (3) (2004) 277–290.
[21] T. Jiang, S. Myngheer, D.J.W. De Pauw, H. Spangers, I. Nopens, M.D. Kennedy, G. Amy, P.A. Vanrolleghem, Modelling the production and degradation of soluble microbial products (SMP) in membrane bioreactors, Water Res. 42 (2008) 4955–4964.
[22] B.E. Rittmann, W. Bae, E. Namkung, C.J. Lu, A critical evaluation of microbial product formation in biological processes, Water Sci. Technol. 19 (3–4) (1987) 517–528.
[23] P. Mendes, GEPASI: A software package for modelling the dynamics, steady states and control of biochemical and other systems, Comput. Appl. Biosci. 9 (1993) 563–571.
[24] D. Jenkins, Towards a comprehensive model of activated sludge bulking and foaming, Wat. Sci. Technol. 25 (6) (1992) 215–230.
[25] J. Wanner, Activated Sludge Bulking and Foaming Control, Technomic Publishing Company, Inc., Lancaster, 1994.