BIOLOGICAL TREATMENT OF A CONTAMINATED GASEOUS EMISSION CONTAINING MONOCHLOROBENZENE

F.S.C. BASTOS[1], A.O.S.S. RANGEL[1], P.M.L. CASTRO[1*] AND R.M. FERREIRA JORGE[1,2]

[1]Escola Superior de Biotecnologia - Universidade Católica Portuguesa, R. Dr. António Bernardino de Almeida, 4200 – 072 Porto, Portugal
[2]SIA - Sociedade de Inovação e Ambiental, Lda. CEBI - Centro Empresarial de Biotecnologia R. Dr. António Bernardino de Almeida, 4200 – 072 Porto, Portugal

ABSTRACT

This study presents the operation of a biotrickling filter when treating a monochlorobenzene (MCB) contaminated gaseous emission. Treatment dynamics were characterised by exposing the reactor to various MCB Organic Loads (OL). The use of different growth support materials, namely limestone, sand, ceramic and PVC pall-rings, was investigated. Limestone led to clogging of the reactor due to the accumulation of surface precipitates, but PVC pall-rings allowed for a uniform biofilm growth. The biotrickling filter presented maximum removal efficiency (RE, 95%) under OL regimes of 10 g m^{-3}-reactor h^{-1}. Treatment inhibition was observed when the reactor was exposed to OL of 45 g m^{-3}-reactor h^{-1}, with RE reaching a minimum value (8%) and elimination capacity of 8 g m^{-3}-reactor h^{-1}. The first half of the reactor height was the predominant section for MCB biodegradation and increasing the mineral medium recirculation rate was beneficial for the overall treatment.

Keywords: Biological treatment, biotrickling filter, monochlorobenzene, gaseous emissions.

INTRODUCTION

In 1990, the Clean Air Act Amendments introduced the control of Volatile Organic Carbons (VOCs) as a major subject of concern. Generally, these pollutants are generated from chemical industries and their control is required since they can pose potential risks to human health and the environment. Recently, under the Integrated Pollution Prevention Control European directive, Gas Phase Bioreactors (GPBs) have been classified as Best Available Technologies (BATs) for air pollution control from chemical industries [1]. However, GPBs are not found worldwide and are mainly focused in north and central Europe [2].

Biological treatment of gaseous emissions contaminated with VOCs offer advantageous solutions because i) they are natural treatment systems, almost without waste generation; ii) there is little consumption of energy and chemical supplements; iii) they are well accepted by the public. Main waste products include waste-water generation and biomass sludge that require further treatment. In a biotrickling filter for VOCs treatment, an aqueous-phase is continuously recirculated through a packed bed. The performance of biotrickling filters is strongly affected by the choice of the packing material [3-6]. The surface should allow for an adequate biofilm growth and, in the event of excessive biomass formation, should avoid clogging of the reactor. The pollutants and the oxygen present in the gaseous effluent are absorbed by the aqueous phase and transported to the biofilm, where biodegradation takes place and pollutants are converted to simple compounds (carbon dioxide and water).

The biological treatment of contaminated gases containing monochlorobenzene (MCB) has been reported [7-9]. Aiming at the simulation of industrial emissions, the treatment of VOCs mixtures, such as MCB and dichlorobenzene [7,9], and acetone and methylacrylate [10], has been achieved. GPBs used for air pollution control

present, however, a limited application when considering highly loaded emissions [1-4,6]. The effectiveness of a biotrickling filter is determined from the inlet and outlet gaseous concentrations, as well as by controlling the aqueous phase composition, particularly when biodegradation products are generated. On-line methods for monitoring biodegradation products, such as chloride, could allow for the development of control strategies of GPBs operation, which often decrease their efficiency due to biomass overgrowth and subsequent clogging [11]. Sequential Injection Analysis (SIA) presents several advantages when compared to classical methods or other automatic flow methodologies for the automation of wet analytical procedures [12]. SIA allows for monitoring of chemical parameters, such as chloride, in a reduced time (less than 60 s) with reproducible results and considerable saving of reagents [13].

The objective of this study was to evaluate the performance of a biotrickling filter for removal of gas-phase MCB. The effects of MCB organic loading, recirculation flow, and growth support material, on the overall treatment performance were investigated.

MATERIALS AND METHODS

Inoculum and Mineral Medium

A mixed microbial culture previously enriched on MCB was used. During the experiments, no aseptic conditions were maintained. The mineral medium (MM) used in these experiments contained the following compounds per litre (pH = 6,5): $Na_2HPO_4.2H_2O$ (2.67 g); KH_2PO_4 (1.4 g); $MgSO_4.7H_2O$ (0.8 g); $(NH_4)_2SO_4$ (0.5 g); and 10 ml of a trace elements solution. The trace elements solution contained the following compounds per litre: NaOH (2 g); $(Na_2)EDTA.2H_2O$ (12 g); $FeSO_4.7H_2O$, (2 g); $CaCl_2$ (1 g); Na_2SO_4 (10 g); $ZnSO_4.7H_2O$ (0.4 g); $MnSO_4.4H_2O$ (0.4 g); $CuSO_4.5H_2O$ (0.1 g); $Na_2MoO_4.2H_2O$ (0.1 g); H_2SO_4 concentrated (0.5 ml).

GPB Operation

A biotrickling filter was operated for treating a MCB contaminated gaseous effluent. The experimental set-up is schematically shown in Figure 1 and experiments were at least repeated. The biotrickling filter consisted of an 80 cm

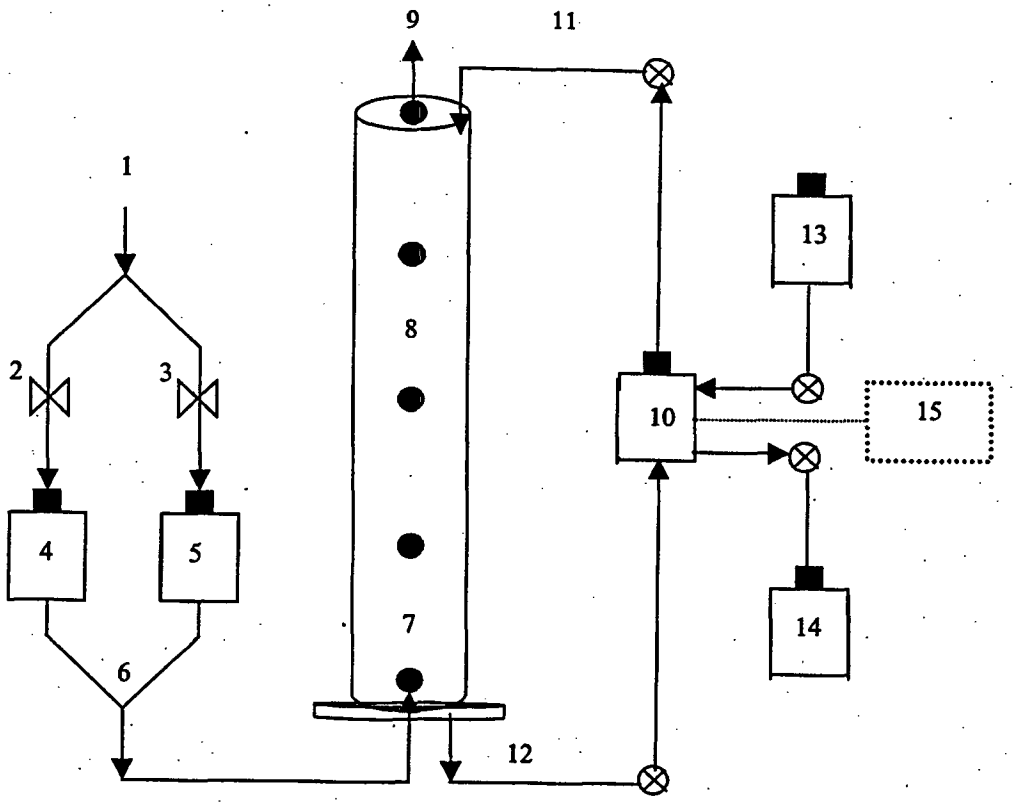

Figure 1. Schematic representation of the GPB. Figure legend: 1 - pressurised air; 2,3 - gaseous mass-flow controllers; 4,5 - saturation vessels; 6 - laden-flow mixture point; 7 - gas inlet; 8 - GPB; 9 - gas outlet; 10 - recirculation vessel; 11 - MM GPB inlet; 12 - MM GPB outlet; 13 - MM feed; 14 - MM waste, 15 - SIA.

height and 9 cm internal diameter cylindrical stainless steel column. A perforated stainless steel plate was placed at the bottom of the column to allow for a better distribution of the gaseous effluent through the column. A water nozzle (DANFOSS, ref. 030F4144) was used to homogeneously disperse the recirculating MM. Apart from the gaseous inlet and outlet-sampling ports, three additional sampling ports were located along the filter bed at 20, 40 and 60 cm from the bottom.

For biofilm establishment, an aqueous solution of MM containing 100 mg l^{-1} MCB was inoculated with 500 ml of MCB-degrading culture, previously grown in 250 ml batch reactors to biomass concentrations of 25 mg l^{-1}, and continuously circulated through the biotrickling filter for three days at a flow rate of 50 ml h^{-1}. Biomass concentration was determined using a previously established dry weight calibration curve. During GPB operation, the gaseous effluent was continuously fed to the reactor in a countercurrent mode with the liquid flow. The required MCB inlet gaseous concentration was achieved through a controlled mixture of a MCB-laden gas stream with a water-laden gas stream, as previously described [14]. Both laden-streams were obtained after a single passage of a controlled flow of pressurised air through independent saturation vessels, containing either MCB or water. By changing the ratio of the laden streams, different MCB inlet gaseous concentrations could be achieved. The recirculation flow was initially set at 250 l h^{-1}. In Experiment I, MM was replaced every 5 days and a total volume of 1 litre was renewed in the recirculation vessel. In Experiment II, similar conditions were maintained until day 70 when MM was continuously fed at 50 ml h^{-1}. The Empty Bed Residence Time (EBRT) was maintained at 2.5 min throughout the experiments. Samples were periodically withdrawn from the sampling points, allowing for the characterisation of the gaseous effluent concentration through the reactor column height (at inlet – 0%, 25%, 50%, 75% and outlet – 100%, of the column height). The total and partial Removal Efficiencies (RE, %), as well as the Organic Load (OL, g m^{-3}-reactor h^{-1}) and the reactor Elimination Capacity (EC, g m^{-3}-reactor h^{-1}), were determined.

Growth Support Materials

Different growth support materials were tested: sand, pall rings made of PVC, limestone and ceramic. In Experiment I, each reactor section was filled with 5 cm layers of each support material in the following order, starting from the bottom: sand, ceramic, pall rings and lime, allowing for an even distribution of growth support materials per reactor section. Tiles were hand-broken into small pieces in order to increase the surface area available for biofilm growth. In Experiment II, the reactor was filled with a 5 cm sand layer at the bottom and the rest of the column height (ca. 75 cm) was filled with pall rings. Preliminary batch tests were carried out in shake-flasks containing MM supplied with 100 mg l^{-1} MCB and 10 g of each growth support material, in order to investigate whether there were any inhibitory effects of the growth support material on the MCB culture degradation capacity; this was achieved by monitoring the evolution of chloride and suspended biomass concentrations.

Analytical Methods

MCB in the gas phase was analysed using a gas chromatograph (Hewlett Packard 5890, UK) equipped with a flame-ionisation detector. A 50 m long packed column (type Column CP-WAX 57CB) with 0.25 mm inner diameter was used at a carrier gas (hydrogen:argon 50:50) flow rate of 8 ml min^{-1}. The column was heated isothermally at a temperature of 80 °C. Gaseous samples of 0.5 ml were collected daily from the in- and outlet-stream, as well as from three sample ports over the height of the reactor column, with 0.5 ml – gas-tight syringe and immediately analysed. All samples were analysed at least twice. MCB in the recirculating MM was also analysed [10].

Biodegradation was detected through the measurement of the chloride ion release. Chloride concentration was assayed colorimetrically [15]. Biomass was removed previously by centrifugation at 14,000 rpm for 5 min. The chloride concentration was calculated from a standard calibration curve ranging from 0 to 100 mg l^{-1} in chloride. The uncertainty of this assay was ± 5 % at the 10 mg l^{-1} level. A SIA system previously described [10] was implemented to allow for on-line monitoring of chloride (Fig. 1).

Chemicals

All chemicals used in the preparation of the MM were obtained from BDH and were of AnalaR grade. All the organic solvents were obtained from Sigma.

RESULTS AND DISCUSSION

GPB Operation - Experiment I

After the three days start-up period, the biotrickling filter was exposed to a contaminated gaseous effluent containing MCB at an OL of 13 g m^{-3}-reactor h^{-1}. After an initial period of adaptation, the reactor showed RE higher than 60 % (Fig. 2). On day 10, the OL was increased to 20 g m^{-3}-reactor h^{-1} and the RE stabilised at ca. 60 %. When the OL was further increased to 25 g m^{-3}-reactor h^{-1} (day 23), the RE was initially decreased to ca. 45% and then recovered and was maintained at RE 65 % (day 30). From day 32, the RE was significantly decreased and clogging of the GPB occurred (day 36).

Figure 2 also shows the evolution of MCB removal efficiency throughout the reactor column height, along with the EC. The high EC observed from day 11 to day 21 was coupled with a predominance of the treatment at the first half of the column height, mainly the first quarter. However, when

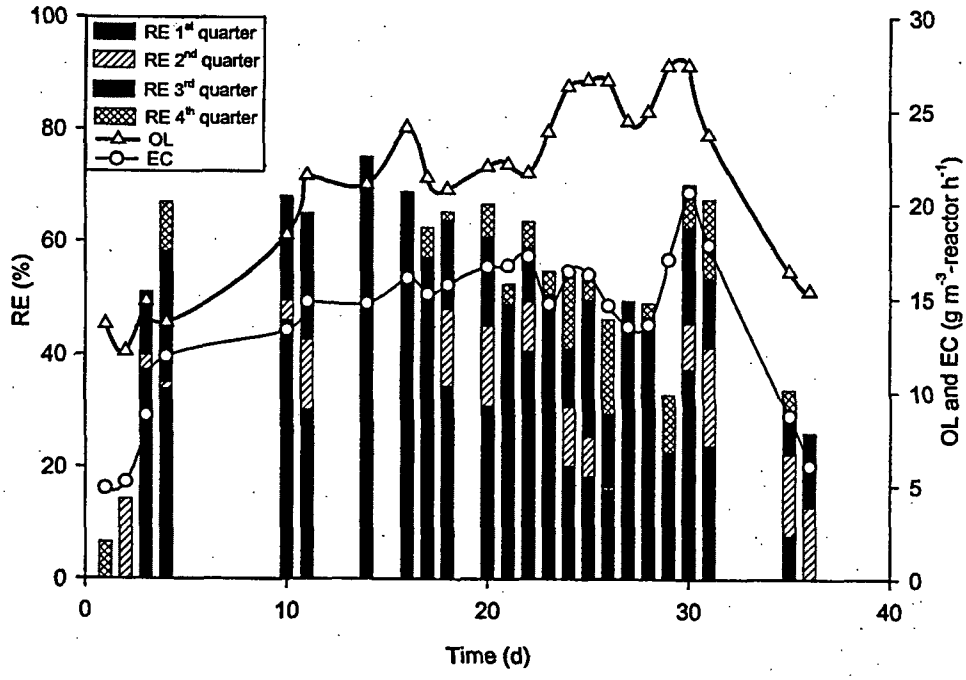

Figure 2. Partial MCB Removal Efficiency (RE, %) versus Organic Load (OL, g m^{-3}-reactor h^{-1}) and Elimination Capacity (EC, g m^{-3}-reactor h^{-1}) obtained during GPB operation in Experiment I.

the reactor was exposed to higher OLs (from day 22), with a subsequent decrease in the RE, little differences were observed between the contribution of each section to the overall treatment. Chloride and suspended biomass concentrations in the recirculating liquid increased from the start of the experiment (data not shown). During Experiment I, chloride and biomass concentrations were maintained at ca. 600 and 15 mg l^{-1}, respectively, although there were significant fluctuations in both concentrations due to the periodical MM renewal. However, a lower biomass release was observed at the last stages of operation (ca. 5 mg l^{-1}), and immediately before the clogging of the reactor occurred, a higher value for suspended biomass in the recirculating MM was noticed (day 35, 40 mg l^{-1}).

Removal of the growth support materials from the GPB on both experiments proved to be a difficult task, due to the limestone layer. The basic properties of lime are often used to adjust the pH of filter beds [16], particularly when treating halogenated compounds [3]. The particles that composed the 5 cm layers of this support became strongly connected, similar to a solid rock, with the formation of a precipitate on its surface. This precipitate may have originated from dissolution of calcium carbonate from the limestone due to acidic conditions, as degradation of MCB generates hydrochloric acid [17], and subsequent re-precipitation. The use of a low recirculation flow could have led to a pH gradient along the column height [4], which could have favoured the accumulation of this precipitate on the limestone surface, thus explaining the clogging of the reactor and the inadequacy of this material for GPB operation in a trickle-bed mode when treating halogenated VOCs.

Ceramic material, specifically waste tile products, were also investigated for growth support adequacy. Absence of biofilm on this growth support material was visually observed upon opening of the reactor. Ceramic monoliths have been investigated as growth support for air pollution abatement, however showing a weak capacity for biofilm adhesion [18]. This support material has been advanced as a non-viable option for biofiltration applications [17]. The results obtained on the present study support the limitation of ceramic matrix for use as a biofilm growth support material. The same was observed for sand. Pall rings showed extensive biofilm growth and a uniform biofilm distribution, based on visual observation upon opening of the GPB.

GPB Operation - Experiment II

Based on the results of Experiment I, the experimental conditions of GPB operation were altered. The growth support material inside the GPB consisted of a 5 cm layer of sand, to better disperse the gaseous effluent through the column, and of a uniform layer of PVC pall-rings. The recirculation flow was increased to 500 ml h^{-1} on both experiments carried out, and on the last repetition the MM was supplied continuously at a rate of 50 ml h^{-1} from day 70.

The reactor was initially exposed to an OL of 10 g m^{-3}-reactor h^{-1}. Generally, the RE during the first month of operation was never higher than 50% (Fig. 3.A). At the end of

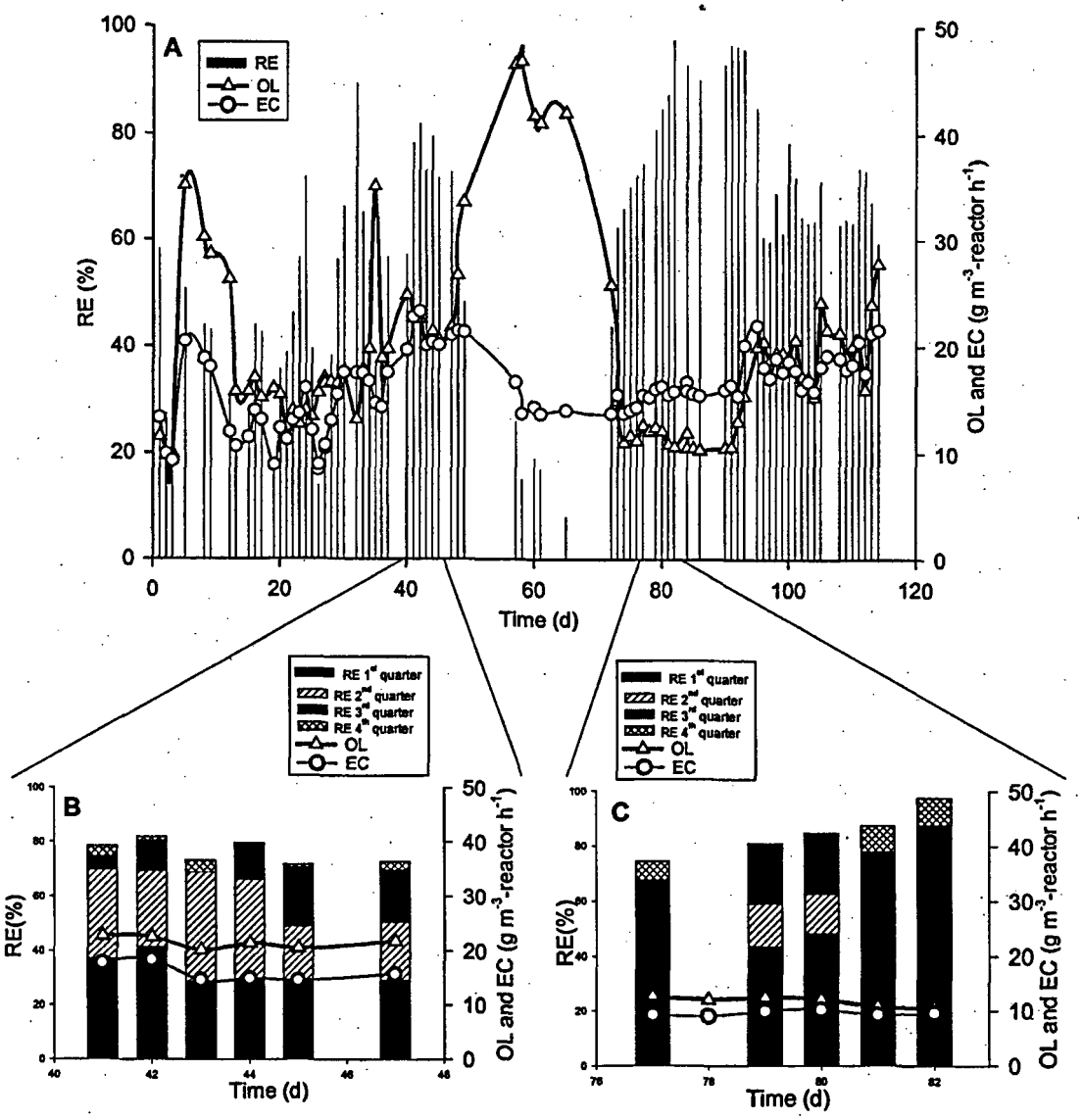

Figure 3. MCB Removal Efficiency (RE, %) versus Organic Load (OL, g m^{-3}-reactor h^{-1}) and Elimination Capacity (EC, g m^{-3}-reactor h^{-1}) obtained during GPB operation in Experiment II (Fig. 3.A). Partial MCB Removal Efficiency (RE, %) obtained between days 40 - 48 (Fig. 3.B) and days 76 – 82 (Fig. 3.C).

the first month, a steady increase in the RE, up to 90 % on day 33, was observed, but that was followed by a sharp decrease (day 38) when a sudden increase in the reactor OL was observed. From day 40, the treatment process stabilised at a RE of ca. 70%, when the reactor was exposed to an OL of 22 g m^{-3}-reactor h^{-1}. From day 50, the OL was gradually increased to 45 g m^{-3}-reactor h^{-1}. The RE decreased accordingly, reaching a minimum value of 8% on day 65. When the OL was gradually reduced to the initial value of 10 g m^{-3}-reactor h^{-1} (day 71), a steep increase in the RE was observed, stabilising at 95% (day 92). When the OL was again increased to 20 g m^{-3}-reactor h^{-1} (day 96), the RE decreased and stabilised at 70%.

The partial removal of MCB through the reactor height was also characterised (Fig. 3.B and 3.C). Generally, the contribution of the first reactor section predominated. In accordance with results obtained in Experiment I, under high OL operating regimes equivalent contributions to the reactor overall treatment efficiency were observed along the column height (Fig. 3.B). Under low OL operating regimes, a predominant contribution of the first reactor section to the overall treatment was evident (Fig. 3.C). Similar results showing the predominance of the first reaction section to the

overall treatment when operating GPB for treatment of several VOCs have been published [10,19-23]. The main explanations advanced for such predominance include enhanced mass-transfer conditions, leading to the presence of more carbon sources, moisture content and nutrients, that contribute to a higher metabolic reaction given by a higher biomass concentration, and thus a higher biodegradation rate. During periods of lower RE, there was no clear difference between the contribution of each section to the overall RE. A similar behaviour was observed along filter beds exposed to MCB [7] and phenol [24].

Evolution of chloride and suspended biomass concentrations in the MM is shown in Figure 4. During the first two months of operation the fluctuations observed in chloride concentrations were due to the periodical renewal of the MM from the recirculating vessel. The high peaks of suspended biomass observed at some stages of operation may have been due to the release of attached biofilm portions. From day 70, MM was fed continuously to the GPB, and the SIA methodology for on-line chloride monitoring was coupled to the system. With this new operating regime, characterised by a continuous replacement of MM in the system, the evolution of chloride concentration in the MM at the outlet of the GPB, presented a more stable behaviour. A mass-balance carried out under constant OL operational regimes (between days 79-85 and days 96-104) showed that the chloride liberation accounted for more than 99% of the MCB removed, as determined by analysing the GPB inlet and outlet MCB gaseous concentrations. The GPB clogged on day 114. No abnormal concentrations of suspended biomass were observed.

An improvement on the overall reactor performance was observed from Experiment I to Experiment II. Apart from the selected growth support material, the increase in the recirculation flow might have improved the reactor operational conditions. Increases in the recirculation flow have been shown to improve the EC of filter beds [7,8]. The major roles of the liquid medium on a biotrickling filter include: i) a transport carrier for inorganic nutrients supply; ii) a barrier for mass transfer; iii) an additional reaction zone [18,25]. Therefore, the beneficial effects produced from MM recirculation may be explained by an increase in the reaction zone promoting larger active specific biofilm surface area, obtained through the creation of favourable growth conditions for the biomass and better moisture control [9]. The quantification of the partial RE along the reactor height

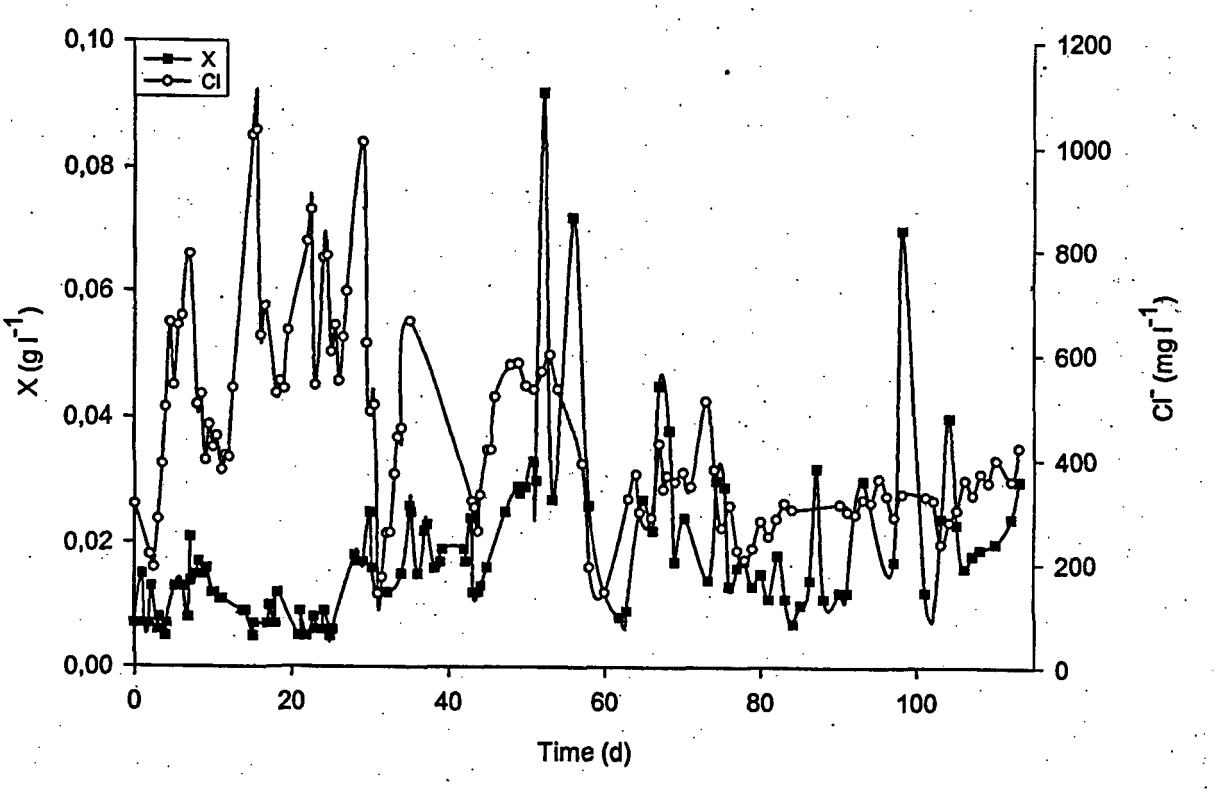

Figure 4. Evolution of suspended biomass (X, mg l^{-1}) and chloride (Cl^-, mg l^{-1}) concentrations obtained in the recirculation vessel during GPB operation in Experiment II. From day 70, chloride concentrations represent daily average values.

allowed for the identification of the first reaction section as the predominant contributing section, particularly at low OL regimes. The positive effect of high recirculation rates and the predominant contributing section should be considered when scaling-up biological processes, as the overall dimensions of the treatment unit can be significantly reduced.

Development of on-line monitoring systems, when compared to classical techniques, would be a step-forward towards the optimal strategy for GPB monitoring. SIA methodology for on-line monitoring of chloride proved to be accurate, precise and fast, being an advantageous alternative to the time-consuming reference procedure usually applied for chloride monitoring. The low detection and quantification limits that the methodology allows [13], supports its application for the quantification of trace amounts of compounds often present in industrial effluents.

Treatment Inhibition

For characterisation of the treatment process, the OL was compared to the EC obtained at steady-state, represented by the stabilisation of removal efficiencies at constant OL operating regimes, during the experiments carried out (Fig. 5). The similarity of results obtained for each OL amongst the different experiments shows the reproducibility of the GPB behaviour when exposed to similar operating conditions. Despite the low EC values, the curve shape is in accordance with literature published elsewhere [8,10,21,22], characterised by a diffusion limited zone, where a linear relation between EC and OL at lower OL values was observed, and a reaction limited zone, where with increasing OL a constancy in the EC levels was observed. Under this reaction limited zone, kinetic inhibition seemed to occur when the reactor was exposed to higher OLs (> 40 g m^{-3}-reactor h^{-1}), with a subsequent decrease in EC. A similar behaviour has been observed during the biological treatment of benzene and toluene in a biofilter [26].

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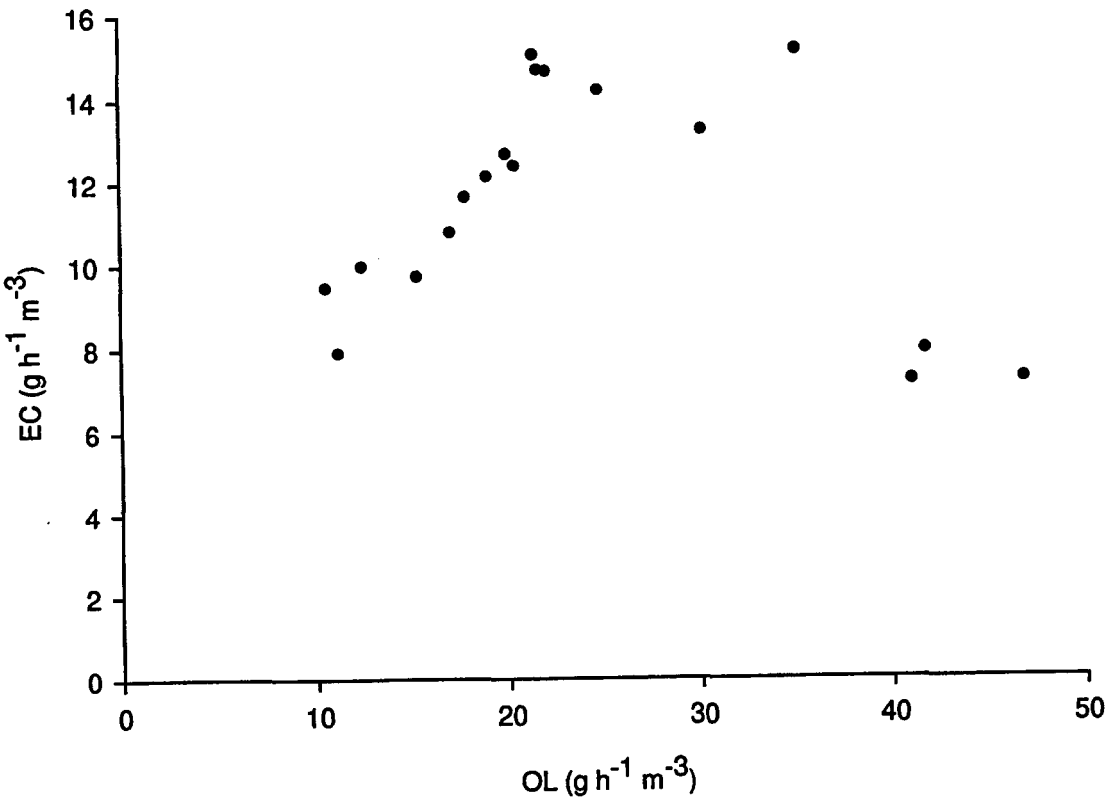

Figure 5. Elimination capacity (EC, g m^{-3}-reactor h^{-1}) versus organic load (OL, g m^{-3}-reactor h^{-1}) fed to the GPB.

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