



Comparison of UASB and EGSB performance on the anaerobic biodegradation of 2,4-dichlorophenol

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ABSTRACT

The anaerobic degradation of 2,4-dichlorophenol (2,4-DCP) in upflow anaerobic sludge blanket (UASB) and expanded granular sludge bed (EGSB) reactors using glucose as main carbon source was studied. The performance of both systems was compared in terms of 2,4-DCP and COD removal efficiencies, methane production, stability, granular sludge adaptability as well as reversion of the bacterial inhibition. Both organic and 2,4-DCP loading rates were incrementally varied through the experiments. With loading rates of 1.9 g COD L⁻¹ d⁻¹ and 100 mg 2,4-DCP L⁻¹ d⁻¹, 75% and 84% removal efficiencies of this compound, accompanied by COD consumption efficiencies of 61% and 80% were achieved in the UASB and EGSB reactors, respectively. In these conditions, methane production reached 0.088 L CH₄ g⁻¹ COD in the EGSB reactor whereas in the UASB reactor was almost negligible. Decreasing the 2,4-DCP loading rate to 30 mg L⁻¹ d⁻¹ an improvement in the methane production was observed in both reactors (methanogenic activity of 0.148 and 0.192 L CH₄ g⁻¹ COD in UASB and EGSB reactors, respectively). Efficiency of dechlorination was improved in both reactors from around 30% to 80% by reducing to one-half the COD due to a decreasing of the 4-chlorophenol concentration accumulated in the effluents of both reactors. The dechlorination efficiency of the UASB reactor was dramatically inhibited at a 2,4-DCP feed concentration above around 210 mg L⁻¹ because of 2,4-DCP accumulation in the effluent. SEM studies revealed no significant morphological changes in the sludge granules.

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1. Introduction

Chlorophenols are toxic and recalcitrant compounds that can be present in industrial wastewaters and in subsurface water because they are used in the production of herbicides, insecticides, antiseptics, disinfectants and wood preservatives (Krumme and Boyd, 1988; Ning et al., 1997). Due to their toxicity, some of them are included in the United States Environmental Protection Agency list of priority pollutants and in the European framework of water policy established in the 2000/60/CE Directive.

Removal of chlorophenols from water has been investigated in a number of studies. Adsorption, the most commonly used non-destructive method, concentrates the chlorophenols on the solid phase, transferring the problem to a solid waste (Dabrowski et al., 2005). Destructive methods, chemical and biological, allow chlorophenols mineralization and are sometimes used in combination. The chemical oxidation methods are faster (Pera-Titus et al., 2004), although they can generate some intermediates that can be even more toxic than the starting pollutants. Biological treat-

ments, aerobic and anaerobic, have been extensively used in the wastewater field because they can work at high efficiencies and low costs. Nevertheless, when toxic and recalcitrant species are present conventional biological treatments are not suitable (Speece, 1996). In anaerobic processes reductive dechlorination and halorespiration of chlorine atom from chlorophenols takes place producing less hazardous compounds, while in aerobic conditions substituted catechols and other refractory intermediates can appear if oxidation is incomplete (Annachatre and Gheewala, 1996).

2,4-Dichlorophenol (2,4-DCP) is one of the most environmentally representative chlorophenols because it is used as intermediate in the production of 2,4-dichlorophenoxyacetic acid, a well-known herbicide. Anaerobic biodegradation of 2,4-DCP is preferable to aerobic because the activity of the aerobes is rapidly inhibited at 2,4-DCP loading rates above 100 mg L⁻¹ d⁻¹ (Sahinkaya and Filiz, 2007).

As has been previously reported, 4-chlorophenol (4-CP) dechlorination is the limiting step in the anaerobic dechlorination of 2,4-DCP because the time required for the adaptation of the sludge to 4-CP is fairly long, often higher than 30 d (Kennedy et al., 1996). This has been explained as a consequence that only few bacteria are able of dechlorinating chlorophenols on *p*-position (Magar et al., 1999). Even *Desulfitobacterium* genus, one of the most studied

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dechlorinating genera, is unable to dechlorinate 4-CP (Villemur et al., 2006). Despite of this fact, complete biodegradation of 4-CP is possible (Majumder and Gupta, 2008).

It has been proved that the addition of another carbon source in an anaerobic medium allows to mitigate the toxic effects of chlorophenols, either with a sole organic source (Atuanya and Chakrabarti, 2003), or with mixtures (Ye and Shen, 2004). Anaerobic biodegradation of 2,4-DCP in the presence of glucose as co-substrate has been studied by Atuanya and Chakrabarti (2004). The results showed that biodegradation of 2,4-DCP strongly depends on the glucose concentration. A high efficiency was obtained at 2,4-DCP concentrations up to 150 mg L^{-1} and beyond that value a significant decrease was observed. At 124 and 500 mg L^{-1} of 2,4-DCP and glucose, respectively, and 13.2 h hydraulic retention time (HRT), 70% 2,4-DCP removal was achieved.

The upflow anaerobic sludge blanket (UASB) reactor has been widely used for the treatment of industrial wastewaters. This system has proved to be highly effective for medium and high strength wastewaters within a wide range of HRT (3–48 h) (Seghezzo et al., 1998). It is one of the most extended systems for the biological treatment of phenolic wastewaters (Veeresh et al., 2005). The expanded granular sludge bed (EGSB) reactor is a modification of the traditional UASB reactor. Both are inoculated with granular sludge, but the hydrodynamic conditions are different. Superficial velocity in EGSB ($2\text{--}10 \text{ m h}^{-1}$) is higher than in UASB due to a high height to diameter ratio and a high recirculation rate. These characteristics improve the mixing and the contact between the wastewater and the sludge in the EGSB reactor (Franklin et al., 1992; Zoutberg and Frankin, 1996).

In this work, results on the anaerobic biodegradation of 2,4-DCP in UASB and EGSB reactors using glucose as carbon source are presented. The two types of systems are compared in terms of COD consumption, 2,4-DCP removal, methane production, process stability and microorganisms adaptability.

2. Materials and methods

2.1. Reactors configuration

The experiments were performed at $30 \pm 1^\circ \text{C}$ in two 5.4 L continuously fed UASB and EGSB reactors. These had an internal diameter of 10 cm and a height of 72.5 cm. The three-phase separator was located 15 cm below the top of each reactor. The feed was supplied with peristaltic pump as well as the recirculation in the case of EGSB, giving a superficial velocity of 2.5 m h^{-1} . CO_2 was removed from biogas using a Mariotte flask with a 4 M NaOH solution trap, and methane was measured with a wet gas-meter.

2.2. Source of biomass

The reactors were inoculated with 100 g of volatile suspended solids (VSS) of a 1:1 mixture of two different anaerobic granular sludges. The first was retrieved from a lab-scale UASB reactor, where it was acclimated to treat cosmetic wastewater for 180 d. These granules presented an average diameter of 1 mm and a specific methanogenic activity (SMA) of $0.73 \text{ g COD g}^{-1} \text{ VSS d}^{-1}$. The second was obtained from a full-scale UASB reactor treating pulp bleaching wastewaters. The granules had a diameter of 1.5–2 mm and the SMA was $0.46 \text{ g COD g}^{-1} \text{ VSS d}^{-1}$.

2.3. Wastewater preparation

2,4-DCP (Sigma–Aldrich) was dissolved in NaOH 0.1 M to a concentration of 5 g L^{-1} and aliquots of this solution were used to prepare the synthetic wastewater. The macronutrients and micronutrients media were prepared according to previous work (Sanz

et al., 1996). The basal medium was supplied with glucose as main carbon source and with 2,4-DCP solution. Sodium bicarbonate was added at $1 \text{ g NaHCO}_3 \text{ g}^{-1} \text{ COD}$ to provide alkalinity and maintain a pH in the range of 7.0–7.5. The synthetic wastewater was stripped with a 80:20 mixture of $\text{N}_2:\text{CO}_2$ to remove dissolved oxygen. The medium was stored at 4°C and used immediately to avoid fermentation. The samples were taken from the top of both reactors, filtered and stored at -20°C before analyses.

2.4. SMA tests and batch experiments

Previous SMA tests were performed with the sludge to be used in the reactors, using the James et al. (1990) procedure. The SMA values were estimated using the Roediger equation (Edeline, 1980). In order to evaluate the effect of glucose on the anaerobic dechlorination of 2,4-DCP, some batch experiments were carried out, where 300 mL serum bottles were inoculated with 1.5 g VSS L^{-1} of 2,4-DCP-adapted granular sludge from the EGSB reactor. Methane was measured by the aforementioned method. Glucose at 4 g L^{-1} was used as carbon source and 2,4-DCP was tested at different concentrations ranging from 10 to 250 mg L^{-1} in duplicate runs. The batch tests were maintained until complete glucose depletion.

2.5. Continuous experiments

A HRT of 48 h was used in the continuous experiments. Reactors were started up with a glucose concentration equivalent to 8 g COD L^{-1} and 10 mg L^{-1} of 2,4-DCP, with the aim of acclimating the biomass to this compound. Biomass was considered acclimated when a COD and 2,4-DCP removal efficiencies of 85% and 90%, respectively, were reached and maintained. In these conditions, methane production was $0.15 \text{ L CH}_4 \text{ g}^{-1} \text{ COD removed}$.

2.6. Analytical procedures

Analyses of total and soluble COD and VSS were performed according to the APHA Standard Methods (1992).

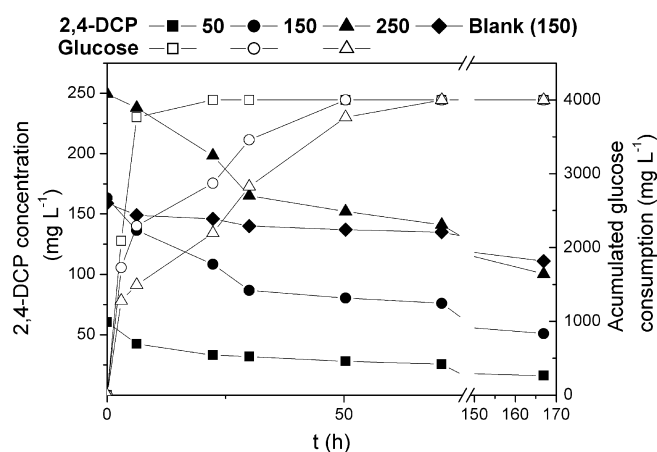


Fig. 1. Time evolution of 2,4-DCP concentration and accumulated glucose consumption in the batch experiments.

Table 1
Operating conditions in the UASB and EGSB reactors for the continuous runs.

Stage	I	II	III	IV	V	VI	VII	VIII	IX	X
Length (d)	20	8	8	9	28	30	50	17	6	15
Glucose (g COD L^{-1})	8	8	8	8	8	4	4	8	8	12
2,4-DCP (mg L^{-1})	10	20	50	85	115	130	210	110	55	55

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