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ORIGINAL PAPER

Feasibility study of degradation of phenol in a fluidized bed bioreactor with a cyclodextrin polymer as biofilm carrier

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Abstract This work is focused on the evaluation of a β-cyclodextrin polymer as a carrier medium in a fluidized bed bioreactor treating aqueous phenol as a model pollutant. The insoluble polymer support was obtained in the shape of spherical beads by crosslinking β-cyclodextrin with epichlorohydrin. A batch of swollen polymer particles was loaded into the reactor and inoculated with a mixed bacterial culture. Bacterial growth on the polymer beads was initially stimulated by glucose addition to the medium, and then gradually replaced with phenol. The operational variables studied after the acclimation period included phenol load, hydraulic residence time and recirculation flow rate. Low hydraulic residence times and moderate phenol loads were applied. The elimination capacity was usually about 1.0 kg-phenol/m^3d, although a maximum of 2.8 kg-phenol/m^3d was achieved with a retention time of only 0.55 h. The depuration efficiency was not affected by the recirculation flow rate in the range studied. Neither operational nor support stability problems were detected during the operation. A high degree of expansion was achieved in the bioreactor due to the hydrogel nature of the cyclodextrin polymer and, consequently, a low energy requirement was necessary to fluidize the bed.

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Keywords Phenol · Cyclodextrin polymer · Fluidized bed bioreactor

Abbreviations

CD	Cyclodextrin
CDP	Cyclodextrin polymer
FBBR	Fluidized bed biological reactor
HRT	Hydraulic residence time

Introduction

Phenol is an aromatic organic compound that is toxic by ingestion, contact or inhalation, and harmful to aquatic organisms. Phenol and its derivatives are present in several industrial sectors, such as petroleum refining, chemical and parachemical industries or wood processing. These compounds have been usually removed by adsorption or biological treatments. The latter are especially suitable for the processing of low concentration effluents, as in fact occurs in most phenolic wastewaters. Effluents containing phenol in the range about 5–500 mg/l are in principle good candidates to be treated biologically.

Different configurations have been evaluated in the literature for the biodegradation of phenolic compounds, both in suspended cultures (Annadurai et al. 2003; Okaygun et al. 1992) and immobilized

ones (Chen et al. 2002; González et al. 2001; Hecht et al. 2000; Mordocco et al. 1999). Compared to suspended-culture systems, immobilized biomass has been shown to be more effective, more resistant to pollutant overload and operationally more stable (Junter et al. 2003). Fluidized bed biological reactors (FBBR) are high-load water treatment systems, which have been studied by numerous authors (Chen et al. 2002; Lao 2002; González et al. 2001; Kargi and Karapinar 1997). Fluidization provides a favorable gas-liquid mass transfer, which promotes good pollutant-biomass contact and suitable oxygen transport rate (minimizing anaerobic zones). Moreover, liquid fluidization produces little particle attrition and also reduces operational problems such as formation of preferential flow paths and bed clogging by growing biomass. Materials with high specific surfaces and good physicochemical and fluidodynamic properties are typical supports used in these reactors. A variety of matrices have been applied for this purpose: activated charcoal (Lao 2002), wire-mesh sponge (Kargi & Karapinar 1997), polyurethane foam (Brányik et al. 2000), polypropylene (Sokol and Korpal 2005), calcium alginate (González et al. 2001), porous silicone (Hecht et al. 2000) or polyacrylamide (Chen et al. 2002), among others.

In this work, a cyclodextrin polymer (CDP) has been tested as a biomass carrier for degrading phenol in a FBBR. Cyclodextrins (CDs) are cyclic oligosaccharides made of six, seven or eight units of glucose (respectively α-, β- and γ-CD) linked by glucosidic bonds (Szejtli 1998). Their shape resembles a truncated cone with a hydrophilic exterior (which promotes their solubility in water) and a hydrophobic cavity (which facilitates the formation of inclusion complexes with hydrophobic molecules in aqueous media). Due to this feature, cyclodextrins are regularly used in the food and pharmaceutical industries (Szente and Szejtli 2004, Fromming and Szejtli 1994). Being a more polar compound, the affinity constants of cyclodextrins for phenol are similar than for other non-polar compounds such as benzene and toluene (Liu and Guo 1999). As a consequence, cyclodextrin polymers can be effectively used to retain phenol (Romo et al., 2007). In spite of having good sorptive properties, the application of cyclodextrins for removing pollutants is still recent (Molnar et al. 2005; Garon et al. 2004; Szente et al. 1999; Wang et al. 1998; Crini et al. 1998). Nevertheless, their use as a bacterial support requires that the CDs should be incorporated into insoluble polymeric matrices to avoid being carried away by water. Likewise, the use of a biomass support with sorptive properties allows to combine two pollutant removal mechanisms (sorption and biodegradation), and it could also protect biofilms against starvation or shock-loading episodes. In addition, some cyclodextrin polymers are hydrogel materials, which exhibit a high water absorption ability. As their swollen density is slightly higher than water, CDPs can be easily fluidized with a low energy requirement. Since fluidization of conventional supports usually requires a high pump energy, the use of a low density support can also improve the inherent advantages of fluidized bed bioreactors (Nicolella et al. 2000). Despite all these interesting characteristics, CDPs have been scarcely used as biofilm attachment media for wastewater treatment (Sevillano et al. 2002).

Materials and methods

Biomass support

A batch of insoluble CDP particles (nearly spherical in shape) was synthesized by crosslinking β-cyclodextrin with epichlorohydrin (EP). The main polymerization conditions were a CD:EP mole ratio of 1:16 and a reaction temperature of 50°C. A detailed description can be found in Romo et al. (2006). The swollen polymer particles thus obtained were wet sieved and the fraction between 1.25 and 1.60 mm was chosen for this study. About 100 ml of swollen beads (corresponding to 0.190 m of bed height, i.e., 12.5 g of dry CDP) were placed in the reactor. In order to promote heterogeneous microbial populations, this bed was inoculated with a mixed culture. The original inoculum was obtained from a small polluted river with industrial and farming activity, and it was then enriched in a batch suspended culture for a year.

Experimental system

A scheme of the FBBR configuration is provided in Fig. 1. A glass column (inlet diameter 26 mm; height 0.94 m) was used as bioreactor. The column had an

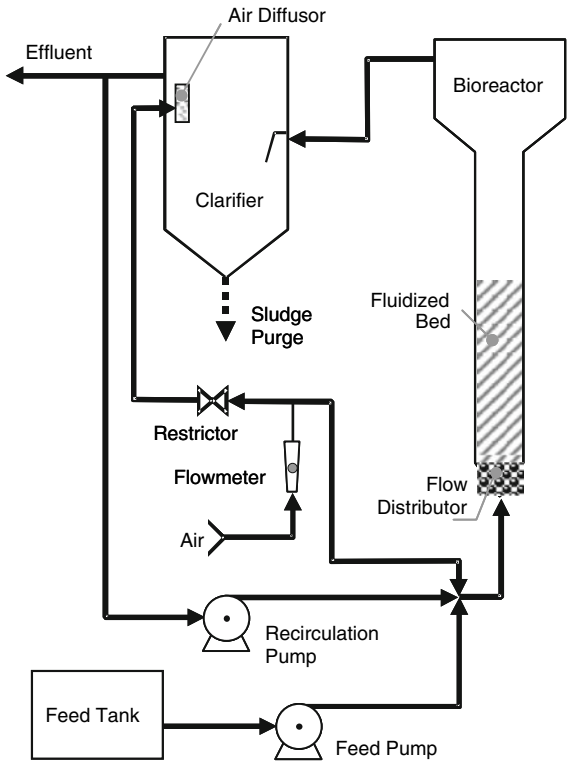

Fig. 1 Experimental arrangement of the FBBR

enlargement at the top (diameter 74 mm; height 0.15 m) to avoid a possible elutriation of the CDP particles. The influent was pumped upwards in the reactor with a multichannel peristaltic pump (Masterflex L/S). The effluent was settled into a clarifier (diameter 51 mm; height 0.66 m) to remove the biomass flocs detached from the support particles. A portion of the clarified effluent was recirculated to the bioreactor with a second pump in order to maintain the fluidization of the bed. Both feed and recirculation streams were aerated to maintain the dissolved oxygen above 3 mg/l. The whole system (including bioreactor, clarifier and tubing) had a total volume of about 1.8 l.

Wastewater

A synthetic wastewater with a variable phenol concentration (5–125 mg/l) was applied. Although phenol was the target pollutant studied, glucose (150–1,000 mg/l) was also used as the carbon source only during the initial start-up of the FBBR. This medium was equilibrated with essential macronutrients (mg/l: K_2HPO_4, 17; KH_2PO_4, 17; Na_2HPO_4, 5.6; NH_4Cl, 0.125; $FeCl_3{\cdot}6H_2O$, 0.060) and micronutrients (μg/l: $ZnSO_4{\cdot}7H_2O$, 1.45; $MnCl_2{\cdot}4H_2O$, 1.00; $Cu(CH_3COO)_2$, 0.22; $CoSO_4{\cdot}7H_2O$, 0.285; H_3BO_3, 0.285; $Na_2MoO_4{\cdot}2H_2O$, 0.050).

Start-up phase

In order to promote a faster growth of the biomass on the support particles, and before feeding phenol, glucose was used during the initial start-up of the FBBR. Then, when the colonization of the CDP particles was visually evident after almost 8 weeks, glucose was progressively replaced by phenol. Finally, acclimation to phenol as the sole carbon source was carried out for eight additional weeks before beginning trials. An inlet phenol concentration as low as 5 mg/l and a hydraulic residence time (HRT) of 0.55 h were used during this starting period.

Operating conditions

The FBBR was operated at room temperature and the air-flow was always enough to assure a proper oxygen saturation level in the liquid phase. The operational conditions used following the bioreactor start-up are summarized in Table 1. Each trial was performed until the effluent phenol concentration remained relatively stable for at least a week. Steady state was considered to be reached when the variations in removal efficiency were less than 15%, at least for a week, and with a minimum phase duration of 2 weeks. Thus, the duration of Phases I and III was about 2 weeks each while Phases II and IV lasted more than 4 weeks (see Table 2). The FBBR was fed with a low concentration of phenol along the first three phases in order to study its evolution without compromising the development of the microbial population. The effects of feed and recirculation flows on the phenol removal capability were evaluated in Phases II and III, respectively. Finally, the inlet concentration of phenol was increased in Phase IV to analyze the behaviour of the bioreactor under a phenol shock loading.

Table 1 Operational conditions in trial performance

	Phase I	Phase II	Phase III	Phase IV
Inlet phenol concentration (mg/l)	55.6 ± 3.6	58.0 ± 3.3	50.2 ± 3.2	133 ± 7.5
Hidraulic residence time (h)	0.55 ± 0.05	1.12 ± 0.08	1.66 ± 0.10	1.69 ± 0.06
Inlet flow (ml/min)	4.0	2.5	2.5	2.5
Recirculation:feed ratio (–)	15	24	32	32
Air flow rate (ml/min)	25.8 ± 3.8	23.8 ± 2.9	76.2 ± 5.4	116.9 ± 6.0

Table 2 Average operating variables

	Phase I	Phase II	Phase III	Phase IV
Operating time (d)	15	27	18	26
Fixed bed height (mm)	202 ± 15	243 ± 12	290 ± 17	345 ± 6
Expanded bed height (mm)	239 ± 24	316 ± 23	462 ± 26	481 ± 19
Temperature (°C)	18.1 ± 1.1	21.5 ± 1.7	21.3 ± 1.3	22.9 ± 1.2
Dissolved oxygen (%sat.)	31.5 ± 5.7	43.3 ± 9.6	37.0 ± 5.0	35.6 ± 8.2
Inlet phenol load (kg/m^{3}d)	2.52 ± 0.46	1.02 ± 0.26	0.72 ± 0.06	1.88 ± 0.13
Outlet phenol load (kg/m^{3}d)	0.61 ± 0.22	0.17 ± 0.05	0.08 ± 0.01	0.93 ± 0.13
Phenol removed (kg/m^{3}d)	1.92 ± 0.35	0.91 ± 0.07	0.64 ± 0.03	0.96 ± 0.11
Removal efficiency (%)	74.6 ± 10.9	83.8 ± 4.2	88.2 ± 2.1	51.0 ± 6.8
Effluent suspended solids (mg/l)	8.7 ± 3.5	13.9 ± 6.7	13.1 ± 5.9	8.2 ± 4.1
Settled solids in clarifier (mg)	248	811	344	974
Biofilm thickness (μm)	47.2 ± 20.7	101.4 ± 14.4	155.7 ± 18.8	213.3 ± 6.1
Attached biomass (ml)	11.1 ± 6.0	25.5 ± 4.5	42.0 ± 6.3	61.8 ± 0.2

Due to the support properties, the common methods for measuring the amount of biomass covering the CDP beads could not be applied. Thus, gravimetric analysis was not valid because of the non-refractory nature of CDP. Furthermore, the combination of ultrasonic waves and strong acids caused the disaggregation of the solid, without detaching the biofilm completely. Finally, an indirect method to estimate the biofilm thickness based on static bed heights was chosen instead (Ngian and Martin 1980). This method assumes that the porosity of the static bed keeps constant while the biofilm is growing around carrier beads, that the particles keep the original shape, and also that no particles are elutriated from the reactor along the FBBR performance. Therefore, the static bed height was periodically measured to estimate the biofilm growth (calculated as average biofilm thickness) on the CDP beads.

Because most of the active biomass was covering the CDP beads, the expanded bed height was used to calculate some of the operational parameters (mainly phenol load and HRT). As the aeration flow generated some turbulences in the gas-liquid-solid fluidization, the expanded bed height could not be accurately determined. Furthermore, the bed contraction due to air bubbles could be considered negligible, so the liquid-fluidized bed height was chosen as a reliable indicator of the expanded bed volume. Air and water flows were momentarily shut off to measure static bed heights, while liquid-fluidized bed heights were determined by keeping the water flow only.

Analytical methods

Phenol concentrations were determined in filtered samples (1.2 μm) by UV/visible spectrophotometry (Perkin-Elmer Lambda 2) at 270 nm. The observed concentrations were in total agreement with those measured by HPLC, and no retention of phenol was detected due to filtration of the samples. Inlet and

outlet organic loads were monitored by COD measurements (APHA 1992). Suspended solids in the effluent and total solids in the clarifier were measured according to Standard Methods (APHA 1992). Dissolved oxygen (Hanna Instr. HI98410), pH (Hanna Instr. HI98150) and conductivity (Crison 524) were measured daily both in the influent and in the effluent. Bed temperature (Hanna Instr. HI92804C) was recorded every 30 min.

Results and discussion

Phenol was successfully removed from a synthetic wastewater in a FBBR using CDP particles as biomass carrier. The testing period including the start-up phase was seven months. The reactor exhibited a good operational stability since the fluidization of the beads was very homogeneous. Although non-coated CDP beads were transparent, browning was observed in many particles approximately 20 days from start-up, and all the particles became dark and opaque about 3 weeks later. So, microbial colonization of the CDP beads was evident along the start-up phase and a significant biofilm growth was observed. In contrast, a small loss of fine CDP particles (less than 1.00 mm in diameter) was elutriated from the bed during the first days of the start-up, which led to a slight decrease (of about 5 mm in 2 days) in the static bed height. As a consequence, extremely high values of COD (even higher than those in the influent) were measured at the beginning of the start-up in the effluent (data not showed). These phenomena were not observed afterwards. Thereafter, COD (total and filtered) and phenol concentration values were always concordant.

Prior to FBBR start-up, batch biodegradation assays were carried out in respirometer flasks, with and without an extra carbon source. Triplicate samples of polymer beads (dry weight about 50 mg) were placed in aerated stirred flasks containing nutrient solution (400 ml), inoculated with an acclimated microbial culture (40 mg/l), and incubated at 20°C. Glucose (150 mg/l) was added in extra carbon source tests. Blanks were performed in the same way but without polymer. The BOD values were compared with the theoretical oxygen demand to obtain the biodegradation degree. A theoretical factor of 1.295 mg DO/mg CDP was deduced from the polymer composition (46.0% CD, 54.0% EP). CDP mass losses of less than 1% per month were obtained when using glucose, and of less than 6% in 21 days without extra carbon source. This good support stability, despite its hydrocarbon character, can be explained considering the complex structure due to crosslinking, which complicates the biodegradation of this material. Besides, cyclodextrins are characterized by their outstanding resistance towards the usual starch-hydrolyzing enzymes (Szejtli 1996). In any case, no additional amounts of polymer were added to the FBBR during the whole operation period with phenol.

Average operating parameters for phenol biodegradation are summarized in Table 2. Since the concentration of suspended solids in the liquid medium was almost negligible, the elimination capacity was calculated according to the expanded bed volume (between 0.10 and 0.25 l, approximately, depending on the phase considered) instead of using the total volume (about 1.8 l). Thus, the active bed volume in different stages ranged from 6.4% to 15% of the total volume depending both on the biofilm thickness variability and on the bed expansion. Consequently, a little fraction of the total volume has been responsible for the phenol biodegradation. Apart from the variables that characterize the biodegradation, no significant variations were observed in the other parameters measured (data not shown). For example, pH ranged between 6.4 and 6.7 and the conductivity values were from 167 to 204 μS/cm. Density of fully covered bioparticles was measured by flotation at the end of Phase IV. An average density of 1.034 g/ml was found using glycerol-water and ethylenglycol-water mixtures. Previously, a value of 1.052 g/ml had been obtained for biomass-free particles. Thus, considering a biofilm thickness of 212 μm, a wet-biomass density was calculated as 1.02 g/ml.

Experimental fixed and expanded bed heights and calculated biofilm thicknesses are displayed in Fig. 2. The three profiles show an increasing trend with time during the first three phases, while they became stabilized (or even slightly decreased in the case of the expanded height) in the last one. Notice the abrupt enlargement in the expanded height at the beginning of Phase III caused by the increase in the recirculation flow rate applied. The static bed height development was more important during

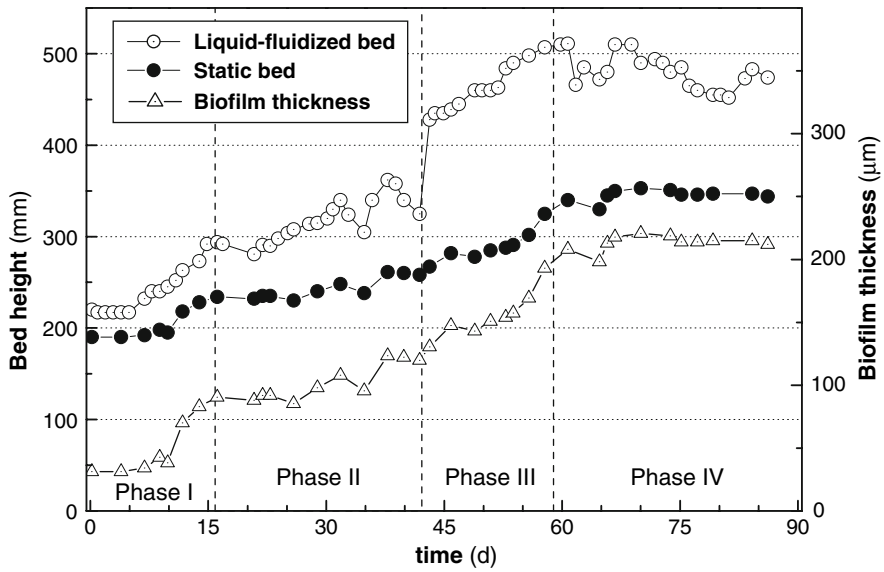

Fig. 2 Experimental bed heights and calculated biofilm thicknesses in the FBBR

Phases I and III (mean growth of 2.7 and 3.1 mm/d, respectively) than in Phases II and IV (1.2 and 0.2 mm/d, respectively). Logically, this in perfect agreement with the evolution of the mean growth of biofilm thickness, calculated as 3.7, 1.5, 3.4 and 0.2 μm/d, for Phases I–IV, respectively. The same tendency was observed for the liquid-fluidized bed height. This biofilm growth causes the bioparticles to reduce their density and increase the bed expansion (Nicolella et al. 1996). The biomass volumes in Table 2 were calculated from the corresponding biofilm thicknesses. Furthermore, Phases I and III produced less solid settlement in the clarifier (accumulated mean of 16.5 and 19 mg/d, respectively) than the other two (30 mg/d in Phase II and 37.5 mg/d for Phase IV). The biomass evolution, together with the high phenol biodegradation efficiencies achieved, demonstrate that the operating conditions favoured the biofilm development, which reduced the particles' density and, as a consequence, increased the bed expansion. However, the small decreasing trend in the expanded bed height, together with the stability of the fixed bed height, suggests that the bioparticle density has been slowly increasing during Phase IV, which may be indicative of a more mature biofilm. Moreover, since the oxygen solubility in water is very low, the availability of oxygen in the inner biofilm layers could be limited by large biofilm thicknesses, which in turn could increase biomass detachment from support media and probably contribute to growth stagnation in attached biomass during the last phase. On the other hand, Fig. 2 also allows us to confirm that low energy requirements are needed to expand considerably the bed. For example, bed expansions of 15–40% were achieved with a water velocity of only 2.0 mm/s (empty bed velocity) in the first two phases.

Figure 3 shows the inlet loading rate, the removed load and the elimination efficiency of phenol during the operation period. As the inlet concentration of phenol was more than ten times higher than that used in the start-up, keeping HRT constant, a phenol load of 2.52 kg/m^{3}d was applied in Phase I. Thus, the FBBR was operated under medium load and low HRT when compared with other reactors reported in the literature (González et al. 2002; Juárez-Ramírez et al. 2001). Comparatively, these authors treated high polluted wastewaters (phenol from 500 to 3,000 mg/l), although large HRTs (2–4 days) and specific microorganisms were used. The variability in the system activity observed in this first phase was due to fluctuations in the inlet concentration of phenol caused by a microbial contamination problem in the feed tank. The system showed a high efficiency, and most of the phenol load fed to the bioreactor was removed.

Phase II involved a notable reduction (−44%) in the phenol load fed to the reactor and a significant increase (+60%) in HRT with respect to the first phase. These changes implied a higher removal

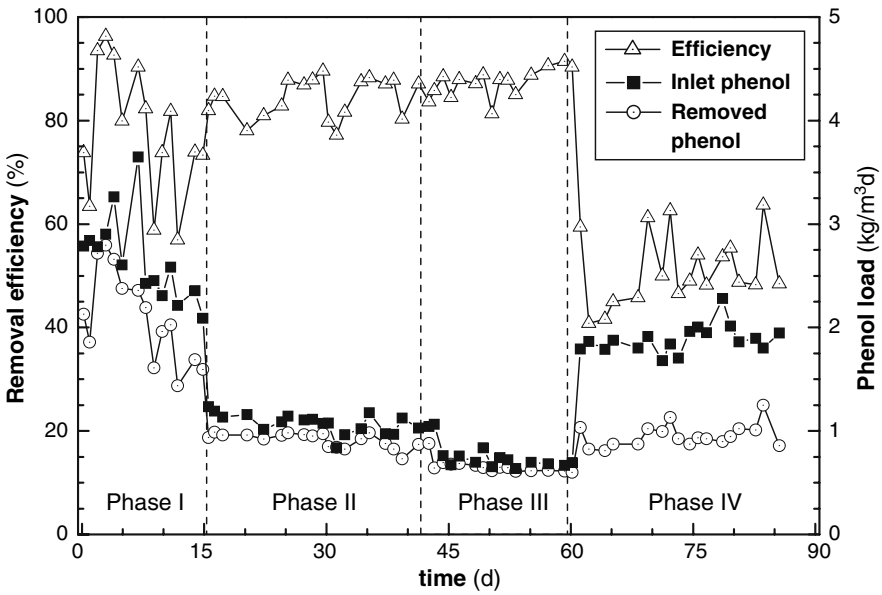

Fig. 3 Phenol loading rates and elimination efficiency

efficiency and a lower elimination capacity, but without affecting the biomass development. Additionally, more stable phenol profiles were obtained at these operational conditions. The recirculation rate in Phase III was increased in 33% with respect to the previous phase, which slightly improved the phenol load removed and the depuration efficiency.

Variations between Phases I and III, with a double recirculation rate for the latter, did not improve much either the phenol load removed or the elimination efficiency. Consequently, the bioreactor activity was not significantly affected by the recirculation rates applied. It is likely that higher recirculation flows may be necessary to detect appreciable changes in the bioreactor performance. Nevertheless, as the CDP is a very light support, application of too high recirculation flow rates could cause elutriation of bed particles.

Phase IV deserves a special attention because of the strong increase in the phenol loading rate (+265%) with respect to Phase III. An average inlet concentration of 133 mg/l phenol was supplied in this stage while only 50 mg/l was fed in the previous one. Both phases were performed at the highest HRT and the highest recirculation rate of the total operating period. Although the system quickly reached a steady state, a sudden fall in the system depuration efficiency was observed at the beginning of this last phase. As explained before, the excessive biofilm development observed in Phase IV could probably reduce the amount of active biomass and cause the decrease in the removal efficiency. The inhibitory nature of phenol to the microorganisms and the low HRT applied could also explain this depuration efficiency decrease. However, despite this decrease, a slight improvement in the depuration capacity was achieved (see Fig. 3), even though the phenol concentration in the effluent remained relatively high. This fact might be attributed to the higher concentration of phenol present in the liquid medium which could generate a higher driving force sufficient for a deeper penetration of substrate within the biofilm. Nevertheless, more appropriate operational parameters (higher HRT and recirculation flow) could have improved the FBBR activity in this phase.

A comparison of our results with those of other studies is not straightforward because of differences in the operational parameters. Considering the nature of the bacterial inoculum used (mixed, non selected) and the low operating temperature and HRTs applied, the FBBR efficiency has remained in acceptable levels when compared to other bioreactors (González et al. 2001; Chen et al. 2002; Juárez-Ramírez et al. 2001). The use of specific cultures with a demonstrated ability to uptake phenol (mainly belonging to the *Pseudomonas* and *Candida* species) allowed these authors to increase the inlet concentrations up to one gram of phenol per litre without exhibiting inhibitory

effects. Mordocco et al. (1999) applied an inlet concentration as low as in this study but using *Pseudomonas putida*. In fact, the toxicity of phenol to mixed cultures can be, depending on its origin and nature, as low as 50 mg/l (Chen et al. 2002).

Surprisingly, the system reached the highest phenol load removal rate in Phase I, in spite of working with both the lowest HRT and recirculation rate. In fact, a maximum elimination capacity of 2.8 kg/m^{3}d was reached at the beginning of the first phase. A possible contribution of the sorption mechanism to the phenol removal can be discarded at that moment because the CDP bed was saturated after the 8 weeks of acclimation to this contaminant. The values of elimination capacity achieved are low compared to those of other works (González et al. 2001; Chen et al. 2002; Mordocco et al. 1999). Nevertheless, our results can not be easily compared with the rest because of the low HRTs applied. Notice that HRT values ranged from 0.55 and 1.7 h, whereas it was in the order of days in other studies. For instance, Juárez-Ramírez et al. (2001) reported phenol load removal capabilities similar to ours, although they used a specific culture (*Candida tropicalis*) and a much higher HRT (50–60 h). This suggests that a higher HRT could increase the ability of this CDP-FBBR to remove phenol.

Conclusions

The feasibility of a β-cyclodextrin polymer as biomass carrier in a fluidized bed bioreactor for aerobically degrading aqueous phenol has been successfully tested. Neither operational nor support stability problems were detected after a testing period of two months with glucose and almost five months with phenol. Biomass growth on the CDP particles was evident after the acclimation period. In fact, the biofilm thickness grew with time during the operation with phenol, as deduced from the mean increase of 2 mm/d in the fixed bed height measurements. Additionally, the slight decreasing trend in the expanded bed height during the last phase, together with the stability of the fixed bed height, suggests that the bioparticle density has been slowly increasing, which may be indicative of a more mature biofilm. In the last phase, diffusional limitations in oxygen transfer could be also possible due to the high biofilm thickness reached (about 210 μm).

Compared with other bioreactors reported in the literature, the system was operated under medium phenol load and low HRT. The elimination capacity (referred to the expanded bed volume) was typically around 1.0 kg-phenol/m^{3}d, with a maximum value of 2.8 kg-phenol/m^{3}d achieved working with an HRT as low as 0.55 h. This suggests that a higher HRT could increase the ability of this CDP-FBBR to remove phenol. The bioreactor performance was not significantly affected by the recirculation flow rate in the range tested. Low flow rates were necessary to provide adequate fluidization because of the small difference between the densities of water and the swollen CDP beads. For example, bed expansions as high as about 20–30% were observed using water velocities of only 2.0 mm/s bed. This fact characteristic of light particles is interesting in order to reduce the operational costs associated with the pumping energy required to fluidize a particulate bed.

Currently, the FBBR keeps working in order to study how the operation conditions can improve the efficiency of this system. Some of these factors have been identified in this work, such as the application of higher HRTs and the use of specific microorganisms for this biodegradation process. In addition, the analysis of the combined effect of biodegradation and sorption will be particularly interesting to enhance the removal capacity of aqueous pollutants by CDP particles.

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