Biochemical Engineering Journal 31 (2006) 107–112

Biochemical Engineering Journal
www.elsevier.com/locate/bej

Solid phase micro extraction fibers, calibration for use in biofilter applications

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Received 1 July 2005; received in revised form 19 January 2006; accepted 12 May 2006

Abstract

The main purpose of this study is to develop a SPME calibration method suitable for use in evaluation of concentrations of hydrophobic substances in environmental samples.

The analyte used in the experiments was alpha-pinene, a hydrophobic organic compound commonly found in wood, and therefore found in wood storage facilities, wood processing industries and wood based biofilters. The SPME fibres were calibrated for different concentrations of alpha-pinene at different temperatures and relative humidities. The method was used to evaluate the removal efficiency of a lab-scale biofilter.

Keywords: SPME; Biofilters; Alpha-pinene; Bioprocess monitoring; Mass transfer; Absorption

1. Introduction

Emission of volatile organic compounds (VOCs) is an environmental problem; it may contribute to air/water pollution as well as causing health problems.

Alpha-pinene is a mono-terpene, a hydrophobic VOC, which is present naturally in softwood, and emitted by the forest product-, pulp- and paper- and fragrance industries [1–4]. It can react in the atmosphere to form free radicals and deplete the ozone layer, cause health effects, and also become a human nuisance in the form of an odorous compound [5–11].

The use of a biofilter to remove alpha-pinene from the gas-stream before emitted into the air is a possible solution for small-scale industries, e.g. local sawmills (emissions from wood drying). Since alpha-pinene is a hydrophobic compound, with water solubility less than 2.5 ppm at 23 °C [6,8], high water content in the packing materials, which is one of the requirements of successful operation in biofilters, may present difficulties in bed performance due to higher diffusion resistances.

Conventional sampling methods for sampling VOCs in air or water include passive or active sampling on sorbtion tubes or filters. There is a need for a simple inexpensive and efficient method to monitor and evaluate the in- and outdoor environment.

When using a biofilter to lower the emissions from a small-scale industry, there is a need to find a quick and simple method to measure the concentrations of pollutants both before and after the biofilter, i.e. to monitor the effectiveness of the biofilter.

Solid phase micro extraction (SPME) is a sampling technique developed during the 1990s [12,13]. SPME is a solvent free sampling method for volatile organic compounds [14].

SPME with poly(dimethylsiloxane) (PDMS) has been used in environmental analytical chemistry to sample VOCs in surface water, wastewater and air samples [4,5,15–17], and methods to quantify VOCs in air have been developed [14,16,18–20]. The analytes are pre-concentrated in the SPME fibre before thermally desorbed in an injector of a gas chromatograph (GC). Sampling times can range from a few seconds to days depending on when equilibrium is reached. SPME could be considered to be an attractive alternative to conventional air sampling methods. Extraction of analytes on PDMS is done through absorbtion, the absorbtion is based on partitioning equilibrium between the SPME coating and the sample matrix, making the calibration

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doi:10.1016/j.bej.2006.05.007

into a challenge. The calibration is dependant on temperature, relative humidity and sampling time.

Since the concentration of an organic compound in an air or water system can be easily controlled and calculated, the calibration of an SPME–GC system versus analyte concentration is a feasible alternative [21].

The main objective of this work is to develop a reliable method for quantification of alpha-pinene from different gaseous and headspace matrices with SPME sampling. The results from the SPME calibration were used to measure the alpha-pinene degradation during the operation of a lab-scale biofilter set-up.

The obtained results must represent the functionality of alpha-pinene concentration (ppm, mg/l) from GC–MS response (Mcounts). In addition, the dynamic behaviour of SPME fibres are also investigated. Finally, obtained results will be used in the concentration detection of alpha-pinene along the biofilter bed in different operational conditions. For a greater accuracy of results, an On-Line FID, in addition to SPME–GC–MS method, detects the outlet concentration.

2. Materials and methods

2.1. Biofiltration set-up

The biofilter consisted of a vertical cylinder made of glass with inner diameter of 0.14 m and total height of 0.6 m. There are five sampling ports along the biofilter column, with equal separation distances, in order to monitor the concentration, humidity, temperature and pressure of the gas phase. The diameter of each port is 18 mm and is connected to a perforated straight elastic tube inside the bed, which allows the passage of the gas phase and avoids the packings (Fig. 1). More detailed description of the biofilter construction and side equipments is presented elsewhere [22].

Calibration apparatus: calibration set-up consisted of a simple five-neck bottle (5.5 l in volume), an electrical heater and monitoring devices (Fig. 2). One of the openings was equipped with a plastic seal stopper, with a septum inside, which enabled us to insert the SPME device into the sample matrix. Two temperature and humidity detectors were placed from two other openings inside the bottle. By these detectors, it becomes possible to monitor the exact amount of these parameters. The temperature of the system is manipulated by the electrical heater, which is located under the bottle.

Different humidities are created by the different saturated salt solutions inside the system. According to thermodynamical relations for partial pressure of mixed compounds in the equilibrium (Raoult's law, Henry's law), relative humidity, above a saturated solution of solid salts in any pure solvent, i.e. water, in any closed system, will remain constant, numerically less than the humidity of pure solvent. During all evaporation periods of solvent, any change will not happen in the dominant equilibrium between solid/liquid–gas phase, since the residue of salt is in the solid state and sediment at the bottom of the container.

The humidity calibration was performed using the concept of a sample reservoir containing an open container with a special salt solution. After a short period, equilibrium is achieved between the gaseous atmosphere and salt solution. By using different solutions, various relative humidities could be prepared. To ensure the resultant humidity, a humidity detector is placed on the system by which the exact amount is monitored.

To prepare samples with different concentrations, a definite amount of alpha-pinene is weighted in special ependorff tubes and dropped inside the bottle. Proper salt solutions also are located inside the bottle corresponding to the desired relative humidities. After 1 h, an equilibrium condition is reached in the system for both organic compound and salt solution. For sampling from this gaseous matrix, which contains organic volatiles, the SPME syringe is pushed through the septum and the fibre

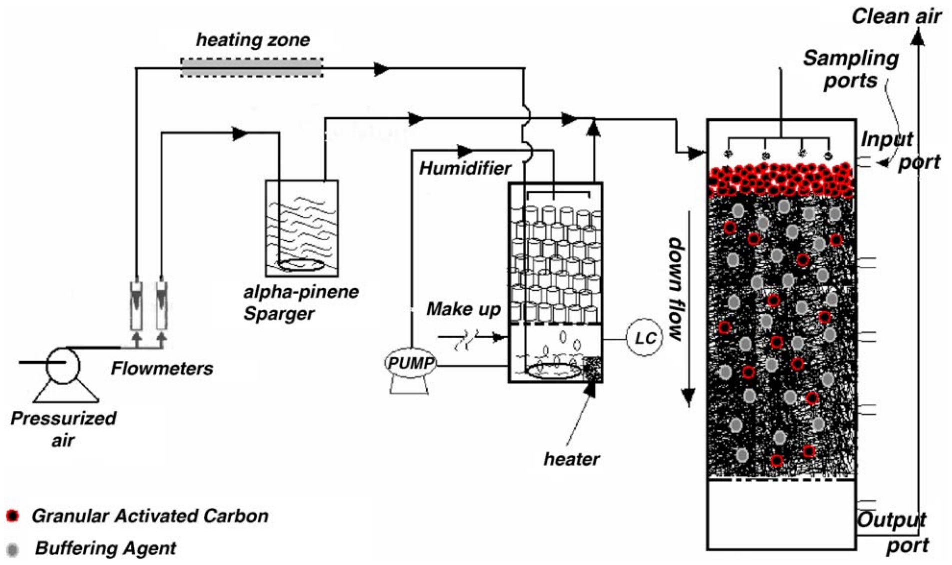

Fig. 1. Schematic diagram of biofiltration set-up and side devices, used for alpha-pinene treatment.