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BIODEGRADATION OF TOXIC WASTEWATERS IN AN OPTIMALLY CONTROLLED DISCONTINUOUS REACTOR

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ABSTRACT

The paper presents several attempts to solve the problems of concentration peaks, microbial activity diminution due to substrate starvation, as well as the maintenance of a reliable performance of an aerobic sequencing batch bioreactor degrading inhibitory wastewaters. Two main solution lines have been followed: on one side, several control strategies, based on the measurement of the dissolved oxygen concentration, have been proposed. On the other side, the use of fixed biomass, or a mixture of suspended and fixed biomass, instead of suspended biomass has been pursued in order to overcome the problems mentioned above. It was observed that if no especial control strategy is designed the SBR systems with attached biomass have a better resistance against concentration peaks and toxic starvation than the suspended biomass systems. However, these solutions are not enough to increase sufficiently the performance of the SBR under extreme operating conditions. It was observed that sophisticated control strategies as the time optimal control greatly increased the robustness and performance of the SBR to levels never obtained before without them.

KEYWORDS

Optimal control, dissolved oxygen, 4-clorophenol, sequencing batch bioreactor, toxic wastewater.

INTRODUCTION

The biological treatment of toxic wastewater with high concentrations of toxic compounds, such as that produced by the chemical and petrochemical industries is a difficult and challenging task. Aerobic sequencing batch reactors (SBR) have demonstrated their superiority with respect to the continuous reactors due to their better efficiency and flexibility. The term SBR is used as a synonym of the wastewater treatment technology, where the volume of the reactor tank is variable in time (Wilderer et al. 2001). It can work with suspended or attached biomass. In general, the SBR process presents three major characteristics: periodic repetition of a sequence of well defined phases; planned duration of each process phase in accordance with the treatment result to be met, and progress of the various biological and physical reactions as a function of time. Another characteristic of SBR systems, because of their flexibility in control strategy, is that they are effective for fully automated computer controls.

However, standard operation modes of SBRs face several key problems in the treatment of toxic wastewaters:

1. The behavior under sudden increase of the toxic substrate concentration (concentration peaks) in the wastewater that severely affects the operation of the wastewater treatment plant (WWTP). They are frequent because of intermittent industrial operation, that generates concentration peaks when, for example, the containers and reactors are cleaned.

2. The toxic nature of the substrate makes it necessary to previously acclimation of the biomass for degrading the toxics. Moreover, the exposition of the acclimated population to prolonged periods of starvation, usual under common SBR operation policies, produces a decrease of the bacterial activity and, even the death (Coello *et al.*, 2003; Buitrón and Moreno 2002). This problem is usually not taken into account in the operation of biological WWTPs.

3. The adequate control of the SBR requires the on-line monitoring of the toxic concentration in the reactor. However, this is not practically and economically implementable at a WWTP level. To overcome this problem several operation modes have been proposed using either the carbon dioxide evolution rate (Buitrón et al. 1993) or the dissolved oxygen (DO) concentration (Sheppard and Cooper, 1990). They proposed a control strategy, called Self-Cycling Fermentation (SCF), in which the length of the growth period is controlled by the biological activity in an aerobic reactor, and based on the close correlation between DO concentration in the reactor and cellular respiration.

4. The treatment of toxics decreases the time efficiency of the plant, since an increase in the toxic concentration increments the reaction time in a not proportional manner.

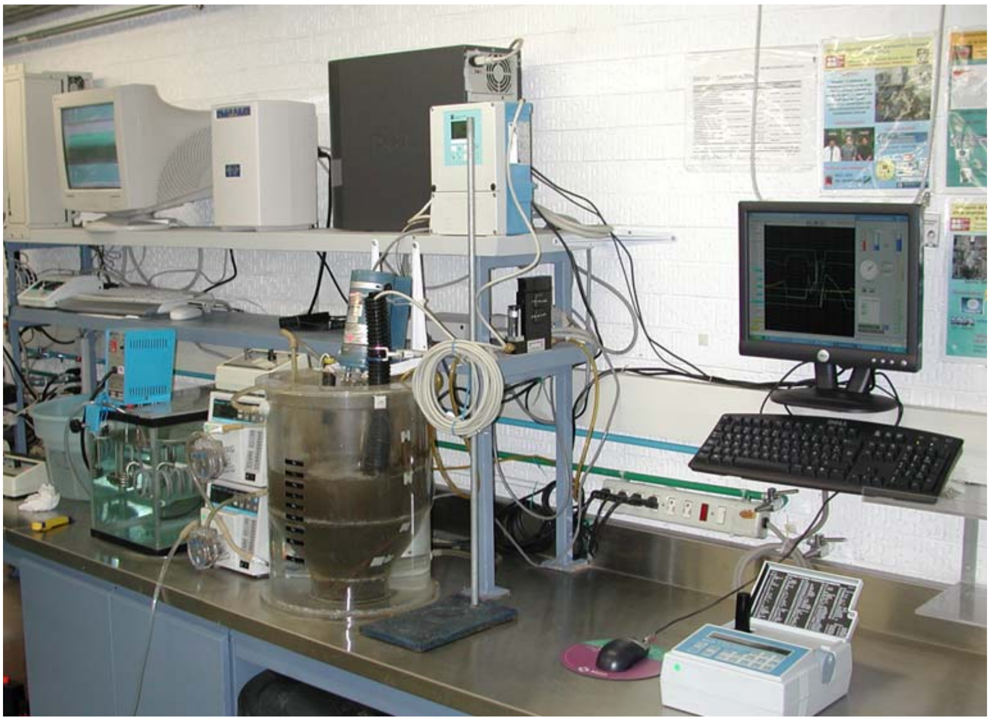
The objective of this paper is to present several attempts of our research group to solve these problems. Two main solution lines have been followed: on one side several control strategies, based on the measurement of the DO concentration, have been proposed. On the other side the use of fixed biomass, or a mixture of suspended and fixed biomass, instead of suspended biomass have been pursued in order to overcome the problems of starvation and concentration peaks, and in view to maintain a high efficiency of removal of toxic contaminants as well as a reliable performance of the system. The results of these proposals will be discussed, and some open problems will be presented.

METHODOLOGY

A pilot system with an aerobic reactor of 7 liters of useful volume (Figure 1) was employed to treat synthetic wastewater containing 4-chlorophenol (4CP) or a mixture of phenolic compounds in an equal proportion (phenol, 4CP, 2,4-dichlorophenol, and 2,4,6-trichlorophenol). Nutrients such as nitrogen, phosphorus, and oligoelements were added following the techniques recommended by ANFOR (1985). The pH was maintained around 7.0. The exchange ratio in the reactor was 4/7 and the airflow is 1.5 liters per minute. An automatic temperature controller based on a recycling water pump was used to maintain a constant temperature of 20 oC inside the reactor (PolyScience model 210). Dissolved oxygen was measured using an electronic meter (YSI model 52) coupled to a computer. The input and output water flows were controlled using peristaltic pumps, which could be read and controlled by the computer (Cole-Palmer model 7523, Masterflex series). Additionally, the computer could also control a mixer and a valve that turned on the aerator. The treatment process used is SBR type with 5 steps: filling, reaction, sedimentation, decanting and an idle period.

The substrate concentration was measured taking samples and processing them offline using colorimetric techniques with 4-aminoantipyrine method (Standard Methods, 1992). To determine the biomass concentration at a given instant, total and volatile suspended solids (VSS) analysis was made (Standard Methods, 1992). Dissolved organic carbon (DOC) analysis was also performed to test whether 4CP was being mineralized (Shimadzu TOC-5050).

Figure 1 - Experimental assembly



Biomass

The reactor was inoculated with microorganisms coming from a municipal activated sludge treatment plant (2000 mgVSS/L). A cell retention time of 20 days was maintained. The biomass was used considering 3 alternatives: Suspended Biomass (SB), a Moving Bed system (MB), which is composed by a mixture of suspended biomass and fixed biomass previously colonized in a polyethylene packing of high density (BCN009 plus from the 2H company, with a superficial area of 963 m2/m3), and Fixed Biomass (FB) being the packing material a porous volcanic rock (puzolane) with a mean diameter from 1.0 to 1.5 cm and 63% of porosity. The biomass was acclimated using the fixed timing control strategy before appliying any of the strategies discused later. Acclimation was done to an initial concentration of 50 mg/L in the reactor. When degradation times were constant, the initial concentration was stepwised incremented up to 200 mg/L in the reactor (350 mg/L in the feed tank). In the case of the mixture of phenos an initial substrate concentartion of 175 mg/L (100 mg/L in the reactor) was used.

Strategies used for controlling the operation of the SBR

Different control strategies can be used to control the fill and reaction phases of the SBR: *Fixed Timing Control* (FTC), *Variable Timing Control* (VTC), *Time Optimal Control Observed Based* (OB-TOC) and *Event Driven Time Optimal Control* (ED-TOC). Next, they are shortly explained because of the space of the paper. For more details references must be consulted.

Fixed Timing Control **(FTC).**

The simplest one is the FTC. This is the usual way in which SBR are operated. Here the duration of each phase is previously fixed according to a programmed strategy. For control purposes in this strategy the reaction phase length is fixed, regardless of the final substrate concentration.

Variable Timing Control **(VTC).**

In the VTC (Figure 2a) the reaction phase duration will be based on the dissolved oxygen concentration (DO) behavior. In a batch process as the substrate concentration decreases, the metabolic activity of the microorganisms increases. Therefore, for a fixed air flow rate, the metabolic activity is traduced in a diminution of the DO concentration (Buitrón et al., 2003). Once the degradation was finished, the DO increases. This behavior is used as reaction’s near-end detector. The only automated variable timing is the reaction time.

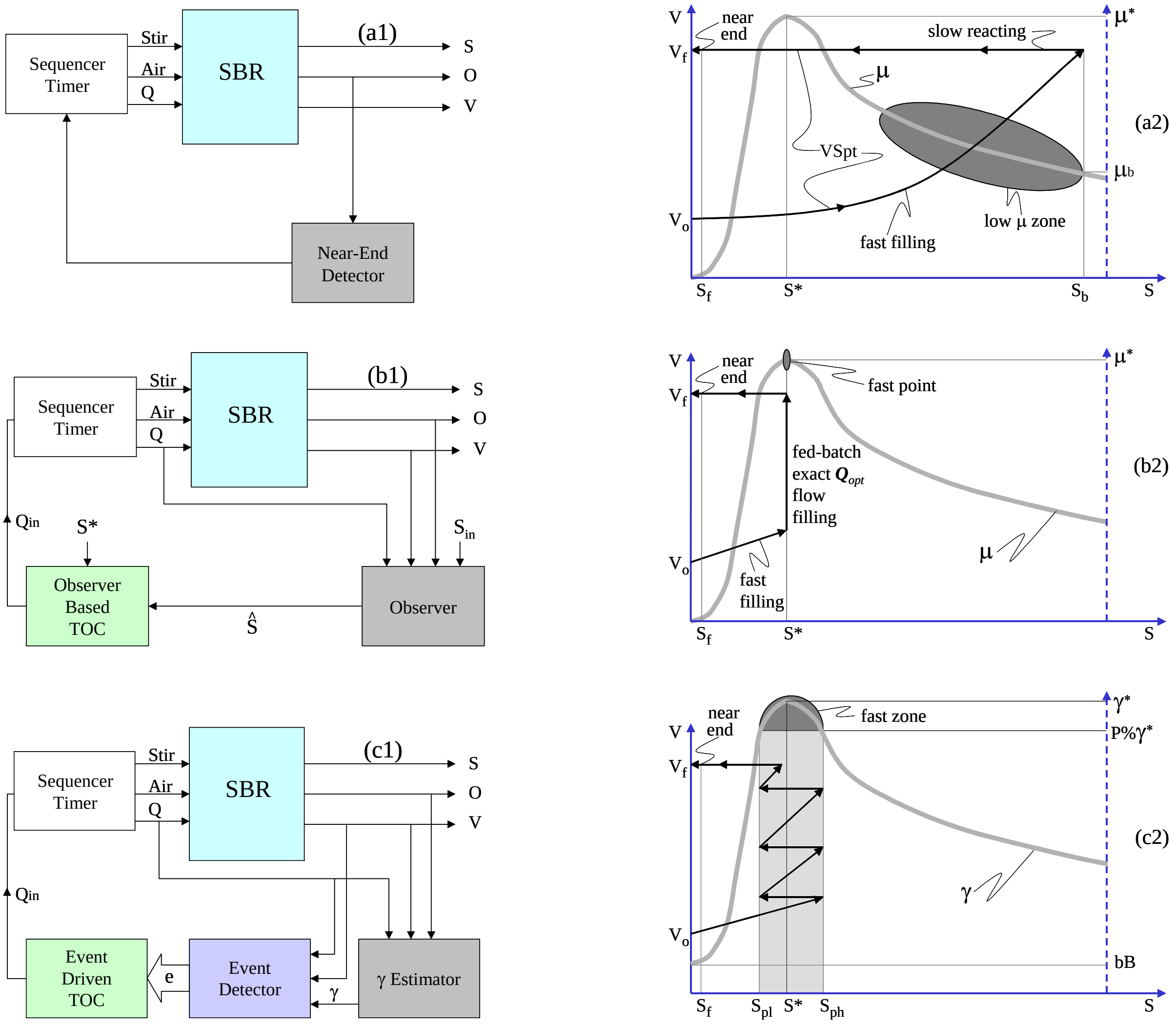
Time Optimal Control Observed Based **(OB-TOC).**

The Haldane law can be considered for the degradation of an inhibitory substrate. Here, there exists a substrate concentration S*, which is associated with a maximal growth rate (or degradation rate). The OB-TOC strategy aims to control the influent flow rate in such a way to maintain the optimal concentration S* in the reactor. The vertical trajectory in Figure 2b means that there is no change in substrate while the volume increases. The problem is that, in practice, the substrate concentration could not be easily measured on line. The *observer based* (OB)-TOC strategy (Vargas *et al*., 2000) solves this problem theoretically, by estimating the substrate concentration by using the dissolved oxygen concentration and the volume in the tank (Figure 2b1). Practical implementation was presented by Buitrón *et al.,* (2005). The drawback of this strategy is that it needs to know exactly the inflow substrate concentration and the constants of the Haldane model. A slight mistake in estimating such parameters renders the observer useless and then the real VSpt will not resemble Figure 2b2. This could make the OB-TOC difficult to apply in practice.

Event Driven Time Optimal Control **(ED-TOC).**

The ED-TOC strategy finds a variable (named γ) related to the reaction rate. Such variable can be estimated in real time by using the dissolved oxygen concentration and the volume of the reactor, as described Betancur *et al.*, (2004). The influent flow rate is controlled in such a manner that the reaction rate stays inside the fast zone (gray zone in Figure 2c2). Such zone is above a P% of the maximum rate. The reaction rate is controlled maintaining the substrate concentration oscillating in a gap during the SBR filling. Every time the substrate concentration tries to leave this gap, an event is issued and the ED-TOC then switches the influent flow on/off, to prevent it. This will work regardless of the substrate influent concentration value and despite changes in most of the SBR parameters. Only the mass transfer coefficient, Kla, and the dissolved oxygen concentration at saturation, Os, are needed to estimate γ and they do not even need to be known precisely. This solution is therefore a good candidate for uses in real industrial environments.

Figure 2 - a) VTC, b) OB-TOC, c) ED-TOC; 1) Control Layout, 2) V-S plane trajectory (VSpt); Secondary dashed axis for μ or γ, respectively. A dark area marks the speed related zone in which the process spends most of its time. Initial S=0 and V=V_o conditions are assumed



Experimental strategy

The main problems identified, as susceptible to be solved, were: lack of robustness of the SBR when confronted to peak substrate concentrations (PSC), loss of activity due to starvation (LOS), and variations in degradation efficiency (DE) because of operating into the inhibition zone. It would be also desirable to test the long-term stability (LTS) of the new solutions.
For testing possible solutions to these problems, a series of experiments in two different directions were conducted. The main philosophy is to increase complexity step-by-step, beginning with the simpler modes. Future experiments (FE) will combine this two research axes. Table 1 shows the experimental strategy.

Table 1 - Experimental strategy based on two different research directions. The problems to be solved in each case are referenced. Future experiments (FE) are also suggested

Control modes Biomass configurations	FTC: Fixed Timing Control	VTC: Variable Timing Control	OB-TOC: Observer based Time Optimal Control	ED-TOC: Event Driven Time Optimal Control
SB: Suspended Biomass	SOC PSC LOS DE	PSC DE	PSC DE FE=LTS	PSC DE FE=LTS
MB: Moving Biomass	PSC LOS DE	FE=All	FE=All	FE=All
FB: Fixed Biomass	PSC LOS DE	FE=All		

In order to obtain comparable data for testing the different control modes, a standard operation condition (SOC) was defined. Here the SOC was the FTC strategy since is the usual mode of SBR operation. For doing any control mode experiment, the reactor was previously running in SOC. Then the experimental kinetics is made and, after that, again a SOC is conducted. This allows comparing the "after" and "before" SOC kinetics to asses the short term impact of the new mode in the SBR parameters.

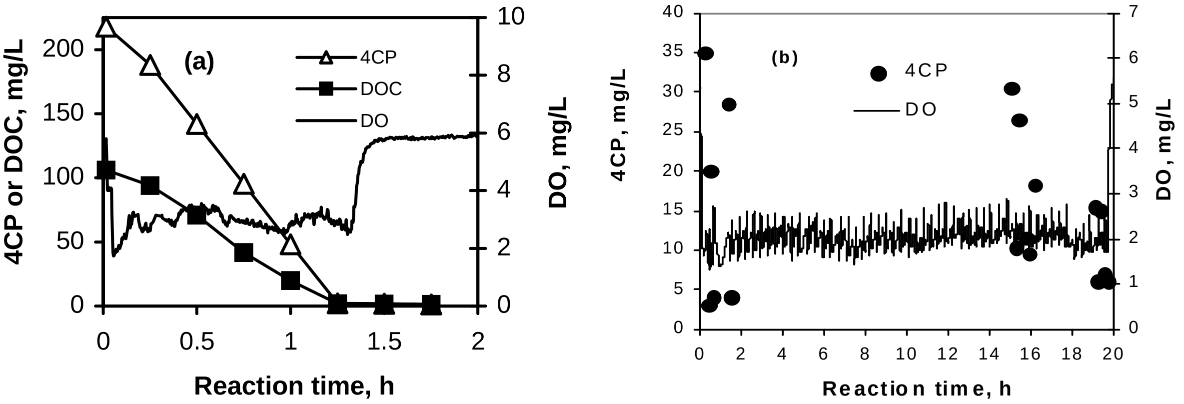
RESULTS AND DISCUSSION

In the paper the initial concentration condition is reported in two forms. The influent substrate concentration present in the storage tank and fed to the reactor is called S_{in}. Once the reactor was fed, the influent substrate concentration becomes the initial substrate concentration (S_o) and depends on the internal dilution (or the volume exchange ratio). Removal efficiencies of 4CP and the mixture of phenols were always superior to 98%, except for the days when the perturbations were introduced (concentration peaks or starvation). Degradation rates were computed taking into account the quantity of substrate degraded, and dividing this by the quantity of VSS and the filling and reaction times. During acclimation degradation rate (q) varied from 20 to 60 mg 4CP/gVSS-h, for the suspended biomass. The sludge volumetric index (SVI) obtained was in average 40 mL/g, indicating the excellent characteristics of the sludge. MLVSS concentration varied between 1800 and 2500 mg/L, as a consequence of the daily purge of sludge to maintain a mean cell retention time of 20 d. Mean concentration was 2000 mgVSS/L.

Once the biomass was acclimated, the reactor was operated under a determined strategy. The decanting time (30 min), idle period (15 min) and drawing (15 min) times were always the same no matter the type of biomass or control strategy used. In the case of the FTC, filling time was 15 min, and reaction time was fixed in 4 h.

Figure 3 illustrated the behavior of the VTC and ED-TOC strategies for the 4CP degradation. Figure 3a presents the behavior of a cycle operated under the VTC strategy using 4CP as substrate (220 mg/L). It is possible to follow the behavior of the DO during the degradation of the substrate. Al the time when no more organic mater is present in the reactor, the DO increases indicating to the computer the end of the reaction period. When the TOC strategy (either for the OB and EV modes) was implemented, filling rate was keep in such a way to maintain the substrate concentration at S*. In this case the reaction and filling phases occurred simultaneously. At the moment when the maximal volume was reached, the filling phase stopped and only reaction phase occurred. When a concentration peak was introduced, the algorithm determines the optimal influent rate allowing the necessary time to biodegrade the volume of the toxic water. Note in figure 3b the example for the ED-TOC strategy. Here the internal concentration in the reactor was maintained oscillating around 20 mg 4CP/L, for an influent concentration (S_{in}) simulating a peak of 5200 mg4CP/L In the same figure it is possible to note the DO evolution.

Figure 3 - Evolution of substrate concentration and dissolved oxygen for the VTC (a) and the TOC-ED (b) strategies



Effect of the concentration peaks

Table 2 summarizes the effect of the concentrations peaks on the performance of the reactor. For all the cases, the best performances were obtained with the ED-TOC strategy. Here, due to the basic principle of operation of the strategy, the microorganisms always will be in presence of a concentration around S*, resulting thus protected against the inspected arrival of shock loads. For this work several initial peaks concentrations were prepared in the feeding tank (1200. 5200 and 11200 mg 4CP/L). In all the cases degradations occurs effectively with this strategy. Thus, it was possible to degrade S_{in}

concentrations up to 11200 mg 4CP/L. Theoretically there is not limit in the initial concentration since the algorithm always will keep the concentration al the optimal value. With the usual control system, based on fixed times, the worst performances were observed. Only 550 mg/L was possible to biodegrade with 100% of efficiency removal.

On the other hand, it is interesting to point out the promissory results obtained with the moving bed (MB) compared with the suspended biomass (SB) system. If the MB and SB are compared using the FTC algorithm, it is observed that the mixture of attached and suspended biomass generates better results than the suspended biomass alone. Up to 1850 mg4CP/L were possible to treat without problems in the degradation efficiency (almost 3 times more than the SB system). The major impact of the toxic peaks was observed for the FTC control strategy. When a new cycle was conducted (at 350 mg/L), the degradation rate obtained with the FTC-SB after the 900 mg/L peak decreases 80%. That means that a waste water treatment plant will need five times more time to degrade the usual influent concentration. On the other hand, the degradation rates were not affected after a sudden introduction of a toxic shock load when the reactor was operated under the time optimal control strategy. Even, in some cases when the event driven algorithm was used a higher degradation rate was obtained (114 mg 4CP/gVSS -h) during the peak.

Effect of starvation periods

Some times, due to variations in product manufacture, the concentration of the toxic compounds present in industrial effluents, may vary. This will generate a starvation period against the acclimated biomass and thus generating a lost of activity (Buitrón and Moreno, 2002). This implies that the efficiency of the treatment would be affected when the toxic enters again to the WWTP. Figure 4 presents the effect of starvation periods on the performance of the reactor when suspended, fixed and a mixture of suspended and fixed biomass is used. It is clear the beneficial impact generated by the fixed biomass. When a mixture of phenols was used, there is only 35 % of increment in the degradation time (against almost 100% for suspended biomass). In the case of 4CP, the impact of starvation is avoided clearly by the use of the carrier material, indicating again the robustness of the process by the attached biomass (Gheewala and Annachhatre, 2003).

Figure 4 - Increase in the degradation time due to different starvation periods, in respect to the degradation time observed before starvation: (a) 100 mg/L of mixture of phenols (25 % each), (b) 100mg/L of 4-CP

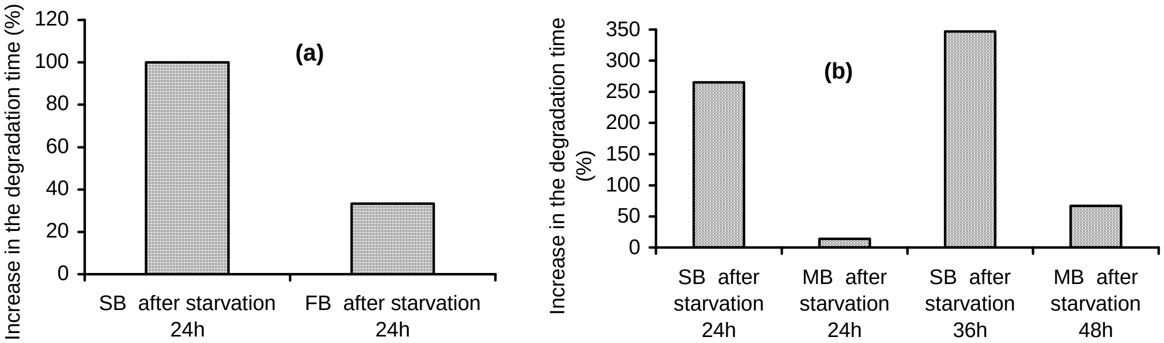


Table 2 - Effect of different operational strategies on the reactor performance under peaks of concentration

Control strategy	Type of Biomass	Peak of 4CP, mg/L (S_{in})	Efficiencies during the peak (%)	Degradation rate before the peak (mg 4CP/gVSS-h) **qb**	Degradation rate during the peak (mg 4CP/gVSS -h) **qd**	Degradation rate after the peak (mg 4CP/gVSS -h) **qa**	Degradation rate ratio after the peak **(qa/qb)**
FTC	SB	550	100	25.0	21.0	22.2	0.9
		760	85	25.0	18.5	11.3	0.5
		900	63	25.0	21.4	7.4	0.2
FTC	MB	850	100	33.3	44.4	33.3	1.0
		1850	100	33.3	24.3	26.7	0.8
		3240	20	33.3	6.9	N.D.	N.D.
VTC	SB	700	100	59.8	44.9	59.8	1.0
		1050	100	59.8	9.0	18.0	0.3
		1400	18.3	59.8	0.9	N.D.	N.D.
OB-TOC	SB	700	100	79.3	57.1	79.3	1.0
		1050	100	79.3	45.1	79.3	1.0
		1400	100	79.3	73.3	79.3	1.0
ED-TOC	SB	700	100	71.4	63.5	71.4	1.0
		1400	100	65.0	91.2	71.4	1.1
		2800	100	95.3	114.3	101.5	1.1
		5600	100	81.6	114.3	71.4	0.9
		11200	100	71.4	114.3	64.5	1.0

N.D. Not enough degradation was archived to compute the degradation rate

CONCLUSIONS

From the results obtained so far, two important results are easily seen:

1. If no especial control strategy is designed (let say FTC strategy) then SBR systems with fixed biomass (MB or FB) have a better resistance against concentration peaks and toxic starvation than SB systems. However, these solutions are not enough to increase sufficiently the performance of the SBR under extreme operating conditions.

2. Sophisticated control strategies as OB-TOC, and specially ED-TOC, greatly increase the robustness and performance of the SBR to levels never obtained before without them. The investigation in developing such control modes is, therefore, very promising.

3. Results showed that it was feasible the practical implementation of the optimal control strategy. A good performance of the reactor operated with the ED-TOC strategy was obtained since the degradation and mineralization of the toxic substrates was efficiently completed. The removal efficiencies were up to 98% as chemical oxygen demand and 100% as 4CP. The ED-TOC strategy

was able to manage increments of toxic concentrations in the influent up to 11200 mg/L of 4CP without any inhibition problem.

Several experiments have to be done to finalize this study. Long-term Stability of the SBR under the TOC strategies has to be studied, before a strong affirmation about their properties can be done. This includes specially the study of the evolution of the properties of the biomass under such control strategies. Our hypothesis is that the combination of suspended and fixed biomass with the Time Optimal Control strategy will give the best results in terms of efficiency and robustness of the whole system. This is part of the future work.

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