

Degradation of solvent mixture vapors in a biotrickling filter reactor: Impact of hydrophilic components loading and loading release dynamic

JAN PACA¹, ONDREJ MISIACZEK¹, MARTIN HALECKY¹ AND KIM JONES²

¹ Institute of Chemical Technology, Department of Fermentation Chemistry and Bioengineering, Technicka 5, 160 28 Prague, Czech Republic

² Environmental Engineering, Texas AM University-Kingsville, MSC 213, Kingsville, Texas 78363, USA

ABSTRACT

Interactions amongst the degradation rates of toluene, xylenes, methyl ethyl ketone (MEK), methyl isobutyl ketone (MIBK), n-butyl acetate (n-BA), and acetone (Ac) were investigated in a biotrickling filter reactor. The reactor was packed with polypropylene High-Flow rings in a counter-current air-water mode of operation. Performance evaluation of the reactor with increased hydrophilic compound loading while maintaining a steady loading rate of hydrophobic components, were evaluated. The dynamic responses of the individual solvent components following a drop of the ketone loading rate are also described in a second phase of experiments.

The degradation rate of aromatics became partially inhibited at OL_{KET} of $15 \text{ g.m}^{-3}.\text{h}^{-1}$; below this level all of the ketones were totally degraded. Once the organic loading exceeded a value of $40 \text{ g.m}^{-3}.\text{h}^{-1}$ the removal efficiency of all the components (except n-BA) began to drop sharply. At OL_{KET} of $85 \text{ g.m}^{-3}.\text{h}^{-1}$ the RE of aromatics dropped to below 10 %, that of acetone to 10 %, MEK and MIBK to 20 %, but n-BA removal remained above 97 %.

A step-decrease of the OL_{KET} from 85 to $5 \text{ g.m}^{-3}.\text{h}^{-1}$ resulted in a rapid increase of RE_{AROM} to 30 % (in 20 min). After the decrease, the level of RE_{KET} quickly reached 90 %, specifically: for MEK this occurred in about 4 min, for MIBK in about 25 min but for acetone, this was not achieved until after a period of 3.5 h. The significantly longer time period of RE_{Ac} to achieve the original value was a consequence of: (1) its slower degradation rate resulting from a degradation competition with the other components, (2) the inhibitory effect resulting from acetone unlimited water solubility, and (3) a high quantity of acetone being accumulated in a circulating aqueous medium.

1 INTRODUCTION

Paint solvents are mixtures of VOCs containing both hydrophobic and hydrophilic components. Their removal from waste air has been studied using biotrickling filters (Webster *et al.*, 1999; Song *et al.*, 2002; Hekmat *et al.*, 2003; Bastos *et al.*, 2003; Chang and Lu, 2003; Kim *et al.*, 2004) and biofilters (Atoche and Moe, 2003, Moe and Qi, 2004; Qi *et al.*, 2005; Moe and Qi, 2005; Qi and Moe, 2006).

The objectives of this study were as follows: (1) To evaluate the simultaneous degradation of the individual hydrophobic and hydrophilic components in a paint solvent mixture. (2) To test the effect of increasing loading by only ketones on the above mentioned degradation. (3) To characterize the reactor's dynamic response after a step-rate ketones loading decrease.

2 MATERIALS AND METHODS

A schematic diagram of the bench-scale biotrickling filter is shown in Figure 1. The height of the reactor was 1.7 m and the internal diameter was 0.15 m. The sump was separated from the column by a perforated plate. The packing material consisted of Pall rings made of hydrophilized polypropylene. The parameters of Pall rings were as follows: 15 x 15 x 1 mm, void volume of 0.8624, specific surface area of 350 m².m⁻³ and a bulk density of 120 kg.m⁻³. The packed bed height was 1 m.

The mixed microbial culture used to inoculate the reactor contained the following bacterial strains: *Sphingobacterium multivorum* (G⁻ rods), *Comamonas testosteroni* (G⁻ rods), *Pseudomonas putida* (G⁻ rods) and *Bacillus cereus* (G⁺ rods). All the bacterial strains were primary toluene and xylene degraders (i.e. each strain was able to use the individual pollutants as the sole carbon and energy source for growth).

Key biodegradation experimental conditions included a temperature of 22°C, a mineral medium (MM) for growth which contained 0.4 g/L (NH₄)₂SO₄, 0.3 g/L KNO₃, 0.1 g/L NaCl, 0.125 g/L K₂HPO₄, 0.085 g/L KH₂PO₄, 0.34 g/L MgCl₂.6H₂O, 0.02 g/L and 1 mg/L trace elements (Weigner *et al.*, 2001). The pH of the circulating water phase was maintained at 7.0, along with a hydraulic loading rate of 0.224 m.h⁻¹.

Mixtures of the following pollutants were applied to the biological treatment systems to simulate air contamination: toluene (TOL), xylenes (XYL), methyl ethyl ketone (MEK), methyl isobutyl ketone (MIBK), n-butyl acetate (n-BA) and acetone (Ac). The pollutants in the gas phase were determined using an Agilent 6890 N gas chromatograph. Details of the conditions have been published (Paca *et al.*, 2006). The reactor had been in operation degrading solvent mixtures for seven months when this experiment started. The reactor loading during this experiment was as follows: The ratio of TOL/XYL was kept constant at 50%w/50%w levels. The ratio of the ketones

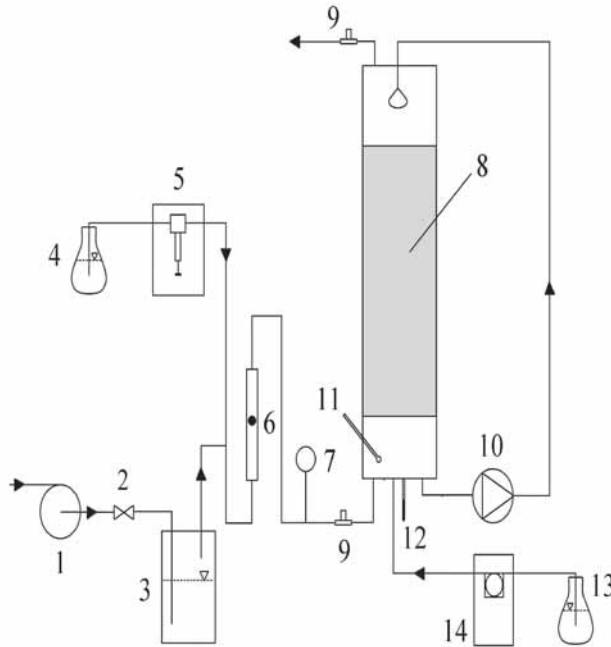


Figure 1. Schematic of the trickle bed reactor set-up

1- blower, 2 - needle valve for air-flow rate control, 3 - humidifier, 4 - vessel with pollutant, 5 - syringe pump, 6 - flow meter, 7 - manometer, 8 - packing, 9 - sampling ports, 10 - membrane pump, 11 - pH electrode, 12 - thermometer, 13 - NaOH solution, 14 - peristaltic pump.

inlet concentrations was kept constant: Acetone/MEK/MIBK/nBA = 1/1.13/0.93/1.43. Their inlet concentrations were changed within a range of 94 – 1500 mg.m⁻³. The empty bed retention time (EBRT) for the experiment was kept at 43 s.

3 RESULTS AND DISCUSSION

3.1 IMPACT OF LOADING RATE BY KETONES

The experiment started on day 220 and lasted 85 days. During this time period, the constant loading rate of aromatics was 4 g_c.m⁻³.h⁻¹ (Fig. 2b). The reactor was loaded by gradually increasing inlet concentrations of ketones (Fig. 2a). At day 226 (A arrow), when a drop of the RE_{AROM} was observed, the syringe pump supplying a mixture of TOL and XYL into the inlet air failed. It resulted in the drop of RE_{AROM} only. At day 256 (B arrow), biomass backwashing was carried out. The biomass removal was followed by a drop of RE of both the hydrophilic and hydrophobic groups of

compounds. However, the recovery lasted only three days. The next decrease of both the groups of components on day 260 was a consequence of the basic nutrients starvation that was eliminated by replacing of the entire volume of aqueous medium on day 265 (C arrow).

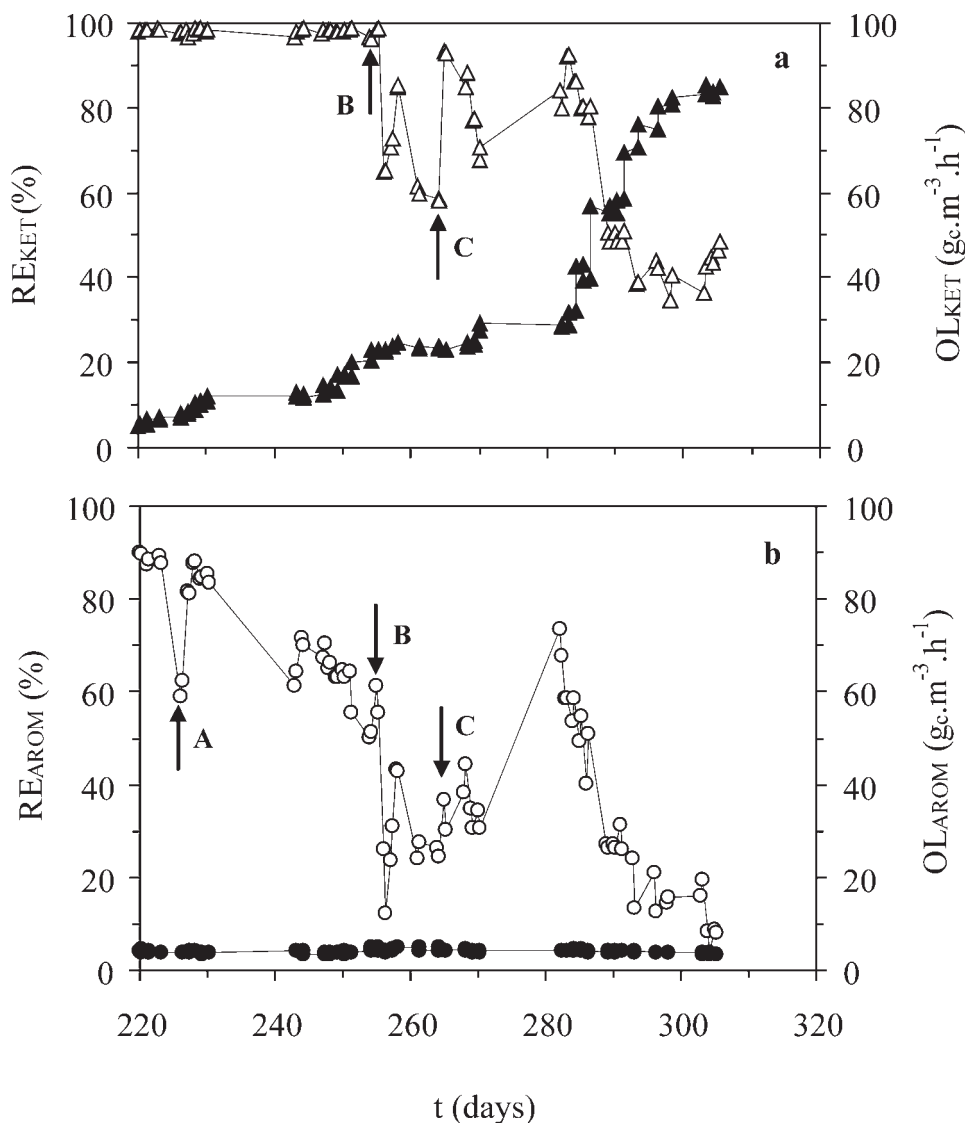


Figure 2. Loading rates (full dots) and their impact on RE (empty dots) of hydrophilic (a) and hydrophobic (b) components.

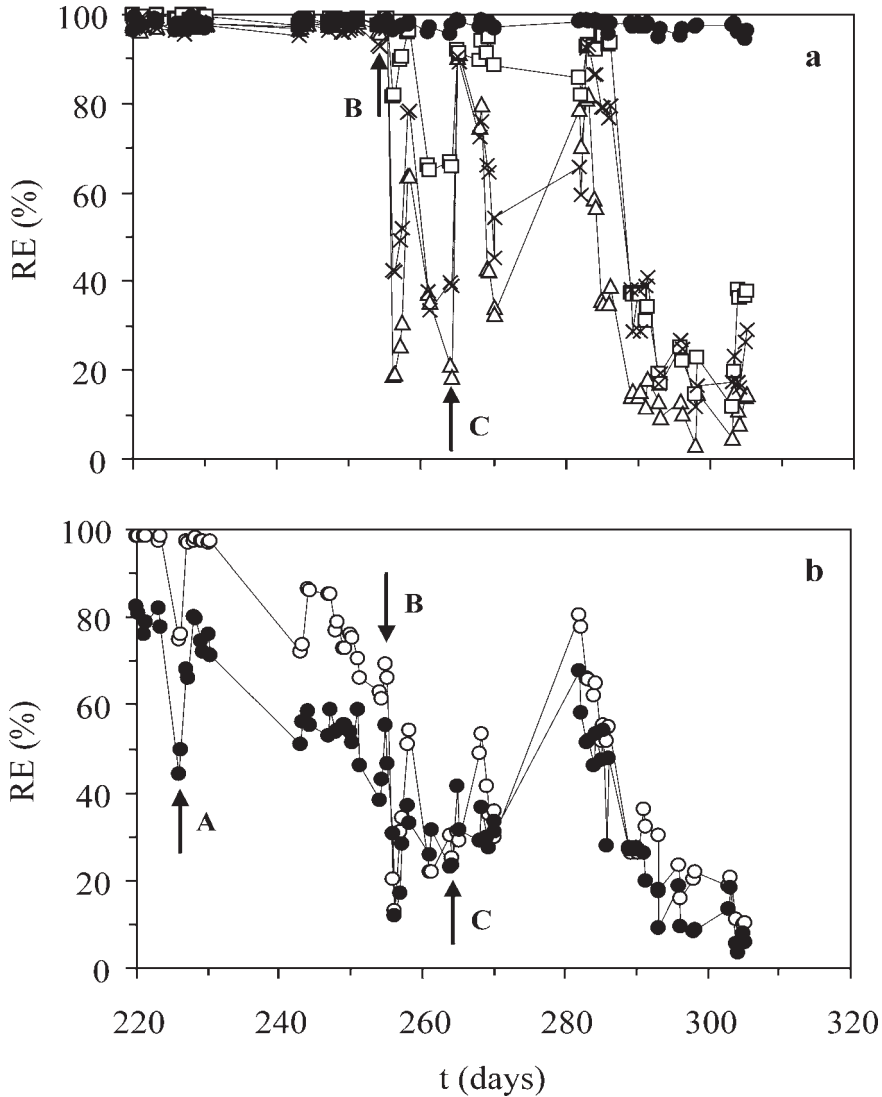


Figure 3. Impact of loading rates on RE of the individual components in the solvent mixture.
 a – (□) MEK; (x) MIBK; (●) nBA; (Δ) Ac b – (○) TOL; (●) XYL

Increasing the OL_{KET} from 6 to $12 \text{ g}_c \cdot \text{m}^{-3} \cdot \text{h}^{-1}$, there was no effect on the RE_{KET} (still above 95 %) but the RE_{AROM} dropped from 85 % to 65 % (on day 245). Looking at Fig. 3 it is evident that the RE of all the individual ketones remained above 95 %. Due to preferentially degraded ketones, the RE of TOL and XYL decreased to 85 %

and 55 %, respectively. Further increase of OL_{KET} to $24 \text{ g}_c \cdot \text{m}^{-3} \cdot \text{h}^{-1}$ still resulted in a low RE_{KET} drop (above 90 % on day 48). The RE_{AROM} dropped to 35 %. Supplying the cells with a sufficient nutrient (day 50 to 63) at the OL_{KET} of $30 \text{ g}_c \cdot \text{m}^{-3} \cdot \text{h}^{-1}$, the gradual decrease of both aromatics as well as the ketones occurred (Fig. 3). Only the RE of n-butyl acetate still was kept above 90 %.

3.2 DYNAMIC RESPONSE TO THE STEP-DROP OF THE LOADING RATE

Figure 4 shows the dynamic response following the release of ketones loading to the original value of $OL_{KET} = 7 \text{ g}_c \cdot \text{m}^{-3} \cdot \text{h}^{-1}$ (before starting this experiment) that was carried out on day 305. As only the OL_{KET} was dropped, and since the OL_{AROM} was not changed the RE_{AROM} increased to 32 % (Fig. 4b). Before reaching the new steady state condition both the RE_{TOL} and RE_{XYL} showed damping oscillations lasting 4 h. The new values were $RE_{TOL} = 37 \%$ and $RE_{XYL} = 28 \%$.

The transient of the RE_{KET} response lasted 10 h. Since the RE_{BA} was not affected by the high OL_{KET} there was no response either. The fastest increase of RE showed MEK that reached 90 % during 5 min while with MIBK it took 25 min. A completely different response was observed with acetone. Due to its unlimited water solubility, the acetone accumulated in five litres of the circulating water medium during the previous loading time period. Therefore, after the loading drop at time 0 (Fig. 4a) the RE_{KET} showed 3 h zero value. From the acetone analyses it was proven that during a time period of 2 h 40 min its concentrations in the outflow air were higher than those in the inflow air. Nevertheless, the RE_{Ac} of 98 % was achieved after the four hours transient phase.

Comparing the final RE values on day 305 with those on day 220 (Figs. 2 and 4) it was found that the cells were able to reach back the original RE value just for ketone degradations. After a period of the high ketone loading rates and despite of a continuous low TOL and XYL loading rates, the RE_{AROM} only achieved 32 % instead of the originally 90 %. This fact can be explained by a reduction of catabolic activity by the microbial cells in degrading the toluene and xylene hence, more slowly degraded compounds. A recovery of the degradation activity to aromatics could be achieved during 2 – 4 days, as it has previously been proven (Paca *et al.*, 2006).

4 CONCLUSIONS

- The cells prefer to dissimilate ketones to aromatic hydrocarbons.
- The lack of nutrients caused a significant loss of the ability to dissimilate xylene, toluene, and acetone. A little bit milder was this effect observed with MIBK and MEK degradations. The degradation rate of nBA was not affected at all by the nutrient limitation.

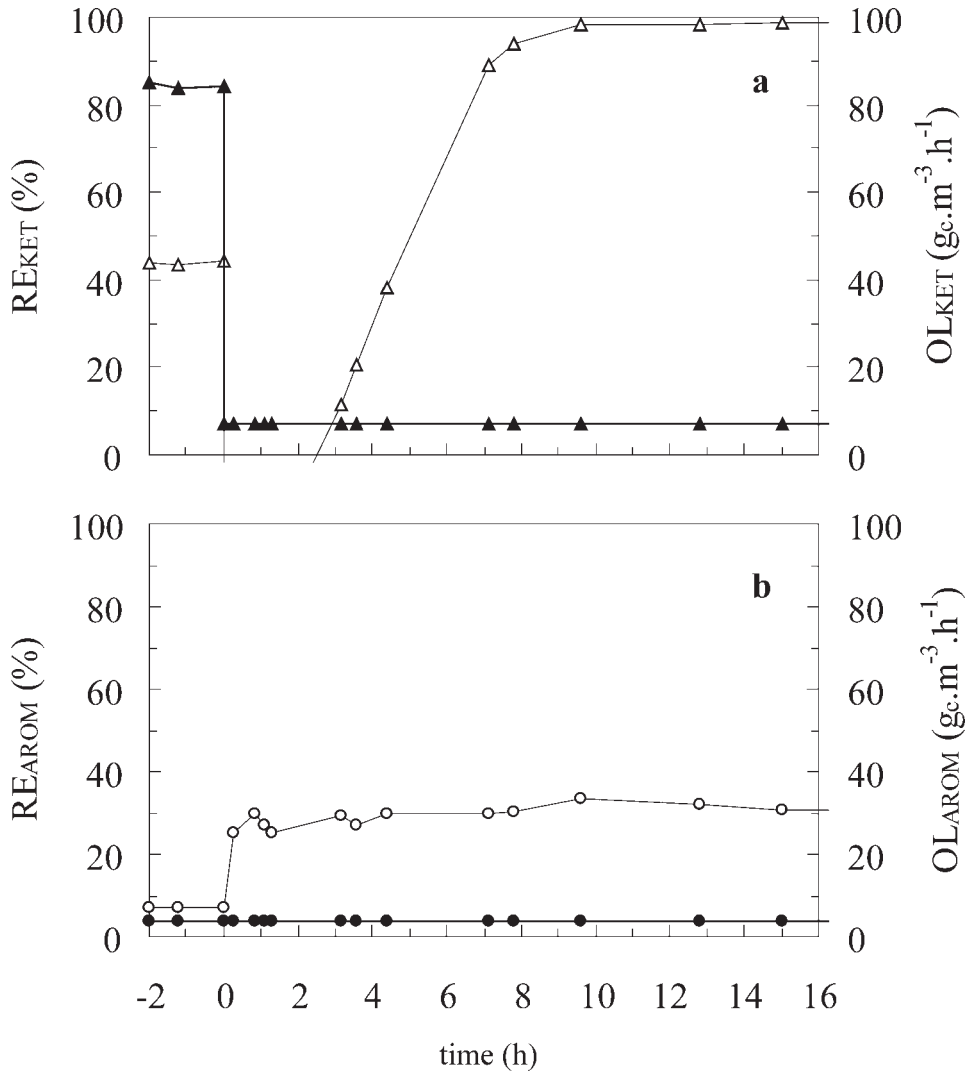


Figure 4. Dynamic response to loading release by ketones on RE_{KET} (a) and RE_{AROM} (b).
 OL – full dots; RE – empty dots. Test carried out on day 305.

- High OL_{KET} of 85 g_c.m⁻³.h⁻¹ suppressed the RE of all the compounds below 20 % with the exception of n-butyl acetate.
- Under conditions of the breakthrough of the solvents (overloading conditions) in the biotrickling filter, acetone can be dissolved into the circulating aqueous medium to a much higher concentrations than the other

solvents with a limited water solubility. After a drop below the overloading conditions, the degradation of acetone, evolved from the aqueous phase, significantly prolongs the transient phase before reaching the new steady state conditions.

5 ACKNOWLEDGEMENTS

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