Remediation of chlorophenol- and phenol-contaminated groundwater by a sequencing batch biofilm reactor

G. Farabegoli, A. Chiavola and E. Rolle

ABSTRACT

The paper describes the results of an investigation aimed at evaluating suitability of a lab-scale Sequencing Batch Biofilm Reactor (SBBR) for the remediation of groundwater contaminated by phenol (P) and 2-chlorophenol (2-CP). Kinetics of compound degradation was determined along the bed height in the absence and in presence of effluent recirculation, and with different influent composition (compounds fed separately or in combination in the same stream). SBBR performances with and without recirculation were very satisfactory for all the influent compositions: the system showed 99% removal efficiencies for both phenol and 2-CP and their complete removal was always achieved far before the end of react. In the presence of recirculation, the concentration gradient established during fill was rapidly eliminated and an even biomass distribution along the bed height was formed. Consequently, an acceleration of the elimination process was observed, particularly for phenol that was mostly removed in the first hour of the cycle. When the compounds were fed simultaneously, 2-CP removal kinetics improved probably due to cometabolism. The adsorption phenomena of the toxic compounds on the packing material were studied also, showing about 50% COD removal after 7 hours contact time.

Key words | biofilm, chlorophenol, groundwater, recirculation, SBBR

G. Farabegoli
A. Chiavola
E. Rolle
Department of Hydraulics,
Transportation and Roads,
Faculty of Engineering,
Sapienza University of Rome,
Via Eudossiana, 18, 00184 Rome,
Italy
E-mail: *geneve.farabegoli@polimi.it*;
agostina.chiavola@uniroma1.it;
enrico.rolle@uniroma1.it

INTRODUCTION

The rapid advances of industrial technology and the development of chemical industries have given rise to a huge consumption of different types of chemicals. The aromatic compounds and aliphatic chlorinated compounds are used as intermediates or final products in most industrial processes. Therefore, it is not surprisingly that they are commonly found in many soils and groundwater (Arcangeli & Arvin 1995). Conventional biological removal processes seldom achieve required performances because these compounds are usually less biodegradable and may exert toxic or inhibiting effects on microorganisms. Effective treatment requires systems which are able to select and enrich bacterial species capable of completely degrading the target pollutants. They also need to possess high operative flexibility so as to adapt the process to variable influent conditions without affecting its efficiency. The attached biomass systems represent a valid alternative to the activated sludge processes for contaminant removal. The main advantages of biofilm systems include: higher volumetric loads, higher specific removal rates, increased process stability and compactness of the reactors due to higher biomass density (Kaballo 1997). Furthermore, these systems are particularly suitable to enrich slow growing-organisms, as those degrading xenobiotic compounds, because sludge age is independent of the mean residence time of the fluid. Degradation capacity of fixed bed biofilm reactors not only depends on the microbial activity but also on the rate of mass transfer into the biofilm (Siegrist & Gujer 1985). Attention has to be paid to reactor specific parameters like hydraulics, reactor configuration or operational features which influence the mass transfer conditions (Boller *et al.* 1994). Operating a plug flow biofilm

doi: 10.2166/wst.2008.398

reactor with continuous flow results in the formation of concentration gradients in the direction of flow. That means that different growing conditions exist in different zones of the reactor (Wilderer *et al.* 1993). Due to this stratification, deterioration of effluent quality was observed in case of strong influent fluctuations as well as in reactors treating industrial wastewater containing xenobiotics (Wilderer *et al.* 1993; Kaballo *et al.* 1995; Wobus *et al.* 1995). Previous studies have demonstrated the Sequencing Batch Reactor (SBR) capabilities to remove compounds difficult to biodegrade such as xenobiotics and also to handle wide variety of influent conditions (Wilderer *et al.* 2001; Chiavola *et al.* 2004). The application of the SBR concept to the attached biomass reactors have led to the introduction of the Sequencing Batch Biofilm Reactor (SBBR) technology (Wilderer 1992; Kaballo *et al.* 1995; Wilderer & McSwain 2004). The SBBR is a compact process that combines advantages of biofilm systems with the periodic discontinuous flow. It can be operated in a very flexible manner by modifying phase durations and the volumetric exchange rate to cope with changing influent concentrations and flow rates. The discontinuous mode of operation results in a more homogenous distribution of bacterial biomass and in similar removal rates in different sections of the reactor. Thereby, a biomass distribution similar to that of a completely mixed reactor can be achieved in a plug-flow reactor (Wobus & Röske 2000).

The aim of the present paper was to study suitability of the SBBR process for the remediation of groundwater contaminated by phenol (P) and 2-chlorophenol (2-CP). These compounds were chosen as models for xenobiotics because they are widespread in the environment. Kinetics studies of the microbial degradation process were carried out with different influent compositions. Besides, the effects of the effluent recirculation on the elimination rates were determined with the aim of selecting the mode of operation achieving best performance.

METHODS

The experimental set-up was composed by an up-flow laboratory-scale SBBR filled with expanded clay Filtralite® (4–8 mm diameter). Four ports were located every 10 cm to allow liquid samplings: the ports are referred to as P1, P2, P3 and P4 from the top to the bottom. In additions, there were also three openings placed every 6 cm to allow packing removal for biomass measurements. The main reactor features are listed in Table 1.

The influent volume, V_F, delivered to the reactor at beginning of each operative cycle was 8 L, whereas the same volume was drawn at the end of the cycle. Consequently, the Volumetric Exchange Ratio (VER), equal to V_F/V_W, was about 53%. As it is well known, the mode of operation of the fill phase controls the maximum concentration established within the reactor at the end of the fill phase, that corresponds to the beginning of the react phase. As a consequence, the kinetics of the removal process are conditioned by the values selected for the fill duration, the influent flow rate and the VER. According to Arnz *et al.* (2000), in the case of xenobiotic compounds, near 68% of the reactor liquid can be exchanged if the concentration of pollutants introduced with the incoming wastewater must to be kept very low in order to avoid inhibiting phenomena. Besides, high exchange ratio grants the operators of the plant a high flexibility concerning the treatment goals. In the present case VER was selected based on the needs to allow high exchange rate and also to avoid inhibition phenomena on bacterial activity due to the compounds used as the sole energy and carbon source. Initially, the lab plant was operated through batch cycles having variable duration, so as to provide microorganisms with a very long aerated period. In order to avoid any accumulation of the compounds within the reactor, which could have induced toxic effects, each batch cycle was started only after complete pollutant disappearance.

When the removal rates became faster, it was possible to progressively reduce the length of the cycle: at regime

Table 1 | Main features of the SBBR plant

Parameter	Units	Value
Inner diameter, D	cm	19
Total height, H	cm	92
Geometric volume, V_T	L	26
Fixed bed volume, V_B	L	7.8
Average liquid volume, V_W	L	15
Initial bed porosity, e	%	29
Hydraulic Residence Time, Θ_H	h	15

conditions cycle duration was fixed at 8 hours. Fill and draw phases lasted about 10 min; therefore, most of the cycle was devoted to react. The reactor was fed with a synthetic mixture containing 40 mg/L phenol (C_6H_5OH) and 40 mg/L 2-CP and macronutrients (in the form of nitrogen and phosphorus salts); micronutrients were provided by diluting chemicals into tap water.

The reactor was equipped with an external loop to allow recirculation of the effluent. The recirculation rate was performed as maximum as possible (1.5 times the influent flow rate) to avoid any influence of mass transfer (Kaballo 1997). Besides, recirculation started immediately after the end of the fill phase and lasted as long as the react phase. Backwash operation was operated only once throughout the experimental activity because the influent stream was lack of solids; moreover, the low growth yield supported by the xenobiotic compounds led to the formation of a thin biofilm layer over the packing material, which reduced clogging problems and therefore backwashing frequency. Aeration was provided through four porous stones located below the bottom of the fixed bed and connected to an external compressor. The air-flow rate was controlled by a flow meter: a high value (i.e. 200 L/h) was used in order to maintain a Dissolved Oxygen (DO) concentration above the bed in the range of 3–6 mg/L. Temperature of the reactor was maintained at 24°C ± 2 by using a water jacket connected to a thermostat bath. The value of pH was continuously monitored during the study and remained always in the range of 7.5–8.0 units. Reactor performances were monitored through periodical analyses on liquid samples from both the influent and the effluent streams. Furthermore, kinetic studies of the biodegradation process were carried out within typical operative cycles. Chlorophenol and phenol concentrations were determined by using the High Pressure Liquid Chromatography (HPLC), whereas Chemical Oxygen Demand (COD) was measured by following Standard Methods for the Examination of Water and Wastewater (2005).

RESULTS AND DISCUSSION

The experimental activity focused on the biodegradation kinetics of the pollutants considered either alone or mixed in the same influent stream (IN), and in the presence and absence of effluent recirculation. Accordingly, after the acclimation phase, the study was scheduled in different operational periods as shown in Table 2. Every condition tested in the study was applied for at least 3 weeks; in the meantime, kinetic tests were being carried our twice a week to follow adaptation of the system to the new set of operative conditions. The results of the kinetic studies shown later on were obtained at steady state conditions. Contribution of the adsorption process to the contaminant removal was also evaluated.

Acclimation period

The reactor was initially seeded with a biomass sample grown on 2-CP alone in a lab-scale SBR. Since a very low growth yield of biomass in the form of biofilm was observed, microorganism density was further increased with a sample of activated sludge from a full-scale continuous flow treatment plant for domestic sewage. Besides, glucose was temporarily added to the feed in order to rise the total COD from 160 mg/L to 460 mg/L with a promptly biodegradable compound. When biofilm was formed, glucose was eliminated and only phenol and 2-CP were provided to the biomass as energy and carbon source. After 18 cycles (corresponding to an operation length of about 2 months since reactor start-up), the system reached steady state performance. The average removal efficiency of the compounds was 99% and it was achieved in less than 5 hours. At this time, the operation was switched into 3 daily cycles, as above described.

Table 2 | Operational periods

Period	Features
1	With recirculation
1.1	IN: 40 mg/L Phenol
1.2	IN: 40 mg/L 2-CP
1.3	IN: Mixture of 40 mg/L 2-CP and 40 mg/L Phenol
2	Without recirculation
2.1	IN: 40 mg/L Phenol
2.2	IN: 40 mg/L 2-CP
2.3	IN: Mixture of 40 mg/L 2-CP and 40 mg/L Phenol

Period 1

Figures 1 and 2 show typical kinetic patterns observed at regime conditions when phenol and 2-CP were fed separately to the reactor. In both cases, a concentration gradient along the bed depth can be noted at time $t = 0$, which corresponded to the end of fill, with higher concentrations established at the top of the reactor. Due to the presence of recirculation, during react the hydraulic conditions of the bulk liquid resembled those of a mixed reactor and an even biomass distribution developed along the bed height. With the up-flow mode of filling in the absence of aeration, the influent volume rose through the bed with minimum contact with the treated liquid volume from the previous cycle. This gave rise to higher concentrations at the top of the bed, which corresponded also to the effluent. The gradients leveled off when recirculation was switched on and very similar concentrations along the reactor height were established after only 5 minutes. Also the sharpest elimination occurred in the first 5 minutes, whereas complete pollutant removal was observed in less than 20 and 40 minutes for phenol and 2-CP, respectively. Recirculation along with the batch mode of operation of the SBBR contributed to achieve a more homogenous distribution of the substrate and microorganisms in the reactor. Therefore, the existence of concentration gradients was limited to the filling phase and to the beginning of the react phase whereas during most of the cycle time the reactor was considered as completely mixed (Kaballo *et al.* 1995; Di Iaconi *et al.* 2002). It is noteworthy that this pattern was always observed in the presence of recirculation.

It is well known that addition of the highly polluted influent to the treated liquid resulting from the previous cycle causes dilution of the incoming concentration, thus affecting also kinetics of the following react phase. In the present case, the concentration reduction in the fill phase due to dilution only (i.e. in the absence of any biodegradation and/or adsorption) was about 47%: consequently, the concentration expected at beginning of the react phase was about 21 mg/L. It can be noted that concentrations of phenol and 2-CP measured at $t = 0$ were lower than the expected values based on VER, particularly in the bottom of the bed. This result suggests that during fill adsorption on the packing material and/or biological degradation occurred.

Degradation profiles of phenol at different ports during react well fitted a first order kinetic, whereas 2-CP degradation followed approximately a saturation order. Since 2-CP is more difficult to degrade than phenol, the time needed for its complete removal was always longer. However, stable removal kinetics were obtained for both compounds.

The results obtained with the mixture of compounds are shown in Figure 3. It can be noted that similarly to the previous phases, a concentration gradient was still present at $t = 0$: however, differently from the periods 1.1 and 1.2, it was not completely eliminated in the following react phase despite recirculation was on. Elimination rate of phenol (P)

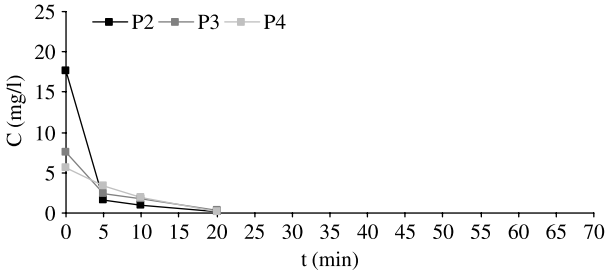

Figure 1 | Typical kinetic pattern of phenol removal in the presence of recirculation (period 1.1).

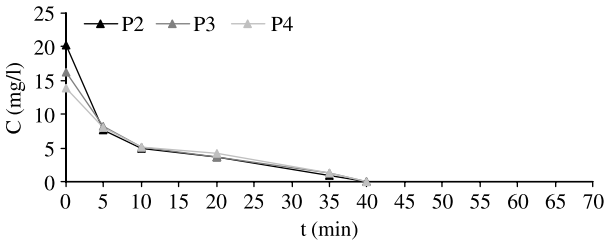

Figure 2 | Typical kinetic pattern of 2-CP removal in the presence of recirculation (period 1.2).

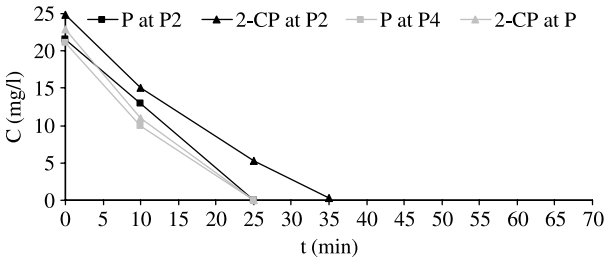

Figure 3 | Typical kinetic patterns of phenol and 2-CP removal in the presence of recirculation (period 1.3).

was still higher than that of 2-CP; consequently, the time for its complete removal was shorter. When fed in combination in the influent, co-metabolism caused appreciable improvement of 2-CP removal kinetics, which became faster. Differently, phenol biodegradation rate was reduced although not significantly. This might be attributed to the higher energy consumption for 2-CP molecule breakdown and/or to a weak inhibition of 2-CP on phenol-degraders.

Period 2

Figures 4 and 5 show concentrations of phenol and 2-CP, respectively, measured along the bed when they were fed separately to the reactor and in the absence of recirculation. In this case, the mixing conditions of the bulk liquid more resembled those of a plug-flow system. A concentration gradient was still present at $t = 0$: however, differently from the previous periods, the lower concentration was always present at the top of the bed (P2), which corresponds approximately to the effluent. Due to the up-flow mode of filling in the absence of recirculation, the biomass developed unevenly along the bed height, with higher density in the lower layers where more substrate and oxygen were available. Consequently, during fill the influent moving upward through the bed was degraded significantly and high reduction of the incoming concentration was achieved. Therefore, concentrations measured at $t = 0$ were always much below the expected values of 21 mg/L, particularly in P2 due to the higher residence time. The lower initial values gave rise to lower elimination rates as compared to the values measured in the presence of recirculation (period 1).

The concentration gradient established during fill persisted in the following react phase because of the absence of recirculation. Anyway, the elimination rates

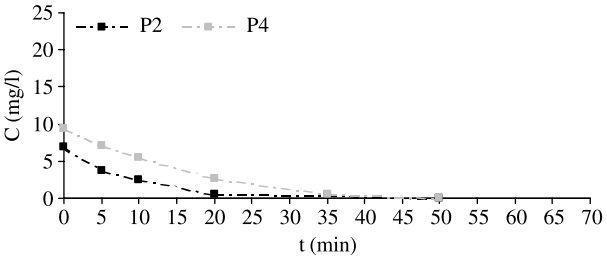

Figure 4 | Typical kinetic pattern of phenol removal in the absence of recirculation (period 2.1).

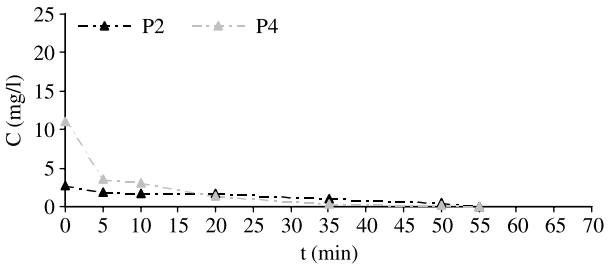

Figure 5 | Typical kinetic pattern of 2-CP removal in the absence of recirculation (period 2.2).

were still fast and complete removal of both phenol and 2-CP was achieved in less than 1 hour in both P2 and P4. Particularly, the process was faster with the influent containing only phenol. In this case, degradation in the react phase followed a first-order kinetic both at the top and at the bottom of the reactor, whereas it always well fitted a saturation order for 2-CP. The results obtained when the mixture of phenol and 2-CP was fed to the plant are shown in Figure 6.

As observed previously, removal rate of phenol was higher than that of 2-CP during both fill and react and well fitted a zero-order kinetic in both ports. However, elimination rates of both compounds decreased appreciably when they were fed simultaneously and a longer time was needed for their complete removal, particularly in the case of 2-CP. The pattern of 2-CP removal indicates the presence of a partial inhibition of its biodegradation which took place until the residual concentration decreased below a non-inhibiting threshold (i.e. after about 25 minutes).

Abiotic phenomena

Contribution of abiotic phenomena on the observed removal was also investigated through several tests carried

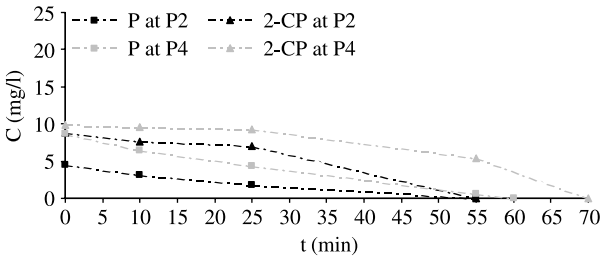

Figure 6 | Typical kinetic patterns of phenol and 2-CP removal in the absence of recirculation (period 2.3).

out in batch vessels filled with the compounds in the presence and absence of the packing materials. In the former case, the support media was previously sterilized by autoclave.

Concentration of both phenol and 2-CP did not change appreciably over time in the absence of packing material, which indicated that autodegradative phenomena did not occur in the vessel.

Conversely, about 50% COD removal was observed after 7 hours contact time between influent solution and packing material. Since this length of time corresponded to the duration of the react phase of the SBBR cycle, then it was assumed that 50% of the observed removal efficiency during the reactor operation was to be attributed to adsorption. However, it must be pointed out that the SBBR may features as a sink-source system: for instance, when fed to the plant, the influent constituents are rapidly stored onto biofilm support media by means of adsorption, thus causing a fast removal of pollutants from the bulk liquid. As the react phase continues, desorption processes make contaminants to be released into the liquid and therefore to be available for biodegradation. Cycles of sink-source processes occurring in a SBBR system provide protection to bacteria against harmful effects caused by potentially toxic influent compounds (Wilderer *et al.* 2000). In the present case, it can be assessed that removal of 2-CP and phenol observed during SBBR operation was the result of both adsorption and biodegradation since progressive improvement of the removal kinetics was measured with time, along with a visible biomass growth onto the packing material. It is likely to assume that adsorption contributed to immediate removal of compounds from the bulk liquid, whereas bacterial activity brought about their progressive degradation.

This phenomenon also allowed cyclic renewal of the adsorptive capacity of the packing material.

CONCLUSIONS

One-year experimental investigation demonstrated suitability of the SBBR technology for remediation of groundwater contaminated by phenol and 2-CP, which were selected as model compounds for xenobiotics. Biomass grown in the plant developed capability of using both compounds as the sole source of energy and carbon. High elimination rates were achieved for both pollutants after a relatively short time of operation since reactor start-up. Average removal efficiency at regime conditions was over 99% for a react phase duration of 7 hours and 40 mg/L as incoming concentration of phenol and 2-CP. These results were obtained in all the operative conditions tested in the study: for instance, when compounds were fed separately and when they were mixed in the same influent stream. As a result, the cycle time can be significantly reduced and exploitation of SBBR capability gets enhanced.

At regime conditions, performances were quite stable and recirculation seemed not to appreciably improve overall reactor efficiency. However, in the presence of recirculation, the concentration gradient established during fill along the bed height was rapidly eliminated and a very uniform removal process was observed during react. Differently, when the recirculation was off, the concentration gradient persisted during all the cycle time and this negatively affected elimination kinetics of both compounds, and mainly of 2-CP. Improvement of 2-CP biodegradation was observed when the compounds were fed in mixture due to the contribution of cometabolism. Finally, adsorption on packing material provided an important contribution to the overall removal process. It can be concluded that the SBBR technology may represent a valid alternative for groundwater remediation, provided that proper operative conditions are selected based upon the nature of the xenobiotics to be removed.

REFERENCES

Arcangeli, J. P. & Arvin, E. 1995 Biodegradation rates of aromatic contaminants in biofilm reactors. *Water Sci. Technol.* **31**(1), 117–128.

Arnz, P., Esterl, S., Nerger, C., Delgado, A. & Wilderer, P. A. 2000 Simultaneous loading and draining as a means to enhance efficacy of sequencing biofilm batch reactors. *Water Res.* **34**(5), 1763–1766.

Boller, M., Gujer, W. & Tschui, M. 1994 Parameters affecting nitrifying biofilm reactors. *Water Sci. Technol.* **29**(10–11), 1–11.

Chiavola, A., Baciocchi, R., Irvine, R. L., Gavasci, R. & Sirini, P. 2004 Aerobic biodegradation of 3-chlorophenol in a sequencing batch reactor. Effect of cometabolism. *Water Sci. Technol.* **50**(10), 235–242.

Di Iaconi, C., Lopez, A., Ramadori, R., Di Pinto, A. C. & Passino, R. 2002 Combined chemical and biological degradation of tannery wastewater by a periodic submerged filter (SBBR). *Water Res.* **36**, 2205–2214.

Kaballo, H. P., Zhao, Y. & Wilderer, P. A. 1995 Elimination of p-chlorophenol in biofilm reactors–a comparative study of continuous flow and sequenced batch operation. *Water Sci. Technol.* **31**(1), 51–60.

Kaballo, H. P. 1997 Shock loading management with the sequencing batch biofilm reactor technology. *Water Sci. Technol.* **35**(1), 35–40.

Siegrist, H. & Gujer, W. 1985 Mass transfer mechanisms in a heterotrophic biofilm. *Water Res.* **19**, 1369–1378.

Standard Methods for the Examination of Water and Wastewater 2005 21st edition, American Public Health Association/ American Water Works Association/Water Environment Federation, Washington DC, USA.

Wilderer, P. A. 1992 Sequencing batch biofilm reactor technology. In: Ladisch, M. R. & Bose, A. (eds) *Harnessing Biotechnology for the 21st Century*. American Chemical Society, pp. 475–479.

Wilderer, P. A., Röske, I., Ueberscär, A. & Davis, L. 1993 Continuous flow and sequenced batch operation of biofilm reactors: a comparative study of shock loading responses. *Biofouling* **6**, 295–304.

Wilderer P. A., Arnz P. & Arnold E. 2000 Application of biofilms and biofilm support materials as a temporary sink and source. *Water Air Soil Pollut.*, 123, 147–158. eds Kluwer Academic Publishers, Netherlands.

Wilderer P. A., Irvine R. L. & Goronszy M. C. 2001 *Sequencing Batch Reactor Technology*. Scientific and Technical Report N. 10, IWA Publishing, London, UK.

Wilderer, P. A. & McSwain, B. S. 2004 The SBR and its biofilm application potentials. *Water Sci. Technol.* **50**(10), 1–10.

Wobus, A., Ulrich, S. & Röske, I. 1995 Degradation of chlorophenols by biofilms on semi-permeable membranes in two types of fixed bed reactors. *Water Sci. Technol.* **32**(8), 205–212.

Wobus, A. & Röske, I. 2000 Reactors with membrane-grown biofilms: their capacity to cope fluctuations inflow conditions and with shock loads of xenobiotics. *Water Res.* **34**(1), 279–287.