Styrene Biofiltration in a Trickle-Bed Reactor

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ABSTRACT

The biological treatment of styrene waste gas in a trickle–bed filter (TBF) was investigated. The bioreactor consisted of a two-part glass cylinder (ID 150 mm) filled with 25 mm polypropylene Pall rings serving as packing material. The bed height was 1m. Although the laboratory temperature was maintained at 22 °C, the water temperature in the trickle–bed filter was slightly lower (about 18 °C).The main aim of our study was to observe the effect of empty-bed residence time (EBRT) on bioreactor performance at a constant pollutant concentration over an extended time period. The bioreactor was inoculated with a mixed microbial consortium isolated from a styrene-degrading biofilter that had been running for the previous two years. After three weeks of acclimation period, the bioreactor was loaded with styrene (100 mg.m^{-3}). EBRT was in the range of 53 s to 13 s. A maximum elimination capacity (EC) of 11.3 g$_C$.m^{-3}.h^{-1} was reached at an organic loading (OL) rate of 18.6 g$_C$.m^{-3}.h^{-1}.

Key words: Biofiltration, styrene, trickle – bed filter, loading by air flow rate

INTRODUCTION

Styrene is a widely produced aromatic hydrocarbon used in many chemical industries, in particular in the production of polystyrene, butadiene–styrene latex, copolymer resins and rubber (Dehghanzadeh et al. 2005; Jorio et al. 2000a; Lu et al. 2001). Approximately 21 million tones of styrene were consumed worldwide in 2000, a 50% increase from 1993 (Chung et al. 2006).

Styrene may leak into the environment during any step of the production process, generating, as a result, great amounts of contaminated effluents and off–gases, which, if not properly treated, may have an adverse impact on air quality. Thus styrene has become a serious threat to public health and welfare (Lu et al. 2001). Recently the metabolism of styrene has been extensively studied in mice and rats in order to obtain relevant toxicological data. Several studies reported both hepatotoxic and pneumotoxic effects (Carlson et al. 2006; Harvilchuck and Carlson 2006). Acute exposure to styrene in humans results in mucous membrane and eye irritations, as well as in gastrointestinal disorders. Chronic contact causes a variety of discomforts including headache, weakness, depression, decreased lung ventilation, possible hearing loss, chronic neuropathy and other neurotoxic effects (Dehghanzadeh et al. 2005; Chung et al. 2006; Lawton et al. 2006). Styrene is a colourless, volatile, strong-smelling liquid, the odour of which is obvious at less than 0.5 ppm (Jorio et al. 2000a).

Although higher concentrations of styrene have been observed in urban areas where there is greater industrial activity, occupational exposure to airborne styrene is modest in most parts of the industry (< 10 mg.m^{-3}). However it tends to be relatively high (40–400 mg.m^{-3}) in the field of reinforced plastics (Nylander-French et al. 1999). In such fields, the microbial purification of

contaminated gases has become economically feasible (Pol et al. 1998). Biofiltration is a promising technology for the treatment of large off–gas volumes of diluted styrene emissions in the air (Tresse et al. 2003). Furthermore, it is environmentally friendly, with contaminants fully converted, at low temperatures, into non–hazardous final products (Zilli et al. 2001). Compared with traditional technologies, biofiltration is also a cost-effective solution for the treatment of low—strength (as well as some medium-strength) waste gases produced by volatile organic compounds (VOCs) (Jang et al. 2005; Kim et al. 2005). Additionally, biofiltration does not produce the further emissions common to conventional waste gas treatment technologies such as carbon adsorption, liquid scrubbing, condensation, thermal incineration and catalytic incineration.

These processes have been commonly used for removing VOCs, but the more stringent environmental regulations of recent years have led to the development of innovative, low-cost treatment technologies based on a biological approach, and biofiltration seems to be the answer (Jorio et al. 2000b).

The biofiltration of styrene waste gas has been the subject of a number of studies, both at bench-scale (Dehghanzadeh et al. 2005; Jorio et al. 2000a; Lu et al. 2001) and pilot-plant scale (Webster et al. 1999). The majority of these studies have conducted experiments using biofilters. Few studies involve trickle–bed filters, for which continuous flow of the liquid phase is characteristic. Trickle–bed filters are often thought to be more efficient than biofilters, but the feeding of nutrients stimulates biomass growth. Clogging by excessive biomass accumulation is one of the main obstacles to the implementation of high-performance trickle–bed filtration (Alonso et al. 1997).

In this study we observed the dependency of removal performance on EBRT for a trickle–bed filter. The goal of our study was to achieve the highest possible elimination capacity at different influent loadings, while maintaining satisfactory removal efficiency.

MATERIALS AND METHODS

Design and operating conditions of bioreactor

A schematic diagram of the bench-scale trickle–bed filter is shown in Fig. 1. The reactor consisted of three cylindrical compartments. The two upper sections were made of tempered glass with total height of 150 cm. The third segment, made of polypropylene, served as a sump for circulating liquid. The sump was separated from the column by a perforated plate. All three sections had an internal diameter of 15 cm. The reactor was packed with polypropylene Pall rings ($25 \times 25 \times 1$ mm) up to a bed height of 100 cm. The cylindrical unit and auxiliary appliances [water circulating pump (Micropump, USA), peristaltic pumps, syringe pumps] were placed in a supporting steel construction. The pH value was set to 7.0 ± 0.2 and this level was maintained by the addition of 0.1 M NaOH solution. A dose of alkaline solution was supplied to the reactor by a peristaltic pump, which, as the reactor had no air humidifier, also had the effect of replenishing the evaporated water content. The trickle–bed filter was operated in up-flow counter-current mode.
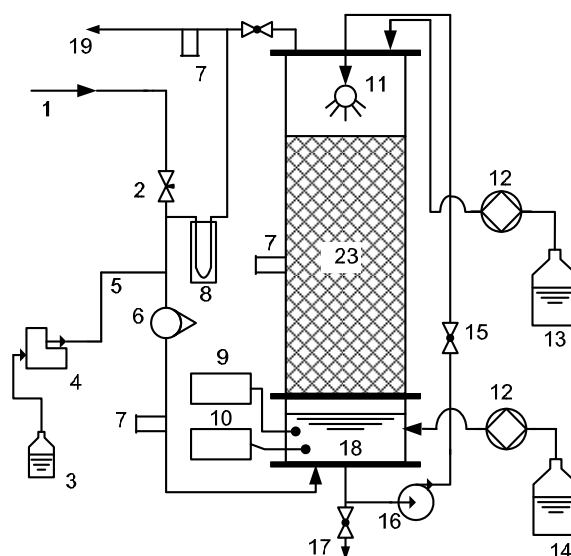
Figure 1 - Schematic diagram of the trickle–bed filter. 1-air inlet, 2-needle valve, 3-pure styren solution, 4-syringe pump, 5-capillary, 6-rotameter, 7-sampling ports, 8-liquid manometer, 9-thermometer, 10-pH–meter, 11-spray nozzle, 12-peristaltic pump, 13-nutrient solution tank , 14-sodium hydroxide solution tank, 15-choke valve, 16-medium circulating pump, 17-drain valve, 18-drain vessel, 19-outlet gas

Inoculum and culture medium

The mixed microbial culture for inoculation was taken from a previously running styrene-degrading biofilter. An inoculum preparation was performed in 250-ml Erlenmeyer flasks containing 100 ml of mineral medium at 27–30 °C on a rotary shaker. After 96 h of fed batch cultivation the cells wereharvested, centrifuged and then re-suspended in fresh nutrient medium for use as an inoculum in the biodegradation experiments. The cultivation and degradation media have the following composition: $(g.L^{-1})$ $(NH_4)_2SO_4$ [2.00]; KNO_3 [1.00]; K_2HPO_4 [4.30]; KH_2PO_4 [3.40]; $MgCl_2.6H_2O$ [0.34]. Trace elements feed composition (µg/L): $FeSO_4.7 H_2O$ [0.16]; $ZnSO_4.7 H_2O$ [0.30]; $MnSO_4. H_2O$ [0.10]; $CuSO_4. 5H_2O$ [0.10]; $Na_2MoO_4. 2 H_2O$ [0.10]; $CaSO_4. 0.5 H_2O$ [0.15]; $CoSO_4. 7 H_2O$ [0.10]; $Na_2B_4O_7. 10 H_2O$ [0.10].

Pollutant supply

The styrene used in this study was a monomer species; 99 % reagent purity grade, inhibited with 0.005 % of 4-tert-butylcatechol (Sigma–Aldrich Chemie, Germany). To generate an air stream contaminated with styrene vapors, the flow of compressed air was forced through a glass T–pipe, at which a pollutant injection point was situated.

A syringe pump (Gilson, France) ensured a continuous feed of styrene.

Analytical methods

Styrene in the influent and effluent gas was determined by GC analysis. Gaseous samples were collected from each of the sampling ports using 500–µL gastight syringes (Hamilton, USA). The gas chromatograph (Hewlett Packard 6890 Series, California, USA) was equipped with a flame ionization detector (FID). A 30 m HP INNOWAX crosslinked polyethyleneglycol capillary column (0.53mm i.d.; 1 µm film thickness) was used for the experiment. GC analytical conditions were as follows: injection and detection temperatures were 250 and 300 °C, respectively, oven temperature was 150 °C, and flow of argon as a carrier gas was 6.3 ml/min. Under these conditions the styrene retention time was 1.9 min.

Evaluation parameters

The parameters studied were calculated from the following equations:

$$OL = \frac{c_{in} \cdot V_g}{H \cdot S} \quad , \quad EC = \frac{(c_{in} - c_{out}) \cdot V_g}{H \cdot S},$$

$$EBRT = 3600 \cdot \frac{V_B}{V_g} \quad , \quad RE = \frac{EC}{OL} \cdot 100$$

where OL is the organic load on the reactor's empty bed volume (g.m^{-3}.h^{-1}), C_{in} and C_{out} are the inlet and outlet pollutant concentrations respectively (g.m^{-3}), V_g is the air flow rate (m^3.h^{-1}), V_B is the filter bed volume, H is the bed height (m), S is the area of the cross section of the reactor (m^2), EC is the elimination capacity (g.m^{-3}.h^{-1}), and RE is the removal efficiency (%).

Temperature settings

The experiment was carried out in an air-conditioned laboratory in order to maintain isothermal conditions of 22 °C. However the water temperature in the trickle–bed filter was slightly lower (about 18 °C).

RESULTS AND DISCUSSION

After three weeks of acclimation period the experiment has been started. The loading test consisted of reducing the EBRT from 53 s to 13 s in several discrete steps. These correspond to the air flowrate of 20, 30, 40, 50, 60, 70 and 80 L.min^{-1}. The styrene inlet concentration was maintained at 100 mg.m^{-3} for the whole experiment runtime.

Figure 2 displays the overall performance of the reactor over time. Each step lasted 10 days in average. Steps of such length were required to achieve steady state conditions at the very beginning of the experiment. Stable removal performance was reached after 25 days of operation. Despite changes to the EBRT, during the period from day 20 to 54 the elimination capacity showed no significant variation (9.3-11.3 g$_C$.m^{-3}.h^{-1}). The reactor, therefore, was not responding to progressive loading. Removal performance dropped off (down to approximately 30 %) with each increase in the gas flow rate. The trickle–bed filter handled loads up to 10–15 g$_C$.m^{-3}.h^{-1} with a relatively high rate of removal, but greater loadings were only partially degraded. Our filtration results are comparable with those of Choi et al. (2004), who reported an average removal rate of 13.3 g$_C$.m^{-3}.h^{-1} in a pilot-scale trickle–bed filter with an organic load of 20.6 g$_C$.m^{-3}.h^{-1} after 5 months of operation.
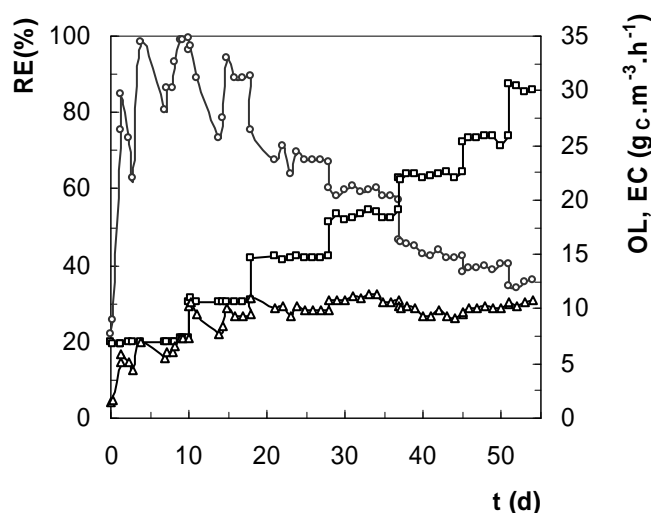

Figure 2 - TBF performance characteristics, RE: ○, OL: □, EC: △

The results from the loading tests are shown in Fig. 3. The reactor worked satisfactorily up to an organic load of 10 g$_C$.m^{-3}.h^{-1}. From that point, however, pollutant breakthrough occurred. Consequently the elimination capacity began to drop from 100 % removal, and for the rest of the experiment remained almost unchanged. The trickle–bed filter was operated at its maximum elimination capacity. Such operating conditions were interpreted by Cox and Deshusses (2002) as

a zero order regime. A similar trend was also observed by Ottengraf et al. (1986), who suggested that it was the result of a low styrene inlet concentration leading to diffusion limitation

in the biolayer. Cox et al. (1997) confirmed this hypothesis, identifying the critical pollutant concentration at the transition point of reaction to diffusion limitation as approximately 60 $mg.m^{-3}$.
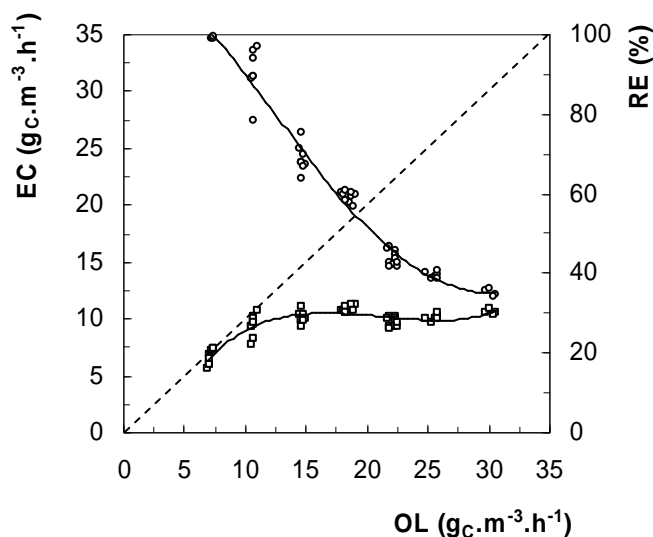
Figure 3 - Elimination capacity and removal efficiency as a function of loading. RE/EC: (○)/(□)

CONCLUSIONS

The results of this study suggest that styrene degradation in the laboratory trickle–bed filter was strongly dependent on the EBRT. The reactor displayed satisfactory styrene removal performance at lower EBRTs of approximately 35 s and more. Therefore our results show the significant potential applicability of trickle–bed filters for the handling of high flow rates of waste gas streams containing low concentrations of styrene.

ACKNOWLEDGEMENTS

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