Biodegradation of high 4-chlorophenol concentrations in a discontinuous reactor fed with an optimally controlled influent flow rate

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Introduction

Many industrial processes generating wastewater containing toxic compounds are characterized by their variability. In the chemical, pharmaceutical, plastic, and petrochemical industries, for some cases, production processes are in batch. Because of the high variations in flow and concentration of contaminants in industrial wastewater, usual treatment processes do not obtain satisfactory removal efficiencies. Besides, due to its toxicity, the biological treatment of industrial wastes containing a high phenol concentration is inefficient because of the inhibition of the microorganisms (Buitrón *et al.*, 2003). To overcome the problems discussed above several operation modes have been presented using the dissolved oxygen (DO) concentration. Betancur *et al.*, (2004) described the mathematical development of a new control strategy called Event-Driven Time Optimal Control (ED-TOC) that measures the dissolved oxygen to robustly control the fill rate of a discontinuous process treating inhibitory compounds. This work presents the results of the application of the ED-TOC strategy to biodegrade, in a discontinuous reactor, a synthetic wastewater constituted with high concentrations of 4-chlorophenol as model of the inhibitory compound.

Methodology

An aerobic automated Sequencing Batch Reactor (SBR) system with a capacity of 7L and an exchange volume of 57% was used. The temperature was maintained at 20ºC inside the reactor. The reactor was inoculated with microorganisms acclimated previously to degrade 4CP. A synthetic wastewater containing 4CP was used as a sole source of carbon and energy. Nutrients such as nitrogen, phosphorus, and oligoelements were added (AFNOR, 1985). Substrate concentration was measured using the colorimetric technique of 4-aminoantipyrine (Standard Methods, 1992). Total and volatile suspended solids (TSS and VSS), Chemical Oxygen Demand (COD) were determined according to the Standard Methods (1992). Dissolved organic carbon (DOC) was determined with a Shimadzu TOC-5050. These analyses were performed to evaluate 4CP mineralization. The metabolite (5-chloro-2hydroxy-muconic acid semialdehyde) which can be inhibitory for the microorganisms, was also determined by spectrophotometry at 380 nm using a HACH spectrophotometer. The experimental design considered four different sets of initial 4CP concentrations in the influent: 350, 3000, 5000 and 7000 mg4CP/L. In order to compare the performances, the SBR was operated under two operational strategies (the conventional and the ED-TOC). The conventional or Fixed Timing Control strategy (FTC) was conducted as follows: Preaeration time: 15 min; filling: 15 min; reaction time: 3 h; and settling time: 30 min. On the other hand, the ED-TOC was operated with the next procedure. Preaeration time: 15 min; filling and reaction time: variable; and settling time: 30 min. The ED-TOC strategy was applied to control the filling and reaction phases. It is known that the behavior of the biomass growth rate (μ) as a function of the toxic substrate concentration (S) can be described by the Haldane law. In this model μ reaches a maximal value, μ*, when the substrate concentration value is S*. Toxic concentrations above or below μ* will generate a diminution in the growth rate and, consequently, also in the reaction rate. If S is kept near S*, the degradation rate can be maintained near to its maximal value.

In the ED-TOC strategy it was developed a manner to estimate a variable (named γ), related to the reaction rate, in such a way that maximizing the former, the later is maximized too, but without measuring it. In this case γ is almost proportional to the reaction rate (or µ). Only two parameters (oxygen mass transfer and the dissolved oxygen concentration at saturation) are needed for control purposes (Betancur *et al.*,2004).

Results and Discussion
Degradation of 4CP by the FTC strategy
The reactor operated under the FTC strategy degraded 350 mg4CP/L in one cycle of 4h (figure 1A). It has been shown that a higher substrate concentrations, inhibition of the biomass starts (Buitrón *et al*. 2003).When high concentrations peaks of 4CP are going to be degraded with the FTC strategy, a dilution of the water is required in order to avoid inhibition, thus several cycles of the SBR are needed. Applying this, the necessary time to degrade the different 4CP concentrations were: 350 mg4CP/L (4 h, 1 cycle), 3000 mg4CP/L (36 h, 9 cycles), 5000 mg4CP/L (60 h, 15 cycles) and 7000 mg4CP/L (80 h, 20 cycles).

Degradation of 4CP by the ED-TOC strategy
The degradation of 350 mg4CP/L with the ED-TOC strategy was obtained in 2h (the total cycle was 3.5h). Figure 1B presents the behavior of the substrate concentration, measured as 4CP, COD, and DOC during a cycle. It is possible to distinguish how the control operates if the substrate evolution and the DO curve are followed. When the substrate is filled the DO decreases until the substrate concentration is higher than S* and an inhibition starts; then, the DO increases, indicating that the maximal degradation rate in the Haldane curve has been passed. At this point the fill is stopped and the degradation rate of the 4CP is near to a maximal. Once the substrate is degraded, the DO starts to increase again and the filling pump is turn on. This behavior is maintained until the total volume of the reactor is reached. The operation mode can be explained as if in the reactor several mini-batches took place during a cycle. At the end of the reaction the DO increases to the saturation value. For the example showed the inhibition never occurred due to the fact that 4CP concentration in the reactor was around S* and never was higher than 50 mg/L during all the reaction, in this case the S* value was around 20 mg/L.
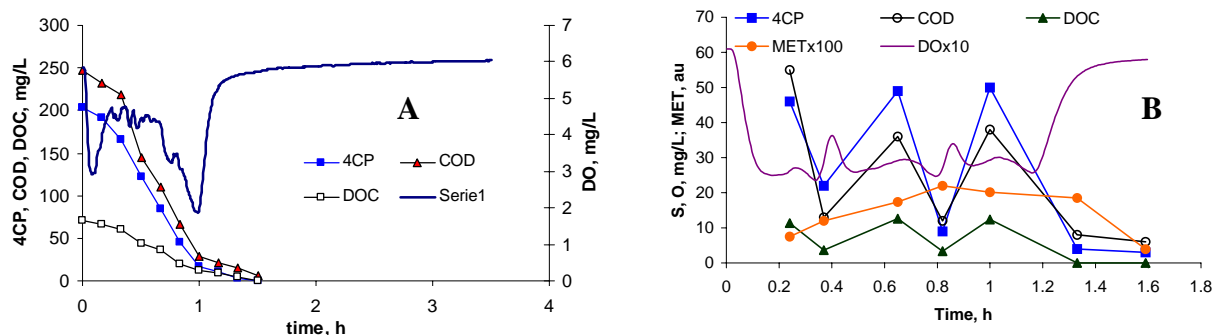

Figure 1. *Behavior of the substrate concentration, measured as 4CP, COD, and DOC during the degradation of 350mg4CP/L using the A) FTC and B) ED-TOC strategy*

The degradation of 3000 mg4CP/L (Figure 2) was reached in 24h (the total cycle was 26h). It is possible to distinguish how the control operates if the substrate evolution and the DO curve are followed as the figure 1B. The behavior of the control and chemical parameters (DO, COD, DOC, 4CP) was similar as the degradation of 350mg4CP/L. In the reactor the concentration of 4CP was never superior to 50 mg/L, except in the first period of fill (the first mini-batch) 70 mg/L where the ED-TOC strategy try to found the S* (around 25 mg/L).
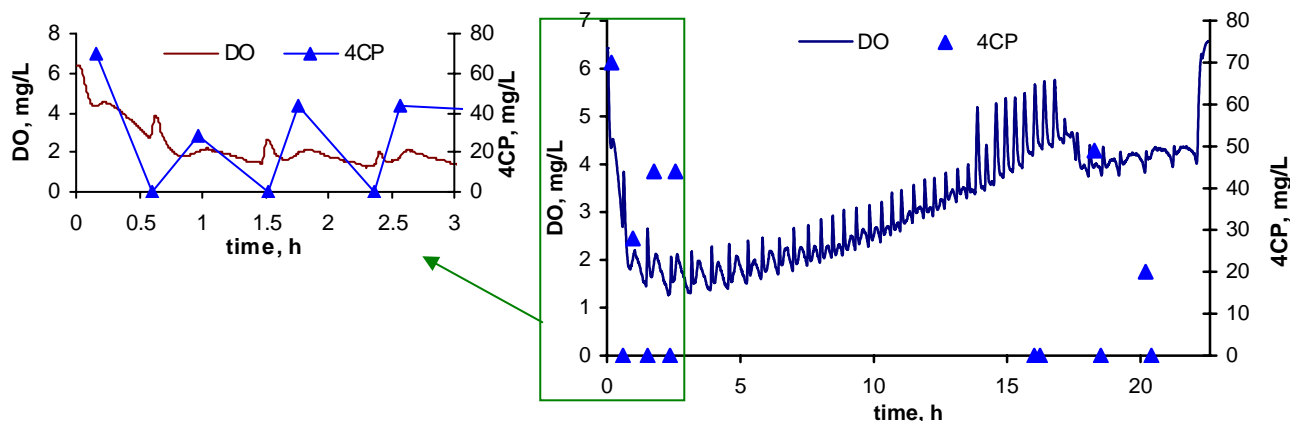
Figure 2. Behavior of the substrate concentration, measured as 4CP, COD, and DOC during the degradation of 3000mg4CP/L using the ED-TOC strategy

The degradation of 5000 mg 4CP/L (Figure 3A) was achieved in 30h. The quantity of 4CP was never superior to 80 mg/L, except in the first period of fill (110mg/L), this concentration of 4CP not causes problems by inhibition of the biomass. The S* was around 30 mg/L. Similar results were observed for the case of 7000 mg4 CP/L (Figure 3B) the reaction time was extended to 42h and the total cycle duration was 43h. It is interesting to note that independently of the influent concentration, no inhibition problems of the biomass were observed for all the cases.
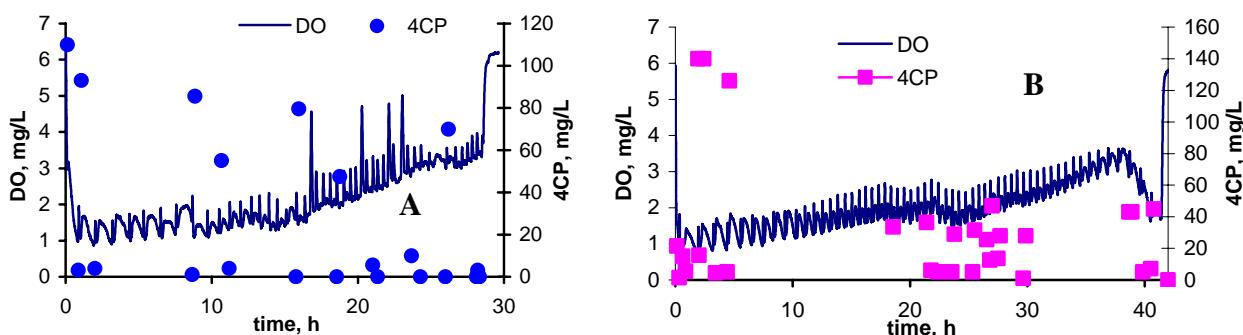

Figure 3. Behavior of the substrate concentration, measured as 4CP, COD, and DOC during the degradation of A)5000 and B)7000 mg4CP/L using the ED-TOC strategy

Comparison of FTC and ED-TOC strategies

With the results obtained it was possible to compare the performances for both strategies and also it was verified the capacity of the ED-TOC strategy to degrade high concentrations of toxic compounds. The comparison of the strategies showed that the necessary time to degrade the same concentration of 4CP is lower with the use of the ED-TOC strategy (figure 4). This time for the ED-TOC is lower from 12% to 52% for the 350 and 7000 mg4CP/L, respectively. The higher the concentration of 4CP the lower the degradation time with the ED-TOC strategy was observed. The maximal specific degradation rate, q_{max}, did not show significant differences when comparing both strategies. For FTC strategy the q_{max} was 50 mg4CP/gVSS/h, and for ED-TOC it varied between 46 and 50 mg4CP/gVSS/h, for the four concentrations studied. This can be explained because although there exists a great difference in the concentration of the wastewater (from 350 to 7000 mg/L), the concentration of the toxic in the bulk of the reactor is not inhibitory (between 50 and 140 mg/L).

It can be observed that for ED-TOC strategy the applied load is of almost the double (table 1) than for the FTC strategy. For the degradation of phenols Herzbrun *et al*., (1985) reported a value of 0.26

kgCOD/m^3/d for a pilot scale reactor. Also, Buitrón *et al*., (1994) reported a value of 1.2 kgCOD/m^3/d for the degradation of 4CP using a strategy similar to the FTC.
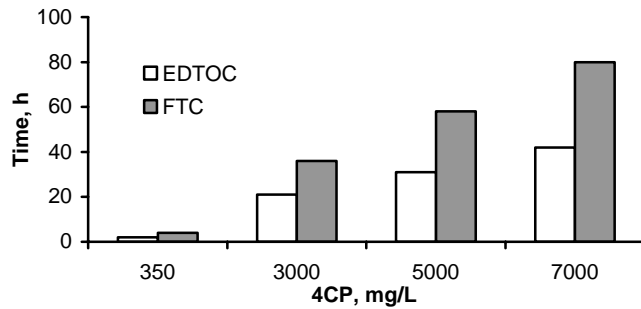

Figure 4. *Comparison of the time necessary for degrade the same quantity of 4CP by the FTC and ED-TOC strategies*

Table 1. Applied load degrade by the different strategies

4CP, mg/L	applied load (kgCOD/m^3/d)	
	FTC (for each cycle)	**ED-TOC**
3000		**4.11**
5000	**2.52**	**4.80**
7000		**4.80**

An important point of discussion is that with the FTC strategy it is not possible to degrade influents with concentrations superiors to 500 mg/L. In addition, it has been observed that inhibition and a total loss of the activity of the microbial consortia was found, when a concentration of 1050 mg/L was applied to the reactor (Buitrón *et al*., 2003). However, EDTOC strategy could theoretically degrade any amount of toxic in the influent. It was showed that it is possible to degrade a concentration of 7000 mg4CP /L. This concentration is 10 times higher to the value that would cause an inhibition using the FTC strategy in the sequential discontinuous reactors.

Conclusions

A better performance of the reactor operated with the ED-TOC strategy was observed when it was compared to the response obtained with the reactor operated under the conventional strategy. The ED-TOC strategy was able to manage increments of toxic concentrations in the influent up to 7000 mg 4CP/L without any problem. It was shown that not only higher concentrations of toxic could be treated with the ED-TOC strategy, but also a reduction in degradation time was obtained (around 52%).

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