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Short communication

Solid-phase microextraction as a source of data for the design of stripping aeration towers

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Abstract

Solid-phase microextraction was used for the analysis of volatile chlorinated hydrocarbons in water. The data were used for the verification of the penetration theory. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

Volatile chlorinated hydrocarbons (VCHs) are a class of very frequent environmental pollutants. They can be found e.g., in heavily polluted ground waters, in drinking water (haloforms), etc. One technological possibility for their removal from water is the use of stripping packed aeration towers.

The design of stripping aeration towers is quite complex and time consuming when actual removal of VCHs is tested in a pilot- or full-plant scale. However, according to the “penetration theory” the ability of the towers for VCH removal can be evaluated according to the kinetics of saturation of water by atmospheric oxygen. There should be an analogy between the kinetics of removal of VCHs from water and the rate of dissolution of atmospheric oxygen in the water under the same conditions.

Measurement of the concentration of oxygen dissolved in water (e.g., by an oxygen probe) is definitely much simpler, quicker and flexible than analysis of VCHs. Concentration of oxygen dissolved in water can be also measured on-line and the data are known immediately. Samples need not be transported to the laboratory, when for example parameters of a full-scale stripping aeration tower are optimized.

The aim of our work was to confirm validation of the recalculation method for VCH removal outlined above. As test compounds chloroform, benzene, trichloroethene, tetrachloroethene, chlorobenzene and bromobenzene were used.

2. Theory

The depth of packing h required to achieve a ratio of influent to effluent concentration of component i in water can be written in the form [1]:

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$$h = \frac{V_L}{k_L a_i S} \left(1 - \frac{m_i V_L}{V_G} \right)^{-1} \ln \left[\frac{m_i V_L}{V_G} \left(1 - \frac{c_{i1}}{c_{i2}} \right) + \frac{c_{i1}}{c_{i2}} \right] \quad (1)$$

where V_L is volumetric liquid and V_G volumetric gas flow-rate ($\text{m}^3 \text{s}^{-1}$), c_{i1} and c_{i2} concentration of component i at inlet and outlet (g m^{-3}), m_i distribution coefficient of component $i (=c_{iL}/c_{iG})$, S cross sectional area of the column (m^2) and $k_L a_i$ volumetric mass transfer coefficient of the component i (1 s^{-1}). Eq. (1) was deduced for counter-current piston flow of both phases in the column, isothermal conditions, linear equilibrium relation and the main mass transfer resistance in liquid phase.

Equation (1) must be valid for all components, including oxygen. Therefore, “oxygen data” can be used to predict removal of compounds to be stripped (e.g., VCHs). It is necessary to know only m_i and $k_L a_i$ values.

The relation between volumetric mass transfer coefficients of oxygen $k_L a_{O_2}$ and of component i follows from the penetration theory of interfacial mass transfer

$$k_L a_i = k_L a_{O_2} \sqrt{\frac{D_i}{D_{O_2}}} \quad (2)$$

where D_{O_2} and D_i are molecular diffusivities of the component i in water.

Eqs. (1) and (2) give relations for recalculation of oxygen to VCH data. The diffusivities and distribution coefficients can be found in literature and/or calculated from Henry’s constants [1], solubilities or infinite dilution activity coefficients [2].

3. Experimental

For the stripping experiments a pilot-plant packed aeration tower was used. Characteristics of the tower and experimental conditions were as follows: counter-current flow of phases, inner diameter of the column 0.29 m, total height of the packing 1.2 m, liquid distributor: disk with 1060 holes (disk diameter 200 mm, diameter of holes 3 mm), water loading rate (variable) 12.7, 20, 40 and 60 $\text{m}^3 \text{h}^{-1}$, superficial gas velocity 0.6 m s^{-1} , gas and liquid temperature 20°C, package of the tower Pall rings. Inlet concentration of each VCH in water was 50 mg l^{-1} .

Chloroform, trichloroethylene, benzene, tetrachloroethylene, chlorobenzene and bromobenzene in water samples were analysed by solid-phase microextraction–gas chromatography–mass spectrometry (SPME–GC–MS). The principle of the method is described e.g., by Arthur et al. [3]. Results of the successful inter-laboratory comparison of organic compounds analysis in water using SPME have been also published [4].

In this work, water samples were collected in all-glass bottles (volume 250 ml). The water samples were free of air bubbles. For the analyses, 1 ml of the aliquot was taken and placed in a screw cap vial. Septum of the vial was PTFE covered. Before the SPME, internal standard (toluene, concentration in water sample 2 mg l^{-1}) was added. SPME fiber (100 μm polydimethylsiloxane coating, Supelco) was then inserted into the vial through the septum by means of a manual holder (Supelco). SPME of the organics from water was performed for 20 min in a vigorously stirred sample. After sampling, the fiber was withdrawn into the needle and transferred into the splitless injection port of the GC instrument (GC 8000, Fisons). Desorption of the organics into the chromatographic system was performed for 3 min at 220°C (temperature of the injection port). For the GC separation of the analytes, a fused-silica capillary column (SPB-1, 4 μm film thickness, 30 $\text{m} \times 0.32$ mm I.D., Supelco) was used. Oven temperature was programmed from 35°C for 3 min (3 min was also period for which the split valve of the injector was closed) to 120°C at 10°C min^{-1} . Helium was used as a carrier gas. The mass spectrometer (MD 800, Fisons) was operated at electron impact (70 eV) and full scan mode ($m/z=35\text{--}300$, 2 scans s^{-1}). Temperature of the interface and ionisation source was 220°C. Concentration of the analytes in the water samples was quantified according to the peak areas of the analytes in chromatograms of the total ionisation current (TIC), with respect to the peak area of toluene. For the qualitative and quantitative confirmation, selected ion chromatograms ($m/z=83$ for chloroform, 78 for benzene, 132 for trichloroethylene, 91 for toluene, 166 for tetrachloroethylene, 112 for chlorobenzene and 156 for bromobenzene, respectively) were also used.

Concentration of oxygen dissolved in water was measured by means of polarographic membrane covered electrode.

Table 1
Repeatability of the SPME–GC–MS method

Compound	S.D. (%)
1,1-Dichloroethene	8.36
<i>trans</i> -1,2-Dichloroethene	9.20
<i>cis</i> -1,2-Dichloroethene	8.28
Chloroform	8.31
1,1,1-Trichloroethane	7.06
Tetrachloromethane	6.77
Trichloroethylene	5.52
Tetrachloroethylene	5.03
Bromoform	2.07
1,1,1,2-Tetrachloroethane	2.83

Concentration of VCHs in water 150 µg/l (prepared from Supelco 4-8001 standard mixture), I.S. toluene, number of determinations $n=3$.

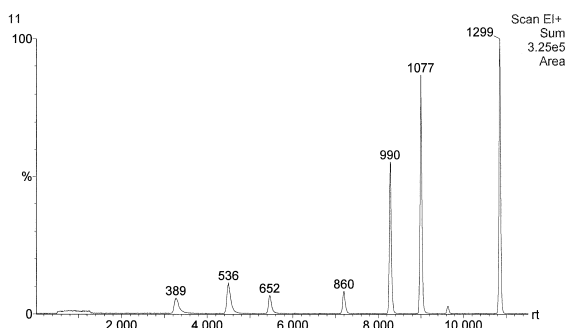


Fig. 1. Analysis of VCHs in water by SPME–GC–MS. Peaks: 389 = Chloroform, 536 = benzene, 652 = trichloroethylene, 860 = toluene (I.S.), 990 = tetrachloroethylene, 1077 = chlorobenzene, 1299 = bromobenzene. rt = Retention time in min.

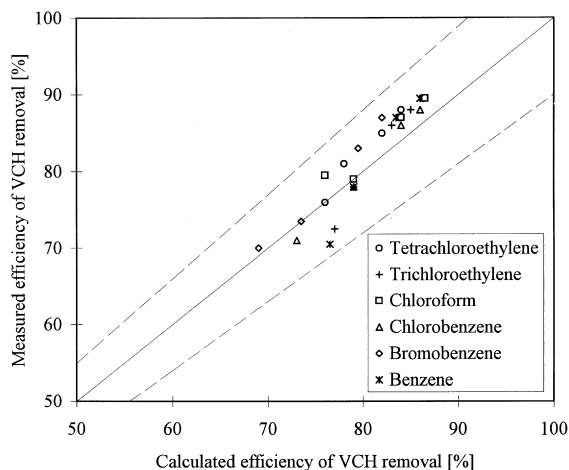


Fig. 2. Comparison of measured and calculated (from oxygen data) efficiencies of VCHs removal (broken line = 10% error).

4. Results

In the beginning of the experiments we verified repeatability of the SPME method. Results of this test are given in Table 1.

It was found that results of the SPME test were satisfactory for our purposes. Moreover, the results shown in Table 1 were obtained for much lower concentrations than actual concentrations of VCHs used during stripping experiments. The result of one SPME–GC–MS analysis is shown in Fig. 1.

The removal efficiencies of different VCHs from water measured in pilot column packed with hydrophilized polypropylene Pall rings (diameter 25 mm) were compared with those calculated according to the “oxygen” data using Eqs. (1) and (2). Results are presented in Fig. 2. It can be seen that the differences between calculated and experimental values did not exceed 10%.

5. Conclusions

(1) It was found that design of packed stripping towers according to the “oxygen” data is reliable. An agreement of the calculated removal efficiencies of VCHs and those observed experimentally confirmed practicability of the design procedure. The differences between them did not exceed 10% and the calculated values were mostly on the safe side of the design (i.e., the calculated efficiencies were lower than the efficiencies measured).

(2) SPME–GC–MS provided accurate, quick and reliable data for the given purposes. It enabled to analyze 3–4 samples per hour, which was almost impossible using “classical” analytical methods.

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