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EXAMINATION OF THE BIOFILTRATION OF AIR POLLUTED WITH METHYL ISOBUTYL KETONE

Biofiltration used for reduction of pollutant atmospheric emissions is difficult to design and hence experimental information about the course of fragmentary processes is still required. Researchers' efforts are thus oriented on the extension of knowledge about them as well as on attempts to generalise the phenomenon's description. This paper presents results of the measurement of biofiltration of the air polluted with methyl isobutyl ketone. Examinations were carried out in a biofilter column, 190 mm in diameter and 1400 mm high. Biofiltration bed, with a volume of 31.5 dm³, was composed of pine bark and compost from urban-industrial waste. Methyl isobutyl ketone concentrations were within the range of 70-770 mg/m³, while superficial flow rate was from 2.16 to 2.35 cm/s. The obtained air treatment degree was 9-100 %, while maximum biofiltration rate amounted to 54 g/(m³·h).

1. INTRODUCTION

In connection with more clearly noticeable depletion of resources and natural materials, the existence and further development of modern societies are inseparably related to the use of products of the chemical industry. It provides us with many end products as well as components used in their production or being part of them. Many of the substances manufactured by the chemical industry do not have their equivalents in nature and have toxic properties. These chemicals are repeatedly released into environment unintentionally or in not fully controlled way. Such substances also include volatile organic compounds used as fuels, solvents for paint products and extractants, and auxiliary substances in various technologies. One of the groups of substances used as solvents are ketones. The most commonly known one is acetone but other representatives of this group such as methyl ethyl ketone or methyl isobutyl ketone are frequently used in modern compositions. More rarely used ones are methyl isopropyl

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ketone, isophorone, mesitylene oxide, or diethyl ketone. Present-day varnish products frequently contain ketone-type solvent additives due to their ability to dissolve polymer compositions used as paint filler and binder and to mix with water being a basic solvent of water based varnishes and paints.

Methyl isobutyl ketone (MIBK) is used as an antioxidant in rubber mixes, extractant in the pharmaceutical and liquor industries and chemical synthesis, ethanol denaturant, in dry cleaning compositions, and in 4-methyl-2-pentanol production. Most frequently however, it is a component of paints and varnishes (about 2/3 of the quantity). Its world production in 1999 amounted to 305 million kg [1]. It is a colourless, poorly water soluble liquid with a characteristic ketone odour. It is stable during typical storage although reacts very readily with many reagents. Opinions on the MIBK toxicity are divided. According to some sources, it is slightly toxic for mammals but due to its relatively high volatility, susceptibility to photo-oxidation and biodegradation is hardly threatening for the environment [1]. According to other sources, it is toxic and carcinogenic for rats and mice [2]. In nature, it occurs in some fruits. It can be removed from emission streams by many methods, including both destructive and non-destructive methods. One of the destructive methods is biofiltration. During its course, undesirable substances are being removed on solid filter beds populated with microbes and other small organisms [3]. Some of them have already been isolated [4, 5], and fungi capable to degradation of MIBK have been described by Qi et. al. [6]. On account of their complex character and despite the continuous progress, these efficient processes are difficult to be modelled and hence experimental information about their course is still required during their designing. Many efforts or researchers are thus oriented on the extension of knowledge about these processes as well as on attempts to generalise their description [7].

2. RESEARCH METHODS

Measurements of the biofiltration of air-MIBK model mixture were carried out on a biofilter column made of hard polyvinyl chloride pipe. Diagram of the test installation is presented in Fig. 1. It worked under ambient conditions, i.e. at atmospheric pressure and the temperature range of 22–25 °C. The biofilter packing was pine bark and industrial compost made from municipal and industrial waste, coming from the solid waste composting plant in Racula near Zielona Góra, mixed at a 2:1 ratio and moistened to the level of water retaining ability. Dimensions of the biofilter column and operating conditions are given in Table 1.

The course of biofiltration was controlled by measuring periodically the MIBK concentrations along its length by the gas chromatography. Samples for analyses were collected from test probes being a termination of five perforated pipes introduced deep into the filter bed to the depth equal to column internal radius and from two probes at the col-

umn inlet and outlet (above and below the filter bed). Six sections of the biofilter bed were separated, without breaking its continuity, which ensured operating conditions of the laboratory column were close to those prevailing in industrial columns with solid filter bed.

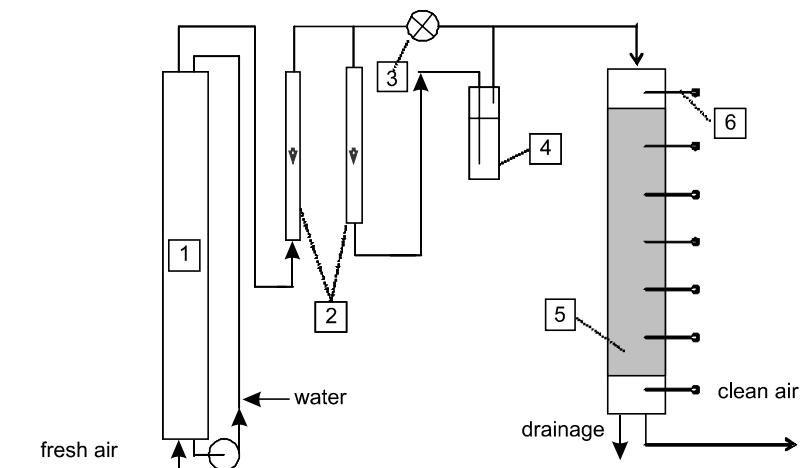


Fig. 1. Scheme of the experimental set up: 1 – humidifying column, 2 – rotameters, 3 – control valve, 4 – scrubber with tested substance (MIBK), 5 – biofiltration column, 6 – sampling ports

Table 1
Biofiltration column dimensions and operating conditions

Diameter, cm	19.0
Column height, cm ²	145.0
Cross-section area, cm ²	283.4
Total bed height, cm	111.0
Total volume of the bed, m ³	0.0315
Total weight, kg	37.6–47.0
Bed weight, kg	±30
Gas flow rate, m ³ /h	2.2–2.4
Humidity of the cleaned gases	above 95%
Final humidity of the bed (vs. to wet mass)	44.25%
Height of the biofilter bed sections, cm	$H_{1-2} = 11.5$ $H_{2-3} = 19.5$ $H_{3-4} = 19.5$ $H_{4-5} = 19.5$ $H_{5-6} = 20.0$ $H_{6-7} = 21.0$

The gas flow rate was also measured and changes in filter bed humidity were determined by systematic weighing of the column. Column pressure drop was measured

by connecting a differential manometer to test probes. The operating conditions of the chromatograph are presented in Table 2.

Table 2
Operating conditions of the chromatograph

Detector	FID
Column (route I)	Packed steel column 1.5 m long and 3 mm in diameter
Column filling	SE – 30 5% on Chromosorb W – HP, 60/80 mesh
Temperature of the sample injector, °C	150
Temperature of the column, °C	110
Temperature of the detector, °C	150
Flow rate of nitrogen, $\text{cm}^3 \cdot \text{min}^{-1}$	40
Flow rate of air, $\text{cm}^3 \cdot \text{min}^{-1}$	100
Flow rate of hydrogen $\text{cm}^3 \cdot \text{min}^{-1}$	30

Based on the results of chromatographic analyses and the data referring to the flow of air–MIBK mixture, the mass loading of the biofiltration column was calculated, as well as total biofiltration efficiency and pollutant elimination capacity (specific biofiltration rate) for the whole column and its virtual sections:

$$M = \frac{GC_i \times 10^{-3}}{V} \quad (1)$$

$$S_u = \frac{(C_i - C_{i+1})}{C_i} \times 100 \quad (2)$$

$$EC = \frac{G(C_i - C_{i+1}) \times 10^{-3}}{V} \quad (3)$$

where: C_i, C_{i+1} – inlet/outlet MIBK concentration (for whole column or its section), mg/m^3 , G – flow rate, m^3/s , V – bed volume, m^3 , M – mass loading of bed with MIBK, $\text{g}/(\text{m}^3 \cdot \text{s})$, S_u – biodegradation efficiency, %, EC – elimination capacity (biodegradation rate), $\text{g}/(\text{m}^3 \cdot \text{s})$.

3. RESULTS AND DISCUSSION

Examination of biofiltration was carried out for six months. The column's starting period, frequently called the adaptation period, lasted for ca. 5 weeks. During this time, the concentrations of analysed pollution (MIBK) at the inlet were usually small, oscillating around the value of 150 mg/m^3 . On single occasions, the MIBK concentration amounted reached 300 and even over 500 mg/m^3 . Biofiltration efficiency at the end of this period was close to 100%. After filter bed adaptation, the substrate concen-

trations at the inlet were increased to an average level of 350–400 mg/m³. Minimum substrate concentration applied during measurements (adaptation period) amounted to ca. 70 mg/m³, while the maximum one to 770 mg/m³. Fluctuations of the superficial gas flow rate were small and within the range from 2.16 to 2.35 cm/s. The results of the measurements are summarized in Fig. 2.

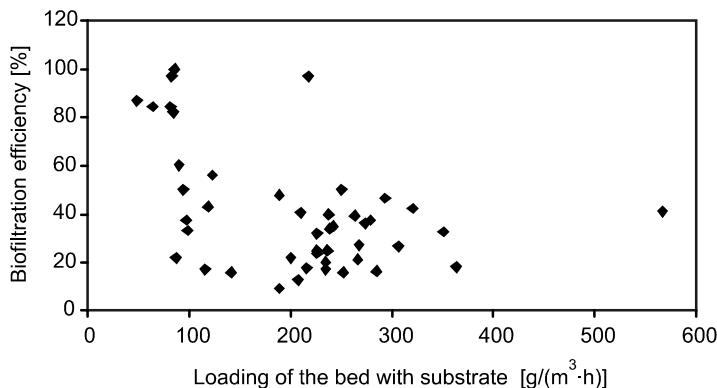


Fig. 2. Dependence of the biofiltration efficiency on the mass loading of the bed

The vertically extended concentration of points at the loading of ca. 100 g/(m³·h) corresponds to the period of the biofilter bed adaptation when the process efficiency increased upon time from ca. 20% to 100%. In the main measurement period, the efficiency of biofiltration was observed at the level of ca. 30%. During measurements, the column weight increased by 9 kg, which must have been mainly related to increase of the biofilter bed moisture from ca. 26% to the final value of 44.25% (Table 1) and partly to biomass gain.

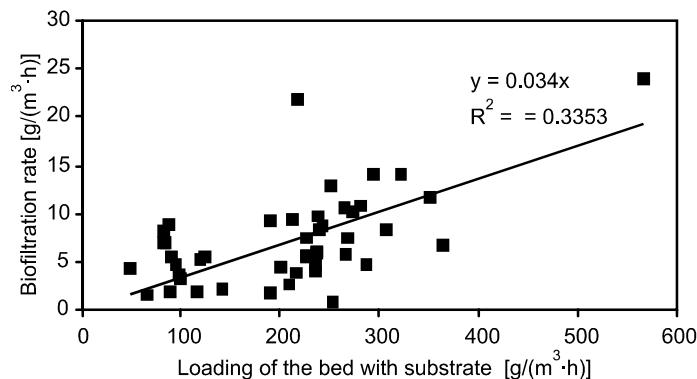


Fig. 3. Dependence of the biodegradation rate on the mass loading of the bed

When averaging the results of many measurements, it is possible to state that the biofiltration efficiency depended linearly on the loading, which is shown in Fig. 3. This is characteristic of the biofiltration proceeding within the area below the critical point [8]. The biofiltration rates being reached and calculated for the whole biofilter bed, and not for its respective layers, were not particularly high. Average values from the whole measurement period amounted to about $7 \text{ g}/(\text{m}^3 \cdot \text{h})$, while the maximum value of $24.04 \text{ g}/(\text{m}^3 \cdot \text{h})$ was attained at the maximum inlet concentration of $770.48 \text{ mg}/\text{m}^3$. The maximum biofiltration rate calculated for one layer (the first one from the gas inlet) amounted to $53.75 \text{ g}/(\text{m}^3 \cdot \text{h})$ at the same concentration and a flow of $2400 \text{ dm}^3/\text{h}$. When compared to literature data, they are similar [4, 5, 9], smaller [10, 11], or definitely smaller [12]. The latter authors obtained MIBK biodegradation rate of the order of $200 \text{ g}/(\text{m}^3 \cdot \text{h})$. However, far reaching conclusions cannot be drawn from such a simple comparison. Most frequently, the maximum experimental biodegradation rate is not the highest possible (theoretical) one due to the method of measurement leading in practice to averaging the results for the whole biofilter bed (its height), i.e. larger rates are being obtained in biofilter beds with a small height. The result similar to the theoretical value may be only obtained when a differential reactor is used or extrapolating the results. For example, the value of $200 \text{ g}/(\text{m}^3 \cdot \text{h})$ obtained from measurements made by Lee et al. [12] is increased to $690 \text{ g}/(\text{m}^3 \cdot \text{h})$ after extrapolation. On the other hand, very high specific biodegradation rates for analysed substances (1400 and $1700 \text{ g}/(\text{m}^3 \cdot \text{h})$) were obtained in measurements made on a thin polyaramide fibre mat [13, 14].

Analysis of the pollutant concentrations along the column's height and the corresponding biofiltration efficiency showed that the order of biofiltration was non-zero for substrate inlet concentrations of about $100 \text{ mg}/\text{m}^3$ and close to zero at higher substrate inlet concentrations. This is visible in Figs. 4 and 5, where the results of exemplary results of measurements are presented (trend lines of the curve or straight type, respectively). Such kinetics is characteristic of the most biofiltration processes [15].

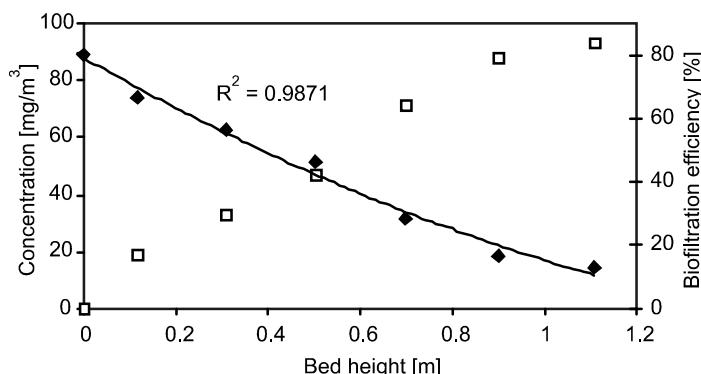


Fig. 4. Biofiltration performance of MIBK on biological bed with pine bark and compost (2:1 v/v ratio) at low concentration of the additive: diamonds – MIBK concentration in the air, squares – biofiltration efficiency; inlet concentration $80.2 \text{ mg}/\text{m}^3$

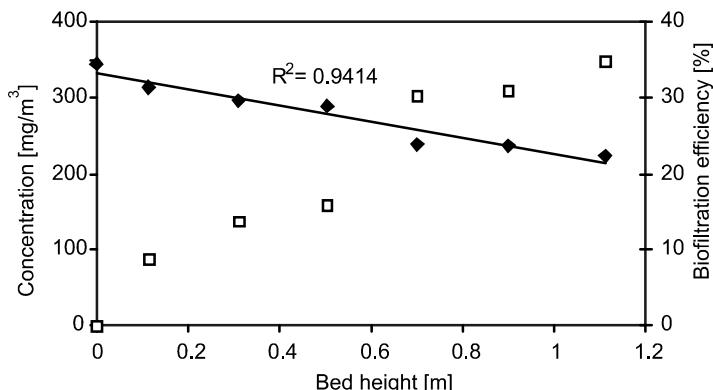


Fig. 5. Biofiltration performance of MIBK on biological bed with pine bark and compost (2:1 v/v ratio) at high concentration of the additive: diamonds – MIBK concentration in the air, squares – biofiltration efficiency; inlet concentration 344.5 mg/m³

Despite small biofiltration rates and efficiencies being obtained for the biofilter bed composed of compost and pine bark mixed at a 1:2 ratio, satisfactory results were attained from another, typically operational point of view. This biofilter bed was mechanically stable and ensured small resistances of the gas flow, maximum of 385 mm H₂O. Average values were definitely more favourable (Table 3).

Table 3
Flow resistance of gases for the whole column and its layers [mm H₂O]

Maximum pressure drop	385
	$\Delta p_{1-7} = 2.5-156.5$
	$\Delta p_{1-2} = 0.5-21.5$
	$\Delta p_{2-3} = 0-31.0$
Mean pressure drops	$\Delta p_{3-4} = 0-64.0$
	$\Delta p_{4-5} = 0-63.0$
	$\Delta p_{5-6} = 0.5-34.5$
	$\Delta p_{6-7} = 0-16.0$

4. CONCLUSIONS

- The stream of air polluted with methyl isobutyl ketone (MIBK) can be relatively efficiently cleaned by using the biofilter bed being a compost and pine bark mixture used in this experiment.
- The MIBK biofiltration proceeded well in the initial stage of biofilter bed operation when almost 100% pollutant loading removal was observed at low inlet concen-

trations. As experiment time went by, after about sevenfold increase of inlet concentration, the efficiency of MIBK removal decreased to about 20%.

- Biodegradation (biofiltration) reaction rates calculated for the whole column and observed during measurements after adaptation period were small and amounted to about $7 \text{ g}/(\text{m}^3 \cdot \text{h})$. Individual biodegradation (biofiltration) reaction rates calculated for separated biofilter bed layers were within a broad range of values. A maximum value, equal to $53.75 \text{ g}/(\text{m}^3 \cdot \text{h})$, was obtained for the MIBK concentration being equal to 770.48 mg/m^3 .

- The biofilter bed made of compost and pine bark mixed at a 1:2 ratio was mechanically stable and ensured favourable conditions for the biofiltration course from the point of view of gas flow resistances.

- The obtained results create a base for research works of the applicable nature.

ACKNOWLEDGEMENTS

This study was supported by financial means of the institution employing the first author as well as a grant from the Ministry of Science and Higher Education No. PBZ-MEiN-5/2/2006

REFERENCES

- [1] Kirk-Othmer Encyclopedia of Chemical Technology, Vol.16, Wiley, 2010.
- [2] STOUT M.D., HERBERT R.A., KISSLING G.E., SUAREZ F., ROYCROFT J.H., CHHABRA R.S., BUCHER J.R., Toxicology, 2008, 244, 209.
- [3] IRANPOUR R., COX H.H.J., DESHUSSES M.A., SCHROEDER E.D., Environ. Prog., 2005, 24 (3), 254.
- [4] PRZYBULEWSKA K., WIECZOREK A., Environ. Prot. Eng., 2008, 34 (4), 61.
- [5] PRZYBULEWSKA K., WIECZOREK A., Arch. Environ. Prot., 2009, 35 (3), 3.
- [6] QI B., MOE W.M., KINNEY K.A., Appl. Microbiol. Biotechnol., 2002, 58, 684.
- [7] SHAREEFDEEN Z., DESHUSSES M.A., Modeling of biofilters and biotrickling filters for odour and VOC control applications [In:] Biotechnology for Odour and Air Pollution Control, Z. Shareefdeen, A. Singh (Eds.), Springer, New York, 2005, 212–231.
- [8] DESHUSSES M., JOHNSON C., Environ. Sci. Technol., 2000, 34, 461.
- [9] DESHUSSES M.A., HAMER G., Bioprocess. Biosyst. Eng., 1993, 9, 141.
- [10] CAI Z., KIM D., SORIAL G.A., Water Air Soil Pollut. Focus, 2006, 6, 57.
- [11] CAI Z., KIM D., SORIAL G.A., Chemosphere, 2007, 68, 1090.
- [12] LEE T.H., KIM J., KIM M.-J., RYU H.W., CHO K.-S., Chemosphere, 2006, 63, 315.
- [13] CURRENT R.W., KOZLIAK E.I., BORGERDING A.J., Environ. Sci. Technol., 2001, 35, 1452.
- [14] KOZLIAK E.I., OSTLIE-DUNN T.L., JACOBSON M.L., MATTSON S.R., DOMACK R.T., Biorem. J., 2000, 4 (1), 81.
- [15] SCHROEDER E.D., Rev. Environ. Sci. Biotechnol., 2002, 1, 65.