Optimal biodegradation of phenol and municipal wastewater using a controlled sequencing batch reactor

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Abstract This work presents the results of the application of an optimally controlled influent flow rate strategy to biodegrade, in a discontinuous reactor, a mixture of municipal wastewater and different concentrations of phenol when used as a toxic compound model. The influent is fed into the reactor in such a way to obtain the maximal degradation rate avoiding the inhibition of the microorganisms. Such an optimal strategy was able to manage increments of phenol concentrations in the influent up to 7000 mg/L without any problem. It was shown that the optimally controlled influent flow rate strategy is a good and reliable tool when a discontinuous reactor is applied to degrade an industrial wastewater.
Keywords Optimal control strategy; phenol; SBR

Introduction

Industrial processes such as oil refineries, pulp and paper manufacturing plants, resins, ceramic and coke manufacturing, steel plants, coal conversion processes, and pharmaceutical industries generates wastewater containing toxic compounds which are characterized by their variability (Santos and Linardi 2004). 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 high phenol concentrations is inefficient because of the inhibition of the microorganisms (Buitrón *et al.*, 2003). One of the main compounds in this kind of wastewater is the phenol. Wastewater containing phenol discharged into a receiving body of water would produce several change in biochemical functions in fish endanger fish life, even at relatively low concentration, e.g. 5–25 mg/L (Chung *et al.*, 2003). In the human case blood changes, liver and kidney damage, and cardiac toxicity including weak pulse, cardiac depression, and reduced blood pressure have been reported in humans acutely exposed to phenol by the oral route. Ingestion of 1 g phenol is reported to be lethal for humans (Nuhoglu and Yalcin, 2005). Moreover, there exists an increasing concern that consumption of water containing high concentration of phenolic compounds may lead to cancer. Other effects of phenol including permeabilization of cellular membranes and cytoplasmic coagulation, phenolic contaminants can damage sensitive cells and thus cause profound health and environmental problems (Tziotzios *et al.*, 2005). Due to these adverse health effects of phenols, the World Health Organization has set a limit level of 1 mg/L to regulate phenol concentration in drinking waters (Hannaford and Kuek, 1999).

Different methods exist for the elimination of phenol in wastewater. However, in contrast with physical and chemical methods, biological methods of phenol removal are preferable in the wastewater treatment process due to relatively low processing costs

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(Zumriye *et al.*, 1999). In spite of phenolic toxic properties, activated sludge and several numbers of microorganisms can utilize phenol under aerobic conditions as a sole source of carbon and energy. For example, Fialova *et al.* (2004) and Yan *et al.* (2005) reported that some microorganisms of genus *Candida* have a phenol-degrading potential up to 1700 mg/L. In the case of a mixed culture Tziotzios *et al.* (2005) reported that in batch reactors concentrations above 1200 mg/L could produce a strong inhibitory effect on activated sludge. In the case of a shock load of 1850 mg phenol/L more than 300 hours were needed to degrade the compound in the batch reactor. Yoong *et al.* (2000) reported the same behavior since they found that concentrations higher than 1300 mg/L in an activated sludge treatment produces inhibition of the system. In some chemical and petrochemical wastewaters, typical phenols concentrations varied from 35 to 400 mg/L for oil-refining, pharmacy, electroplating, paper making, cooking and iron smelting industries (Chen *et al.*, 1997). In this case the biological treatment may be an economical way to treat this hazardous wastewater.

However, in some petrochemical wastewaters, like the spent caustic liquors, the total phenols concentration may reach values up to 30,000–50,000 mg/L (Olguín-Lora *et al.*, 2003). It has been reported, for the case of a Mexican refinery, producing 14 m^3/d of spent caustic wastewater, that the phenol concentration was as high as 30000 mg/L (Olguín-Lora and Ruzo-Flores, 2004). In these extreme cases the use of biological process is limited.

The sequencing batch reactor (SBR) is a bioreactor that operates under five well-defined phases: fill, react, settle, draw, and idle. In the standard operation mode, the duration of these phases is typically determined by an expert operator based on his/her experience and exhaustive testing in the laboratory with a pilot plant. In particular, the reaction phase is sufficiently long to allow the toxic substances to be effectively biodegraded. The settle and draw phases are fixed in duration by the characteristics and constraints of the activated sludge and the reactor itself. A SBR operated under standard operation mode presents several constraints when applied to toxic wastewater degradation such as inhibition of the microorganisms, problems with shock loads of toxic compounds, deacclimation, and low efficiencies regarding the removal of toxic compounds (Buitrón and Moreno, 2002). In order 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 strategy called Event-Driven Time Optimal Control strategy (ED-TOC) to robustly control the influent flow rate in such a way to try to maximize the reaction rate of a discontinuous process treating inhibitory compounds. This strategy proved its practical application for the degradation of a synthetic wastewater containing 4-chlorophenol (Moreno-Andrade *et al.*, 2006).

This work presents the application of the ED-TOC strategy to biodegrade, in a discontinuous reactor, a mixture of municipal wastewater containing high concentrations of phenol.

Methodology

An aerobic automated SBR system of 7L and an exchange volume of 57% was used (Figure 1). The airflow rate was 2.0 L/min and the temperature was maintained at 20 °C inside the reactor. The reactor was inoculated with 500 mgVSS/L from a municipal activated sludge wastewater treatment plant. A mixture of municipal wastewater and high concentrations of phenol was used as a sole source of carbon and energy. Nutrients were added according to AFNOR (1985). Phenol concentration was measured taking samples and processing them off-line using the colorimetric technique of 4-aminoantipyrine (*Standard Methods*, 1998). Total and volatile suspended solids, as well as chemical

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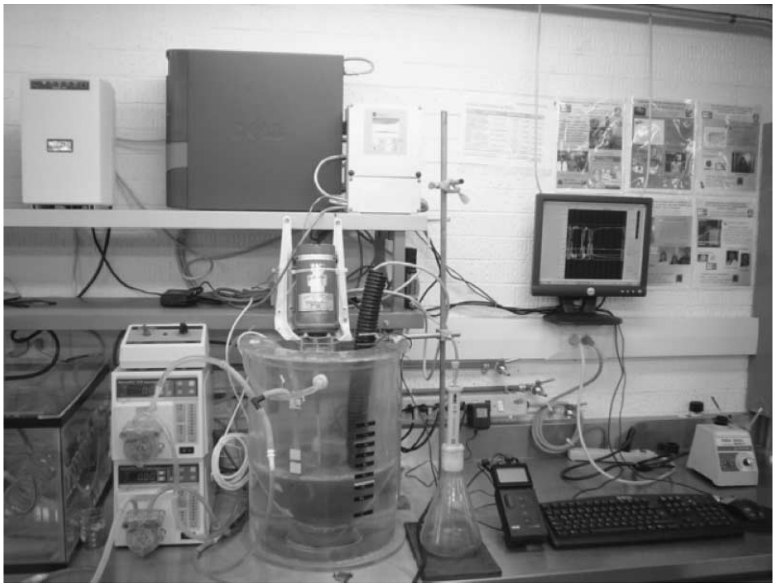

Figure 1 Experimental assembly showing the reactor set-up

oxygen Demand (COD), were determined according also to the *Standard Methods* (1998). Dissolved organic carbon (DOC) was determined with a Shimadzu TOC-5050 analyzer.

The experimental design considered five different sets of initial concentration of phenol (350, 700, 1500, 3000 and 7000 mg/L) in the mixture with municipal wastewater. The concentration of 350 mg of phenol/L was used as standard condition for comparison purposes. The concentration peaks of 700, 1500, 3000 and 7000 mg/L of phenol were tested in a punctual cycle. The acclimation of the reactor was using variable cycles time strategy (Moreno and Buitrón, 2004). After that, and before applying the ED-TOC strategy, the SBR was operated using the standard operation mode. For this case the SBR was operated under the following strategy: preaeration time (15 min.), filling time (5 min.), reaction time (variable depending on the necessary time to reach a total degradation of the mixture) and settling time (30 min.).

Once the operation of the reactor was stable (indicated by constant degradation times), the ED-TOC strategy was applied to control the reaction phase. The ED-TOC strategy finds a variable related to the reaction rate. Such a variable can be estimated in real time by using the DO concentration and the volume of the reactor, as it was described in detail by Moreno-Andrade *et al.* (2006). The influent flow rate is then controlled in such a manner that the reaction rate is close to the maximal value. This is obtained by maintaining an optimal substrate concentration in the reactor due as a consequence of the controlled filling. Considering a Haldane law, the optimal substrate concentration is the $S*$, i.e. the value at which the maximal growth rate or substrate degradation rate is observed. The controller tries to maintain the substrate concentration around $S*$ in order to avoid biomass inhibition.

Results and discussion

The characterization of the municipal wastewater gave the following values: TSS $= 141.5 \pm 25.3$ mg/L, COD (without phenol) $= 270 \pm 52$ mg COD/L and 1227 ± 8 6 mg COD/L in the mixture of wastewater and 350 mg/L of phenol.

The application of the ED-TOC strategy showed that it was possible to degrade a mixture of municipal wastewater and phenol. The mixture presented a total COD of 1227, 2087,

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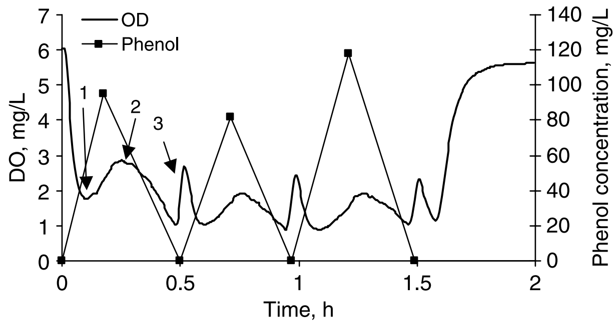

Figure 2 Degradation kinetics of a mixture of municipal wastewater and 350 mg/L of phenol using the ED-TOC strategy. See the explanation in the text

4350, 6380 and 14470 for the five initial phenol concentrations (350, 700, 1500, 3000 and 7000 mg/L), respectively. Note that the increase in COD is due to the increase of phenol.

The reactor operated under the ED-TOC strategy degraded efficiently 350 mg4CP/L in the influent, the reaction time took around 2 hours (total cycle time of 4 hours). This condition was applied during all the experimental operation and was used as a standard condition in the reactor (degradation of a mixture with 350 mg phenol/L). This concentration was studied and used with comparative purposes because it has been shown that at higher substrate concentrations, inhibition of the biomass starts (Buitrón *et al.*, 2003).

Figure 2 shows the degradation of the mixture of toxic wastewater for the case of 350 mg/L of phenol (1227 mg COD/L in the mixture with wastewater). When the substrate is filled the DO decreases (Figure 2, point 1) until the substrate concentration is higher than $S*$ and an inhibition starts. The DO then increases (point 2), 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 phenol is near its maximum. Once the substrate is degraded, the DO starts to increase again (point 3) and the filling pump is turned on. This behavior is maintained until the total volume of the reactor is reached. The operation mode can be explained as if several mini-batches took place in the reactor during a cycle. At the end of the reaction the DO increases to the saturation value. For the example shown, inhibition never occurred due to the fact that phenol concentration in the bulk of the liquid in the reactor was around $S*$ and was never higher than 120 mg/L during the whole reaction. The use of the ED-TOC strategy can minimize the volume of the reactors because it is not necessary to dilute high concentrated toxic wastewater as in the usual operation mode in order to avoid inhibition.

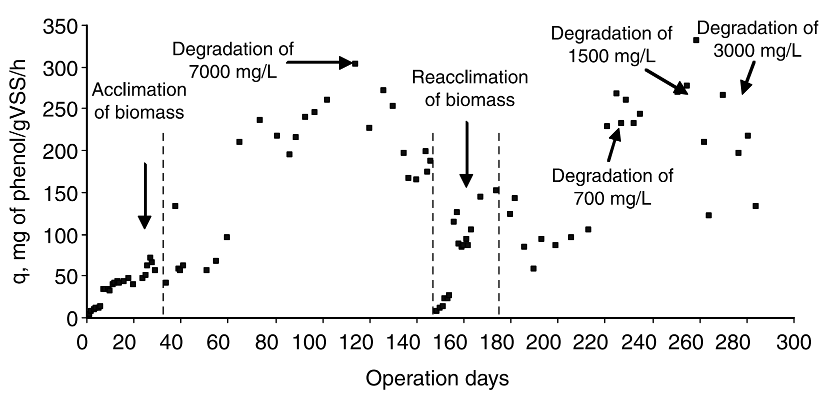

Figure 3 Specific degradation rate (*q*), during the operation of SBR

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The SBR operated during 745 cycles (225 days). A stable efficiency was observed, since the removal efficiencies were up to 98% as C.O.D. and 99% as phenol. The effluent presents excellent characteristics: an average value of 38 ± 13 mg TSS/L, 19.5 ± 15.0 mg DOC /L and 39 ± 24 mgCOD/L. Residual phenol concentration in the effluent was less than 1 mg/L in all the operation cycles. In general, the activated sludge presented excellent biomass proprieties since the sludge volumetric index was 114 ± 36 mL/g. The specific degradation rate (q) of phenol was 238 ± 51 mg phenol/g VSS/h, during the operation with ED-TOC strategy. Figure 3 presents the q value during

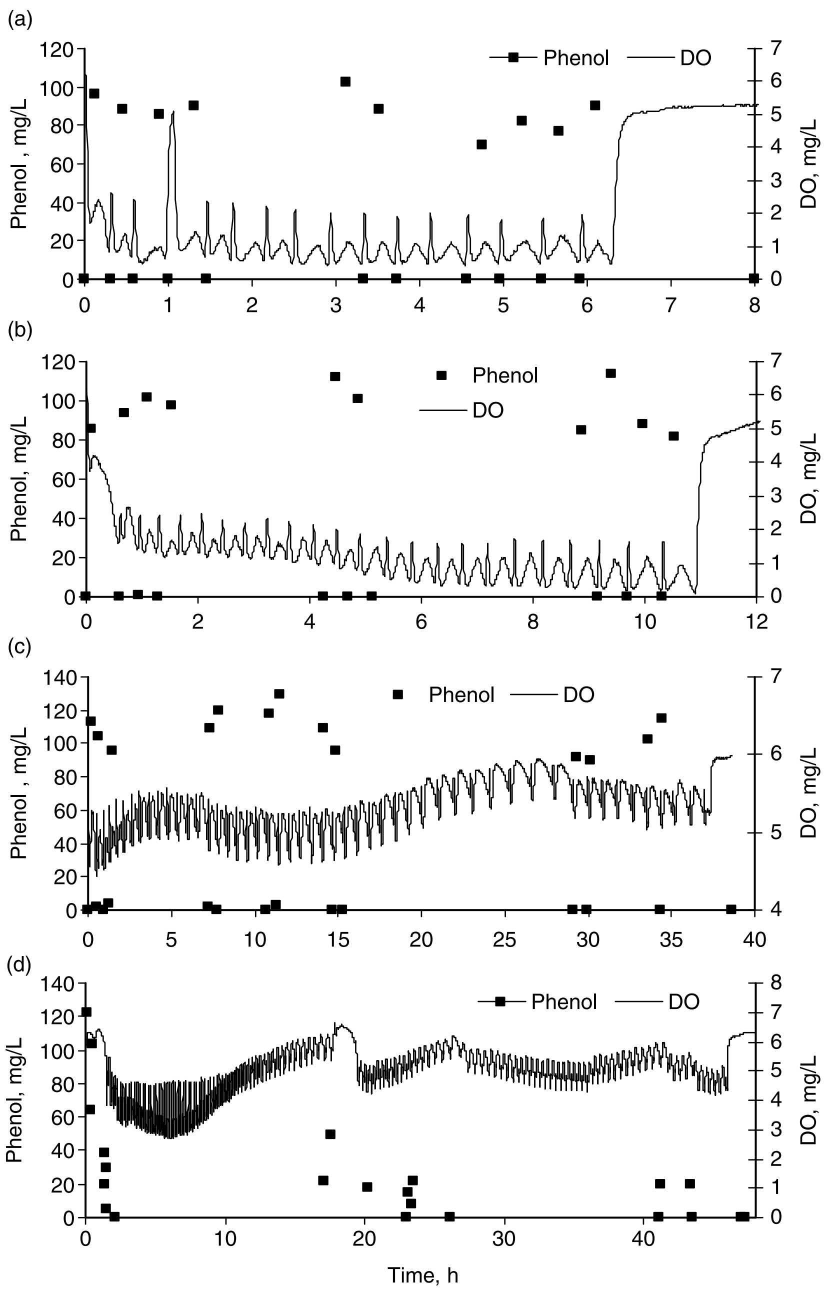

Figure 4 Degradation kinetic of a mixture of municipal wastewater: (a) 700; (b) 1500; (c) 3000; and (d) 7000 mg/L of phenol using the ED-TOC strategy

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the operation of SBR, at the beginning the biomass was acclimated to the wastewater degradation, this acclimation takes around one month using the variable time strategy an after the standard operation strategy. During this period there is a selection and a multiplication of specialized microorganisms (Moreno-Andrade and Buitrón, 2004). Also, physiological transformations occur in the metabolic system of the microorganisms, i.e. alterations at the enzymatic level, regulation and production, mutations, etc. Due to this changes the microorganisms can utilize the mixture of municipal wastewater and the toxics compounds (as the phenol) as source of carbon and energy. After the acclimation period the reactor operates with the ED-TOC strategy. During the operation of the reactor four concentration peaks were applied in the reactor (arrows in Figure 3).

Degradation of shock loads

It was possible to biodegrade shock loads of 700, 1500, 3000 and 7000 mg/L of phenol contained in the municipal wastewater without any inhibition problems. In other studies using SBR it has been reported that the degradation of phenol concentrations as high as 1300 mg/L cause problems of inhibition and a total loss of the activity of the microbial consortia is presented (Yoong *et al.*, 2000). The removal efficiencies during the degradation of the shock load were up to 98% as chemical oxygen demand and 99% as phenol. Figure 4 shows the kinetic degradation of a shock load for degradation of 700, 1500, 3000 and 7000 mg of phenol in the mixture. It is possible to observe the same behavior in the control strategy as in Figure 2.

An important point of discussion is that with the standard operation mode strategy it was not possible to degrade influents with concentrations higher than 1300 mg/L in an activated sludge treatment (Yoong *et al.*, 2000). However, the ED-TOC strategy could theoretically degrade any amount of toxic in the influent, without even measuring it. It is shown that indeed it is possible to degrade a concentration of 7000 mg of phenol/L in the mixture. This concentration is more than five times higher than the value that would cause a permanent and possibly lethal inhibition using the standard strategy in the sequential discontinuous reactors.

Figure 5 shows the degradation kinetics of a shock load of 7000 mg of phenol in the mixture. It is possible to observe the same behavior in the control strategy as in the degradation of 350 mg of phenol in the mixture, as shown in Figure 2. It can be observed that phenol concentration never was higher than 120 mg/L, as in the case of 350 mg/L. These results confirm that higher phenol concentrations, which in a usual batch operation would be inhibitory, can indeed be treated with the proposed strategy. In theory, any phenol concentration could be degraded by this control strategy.

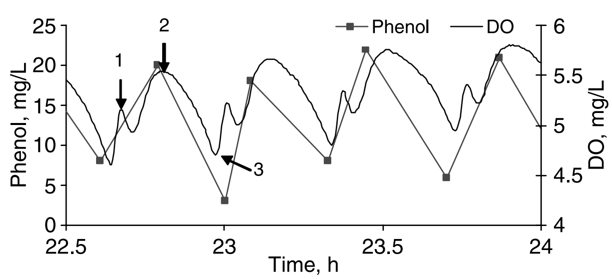

Figure 5 Detail of degradation kinetic of a mixture of municipal wastewater and 7000 mg/L of phenol using the ED-TOC strategy. The points correspond to the explanation of the points in Figure 2

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Conclusions

The application of an optimal control strategy in a discontinuous reactor (ED-TOC) for the degradation of a mixture of municipal wastewater and phenol was presented. Excellent performance of the reactor operated with the ED-TOC strategy was obtained since the degradation and mineralization of the mixture with a high load of phenol was efficiently completed. The ED-TOC strategy was able to manage increments of toxic concentrations in the influent up to 7000 mg/L of phenol in the municipal wastewater without inhibition problems.

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