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Short communication

Determination of methacrylic acid in the drain of a biotrickling filter using isotachophoresis and capillary zone electrophoresis

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Abstract

The performance of a biotrickling filter for treatment of concentrated waste gases was investigated. The macrokinetics of methylmethacrylate degradation in the biotrickling filter is studied by measuring the degradation product methacrylic acid in the drain of the filter. The drain was analysed using isotachophoresis (ITP) and capillary zone electrophoresis (CZE). The CZE analyses were carried out in an I.D. 75 μm capillary at 20 kV (negative inlet polarity) using a 0.01 *M* Tris–acetate buffer of pH 4.45. The electroosmotic flow (EOF) was suppressed by addition of CTA and PVA to the buffer. Detection was at 214 nm. After filtration through a 0.45-μm filter, samples were directly injected. The calibration graph was linear between 10 and 800 mg/l methacrylic acid, with an analysis time under 2 min.

Keywords: Biotrickling filter; Methacrylic acid

1. Introduction

One of the research subjects of the group of Chemical Process Engineering at the Eindhoven University of Technology is biological waste gas treatment. In the early 1980s the BIOTON biofilter was developed and introduced to the market by ClairTech B.V., a company that was a spin-off of the research efforts of the group. Current research at Eindhoven focuses upon the treatment of waste gases in biotrickling filters (BTFs). Design and scale up of BTFs is investigated, as well as obstacles that hamper the widespread application of BTFs in practice. Notably, the treatment of concentrated waste gases [1,2] and of mixtures [3] are subjects of study.

The solvent dichloromethane (DCM) is extensively used in industry and its yearly emission is high due to its high vapour pressure at atmospheric conditions. Because of its harmful effects upon the environment its emission has to be reduced. Previous research at the Eindhoven University of Technology [4,5] has shown that DCM can efficiently be removed from a contaminated air stream in a biotrickling filter if it is the only carbon source present. The research also showed that the biotrickling filter could be operated in a steady state for a long period (±5 years) running on an inlet concentration of 2 g DCM/m^3.

Industrial waste gases are usually polluted with more than one compound, however, and knowledge about the treatment of multicomponent waste gases is desirable. The biological treatment of these mix-

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tures poses a number of problems. Undesirable species interactions may occur, e.g., the formation of a diffusion barrier due to a layered biofilm structure. Due to substrate competition, which includes competition for oxygen, a target compound may not be degraded before other compounds are removed. This leads to an undegraded target compound or unacceptably large installations. These problems may limit the practical applicability of this intrinsically environment-friendly technique.

In earlier studies the performance of a BTF eliminating a mixture of DCM and other compounds has been investigated [6–8]. It appeared that the DCM elimination efficiency decreased drastically after the introduction of methylmethacrylate (MMA) or acetone as a secondary substrate in the waste gas. One of the aims of the current research on the treatment of the mixture is to identify our knowledge of the processes responsible for the decrease in filter performance. The macrokinetics of the DCM and MMA degradation in the BTF are studied when both substrates are present in the waste gas and are degraded in parallel reactions. Also clogging of the filters has been investigated and an upper limit of the maximum allowable carbon load to a filter was investigated [3].

In the biotrickling filter the waste gas is introduced at the bottom of the column. The trickling liquid is sprayed on top of the column. At the bottom, the pH of this liquid is measured and part of the flow is automatically adjusted by addition of either NaOH or HCl, subsequently thermostated and recycled at the top.

In this paper, the results are published of an undergraduate research project that has been carried out in the research group that aims to further elucidate the degradation of MMA in the filter. In the filter, MMA is hydrolysed into the reaction intermediates methanol and methacrylic acid. The response of the filter upon a sudden loading of MMA is investigated by following the concentration of these intermediates in the liquid recycle. Using a special set-up that allows the continuous registration of the mass of the filter monitors the biomass hold-up in the system (biomass, free flowing liquid). For the experiment a filter (4 m in height, 0.4 m in diameter) was used that had been running for over 1.5 years on 2 g DCM/m^3, superficial gas and liquid velocities, 163 and 7.3 m/h, respectively. The set-up has been previously described elsewhere [1].

In a previous paper [9] the suitability of isotachophoresis (ITP) for methacrylic acid analysis in similar samples was already determined. In that case the analysis conditions were optimised for conductivity detection, measuring the steady-state ITP zonelengths for quantitation. Other methods for methacrylic acid analysis were also reported in the literature. In a study of polymer samples for residual monomer [10], pyrolysis-trapping was used as a sample preparation technique. Subsequent analysis was carried out using either gas chromatography–flame ionisation detection (GC–FID) with a polar fused-silica capillary column (analysis time 13 min, detection limit 2.58 pg) or high-performance liquid chromatography–UV detection (HPLC–UV) with an acid exchange column and 0.005 *M* H_2SO_4 as mobile phase (analysis time 7 min, detection limit 7.14 pg). In another paper [11] on the determination of residual methacrylic acid in packaging material, reversed-phase HPLC–UV was used with a C_{18} column and acetonitrile–phosphate buffer–water (detection threshold 0.03 mg/l).

In the present contribution, ITP and capillary zone electrophoresis (CZE) are compared and the latter optimised in terms of detectability and analysis time.

2. Experimental

2.1. Equipment

ITP was performed using laboratory-made ITP equipment [12]. The separation capillary was made of PTFE with total length of 400 mm [length to the 254 nm UV detector 320 mm (380 mm to the a.c. conductivity detector)]×0.4 mm I.D. The driving current was stabilised at 100 μA. Samples of ca. 1–3 μl were injected manually through a septum at the leading/terminator interface.

All CZE measurements were carried out on a Beckman P/ACE 2000 capillary electrophoresis instrument (Beckman Instruments, Fullerton, CA, USA). Operating conditions were: fused-silica capillary of 307 mm (length to the detector 241 mm)×75 μm I.D., separation voltage 20 kV with negative inlet polarity. UV absorption–detection at 214 nm.

2.2. Chemicals

Caprylic acid (CAS 124-07-2), ϵ-aminocaproic acid (CAS 60-32-2), Tris(hydroxymethyl)methylamine (Tris) (CAS 77-86-1), acetic acid (CAS 64-19-7) and cetyltrimethylammonium bromide (CTA) (CAS 57-09-0) were analytical reagent grade purchased from Merck (Darmstadt, Germany). Poly(vinyl alcohol) (PVA) (CAS 9002-89-5) (tradename Mowiol 88-8) was obtained from Hoechst (Frankfurt, Germany). Methacrylic acid (CAS 79-41-4) was 98.5% purity, stabilised with 250 ppm hydroquinone monomethylether (MeHQ) and obtained from Janssen (Geel, Belgium)

2.3. Electrolytes for electrophoresis

Electrolytes for ITP were: leading electrolyte, 0.01 *M* chloride buffered to pH 4.1 with ϵ-aminocaproic acid and terminating electrolyte, 0.005 *M* caprylic acid.

Buffer solution for CZE experiments was 0.01 *M* Tris, with acetic acid added to pH 4.45. The electroosmotic flow (EOF) was suppressed by adding CTA and PVA to the buffer solution, with a final concentration of $5 \cdot 10^{-5}$ *M* and 0.025%, respectively. Both CTA and PVA were added as 1% (v/v) from hundred-fold concentrated stock solutions.

3. Results and discussion

3.1. Isotachophoresis

Besides methacrylic acid, the samples contained about 4 g/l ammonium sulphate, 0.15 m*M* NaCl, 0.5 g/l K_2HPO_4 and methanol, which is an hydrolysis-product of methylmethacrylate. An initial ITP analysis was performed to test the samples for possible disturbing factors. Chloride and sulphate were not detected as such, as they co-migrate with the leading electrolyte. A large phosphate zone is detected, see Fig. 1. Therefore, conditions had to be optimised to separate the zones of methacrylic acid and phosphate far enough for them not to form a mixed zone. Although in the isotachopherogram this was not yet the case, we decided to switch to CZE. Several reasons can be given. First, the CZE equipment was fully automatic whereas ITP has to be carried out by manual injection and instrument operation. Second, as the ITP analysis time was at least 12 min, in CZE it was expected that (with the sufficient mobility differences given) the analysis could be further optimised in terms of analysis time. Finally the dynamic range and detection limit in CZE were expected to be superior.

3.2. Capillary zone electrophoresis

The pH of the buffer was chosen close to the pK_a of methacrylic acid in order to make use of the relatively high coefficient of extinction of the undissociated methacrylic acid. Using much higher pH values (we tried for example a Tris–acetate, pH 8 system, to achieve a shorter time of analysis and an even better separation between phosphate and methacrylic acid) resulted in a much lower coefficient of extinction, and correspondingly lower detector response of the dissociated methacrylic acid. The operating conditions could be optimised so far as to minimise the time of analysis to about 2 min. In view of the rinsing time of the capillary (1 min), further reduction of the time of analysis was not considered necessary.

The detector wavelength was selected to obtain a high response for methacrylic acid. Some test runs were performed using detection at 200 nm, but although the peaks were twice as high, the baseline was far worse. Therefore the final wavelength was selected at 214 nm. Fig. 2 shows an example of a CZE-run of standard solutions of methacrylic acid of widely varying concentration. The logarithmic response axis in this and the next figure were chosen to illustrate that the migration time is constant in the dynamic range, in spite of the fact that the sample load adversely affects the peak widths. Fig. 3 shows the electropherogram of two typical drain samples. It can be seen that the resolution is excellent. Phosphate incidentally, although it has no UV, is detected as well. This is due to the Kohlrausch law regulated displacement of acetate in the buffer and the fact that acetate shows some residual absorbance at 214 nm. Phosphate, as a very broad, triangular peak, migrates well in front of methacrylic acid (Fig. 3).

By adding phosphate to the standard solutions, it was observed that the migration time of methacrylic

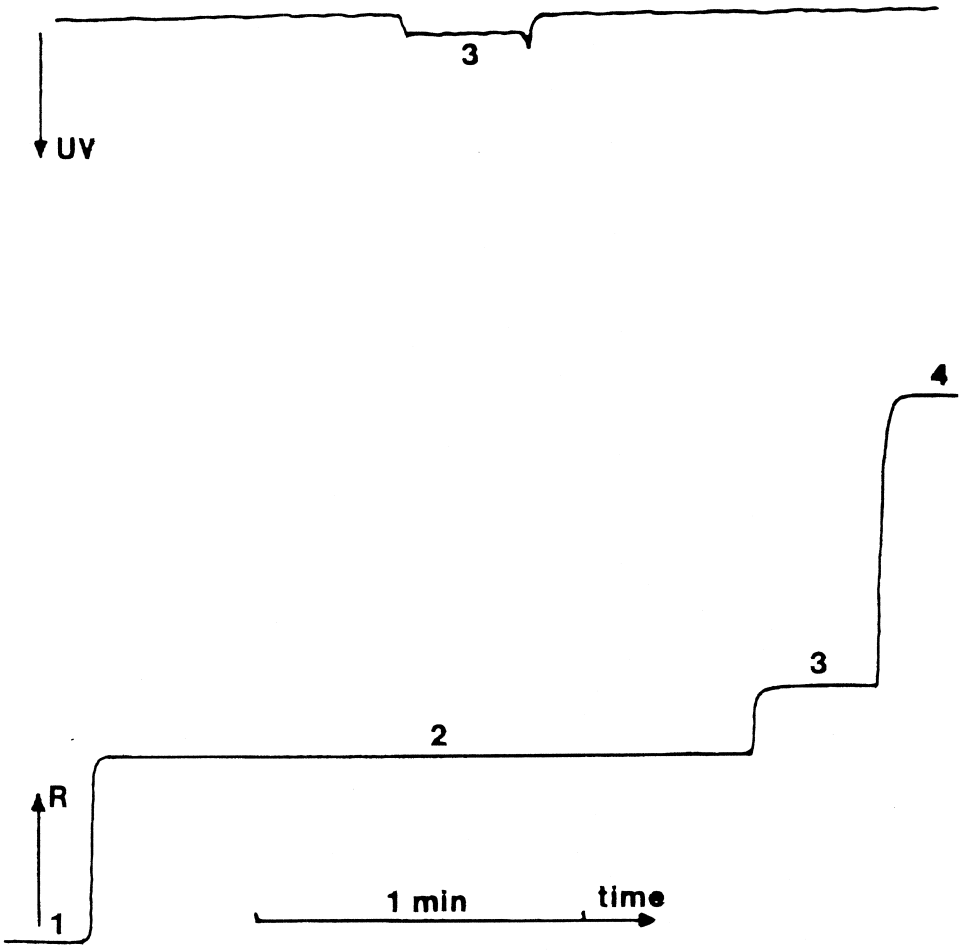

Fig. 1. ITP analysis of a typical drain sample with a.c. conductivity (bottom trace) and UV absorption detection at 254 nm (top trace). Identification of zones: 1=chloride (leading), 2=phosphate, 3=methacrylic acid, 4=caprylic acid (terminator).

acid was slightly changed. Therefore, peak areas were corrected with migration times.

Initial experiments for this investigation[1] indicated that after fraction collection at the biotrickling filter drain, some biomaterial from the system must have been present in the collected sample solutions. Measuring such a sample repeatedly showed an exponential decrease of methacrylic acid concentration in time, with a time constant of 10 h, while ideally such biodegradation reactions would have to be terminated after sample fraction collection.

It was verified that filtering the samples over a 5-μm filter achieved that aim. Samples were subsequently frozen at −20°C. Directly after defrosting the samples, a 1-ml amount was transferred to a 1.5-ml Eppendorff cup and centrifuged. After that, the cups were stored in a refrigerator at 7°C until analysis. The samples were taken and injected in the CZE one by one instead of using a sequence, to minimise the time spent outside the refrigerator. Identical samples analysed at 30 min intervals yielded identical results.

A calibration graph was constructed by injecting standard solutions of 8, 80 and 800 mg/l, using injection times between 2 and 10 s. The combination of different concentrations and injection times yield-

[1]http://intranet.chem.tue.nl/6N220-9

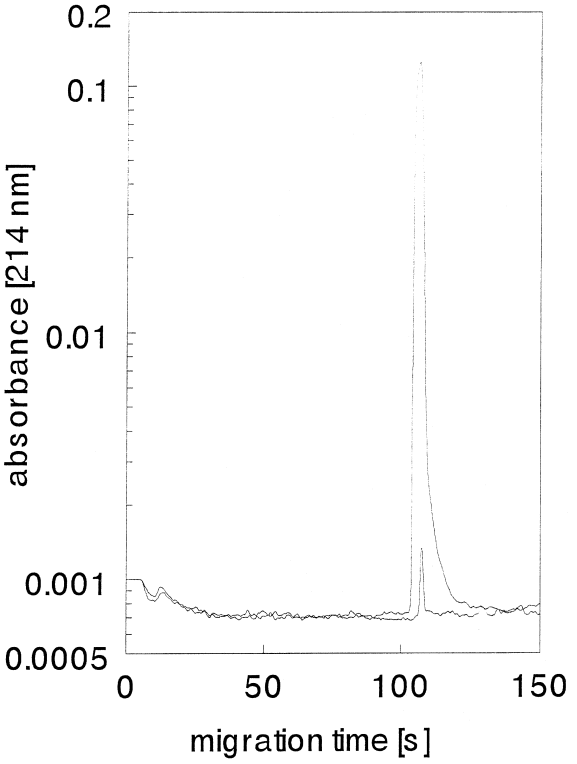

Fig. 2. Electropherogram of two standard solutions of methacrylic acid. The logarithmic response axis was chosen to illustrate that the migration time is constant in the dynamic range.

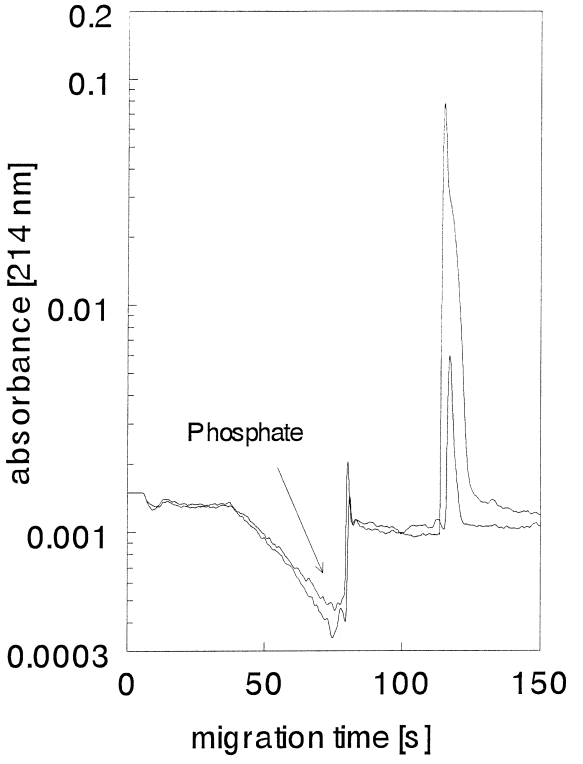

Fig. 3. High-speed selective methacrylic acid analysis of two typical drain samples with CZE. Access phosphate is well separated from methacrylic acid, as it is detected between 40 and 75 s. See legend of Fig. 2.

ed excellent calibration graphs (coefficient of correlation 0.9994 for $n=7$) for the latter two standard solutions, corresponding to a 2 decade dynamic range in terms of injected amount. The minimum concentration that could be determined was 10 mg/l. Sample concentrations were in the range between 10 and 800 mg/l methacrylic acid, and consequently did not require further dilution.

4. Conclusions

Both CZE and ITP have proven to be suitable and flexible techniques to analyse samples from a column on their methacrylic acid concentration. CZE enabled methacrylic acid determination within 2 min by directly injecting filtered samples from a biotrickling filter drain, enabling fast routine checks for bioreactor performance.

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