

Article

# Simultaneous Removal of Hexane and Ethanol from Air in a Biotrickling Filter—Process Performance and Monitoring Using Electronic Nose

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**Abstract:** Biofiltration is a well-accepted method for the removal of malodorous compounds from air streams. Interestingly, the mechanisms underlying this process are not fully understood. The aim of this paper was to investigate the simultaneous removal of hydrophobic hexane with hydrophilic ethanol, resulting in the enhanced removal of hexane in the presence of ethanol. Investigations were performed in a peat-perlite packed biotrickling filter and the process performance was monitored using both gas chromatography and electronic nose techniques. The results indicate that the length as well as the efficiency of biofiltration during the start-up period depend on the feed composition, with higher efficiency obtained when hexane and ethanol were fed together from the process initiation. The experiments in the steady-state period present the biofilter performance when different ratios of hydrophilic to hydrophobic compounds were fed to the biofilter. The obtained results show the synergistic effects of the addition of a hydrophilic compound on the removal efficiency of hydrophobic hexane. The influence of the ratio of hydrophilic to hydrophobic compounds is discussed in terms of enhancing the mass transfer phenomena for hydrophobic volatile organic compounds.

**Keywords:** biotrickling filtration; biofiltration; hexane; ethanol; electronic nose

## 1. Introduction

The problem of malodorous gases polluting the ambient air is a rising problem for developed countries and especially for large urban agglomerations, with the odor sources including municipal waste and waste water treatment plants as well as industrial facilities. The urgent need to reduce emissions of odorous substances necessitates both the use of efficient deodorization methods as well as the introduction of legal regulations on the allowable odorous quality of air. Currently, only eleven countries belonging to the European Union (EU) possess legal regulations counteracting the odor nuisance and determining the odor standards of atmospheric air [1,2]. It is commonly accepted that the assessment of odor emissions is performed according to the EU norm EN 13725:2003 on the determination of odor concentration by dynamic olfactometry. However, when the assessment of odorous quality of air is considered, other analytical methods may be employed including gas chromatography or electronic noses [3–5].

Among the methods intended for the deodorization of air including, in general, adsorption, absorption, incineration, masking or non-thermal plasma [6], biological methods exhibit several distinctive advantages such as low operating costs, the ability to treat large air streams and very low secondary waste generation when compared to physical methods. It is worth noting that the efficiency of biological methods may be increased when they are applied in combination with other

methods (e.g., UV oxidation [7–9] and non-thermal plasma [10,11]). The use of biological methods, especially biofiltration, to treat the air polluted with odorous volatile organic compounds (VOCs) has been practiced for many years. Biofiltration is regarded as a sustainable treatment technology and its application in waste gas treatment is supposed to increase in the near future [12–14]. When the biofiltration process is realized using so called biotrickling filters, a more complete process control can be achieved than in a conventional biofilter. Additionally, these biofilters may operate at very dry or even very wet conditions because they are adapted to a wide range of water management levels. This is why biotrickling filtration can result in higher degree of air deodorization and enables relatively quick adjustment of process parameters (pH, flow, and composition of the liquid phase) in the case of disturbances such as the lack of air flow or an increase in the concentration of odorous compounds in treated air stream in comparison to other biological methods.

During biotrickling filtration (BTF), polluted gas is passed through a packed bed that is continuously or periodically trickled with a liquid. The packed bed is usually initially inoculated with microorganisms, either obtained from activated sludge or intentionally selected for a given system, or may be partially composed of organic media, thus taking advantage of naturally occurring microflora. The growth of microorganisms, enhanced by mineral salts included in the trickling liquid, results in the formation of a biofilm covering the elements of the packing. The general mechanism of BTF consists of two simultaneously occurring processes of the absorption of target compounds in the liquid surrounding the biofilm and their adsorption onto the biofilm-covered particles, followed by the subsequent biodegradation of the compounds in the biofilm [15]. It is worth noting that biotrickling filters, compared to other modes of biological filtration, offer a high specific area for biofilm growth and a high density of biomass, resulting in high gas to liquid and gas to biofilm mass transfer coefficients [16]. These features make biotrickling filters especially suitable for the treatment of air polluted with volatile odorous compounds.

Hexane and ethanol are common air pollutants found, for example, in the post-processing gases coming from solvents production (hexane) or bakeries (ethanol). The selection of the above-mentioned VOCs in this study is attributed to their different solubility in water, thus presenting a binary system of hydrophobic and hydrophilic compounds simultaneously treated in the biofiltration process. While ethanol is easily removed from air via biofiltration, the removal of hydrophobic hexane is rather inefficient. The biotrickling filtration of air polluted with hexane was investigated by Tu et al. [17] and Hassan and Sorial [18]. In the study by Tu et al., a biotrickling filter packed with polyurethane sponges was inoculated with activated sludge from a wastewater treatment plant. Elimination capacity reaching about  $95 \text{ g m}^{-3} \text{ h}^{-1}$  was obtained when saponins were applied to enhance the biofiltration process. Hassan and Sorial reached the elimination capacity of about  $40 \text{ g m}^{-3} \text{ h}^{-1}$  when an acidic (pH = 4) trickling liquid was applied. Removal of ethanol from air in biotrickling filters was studied by Cox et al. [19], who observed an elimination capacity of  $250 \text{ g m}^{-3} \text{ h}^{-1}$  when thermophilic biotrickling filtration was applied. Christen et al. [20] obtained an elimination capacity of about  $107 \text{ g m}^{-3} \text{ h}^{-1}$  when conventional biofiltration using *Candida utilis* growing on sugar cane bagasse was applied. Biotrickling filtration of ethanol in a mixture with other volatile organic compounds has also been investigated [21,22].

The treatment of real-life waste gas streams may almost always be understood as the treatment of gas mixtures, containing either a lower or higher number of components. This situation poses two important challenges regarding the research on biotrickling filtration. First, the process mechanism of the biofiltration of compounds with different hydrophobicity is not fully understood, revealing a considerably lower number of scientific papers discussing the biotrickling filtration of gas mixtures compared to the results of treating air polluted with a single component [23]. Second, real gas mixtures contain components with different chemical properties (affinity to aqueous phase, among others), thus resulting in a varied elimination capacity, depending on the types of compounds present in a gas stream [24–29].

In general, volatile organic compounds treated in biofilters are classified into two groups. The division is based on the availability of the compounds to the microorganisms existing in the biofilm. The classification is thus related to the mass transfer or kinetic limitations and the resulting resistance for the compounds to undergo the biodegradation. According to Ferdowsi et al. [30], mass transfer and kinetic limited air pollutants are defined by the pollutants' bioavailability in the biofilm phase in a pseudo gas–liquid equilibrium in the biofilter. Compounds with a high ability to transfer into the biofilm phase (e.g., alcohols or ketones) are categorized as kinetic-limited pollutants and the efficiency of the biofiltration is mainly governed by their biodegradation rate. On the other hand, mass transfer-limited pollutants are generally hydrophobic compounds with a relatively low tendency to dissolve into the biofilm phase [31]. Thus, even if given, hydrophobic compounds may be easily biodegraded by a specific microorganism, and mass transfer and solubility limitations may negatively affect their biodegradation within the biofilter. Taking into account the limited efficiency of aqueous-based biofiltration systems in the treatment of hydrophobic compounds, several measures have been postulated to improve the process efficiency [24,25] including the addition of surfactants, the application of fungi, pretreatment operations (e.g., UV radiation, application of not-thermal plasma), or the utilization of hydrophilic compounds. However, the positive effect on the biofilter performance is not always observed because an antagonistic effect may also be observed [25]. Additionally, BTF performance is dependent upon both the gas phase composition and the loading pattern. Kim et al. [32] observed that the biofilter response and the reacclimation period were variable when interchanging VOCs were fed to a biotrickling filter, while Mohammad et al. [33] observed higher removal efficiencies for benzene in comparison to the alkylbenzene compounds at the same initial load. The effect of the preferred degradation of the oxygenated rather than the aromatic compounds was also observed [34,35]. The enhanced removal of hydrophobic compounds by the addition of hydrophilic ones is poorly evaluated in the literature, however, it may have a great practical potential when exhaust gasses of different origins can be mixed together and treated simultaneously. Such an operation may result in a better process performance than the separate treatment of different gas emissions that are highly enriched in one or few compounds because the interactions among pollutants with different properties may synergistically alter the biodegradation rate, resulting in an enhanced biofiltration performance [25].

When mixtures of volatile organic compounds are considered, an important aspect of the process realization and efficiency assessment is analysis and monitoring. It is crucial to continuously monitor process efficiency to obtain precise information on the system performance and its response to variable conditions. The most frequently used analytical techniques to evaluate the performance of biofiltration process are gas chromatography techniques. These methods enable the separation and determination of concentrations of individual components of the mixture. However, the cost of using gas chromatography to monitor the process online is relatively high. For this reason, it seems reasonable to use electronic noses, which, thanks to the short analysis time and low cost, are able to monitor the deodorization process on a continuous basis, which is of great value when mechanisms of simultaneous removal of multiple air components are studied.

To the best knowledge of the authors, simultaneous biotrickling filtration of hexane and ethanol has not yet been studied from the perspective of mutual interactions and improved removal of hexane in such conditions. Additionally, the literature does not respond to the question about what the optimal ratio of hydrophilic to hydrophobic compounds resulting in the increased removal of the hydrophobic one. This work is an attempt to at least partially answer the stated question. The aim of this study was to evaluate the performance of a biotrickling filter treating a mixture of hexane and ethanol for varied composition ratios including a focus of the biofilter start-up period and its dependence upon the feed composition, resulting in enhanced removal of hydrophobic hexane as a result of co-treatment with hydrophilic ethanol. In this paper, two methods were applied for the process performance monitoring (i.e., gas chromatography and electronic nose). The selection of an electronic nose is based on its

ability for continuous process monitoring as well as its proven application in the assessment of the biofiltration efficiency of air deodorization [23,26,36,37].

## 2. Materials and Methods

Experiments were performed in a counter-current Plexiglass biotrickling filter with an internal diameter of 0.08 m and a height of 0.68 m. The mixture of air and odorous volatile organic compounds was supplied from the bottom while the trickling liquid was sprayed over the packing from the biofilter top. The biofilter was packed with a peat and perlite mixture (Compo Sana, Compo GmbH, Münster, Germany). The peat and perlite mixture was sandwiched between a bottom and top layers of ceramic Raschig rings to prevent the bed clogging and ensure the uniform down flow of trickling liquid. The peat and perlite packing was used without special inoculation, taking advantage of the naturally present diversified microflora. A more detailed description of the experimental set-up is provided in [26].

The mixture of air with hexane (Merck, Darmstadt, Germany) and ethanol (POCH, Gliwice, Poland) was obtained using an automatic gas mixture generator as described previously [26]. The gas flow rate was controlled using a precise mass flow controller (Vögtlin, Aesch, Switzerland). The biotrickling filter worked with the gas flow rate of  $2.5 \text{ L min}^{-1}$ , corresponding to the empty bed residence time (EBRT) equal to 1 min.

A BTF packing was conditioned for a period of one week prior to the introduction of a treated gas mixture. During the conditioning, the biofilter was fed with air and trickled with a buffered peptone water medium (Merck, Darmstadt, Germany). During the regular investigations, the biofilter packing was trickled with a mineral salt medium (MSM) containing  $\text{Na}_2\text{HPO}_4 \times 2\text{H}_2\text{O}$ ,  $\text{KH}_2\text{PO}_4$ ,  $\text{NaCl}$ , and  $\text{NH}_4\text{Cl}$  (POCH, Gliwice, Poland) dissolved in distilled water and kept at  $\text{pH} = 7.0$ . Total volume of the trickling liquid was replaced each seven days and autoclaved (Prestige Medical, Blackburn, England) prior to the introduction to the BTF. The trickling liquid was sprayed over the biofilter packing using a peristaltic pump with a trickling flow rate of  $0.2 \text{ L min}^{-1}$  and a trickling frequency of 15 s per each 90 min during the process duration.

In this paper, the process performance and efficiency was monitored using both gas chromatography and electronic nose simultaneously. Inlet and outlet gas lines were equipped with sampling ports and connected to the electronic nose. At prescribed time intervals, inlet and outlet gas samples were taken to Tedlar bags and the concentrations of hexane and ethanol were determined using a gas chromatograph equipped with a flame ionization detector, FID (Varian CP-3800, Varian Analytical Instruments, Walnut Creek, CA, USA). A capillary column DB-WAX  $30 \text{ m} \times 0.53 \text{ mm} \times 1 \mu\text{m}$  (Agilent Technologies, Santa Clara, CA, USA) was applied using nitrogen as a carrier gas. The parameters of the analytical program were as follows: oven temperature:  $100 \text{ }^\circ\text{C}$ ; FID detector temperature:  $200 \text{ }^\circ\text{C}$ , carrier gas flow rate:  $3 \text{ mL min}^{-1}$ ; split ratio: 10.

The prototype of an electronic nose (Gdańsk University of Technology, Poland) was used for the online monitoring of the biofiltration process. Every minute, samples from the biofilter inlet and outlet streams were sucked using a membrane pump to a PTFE chamber where the sensor matrix was placed. In this prototype, the sensor matrix consisted of eight chemical gas sensors: one photoionization sensor (MiniPID, Ion Science, Royston, UK), two electrochemical sensors (FEC44-100 and FECS50-100, Figaro USA, Inc., Arlington Heights, IL, USA), and five metal-oxide semiconductor sensors (TGS2600, TGS2602, TGS2603, TGS823 and TGS8100, Figaro USA, Inc., Arlington Heights, IL, USA). The characteristics of the applied sensors are provided in Table 1, according to the declarations of the manufacturers. For standard gas mixtures (similar in composition to the tested mixtures), a series of measurements was made with a matrix of about 20 different types of sensors. Then, for all signals, a regression model was developed that resulted in the best fit of sensor signals to the concentrations of individual substances in the mixture. The variance introduced into the model by each sensor was determined, and finally those sensors that collectively contributed to about 95% of the total variance were selected.

**Table 1.** Characteristics of the sensors applied in the electronic nose.

Sensor Type	Sensor Model	Detected Compounds	Detection Range, ppm	Sensitivity	Response Time, s
photoionization	MiniPID	VOCs with ionization potential <10.0 eV	ppm range	>15 mV/ppm	<8
electrochemical	FECS44-100	ammonia	0–100	0.1 $\mu$ A/ppm	60
electrochemical	FECS50-100	hydrogen sulfide	0–100	0.7 $\mu$ A/ppm	30
metal oxide semiconductor	TGS2600	methane, carbon oxide, ethanol, hydrogen	1–100	0.3 ~ 0.6 <sup>1</sup>	30
metal oxide semiconductor	TGS2602	toluene, ethanol, ammonia, hydrogen, hydrogen sulfide	1–50	0.15 ~ 0.5 <sup>1</sup>	30
metal oxide semiconductor	TGS2603	ethanol, methyl mercaptane, trimethyl amine, hydrogen	1–50	<0.5 <sup>1</sup>	30
metal oxide semiconductor	TGS823	methane, n-hexane, benzene, ethanol	50–5000	0.1 ~ 0.4 <sup>1</sup>	30
metal oxide semiconductor	TGS8100	methane, carbon oxide, hydrogen, ethanol	1–100	0.6 <sup>1</sup>	30

<sup>1</sup> Change ratio of sensor resistance in 10 ppm of hydrogen/ethanol to resistance of the sensor in air.

The electronic nose worked in the stop-flow mode. The sample flow time was 40 s and the stop time of the mixture in the sensors chamber was 20 s. After this time, purified air was directed to the measurement chamber for the regeneration of the sensors. The data analysis and other calculations were performed in RStudio Desktop (v. 1.1.463) software [38] using R [39].

Concentrations of the individual components of the mixture (ethanol and hexane) were determined based on the multiple linear regression (MLR) models. Development of the MLR models was as described in our previous works [26,40].

Concentrations of hexane and ethanol in the inlet gas stream were expressed as inlet loading (IL):

$$IL = \frac{Q \times C_{Gin}}{V}, \quad (1)$$

where  $Q$  is the volumetric gas flow rate;  $C_{Gin}$  is the concentration of hexane or ethanol in the inlet gas stream; and  $V$  is the volume of the biotrickling filter packed bed.

Process performance and efficiency were characterized using the values of removal efficiency (RE) as well as elimination capacity (EC), according to Equations (2) and (3):

$$RE = \frac{C_{Gin} - C_{Gout}}{C_{Gin}}, \quad (2)$$

$$EC = \frac{Q(C_{Gin} - C_{Gout})}{V}, \quad (3)$$

where  $C_{Gout}$  is the concentration of hexane or ethanol in the outlet gas stream.

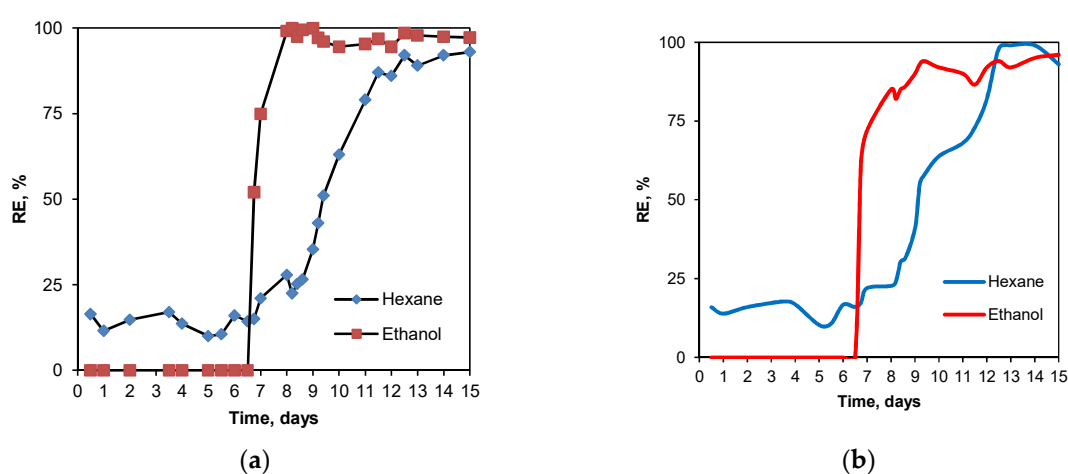
In this paper, a parameter denoted by the Greek letter theta ( $\theta$ ) is introduced to represent the ratio between the concentration of a hydrophilic to hydrophobic compound in the gas phase. For a binary system composed of a single hydrophilic (1) and single hydrophobic (2) compound, a factor ( $\theta$ ) is calculated as follows:

$$\theta = \frac{C_{G1}}{C_{G2}} \quad (4)$$

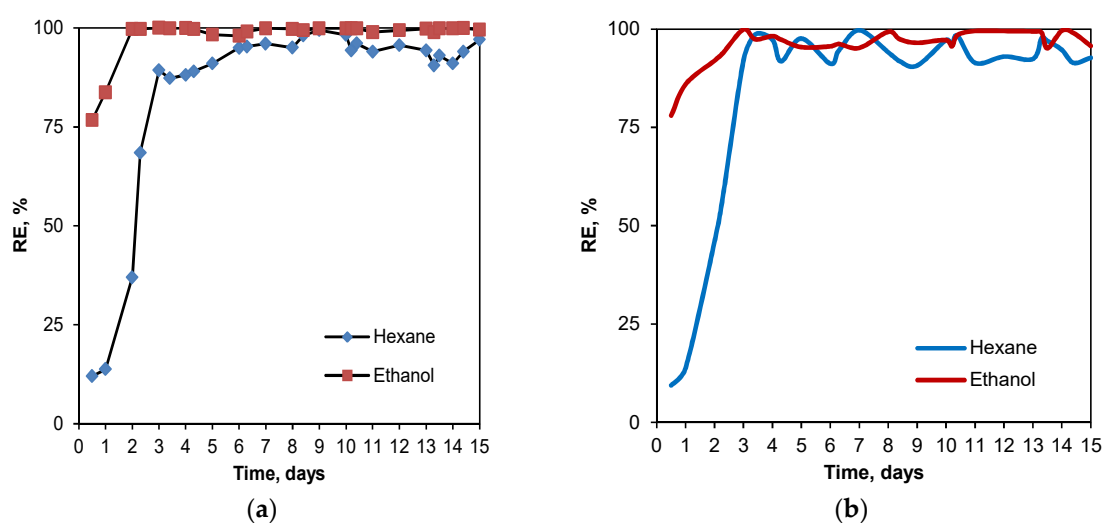
### 3. Results

#### 3.1. Start-Up of a Biofilter

The biofilter performances during the start-up periods are presented in Figures 1 and 2 in order to examine the effect of inlet gas composition on the BTF start-up periods. The removal efficiency of hexane attained values of about 15% from the beginning of the process when no ethanol is fed to the system (Figure 1). The values of RE for hexane were rather stable, unless hydrophilic ethanol was introduced to the gas stream on the sixth day after process initiation. Following the ethanol introduction, values of RE for hexane increased and stabilized, reaching the removal efficiency of about 90% at day 15 of the biofiltration process, which corresponded to the elimination capacity of about  $30 \text{ g m}^{-3} \text{ h}^{-1}$ . At the same time, the values of RE for ethanol attained a level exceeding 90% within the first two days of its biofiltration. The removal of ethanol slightly fluctuated, maintaining RE values between 95 and 99% during the investigated start-up period.



**Figure 1.** Biotrickling filter performance during the start-up period: introduction of hydrophilic ethanol on the sixth day of the process. Inlet loadings:  $34.5 \text{ g m}^{-3} \text{ h}^{-1}$  (hexane) and  $18.45 \text{ g m}^{-3} \text{ h}^{-1}$  (ethanol): (a) process control realized by gas chromatography; (b) process control by electronic nose.



**Figure 2.** Biotrickling filter performance during the start-up period. Inlet loadings:  $34.5 \text{ g m}^{-3} \text{ h}^{-1}$  (hexane) and  $18.45 \text{ g m}^{-3} \text{ h}^{-1}$  (ethanol): (a) process control by gas chromatography; (b) process control by electronic nose.

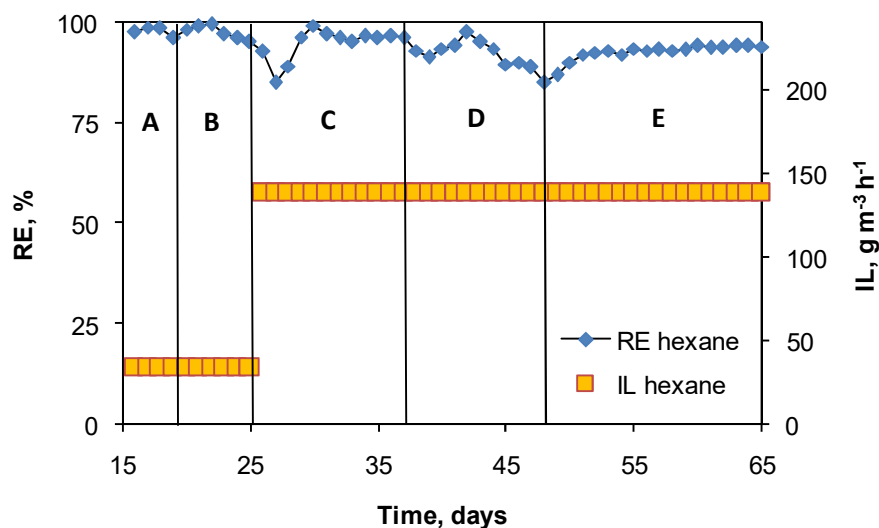


The start-up performance of a biotrickling filter fed with a mixture of hexane and ethanol is shown in Figure 2. The removal efficiency of hexane increased steadily for the first three days from the process initiation and then the values of removal efficiency stabilized (RE about 85%), slightly increased and fluctuated, then reached the value of about 95% on day 15 (EC about  $33 \text{ g m}^{-3} \text{ h}^{-1}$ ). Simultaneously, the removal efficiency of ethanol rapidly increased from about 76 to above 99% in the first two days of biofiltration. Then, the removal efficiency of ethanol stabilized (RE about 99%, EC about  $18.2 \text{ g m}^{-3} \text{ h}^{-1}$ ).

Monitoring and control of the biotrickling filter performance during the start-up period when the biofiltration process follows an unsteady-state pattern is extremely important, mainly because of the biomass growth, biofilm formation, and adaptation of microorganisms. This is why the biofilter performances during the start-up periods were monitored using an electronic nose prototype combined with the MLR calibration model (Figures 1b and 2b) aside from gas chromatography, in order to examine continuously the effect of the inlet gas composition on the BTF performance.

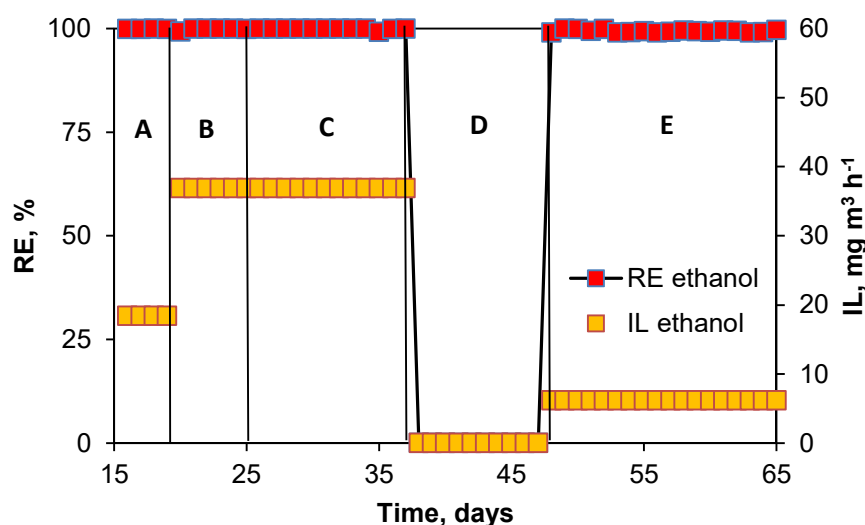
### 3.2. Biofilter Performance in the Steady-State Condition

Figures 3 and 4 present the performance of a steady-state peat-perlite packed biotrickling filter treating a mixture of hexane and ethanol. During the investigated biofiltration duration, inlet loadings of both gas components were varied including the ethanol starvation between the 38th and 47th days of the process, thus affecting the ratio of ethanol to hexane ( $\theta$ ) in the inlet gas stream. The results indicate that the introduced changes affected the biofiltration of hexane, while the performance of a biotrickling filter with respect to ethanol seemed to be stable, resulting in unchanged values of RE. Figure 5 presents the simultaneous removal of hexane and ethanol when the electronic nose was applied as an analytical tool.

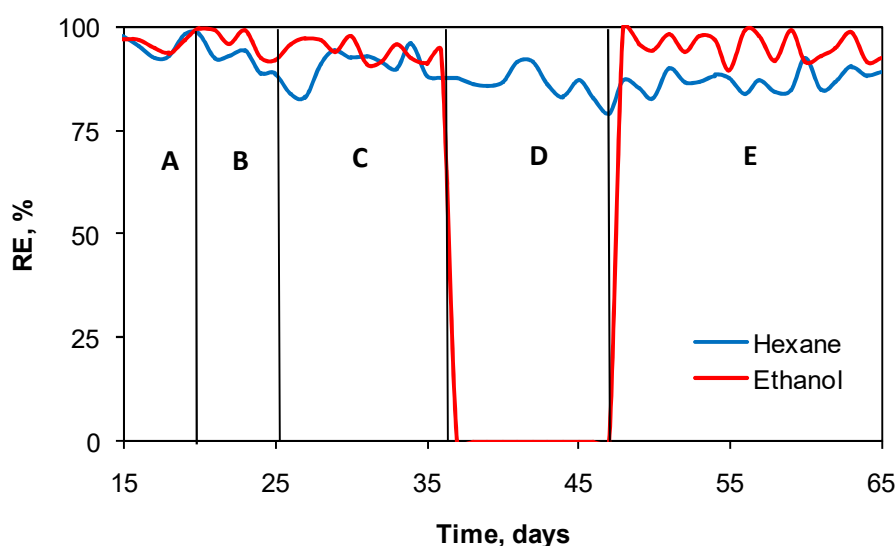


**Figure 3.** The course of the biotrickling filtration of hexane treated simultaneously with ethanol. (A)  $\theta = 1$ ; (B)  $\theta = 2$ ; (C)  $\theta = 0.5$ ; (D) ethanol starvation; (E)  $\theta = 0.25$ .





**Figure 4.** The course of biotrickling filtration of ethanol treated simultaneously with hexane. (A)  $\theta = 1$ ; (B)  $\theta = 2$ ; (C)  $\theta = 0.5$ ; (D) ethanol starvation; (E)  $\theta = 0.25$ .



**Figure 5.** The course of biotrickling filtration of ethanol treated simultaneously with hexane. (A)  $\theta = 1$ ; (B)  $\theta = 2$ ; (C)  $\theta = 0.5$ ; (D) ethanol starvation; (E)  $\theta = 0.25$ . Process performance control using electronic nose.

Since the 15th day from the process initiation, the removal efficiency of hexane exceeded 95% (Figure 3, biofiltration stages A and B). In stages A and B, the values of the ( $\theta$ ) parameter were 1 and 2, respectively, indicating an equivalent or double volumetric concentration of ethanol to hexane, respectively. In stage C, a drop in RE values for hexane was observed, which may be partially attributed to a decrease in ethanol concentration, thus resulting in a worsened mass transfer of the treated gas (more details in the discussion). However, this drop was mainly due a strong increase in hexane loading from about  $25 \text{ g m}^{-3} \text{ h}^{-1}$  to  $140 \text{ g m}^{-3} \text{ h}^{-1}$ . A further increase in biofilter performance around day 28 may have resulted from biomass acclimation to the treated gas mixture. Interestingly, during stage D, the biofilter performance with respect to hexane decreased. It is a reflection of the composition of a treated gas: only hydrophobic hexane is treated where the mass transfer is lower than in the case when the hexane and ethanol mixture is treated. When ethanol was again fed to the system at day 48, the biofilter performance was recovered, however, the RE values of hexane were about 90%



(corresponding to the elimination capacity of about  $125 \text{ g m}^{-3} \text{ h}^{-1}$ ), most likely mainly due to the low value of ethanol to hexane ratio (biofiltration stage E).

During the investigated period of biotrickling filtration (Figure 4), the values of RE for ethanol were about 99%. These are typical values for hydrophilic compounds, indicating the high potential of biofiltration systems in the treatment of air polluted with such compounds. No inhibition of ethanol removal was observed regardless of the corresponding concentrations of hexane in the inlet gas. Moreover, ethanol starvation at stage D did not affect the further removal of ethanol in stage E.

The performance of the simultaneous biotrickling filtration of hexane and ethanol evaluated by an electronic nose (Figure 5) showed similar patterns and observations as described previously with respect to Figures 3 and 4. In general, a lower biofiltration efficiency of hexane than ethanol was observed. The results indicate a higher process performance with respect to hexane for higher values of the ( $\theta$ ) parameter. More exact values presenting the dependence of the process efficiency on the investigated range of ethanol to hexane concentration ratios ( $\theta$ ) are given in Table 2. The results (Table 2) show that the removal of hexane increased when the ethanol concentration in the inlet gas increased. However, it is worth noting that even when  $\theta$  was as low as 0.25, the removal of hexane reached almost 90% and a further increase in the ethanol concentration up to the value of  $\theta = 2$  resulted in only about a 7–9% increase in RE for hexane. It must be stressed, however, that the presented results are based on relatively medium duration experiments (65 days in total) and should be further investigated in long-term experiments as well as for a broader range of the ( $\theta$ ) parameter.

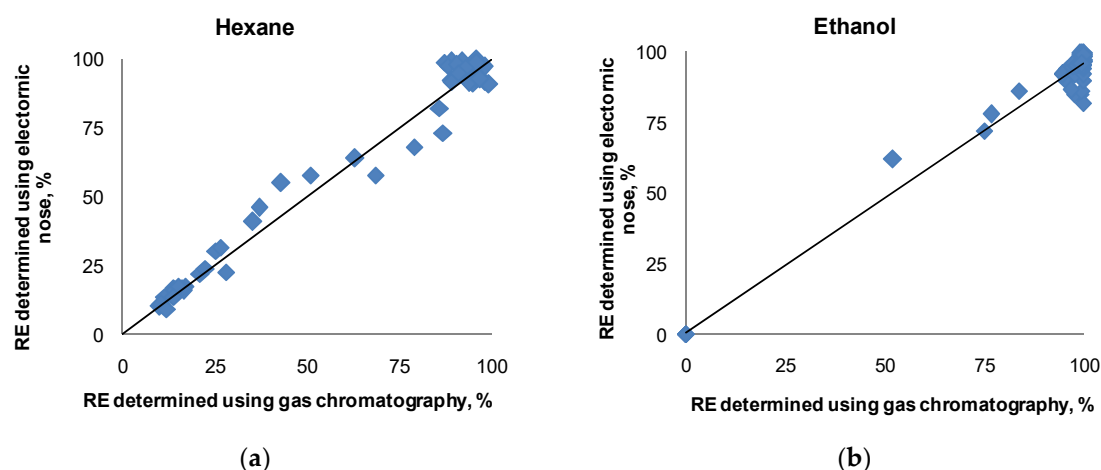
**Table 2.** Influence of ethanol to hexane ratio ( $\theta$ ) on the values of removal efficiency for ethanol and hexane.

$\theta$ , –	RE <sub>hexane</sub> , %	RE <sub>ethanol</sub> , %
0.25	88 ± 4	99 ± 0.5
0.5	93 ± 3.5	99 ± 0.5
1	97 ± 2	99 ± 0.5
2	97.5 ± 1.5	99 ± 0.5

### 3.3. Evaluation of Air Deodorization Efficiency Using Electronic Nose

One of the novelties of this paper is related to the application of an electronic nose for continuous process monitoring. To validate the use of an electronic nose in the proposed application, it is necessary to relate the obtained results with the results obtained from the gas chromatography method accepted as the reference method. The correlation plots for the removal efficiency (RE) determination using an electronic nose and gas chromatography for hexane and ethanol are presented in Figure 6a,b, respectively.

The obtained results show satisfactory correlation between the removal efficiency values determined using the electronic nose and gas chromatography techniques. The greatest dispersion of results was obtained for the highest RE values (>90%). This is especially evident in Figure 6b (ethanol), where the electronic nose underestimated the results. This is due to the inaccuracy in determining very low ethanol concentrations in the outlet gas, which occur at high values of removal efficiency.



**Figure 6.** The correlation plots for removal efficiency (RE) determination using an electronic nose and gas chromatography for (a) hexane and (b) ethanol.

#### 4. Discussion

Biotrickling filtration is an exceptionally efficient technique for the removal of hydrophilic volatile organic compounds from air. However, the process efficiency is lower when hydrophobic VOCs are treated. One interesting approach toward the enhancement of the biofiltration efficiency of hydrophobic compounds is the utilization of hydrophilic compounds. In our previous work [26], we proved that the addition of hydrophilic methanol enhanced the biotrickling filtration of hydrophobic cyclohexane, thus revealing a synergistic effect on the removal of hydrophobic VOC. In this paper, the simultaneous biotrickling filtration of hexane and ethanol was investigated, revealing considerable differences in the course of the process, especially when the start-up period is concerned.

The improvement of the biofiltration of hydrophobic compounds with hydrophilic ones has been proven by the results of several investigations [25], however, the mechanisms of the process are not fully understood and explained. The reason for the process enhancement is usually attributed to the increased biomass growth resulting from the enhanced bioavailability of the hydrophobic compounds in the presence of hydrophilic ones [24,25].

The results presented in Figures 1 and 2 indicate that the start-up period is highly affected by the composition of the feed gas. Presented results indicate the positive effect of ethanol on the biotrickling filtration of hexane. Interestingly, when hexane and ethanol were simultaneously fed to the biofilter from the starting moment of the process, the start-up period was shorter when compared to the case when ethanol was added to the gas stream containing hexane. These results suggest the synergetic effects of hydrophilic compounds on the biofiltration of hydrophobic ones, as proposed by Yang et al. [25]. This may be attributed to the increased biomass growth when hydrophilic compounds are treated. Due to a low barrier for mass transfer from the gas to liquid phase, hydrophilic VOCs are easily transported to the biofilm, thus serving as a carbon source for the microorganisms. As a result, biomass growth proceeds, allowing for the biodegradation of treated VOCs. On the other hand, hydrophobic VOCs account as a barrier for the mass transfer from the gas to liquid phase. Hence, their concentration within the biofilm is low and the biomass growth is much less stimulated than in the case of hydrophilic VOCs. Therefore, the resulting biodegradation is low, and the process efficiency is low.

Sun et al. [41] investigated the biotrickling filtration of styrene with toluene-styrene secondary acclimation. The results of the study show the introduction of toluene as a more accessible compound for the biofilm and enhances the process performance with respect to styrene. When the biofilter reached steady-state conditions for the removal of both toluene and styrene, the flow of toluene was stopped, leaving the biofilter ready for the treatment of styrene solely. This observation is somehow similar to the behavior of the system in stage D of biofiltration when ethanol is removed from the inlet

gas stream. A slight decrease in hexane removal (RE dropped from about 95% to about 85% between the 42nd and 48th days of the process) that was observed during ethanol starvation (Figure 4) must therefore be attributed to some other feature of the system, besides enhanced mass transfer in the presence of gaseous ethanol such as the stability of interactions among the hydrophilic VOCs and the matrix or its effect on microbial metabolism. This relatively small reported decrease in the RE values for hexane during the ethanol starvation may partially result from a too short equilibration time after the process disturbance, which must be considered in future research in this field.

A fluctuating or even slightly increased removal of hexane between days 38 and 42 of biofiltration may also be partially attributed to the carry-over effect, even when ethanol is removed from the inlet gas. Ethanol still present within the trickling liquid, thus acting in similar way as before the ethanol starvation period, may be responsible for this effect. Interestingly, the RE for hexane did not drop drastically to the level of about 15%, as may be expected when comparing it to the beginning of the process. Elucidation of the reason for such system behavior requires further investigations including a longer period of starvation as well as deeper process analytics including the GC-MS analysis of a gas phase (for possible intermediates formation), evaluation of composition and changes of microbial community within the biofilm as well as at least head space analysis of the trickling liquid composition. However, taking into account our previous research [26] as well as unpublished results, even longer starvation periods of hydrophilic compounds than reported in this paper do not result in a considerable drop in process performance with respect to the hydrophobic component of the gas mixture. Thus, further investigations regarding the enhanced biofiltration of hydrophobic compounds resulting from the addition of hydrophilic ones are postulated.

The results presented in Table 2 consider various ratios of concentration of hydrophilic to hydrophobic VOCs. The results indicate that the higher the ratio  $\theta$ , the higher the resulting biofilter performance. A ratio of 1 was proposed as an optimal value in this study. It is interesting when the results are compared with other studies. Zehraoui et al. [42] investigated the simultaneous removal of methanol and hexane for their relative ratios equal to 3:1 and 5:1, respectively. Zehraoui and Sorial [43] studied the removal of hexane, benzene, and ethanol and used the following gas composition of 1:3:6.6, respectively, for the previously mentioned VOCs. Large discrepancies between the above-mentioned results require further investigations on the determination and optimization of the required concentration of hydrophilic compound resulting in the increased performance of biotrickling filters treating hydrophobic VOCs. These investigations should include well-planned studies of the biofilm formation as well as biomass growth and composition, which helps to identify the process mechanisms of the simultaneous biofiltration of VOCs with different degrees of hydrophobicity.

It is known that a bioreactor for gas treatment may be operating under mass transfer or kinetically limited conditions. In fact, in many cases a reactor works under a complex combination of above listed limitations. Mass transfer phenomena are crucial for the bioreactor performance since when the mass transfer is limited, the metabolic rate of microorganisms decreases and the microorganisms may respond adversely to the resulting stress [14].

Mass transfer phenomena govern the bioreactor performance and may be described by the overall mass transfer coefficient  $k_{overall}$  ( $\text{m s}^{-1}$ ):

$$\frac{1}{k_{overall}} = \frac{1}{k_G} + \frac{1}{k_L} + \frac{1}{k_B} \quad (5)$$

where  $k_G$ ,  $k_L$ , and  $k_B$  represent the mass transfer coefficients for the gas, liquid, and biofilm phases, respectively (unit for each coefficient is as given above i.e., ( $\text{m s}^{-1}$ )).

The mass transfer coefficients are dependent upon several factors including the physicochemical properties of pollutants, medium properties, reactor design, or process conditions. When resistance to



the mass transfer is mainly located in the liquid phase and the concentration of the target compound is low [14], then the overall volumetric mass transfer rate  $R(\text{g m}^{-3} \text{s}^{-1})$  may be represented by Equation (6):

$$R = k_L a (C_G - C_L) = \frac{D_{AL}}{\delta_{film}} a (C_G - C_L) \quad (6)$$

where  $k_L a$  is the volumetric mass transfer coefficient ( $\text{s}^{-1}$ );  $a$  is a specific gas–liquid interfacial area ( $\text{m}^2 \text{m}^{-3}$ );  $D_{AL}$  is the gaseous pollutant diffusivity in the liquid ( $\text{m}^2 \text{s}^{-1}$ );  $H$  is Henry's constant (dimensionless);  $\delta_{film}$  is the liquid film thickness (m); and  $C_G$  and  $C_L$  are the concentrations of a target compound in the gas or liquid phase, respectively ( $\text{g m}^{-3}$ ).

Henry's constant ( $H$ ) is a well-accepted factor indicating the hydrophobic or hydrophilic character of a compound, thus determining its bioavailability in the biofiltration processes [44]. The relation between the concentration of a compound in a liquid phase to its concentration in the gas phase may be expressed by Equation (7):

$$C_L = H \cdot C_G \quad (7)$$

Thus, it may be written:

$$C_{G1} = \frac{C_{L1}}{H_1} \quad (8)$$

$$C_{G2} = \frac{C_{L2}}{H_2} \quad (9)$$

where subscripts (1) and (2) depict the hydrophilic and hydrophobic components, respectively.

The concentration ratio factor ( $\theta$ ) defined by Equation (4) may be represented as:

$$\theta = \frac{C_{L1}}{H_1} \cdot \frac{H_2}{C_{L2}} \quad (10)$$

When a hydrophobic component is considered due to its lower mass transfer ability than for the hydrophilic one, Equation (11) may be valid, which is obtained by rearranging Equation (10) and introducing it to Equation (6):

$$R = k_{L2} a (C_{G2} - C_{L2}) = k_{L2} a \left( C_{G2} - \frac{C_{L1} H_2}{H_1 \theta} \right) \quad (11)$$

It is obvious that Equation (11) may be valid only when condition (12) is fulfilled:

$$\theta \leq \frac{C_{L1} H_2}{H_1 C_{G2}} \quad (12)$$

Relation (11) indicates that  $\theta$  affects the mass transfer properties of the hydrophobic compound in the presence of a hydrophilic one. Therefore, an increase in the biofiltration process performance of the hydrophobic component in the presence of a hydrophilic one does not only result from an increased biomass growth in such conditions, but may also be attributed to variations in the solubility of a mass transfer limited component in the liquid phase, and thus its availability for microorganisms occupying the biofilm. The results presented in this paper as well as in other available literature data [43,45,46] suggest that the optimal value of  $\theta$  is system-specific. However, it is highly probable that a general value of  $\theta$  may be proposed for a given group of compounds that have similar  $H$  values as well as similar physicochemical properties (e.g., water solubility, partial pressure, chemical composition). Such a statement is in accordance with the proposal by Zhu et al. [44] regarding the optimal range of Henry's constant values, indicating compounds suitable for efficient biofiltration processes. Thus, deeper investigations are suggested in this field with the aim of modeling  $\theta$  for a more in-depth description of the mechanism of the synergistic biofiltration of binary systems of hydrophobic and hydrophilic compounds.

## 5. Conclusions

Results of investigations presented in this work indicate that the biotrickling filter start-up period is shorter when a mixture of hexane and ethanol is fed to the biofilter, resulting in higher values of hexane removal efficiency obtained in a shorter time when compared to the process when ethanol is supplied to the bioreactor already treating hexane. Such results confirm the synergistic effects of the addition of a hydrophilic compound on the removal efficiency of a hydrophobic volatile organic compound. An increase in the inlet loading of hexane does not affect the process efficiency when ethanol is present in a feed stream, resulting in a rapid biofilter recovery. Ethanol starvation during the steady-state conditions result in a slight decrease of hexane removal, however, the removal efficiency is regained following the ethanol re-supply. Interestingly, the removal of hexane is lower than prior to the system interruption. The results indicate that even for a ratio of ethanol to hexane close to 1, the system performance is satisfactory. Thus, the proposed ratio of the concentration of ethanol to hexane is 1 (on the mass to volume basis). The probable mechanism of an enhanced removal of hexane in the presence of ethanol includes the facilitation of hexane mass transfer to both the liquid and biofilm phases, thus resulting in a greater availability for microbial metabolism and degradation.

The approach proposed in the work may be of industrial use and an approach of “treating waste with waste” is possible with a higher expected efficiency for streams where hydrophobic components predominate. This process enhancement may be achieved upon its mixing with a stream containing mainly hydrophilic components, as compared to the separate biofiltration of gas with dominating hydrophobic components.

The use of an electronic nose to monitor the biotrickling filtration process, thanks to the possibility of online measurements, is especially convenient in terms of monitoring the start-up period or biofiltration system responses to process fluctuations. Satisfactory correlation of the results obtained with the values determined using gas chromatography allows us to state that electronic noses can be an element of a process control system when considering the future design of a pilot-scale BTF system.

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