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Enhancing the Removal Efficiency of Cyclohexane in Biotrickling Filtration Process Monitored by Electronic Nose

Bartosz Szulczyński*, Piotr Rybarczyk, Milena Marycz, Jacek Gębicki

Department of Process Engineering and Chemical Technology, Faculty of Chemistry, Gdańsk University of Technology, 11/12 Gabriela Narutowicza Street, 80-233 Gdańsk, Poland
bartosz.szulczynski@pg.edu.pl

Biotrickling filtration is a cost-effective, efficient and environment-friendly technique for the treatment of waste gases containing low and moderate concentrations of volatile organic compounds. This paper presents the results of investigations of biotrickling filtration of air polluted with vapors of hydrophobic cyclohexane. Process performance was evaluated and controlled using an electronic nose coupled with a modified multiple linear regression (MLR) data processing algorithm. Two methods of enhancing the removal efficiency of cyclohexane were investigated i.e. partial recycling of a treated gas stream and addition of hydrophilic volatile organic compound (n-butanol) to the feed stream. The results indicate that the proposed methods positively affect the process performance, leading to an increase of removal efficiency by about 20% and 40% when recycling approach and addition of n-butanol, respectively, are considered. The study shows that the treatments used to improve the removal efficiency of cyclohexane cause an increase in its removal to 85-90%.

1. Introduction

The use of biological methods for air purification has been known for over 60 years. The devices used for this purpose, mainly biofilters, enable the removal of odorous compounds from gases, e.g. in food processing plants, wastewater treatment plants and municipal waste management facilities. Biofiltration process involves the biodegradation of air pollutants by bacteria or other microorganisms that inhabit the porous packing of the biofilter. The mechanism of the process consists in the diffusion of the pollutants from the gas phase into a biofilm covering the surface of the packing elements. The compounds are thus adsorbed onto the packing elements and absorbed in the biofilm, and then are biodegraded. Finally, purified gas leaves the biofilter (Rybarczyk et al. 2019a). Biotrickling filters have a number of advantages over typical biofilters, including greater process stability, adjustable pH and temperature of the trickling liquid, lower flow resistance and smaller space requirements. Additionally, due to the usage of inert packing materials, biotrickling filters offer much more durable process performance than conventional biofilters. All these features favour the ongoing development of this group of bioreactors for biofiltration processes (Wu et al., 2018).
Research in the field of biofiltration usually involves determining the effect of the bed type, inlet loading or empty bed residence time as well as bioreactor design on the process efficiency, i.e. the removal efficiency or the rate of biofiltration. The basis for determining these parameters is to measure the change in the concentration of removed compounds as a result of the biofiltration process. For this purpose, in laboratory tests, almost exclusively gas chromatography technique coupled with various types of detectors is used. In the case of many odorous compounds, even a high degree of their removal from gas streams does not guarantee that they will be imperceptible to the human sense of smell. Therefore, there is a need to introduce on-line measurements, enabling real-time tracking of biofiltration performance. One of the devices that meets this type of requirement is an electronic nose device (Capelli et al., 2014; Gębicki et al., 2014; Szulczyński and Gębicki, 2019; Szulczyński et al., 2018). In addition, the use of this type of measuring device to assess the effectiveness of treatment allows it to be implemented in the control and monitoring system of the biofiltration process.

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Biotrickling filters exhibit extraordinary performance when the removal of hydrophilic VOCs from air is considered. However, the process efficiency is usually much lower when hydrophobic VOCs are treated. There are several approaches aiming at the increase of biofiltration performance with respect to hydrophobic compounds e.g. selection of microbial populations, addition of surfactants, application of fungal biocatalysts or biofiltration with UV pre-treatment (Cheng et al., 2016). In this paper, two other methods are proposed i.e. treated gas stream recycling as well as the addition of hydrophilic compounds. Recycling of a treated gas stream and mixing it with a feed gas may result in an increase of elimination capacity of a biofilter in the case of excessive inlet loadings. Additionally, the addition of hydrophilic compounds is a known method of improving the biofiltraiton of hydrophobic compounds.
In this paper, the development of an electronic nose coupled with a data processing algorithm is proposed as a toll for the on-line evaluation of biotrickling filtration performance. Air polluted with hydrophobic cyclohexane was treated in a peat-packed biotrickling filter. In the event of disturbances in the operation of a bioreactor and a decrease in the removal efficiency of odorous compounds, the proposed control and measurement system allowed for partial recycling of a treated stream. For the further increase of a process performance, hydrophilic n-butanol was added to the treated gas stream, resulting in the increased removal rate of hydrophobic cyclohexane.

2. Experimental

2.1 Odorous compound selection

Cyclohexane and n-butanol were selected as objects of investigations in this study. These volatile organic compounds are emitted from petroleum industry and solvents production (Salamanca et al., 2017). The selection of above-mentioned compounds is related to their different affinity towards aqueous phase. Henry's constants are $5.3\cdot10^{-5}$ and 1.1 mol m^{-3} Pa^{-1}, for hydrophobic cyclohexane and hydrophilic n-butanol, respectively (Rybarczyk et al., 2019b).

2.2 Selection of electronic nose sensors

Currently, the gas chemical sensor market is very rich in multiple sensor solutions and constructions. However, in the construction of sensor arrays operating in electronic noses, commercially available gaseous chemical sensors of the following types are mainly used: semiconductor (MOS – Metal Oxide Sensors), electrochemical, optical, or photoionisation. Semiconductor and photoionisation sensors are mainly used to analyze streams containing volatile organic compounds (Szulczyński and Gębicki, 2017).
In the presented research, six commercially available MOS sensors were used: TGS823, TGS8100, TGS2600, TGS2602, TGS2603 and TGS2611. These sensors were tested for the possibility of using them to determine concentrations of cyclohexane and n-butanol in the stream of purified air at the inlet and outlet of the biofilter. Two sensor models were selected for the presented application: TGS2600 (Sensor 1) and TGS 2602 (Sensor 2). As a selection criterion, the sensitivity (S) of the sensors to the tested substances and the selectivity coefficient (K) calculated as the ratio of sensitivity of a given sensor model for cyclohexane in relation to n-butanol were used. The values of sensitivity and selectivity coefficients are presented in Table 1. Selected sensor models were characterized by the highest sensitivity to the tested compounds and a high value of the selectivity coefficient.

Table 1: The values of sensitivity and selectivity coefficients determined for the selected MOS sensors

Sensor model	$S_{cyclohexane}$ [mV/ppm]	$S_{n\text{-}butanol}$ [mV/ppm]	K [-]
TGS2600	29.9	20.0	1.5
TGS2602	26.5	20.0	1.3
TGS2603	12.6	11.3	1.1
TGS2611	21.7	14.8	1.4
TGS823	16.9	17.4	0.9
TGS8100	13.9	13.0	1.1

In the next step, calibration (in the cyclohexane and n-butanol concentration range up to 3 g m^{-3}) of the developed sensor matrix was performed. Multiple Linear Regression (MLR) method based on 4 variables was used for this purpose: TGS2600 signal (S_1), TGS2602 signal (S_2), signal multiplication ($S_1\cdot S_2$) and signal division ($S_1\cdot S_2^{-1}$). Table 2 presents the forms of the developed models together with their determination coefficient. These models were used in further studies to monitor cyclohexane and n-butanol concentrations at the inlet and outlet of the biofilter.

Table 2: Developed model parameters

Calibration model	Determination coefficient
$\log C_{cyclohexane} = -4.02 \cdot 10^{-2} \cdot S_1 + 1.03 \cdot 10^{-2} \cdot S_2 + 3.32 \cdot 10^{-5} \cdot S_1 \cdot S_2 + 1.07 \cdot 10^{1} \cdot \frac{S_1}{S_2} - 2.77$	0.981
$\log C_{n-butanol} = 5.61 \cdot 10^{-3} \cdot S_1 - 2.72 \cdot \frac{S_1}{S_2} + 1.65$	0.979

2.3 Experimental setup and biofilter performance

The constructed system together with the electronic nose was used to verify in laboratory conditions the impact of the possibility of recycling part of the purified gas stream and the addition of vapors of hydrophilic compound (n-butanol) on the efficiency of cyclohexane biotrickling filtration.

Investigations were performed in a counter-current two-section plexi-glass biotrickling filter. Working volume of the biotrickling filter was 2.5 dm^3. The biofilter was packed with a peat and perlite mixture (Compo Sana, Compo GmbH, Münster, Germany) sandwiched between two layers of ceramic Rashig rings (6 × 1.5 mm) to provide appropriate conditions for uniform distribution of a trickling liquid. Feed gas, with a constant volumetric flow rate of 2.5 dm^3 min^{-1} was supplied from the biofilter bottom. A trickling liquid (mineral salt medium solution, MSM; Na_2HPO_4 × $2H_2O$, KH_2PO_4, NaCl and NH_4Cl dissolved in distilled water) was sprayed from the top of the bioreactor. The trickling frequency was 15s /60 min with volumetric flow rate of 0.2 dm^3 min^{-1}. The MSM solution was replaced each 6 days during the experiment. The mineral salt medium was autoclaved (Prestige Medical, Blackburn, England) prior to its introduction to the BTF. The processes were carried out at room temperature (23–25°C). All chemicals used in this study, except for cyclohexane (Merck, Darmstadt, Germany), were purchased from POCH (POCH, Gliwice, Poland). A scheme of a laboratory set-up is shown in Figure 1.

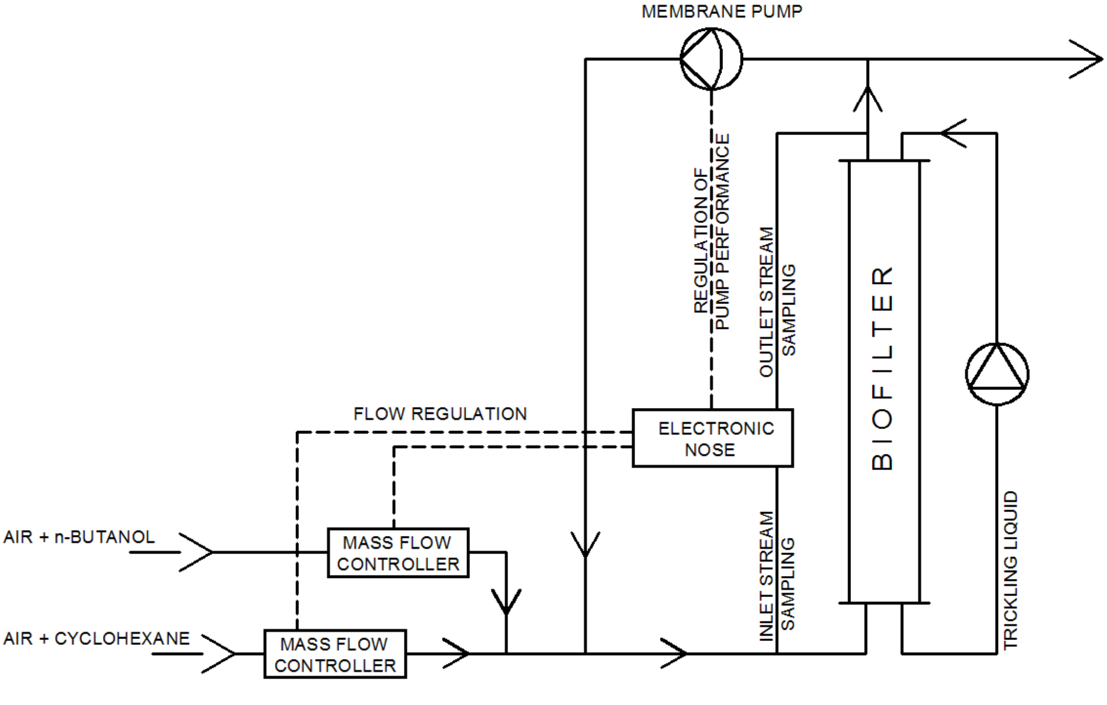

Figure 1: Schematic of the laboratory set-up

The developed electronic nose monitored the inlet and outlet concentrations of cyclohexane and n-butanol every 15 minutes throughout the experiment. The electronic nose was equipped with two additional functionalities: the ability to control the membrane pump (enabling the recycling of the treated gas stream) and the possibility of introducing n-butanol vapors into the inlet gas stream.

The time of the experiment was divided into three 12-day stages:

- standard biofilter operating conditions, including process start-up and stabilization, (stages 1a and 1b),
- operating with recycling part of the outlet stream (stages 2a and 2b),
- operating with recycling part of the outlet stream as well as the addition of hydrophilic compound vapors (stages 3a and 3b).

The following parameters have been determined for each stage: removal efficiency (RE), elimination capacity (EC), inlet loading (IL) and empty bed residence time (EBRT). These parameters were calculated according to the formulae:

$$RE = \frac{C_{in} - C_{out}}{C_{in}} \cdot 100\% \quad (1)$$

$$EBRT = \frac{V}{Q} \quad (2)$$

$$IL = \frac{Q \cdot C_{in}}{V} = \frac{C_{in}}{EBRT} \quad (3)$$

$$EC = \frac{Q \cdot (C_{in} - C_{out})}{V} = \frac{C_{in} - C_{out}}{EBRT} = \frac{RE \cdot C_{in}}{EBRT} \quad (4)$$

where C_{in} is the concentration of cyclohexane in the inlet (feed) gas stream, C_{out} is the concentration of cyclohexane in the outlet gas stream, Q is the volumetric gas flow rate at the biofilter inlet and V is the total volume of a biotrickling filter packing (working volume).The process parameters for all stages together with values of the stream recycling are presented in the Table 3.

Table 3: The determined process parameters for all stages of experiment

Stage	Day	$IL_{cyclohexane}$ [g m^{-3} h^{-1}]	$IL_{n\text{-}butanol}$ [g m^{-3} h^{-1}]	Outlet stream recycling	EBRT [s]	RE [%]	EC [g m^{-3} h^{-1}]
1a	0-6	90	0	0	60	34.2	30.8
1b	7-12	45	0	0	60	53.7	24.2
2a	13-18	90	0	20%	50	74.8	67.4
2b	19-24	90	0	50%	40	63.2	56.7
3a	24-30	90	40	20%	50	81.0	85.9
3b	31-36	180	40	20%	50	88.4	159.2

3. Results and discussion

The performance of the biofiltration process (during all stages) using values of removal efficiency (RE) is shown in Figure 2 and elimination capacity (EC) is shown in Figure 3.

In the stages 1a and 1b, the biofilter is fed with cyclohexane only. In the stage 1a, the inlet loading (IL) was set to 90 g m^{-3} h^{-1} and the system stabilization is reflected by the values of removal efficiency (RE) around 30-35%. To improve the removal efficiency of cyclohexane in the stage 1b, the inlet loading was reduced to 45 g m^{-3} h^{-1}. This approach allowed to obtain the removal efficiency at the level of 50-55%, while reducing elimination capacity (EC) to the level of about 25 g m^{-3} h^{-1}. In the next stage (2a) in order to increase the elimination capacity and the removal efficiency, the inlet loading was set to the initial value of 90 g m^{-3} h^{-1}. Additionally, 20% the outlet stream recycling was introduced to the biofilter system. Such a procedure slightly reduces the EBRT, however both other parameters (RE and EC) increase to the level of about 75% and 67 g m^{-3} h^{-1}, respectively. In the next stage (2b), the possibility of increasing the recycled stream was tested. The outlet stream recycling value was set to 50%. This caused a significant decrease of EBRT, which contributed to reducing the effectiveness of the process (RE = 63%). For this reason, in the next stage (3a) the outlet stream recycling value was set back to 20%. Additionally, n-butanol vapors were introduced into the inlet stream to determine the effect of addition of a hydrophilic compound for the removal efficiency of a hydrophobic compound. The inlet loading of n-butanol was set to 40 g m^{-3} h^{-1}. A further increase in removal efficiency was observed, up to a level of about 80%. In the last stage of experiment (3b), the inlet loading of cyclohexane was doubled. This resulted in a significant increase of elimination capacity. A slight increase of removal efficiency (RE = 88%) was also observed. Similar efficiency of cyclohexane removal was obtained in our previous study (Rybarczyk et al., 2019b) where the n-butanol concentration in the inlet stream was 25%

higher than in this study. These results reflect that the approach of a treated stream recycling together with addition of hydrophilic compound considerably increase the removal efficiency of cyclohexane in the investigated system.

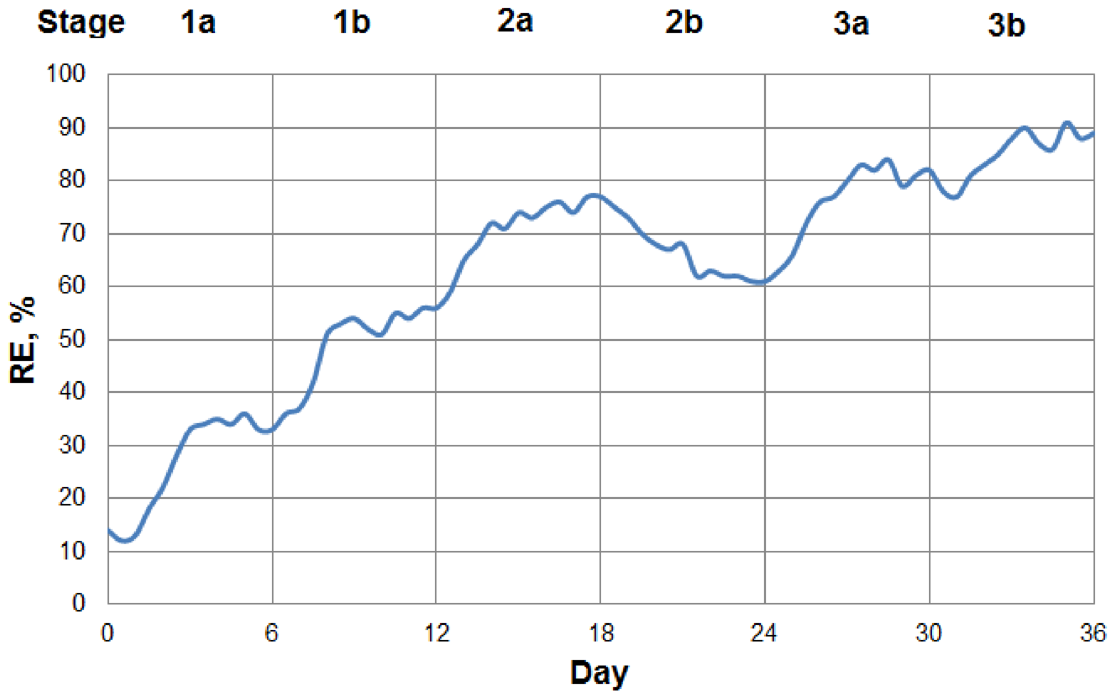

Figure 2: The biofiltration removal efficiency (RE) changes during the experiment

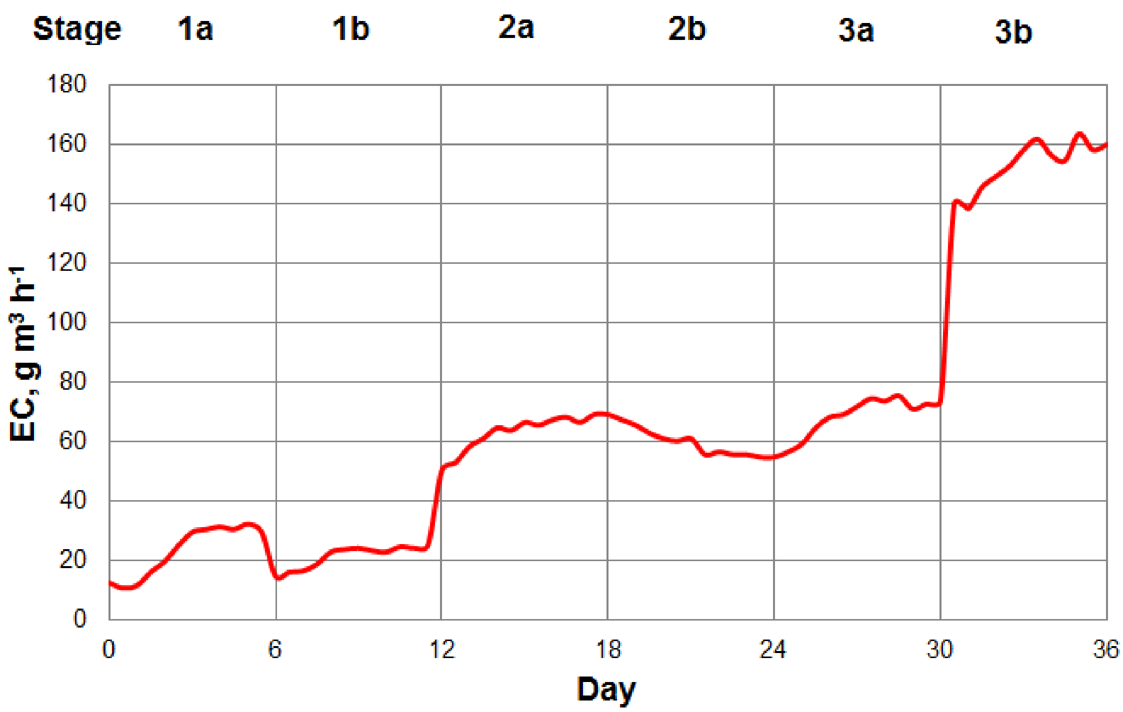

Figure 3: The biofiltration elimination capacity (EC) changes during the experiment

4. Conclusions

This paper presents the results of investigations on the biotrickling filtration of hydrophobic cyclohexane. Electronic nose was used as a monitoring and control tool for evaluation and management of the process performance. Two approaches for the improvement of the removal efficiency of cyclohexane from air were investigated. One approach consisted in the partial recycling of the treated gas stream, while the other was based on addition of hydrophilic ethanol. It was found that the application of both above mentioned methods resulted in an increase of cyclohexane removal efficiency. Partial recycling of a treated gas stream results in an increase of elimination capacity, probably as a result of increased microbial growth, thus increasing the removal efficiency. Moreover, addition of hydrophilic n-butanol, mainly as a result of co-metabolism, also increases the removal efficiency of hydrophobic cyclohexane. Futher studies on the mechanisms of enhanced biotrickling filtration of hydrophobic volatile organic compounds in the presence of hydrophilic ones as well as effects of treated gas recycling on the microbial population are postulated. Moreover, the Authors believe that the application of electronic nose in such studies will enable on-line process monitoring and regulation, presenting a novel approach towards process control and optimization.

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