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Investigations on the Removal of Hydrophobic Odorous Volatile Organic Compounds by Biotrickling Filtration Monitored With Electronic Nose

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The presented paper presents the results of research on the removal of selected hydrophobic volatile organic compounds (VOCs) from their mixture with air by means of a trickled-bed biofiltration. The efficiency of the removal of toluene and α-pinene, as model VOCs, in a three-section biotrickling filter is evaluated using GC-FID and additionally monitored with an electronic nose. The results show that the removal of the model mixture of VOCs occurs with a satisfactory efficiency i.e. exceeding 80% within 21 days after the system start-up when ceramic Rashig rings inoculated with *Candida* species are packed in a biofilter and the trickling liquid is enriched with a surface active substance.

1. Introduction

1.1 Malodours

The main sources of malodours are various types of industrials plants, as well as municipal services, including wastewater treatment plants and landfills. The problem affects especially the inhabitants of large agglomerations due to e.g. the vicinity of municipal waste treatment plants (Lewkowska et al., 2016).
Malodours are volatile compounds sensed by humans and animals by olfactory receptors at very low concentrations and are identified by brain as unpleasant sensations. The malodours include:

- inorganic compounds (e.g. hydrogen sulphide, ammonia, sulphur dioxide, nitrogen oxide, hydrogen fluoride, hydrogen arsenide),
- organic compounds (e.g. thiols, sulphides, disulphides, amines, carboxylic acids, aldehydes, ketones, aromatic hydrocarbons.

Selected odorous compounds, identified in the nearby of municipal waste and wastewater treatment plants are specified in Table 1 (Lewkowska et al., 2016; Cheng at al., 2016).

Table 1: Selected odorous compounds with their basic characteristics

Chemical compound	Chemical group	Hydrophobicity	Smell type	Odour threshold, ppm
Acetone	Ketones	Low	Sharp	0,4 – 42
Triethylamine	Amines	Low	Fish-like	0,0054 – 0,37
Dimethyl sulhpide	Sulphides	Moderate	Rotten	0,0001 – 0,5
Toluene	Aromatic compounds	Moderate	Intensive, pleasant	0,021 – 2,8
α-pinene	Terpenes	High	Forest smell	0,0029 – 0,9
Cyclohexane	Alkanes	High	Characteristic	0,41 – 2,5

The presence of odorous compounds in air is a current issue in the field of environment protection and both efficient and sustainable methods of air deodorization should be implemented and developed.

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1.2 Methods of malodours abatement

Deodorization of gases polluted with odorous compounds may be realized by means of:

- removal of malodorous compounds usually present at trace levels,
- transformation of malodorous pollutants into odourless chemical compounds or the compounds characterised by high odour threshold,
- introduction of additives (i.e. masking compounds) that change the character of the odour or decrease its intensity in terms of the hedonic quality.

Selection of the most effective method of air deodorization depends upon several factors including the emission intensity, concentration of pollutants or odorous character. Pros and cons of the most popular methods of treatment of odorous gases are given in Table 2 (Schiavon et al., 2016; Nanda et al., 2012).

Table 2: Advantages and disadvantages of the most frequently used methods of gas deodorization

Technology	Advantages	Disadvantages
Absorption	Low operating costs	Need for absorbent regeneration and disposal
Adsorption	Possible recovery of adsorbed compounds	Possible secondary emissions
Thermal	Highly efficient deodorization	High energy consumption
neutralization	Simple design, easiness of operation	Generation of secondary pollution (NO_x, SO_x)
Biological	Low operating costs	Microbial biomass overgrowth
treatment	High effectiveness	Usually large surface area of the installation

1.3 Biofiltration of air containing hydrophobic compounds

Biological methods are promising technologies for the treatment of odorous gases (Lebrero et al., 2012). This group of methods is especially applicable to gases coming from food processing plants, sewage treatment plants and landfills. The process of biofiltration is realised in biofilters of various types (conventional biofilters, bioscrubbers, biotrickling filters). Biofiltration consists in the decomposition of contaminants by microorganisms inhabiting the porous packing bed of the biofilter. The process mechanism involves the diffusion of pollutants from the gas phase to the biofilm, covering the surface of the packing elements. The compounds absorbed in the biofilm are being biodegraded and the cleansed gas leaves the biofilter, as shown schematically in Figure 1.

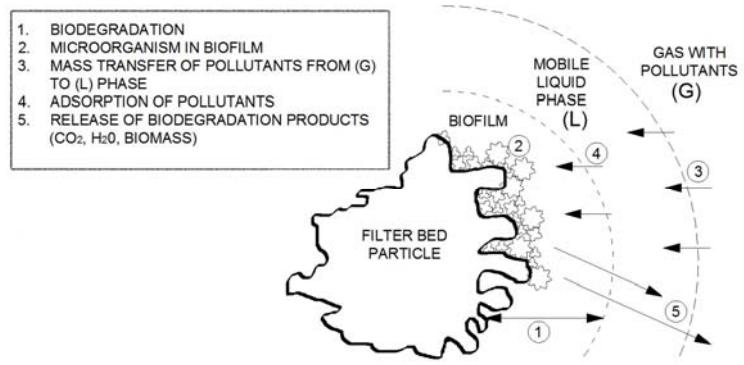

Figure 1: Schematic representation of biofiltration mechanism

Due to e.g. low operational costs and high efficiency of treatment of low-concentrated gas streams and the resulting complete biodegradation of removed pollutants, biofiltration is a superior method for gas deodorization. However, in most of typical cases, elements of biofilters are moisturized with water and thus the resulting biofilm allows for the absorption of hydrophilic compounds. Because of that, the removal of hydrophobic compounds, like toluene, α-pinene or hexane is limited in typical biofilters. It results from the limitation of the process efficiency in terms of low transfer rates of hydrophobic pollutants from the gaseous to the aqueous phase (Lebrero et al., 2012). To increase the efficiency of biofiltration of such compounds, several strategies may be employed, including the addition of surface active substances or other non-aqueous liquid phase (Cheng et al., 2016). The implementation of such approaches is possible in so-called biotrickling filters that are currently regarded as the most efficient bioreactors for the treatment of odorous gas streams (Lebrero et al., 2012).

1.4 Biotrickling filters (BTFs)

In typical biofilter, the contaminated air is humidified in a separate chamber prior to being introduced to the bioreactor. In the case of biotrickling filters, gas stream is introduced to the bioreactor co- or counter-currently with a liquid phase. Therefore, the absorption and decomposition of pollutants take place in one apparatus, the packing of which is trickled with a liquid enriched with nutrients for microorganisms (Schiavon et al., 2016). BTFs are believed to the most promising technology for treatment of odorous gas streams. When compared to other conventional methods of deodorization, BTFs offer lower operating costs, lower environmental impact and high efficiency. Additionally, comparing to traditional biofilters, BTFs are cheaper to operate, offer lower values of required empty bed residence time, lower pressure drop across the packed medium and better control of important process parameters (pH, concentration of nutrients, removal of toxic metabolites) (Lebrero et al., 2012).

1.5 Evaluation of BTF performance

The most often used methods for evaluation of the biofiltration efficiency are the gas chromatographic methods (GC-MS, GC-FID, GC-FPD or GC-NPD). However, due to the high operating costs, they are mainly used in laboratory research. Nowadays, there is a significant increase in the interest in using electronic noses for quantitative and qualitative analysis in environmental monitoring and other applications (Capelli et al., 2014; Gębicki et al., 2014; Gębicki et al., 2016). Due to the low cost and short time of a single analysis, they have become an alternative to gas chromatography. Electronic noses are devices that are supposed to imitate the human sense of smell and are used in many areas of human activity (Wilson, Baietto, 2009). There are four main components of such devices: sampling, detection, data processing and data mining system. The use of electronic noses in quantitative analysis determines the need to use the calibration models. The task of the model is to link the e-nose sensor signals with the concentration of a substance in the analyzed sample. The most commonly used models are: Multiple Linear Regression (MLR), Principal Components Regression (PCR) and Partial Least Squares Regression (PLSR). These methods found successful application for monitoring of changes of odorous compounds concentration in biofiltration process (Szulczyński et al., 2018).

2. Aim of the work

The increase of the efficiency of hydrophobic compounds removal in biotrickling tilters is currently an urgent topic in the field. Therefore, the aim of the presented work was to investigate the efficiency of removal of a mixture of toluene and α-pinene in a three-section BTF packed with ceramic Rashig rings. The selection of above given compounds is justified by their different affinity to aqueous phase i.e. as representatives of moderately and highly hydrophobic odorous compounds, respectively.

3. Materials and methods

3.1 Automatic gas mixture generator

The binary mixture of odorous compounds was mixed with air prior to entering a BTF. The compressed air was passed through a set of filters (molecular sieve 5A, silica gel and activated carbon) and was supplied to an automatic gas mixture generator. This device generates mixtures of a given concentration using the bubbling method and permeation tubes. In presented research, due to the relatively high concentrations of odorants, only the bubbling method was used.

3.2 BTF set-up

Investigations were carried out in a three- section BTF of a total working volume of 4,2 dm^3 (Figure 2). Air mixed with a mixture of model compounds was fed to the bottom of the filter and the trickling liquid was supplied to the biofilter top by means of a peristaltic pump. The volume of the trickling liquid container was 1,5 dm^3. The trickling liquid contained salts and microelements, as listed in p. 3.3 and additionally an anionic surface active substance of concentration C_{SDS} (sodium dodecyl sulphate, SDS). About 20% of the liquid was exchanged for fresh solution every 3 days during the investigated biofiltration process. Basic characteristics of packing elements are listed in Table 3.

Table 3: Basic characteristics of packing material (ceramic Rashig rings)

Section	Dimensions of element, mm	Equivalent diameter, mm	Porosity, -	Specific surface area, m^2/m^3
A	10 x 2,4	10,5	0,56 ± 0,02	1024 ± 46
B and C	6 x 1,5	6,6	0,51 ± 0,02	1456 ± 108

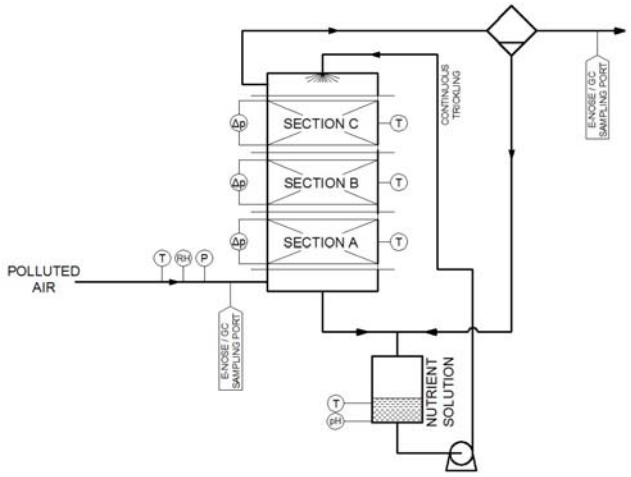

Figure 2: Schematic representation of a BTF set-up

3.3 Inoculation of BTF

A BTF was packed with ceramic Rashig rings inoculated with selected environmental isolates of *Candida* species, taken from the collection of Department of Molecular Biotechnology and Microbiology, Chemical Faculty, Gdańsk University of Technology. The inoculation was realized by immersing the rings in 5 dm^3 of a nutrient solution containing *Candida* species for 4 days. Then, the packing was placed in respective sections of BTF and a nutrient solution (containing K_2HPO_4, $MgSO_4 \cdot 7H_2O$,KH_2PO_4, NH_4Cl and microelements) was subjected to recirculation for additional 7 days prior the start-up of the process.

3.4 Gas analysis

Analysis of gas samples was performed using GC-FID and electronic nose. Parameters of GC method were as follows: HP-1 column (30 m x 0,53 mm ID x 1,5 µm; carrier gas: Nitrogen 0,7 $ml \cdot min^{-1}$; oven program: 50°C (2 min) / 12°C·min^{-1} / 150°C. The external standard method was used as the calibration method. GC analysis were conducted every working day.
For continuous monitoring of the BTF performance, the prototype of an electronic nose was used. The device was equipped with eight sensors (five Metal Oxide Semiconductor sensors, two Electrochemical sensors and one Photoionization sensor). Description of used sensors is presented in Table 4.

Table 4: Models of chemical sensors used to build an electronic nose prototype

No	Manufacturer	Model	Target gases	Sensitivity	Response time, s
S_1	ION Science	MiniPID	VOCs	25 mV/ppm	3
S_2	Figaro	FECS44-100	ammonia	0.1 µA/ppm	60
S_3	Figaro	FECS50-100	hydrogen sulphide	0.7 µA/ppm	< 30
S_4	Figaro	TGS2600	air contaminants	0.3 ~ 0.6[a]	
S_5	Figaro	TGS2602	VOCs and odorous gases	0.15 ~ 0.5[a]	
S_6	Figaro	TGS2603	air contaminants (triethylamine, mercaptanes, etc.)	~ 0.5[a]	~ 30
S_7	Figaro	TGS823	organic solvent vaporous	0.4 ± 0.1[a]	
S_8	Figaro	TGS8100	air contaminants (hydrogen, ethanol, etc.)	~ 0.6[a]	

[a] Sensors resistance in detected gas divided by sensors resistance in the air.

The recorded sensor signals were saved on a computer using the Simex SIAi-8 analog-to-digital converter. Analyzed sample was sucked by the pump and flowed through the e-nose system to the measurement chamber at a constant flow rate of 300 $cm^3 \cdot min^{-1}$. The electronic nose operated in a stop-flow mode: the sample flow time through the chamber was 60 seconds, while the stop time was 30 seconds. Concentrations of the individual components of the mixture were determined using the models based on the Multiple Linear Regression (MLR) models. Development of the MLR models was described by Szulczyński et al. (2018). Developed models together with determination coefficients (R^2) are shown in Table 5.

Table 5: Developed models and their statistical significance

Mixture component	Model	R^2
α-pinene	$\log c = 16.07 + 0.34 \cdot \log S_1 - 1.21 \cdot \log S_2 + 7.83 \cdot \log S_6$	0,87
toluene	$\log c = -13.54 + 9.44 \cdot \log S_1 - 2.25 \cdot \log S_4 + 3.11 \cdot \log S_7$	0,92

3.5 Calculations

The effectiveness of the biofiltration process was assessed based on the values of removal efficiency RE:

$$R_E = 1 - \frac{C_{out}}{C_{in}} \quad (1)$$

where: C_{in}, C_{out} – concentration of toluene or α-pinene at the inlet and outlet of the BTF, respectively.

4. Results and discussion

Basic operational process parameters are listed in Table 6.

Table 6: Basic process parameters of biofiltration

$C_{in(toluene)}$, mg·dm^{-3}	$C_{in(\alpha\text{-pinene})}$, mg·dm^{-3}	Gas flow rate, dm^3·s^{-1}	Empty bed residence time, s	Trickling liquid flow rate, dm^3·s^{-1}	C_{SDS}, mg·dm^{-3}	Trickling frequency
15	15	0,067	62,7	0,001	36	1 min every 12 min

In presented work, on-line monitoring of the process efficiency was applied with the use of an electronic nose. High values of determination coefficient R^2 (Figures 3a and 3b) indicate good correlation of the developed models in comparison to chromatographic results. This confirms the idea that the biofiltration process may be effectively controlled with the use of an electronic nose.

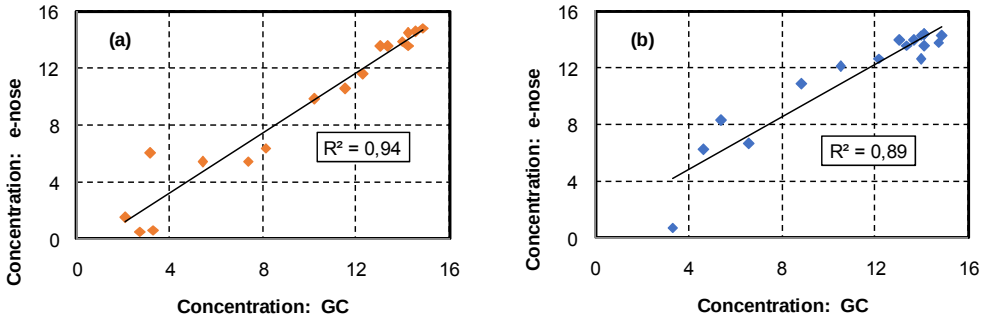

Figure 3: Correlation plots between GC analysis and electronic nose MLR model outputs for toluene (a) and for α-pinene (b)

However, it should be noted that for low values of concentrations of α-pinene, greater estimation error is observed. This may cause errors in determining the effectiveness of biofiltration process in its steady-state conditions. This phenomenon was not observed for toluene due to the use of a PID type sensor, which is intended for the determination of aromatic hydrocarbons.

The results (Figure 4) revealed that toluene and α-pinene may be effectively removed in a BTF with trickling liquid containing an anionic surface active agent (RE above 80% within about 20 days after the process start-up). It was observed that removal of α-pinene is slightly lower than that of toluene. It may be attributed to differences in the hydrophobicity of the compounds. α-pinene is more hydrophobic than toluene (Cheng et al., 2016; Lebrero et al., 2012). Thus, the mass transfer of α-pinene from the gas to the aqueous liquid phase is limited to a greater extent than for toluene. This results in the differences in the removal efficiency of investigated compounds.

Obtained results show that the removal of investigated hydrophobic compounds in the proposed BTF system is more efficient than the results of some literature evidences regarding similar the biotrickling filtration of similar VOCs (Lopez et al., 2013; Salamanca et al., 2017).

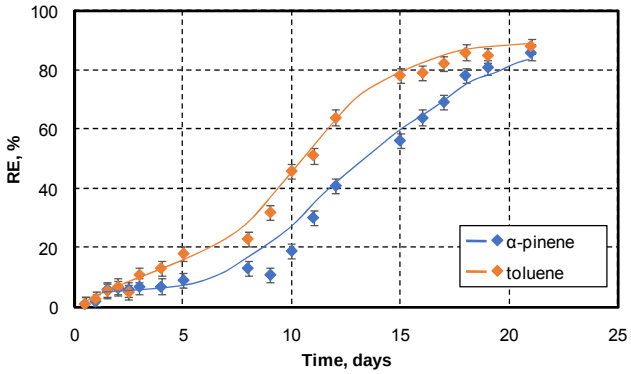

Figure 4: Changes of removal efficiency for investigated compounds as a function of biofiltration time (points – results of GC-FID analysis; lines – results of continuous e-nose monitoring)

5. Conclusions

The research results on the simultaneous removal of toluene and α-pinene in a biotrickling filter are presented. Removal efficiencies exceeding 80% for both compounds were obtained within 3 weeks of a BTF operation. The efficient removal of investigated hydrophobic compounds is attributed to the application of selected species of *Candida* as an inoculum for the BTF packing as well as to the application of a trickling liquid containing a surface active substance that increases the affinity of the aqueous phase towards the removed compounds. The results suggest that an electronic nose may applied for the monitoring and as a possible element of a process control system when considering a future design of a pilot-scale BTF system.

Acknowledgments

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