






# Removal of cyclohexane vapors from air in biotrickling filters: Effects of gas mixture composition and circular economy approach

Piotr Rybarczyk\* , Bartosz Szulczyński , Dominik Dobrzyniewski , Karolina Kucharska ,  
Jacek Gębicki 

Gdańsk University of Technology, Faculty of Chemistry, Department of Process Engineering and Chemical Technology, 80-233 Gdańsk, Narutowicza 11/12, Poland

## \* Corresponding author:

e-mail:

[piotr.rybarczyk@pg.edu.pl](mailto:piotr.rybarczyk@pg.edu.pl)

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## Abstract

This work presents results of investigations on biotrickling filtration of air polluted with cyclohexane co-treated in binary, ternary and quaternary volatile organic compounds (VOCs) mixtures, including vapors of hexane, toluene and ethanol. The removal of cyclohexane from a gas mixture depends on the physicochemical properties of the co-treated VOCs and the lower the hydrophobicity of the VOC, the higher the removal efficiency of cyclohexane. In this work, the performance of biotrickling filters treating VOCs mixtures is discussed based on surface tension of trickling liquid for the first time. A mixed natural – synthetic packing for biotrickling filters was utilized, showing promising performance and limited maintenance requirements. Maximum elimination capacity of about 95 g/(m<sup>3</sup>·h) of cyclohexane was reached for the total VOCs inlet loading of about 450 g/(m<sup>3</sup>·h). This work presents also a novel approach of combining biological air treatment with management of a spent trickling liquid in the perspective of circular economy assumptions. The waste liquid phase was applied to the plant cultivation, showing a potential for e.g. enhanced production of energetic biomass or polluted soil phytoremediation.

## Keywords

biotrickling filtration, cyclohexane, volatile organic compounds, surface tension, circular economy

## 1. INTRODUCTION

Among the gaseous pollutants emitted to the atmosphere, volatile organic compounds (VOCs) and volatile inorganic compounds (VICs) can be distinguished. The former group includes volatile compounds containing carbon in their structures. According to the U.S. Environmental Protection Agency, VOCs are defined as organic compounds with a vapor pressure greater than 0.1 mm Hg under normal conditions (Revah and Morgan-Sagastume, 2005). VICs, on the other hand, are inorganic gases like hydrogen sulfide, sulfur dioxide, carbon disulfide or ammonia.

Pollution of air with volatile organic compounds is a serious problem for both human health and the environment. In this work, cyclohexane, hexane, toluene and ethanol were chosen as target pollutants. The reason for selection of given VOCs was threefold: firstly, these are known as common industrial pollutants with odorous character that can be absorbed via the skin and respiratory system, resulting in pernicious effects on human health, including genotoxicity, hematotoxicity, and leukemia. Secondly, these VOCs present different physicochemical properties (e.g. affinity to aqueous phase) which influence the removal strategies of such compounds from air. Thirdly, cyclohexane removal from air using biotrickling filtration has so far been rarely studied and thus the focus in this work is to investigate the influence of other VOCs on

the cyclohexane biofiltration performance (Rybarczyk et al., 2021; Salamanca et al., 2017; Zhanga et al., 2018). Selected characteristics of the investigated air pollutants are given in Table 1.

VOCs and VICs may be effectively removed from air streams using biological methods, including biofilters, bioscrubbers and biotrickling filtration systems (Wu et al., 2022). Bioscrubbers consist of an absorber sprayed with an absorption liquid and a tank with activated sludge in the form of an aqueous suspension of microorganisms. In the former, there is a mass transfer of target compounds from the contaminated gases to the liquid phase, and in the latter there is regeneration of the absorption liquid due to biodegradation of the absorbed compounds by microbes. One of the main disadvantages of bioscrubbers is short contact time between gas and liquid phases, which limits their application mainly to the removal of contaminants with good solubility in water (Mudliar et al., 2010; Revah and Morgan-Sagastume, 2005). For this reason, bioscrubbers are mainly used for the removal of alcohols and ketones with concentrations in the polluted gases not exceeding 5 g/m<sup>3</sup> (Vikrant et al., 2017). Bioscrubbers require high capital expenditures and are energy intensive. On the other hand, advantages of bioscrubbers include relatively small reactor size and the ease of control of liquid phase parameters such as temperature, pH and nutrient balance (Mudliar et al., 2010).



Table 1. Selected characteristics of hexane, cyclohexane, toluene and ethanol (Botros et al., 2017; Sander, 2015).

Compound	H [mol/(m <sup>3</sup> ·Pa)]	log P <sub>ow</sub>	Water solubility [mg/dm <sup>3</sup> ]	Emission sources	Toxic effects
Hexane	6 · 10 <sup>-6</sup>	3.9	10	Food, leather, textiles production	Skin irritation, sensory disturbances polyneuropathy
Cyclohexane	6 · 10 <sup>-5</sup>	3.44	520	Organic synthesis, textile production	Respiratory tract and skin irritation, liver and kidney damage
Toluene	1.5 · 10 <sup>-3</sup>	2.73	580	Chemicals, drugs, synthetic materials production	Liver damage, dermatitis, nervous system damage
Ethanol	1.9	-0.18	100000	Food, drugs, biofuels production	Liver damage, affects nervous system, addiction if abused

Biofilters are bioreactors with a fixed bed of porous filter material, usually in the form of organic materials such as peat, compost, wood chips, straw loosened soil, bark, which ensure the presence of diverse microbial cultures (Rybarczyk et al., 2019). One of the major drawbacks of biofilters is the periodic need to replace the filter bed, which loses its properties and activity over time. However, with proper maintenance, the lifetime of the bed may be up to several years without significant decrease in the efficiency of the processes (Revah and Morgan-Sagastume, 2005). Among the main factors limiting the use of biofilters are the difficulty in maintaining constant values of numerous parameters, the lack of application in batch processes, and usually large space requirements for installation construction. However, due to their low cost and ability to achieve high efficiencies in removal of VOCs from air, they are often used to treat gases from municipal landfills, wastewater treatment plants, composting units and food processing plants (Schlegelmilch et al., 2005).

Compared to conventional biofilters described above, biotrickling filters (BTFs) offer more complex process control and regulation possibilities, allowing to adjust liquid phase pH, composition or watering frequency as well as offer longer operation times due to application of inert packing materials (Rybarczyk et al., 2019).

In biotrickling filters, polluted air is passed through a porous packing layer. The BTF packing is populated with microorganisms capable of biological decomposition of pollutants. When the gas flows through the layer, the contaminants are sorbed and absorbed by microorganisms, usually growing in a form of a biofilm, and the purified gas stream leaves the biofilter. In order to ensure humid conditions, a trickling liquid, usually containing an aqueous solution of mineral salts, is sprayed on the packing. If inert packing materials are used, microorganisms need to be inoculated on the materials, while natural packings contains various microorganisms, including both autotrophic and heterotrophic ones. The most common bacteria bioactive for organic compounds are: *Pseudomonas*, *Rhodococcus*, *Acinetobacterium*, *Amyko-*

*lata*, *Arhobacter*, *Mycoplana*, *Xanthobacter* and *Bacillus* (González-Martín et al., 2023; Sheoran et al., 2022). In this work, peat was selected as a part of a biofilter packing due to several advantages, including a broad variety of microorganisms, high specific area, presence of intrinsic nutrients, water retention capacity as well as good air permeability (Pachaiappan et al., 2022). The use of a peat mixed with other two different types of material (i.e. perlite and polyurethane foam discs) is a novel approach of using mixed natural and synthetic packing for biotrickling filtration systems.

The biotrickling filtration performance is highly dependent on the solubility of the gas pollutants in the liquid and biofilm phases. It is therefore evident that the more hydrophilic compound, e.g. represented by high values of Henry's constant (Table 1), the higher its bioavailability and expected removal than for hydrophobic compounds. In order to enhance the removal of hydrophobic VOCs in biotrickling filters, various measures have been investigated including addition of surfactants or non-aqueous liquid phase, pre-treatment operations (e.g. photooxidation) or inoculation with selected microbial species, specialized in the removal of hydrophobic VOCs (Cheng et al., 2016; Wu et al., 2023).

Another approach of increasing the biotrickling filtration performance of hydrophobic VOCs, like hexane or cyclohexane, may be their co-treatment with hydrophilic VOCs (Cheng et al., 2020). Interestingly, biodegradation of VOC mixtures can be altered by various interactions between individual compounds when present in a mixture, and thus can reveal positive, neutral or negative effects on e.g. biofiltration performance (Yang et al., 2018; Yoshikawa et al., 2017). In fact, although emissions of VOC mixtures with different physico-chemical properties are typical for many industrial processes, the mechanisms of enhanced biotrickling filtration of air polluted with hydrophobic VOCs in the presence of hydrophilic ones are not fully elucidated.

The enhancement mechanism is already known to be related to increased solubility of hydrophobic VOCs in the aqueous trickling liquid as well as increased biofilm growth and

activity, due to the presence of hydrophilic VOCs (Wu et al., 2022). Hydrophilic VOCs are an easily accessible carbon source for microorganisms and at the same they are easily dissolved in aqueous solution, and thus act as a solvent for hydrophobic ones. This has been investigated e.g. for ethanol and methanol (Meena et al., 2016; Rybarczyk et al., 2021). Interestingly, toluene proved to induce a faster biodegradation of other hydrophobic VOCs when these are simultaneously co-treated. Enhancement of styrene removal efficiency as well as shortening of the start-up time for a biotrickling filter treating styrene-toluene mixture has also been observed (Li et al., 2019). The positive role of toluene as a biofiltration process inducer is attributed to the intermediate metabolite catechol which is responsible for biomass growth. Toluene is also said to be more easily biodegraded into intermediate products than several other VOCs like benzene or xylene.

In this paper, deeper investigations of liquid phase of a BTF were performed. Relations between the liquid phase composition and physico-chemistry on the performance of biotrickling filtration of VOCs have been rarely studied so far (Lee et al., 2021). Thus, surface tension measurements for various investigated systems are presented in order to reveal changes in interfacial tension. The lower the surface tension, the lower the barrier for hydrophobic VOCs to reach the biofilm i.e. the bioavailability of VOCs is increased. It is assumed that the changes in surface tension of the trickling liquid will depend on both the VOCs treated as well as, and primarily, on the specialized microbial species, constituting the biofilm. It may be that due to secretion of metabolic products of some microbes, biosurfactants may be produced, which are said to aid the removal of hydrophobic VOCs in BTFs (He et al., 2019). To the best knowledge of the authors, evaluation of surface tension of trickling liquid has not been previously proposed for description of biotrickling filtration process.

Biofiltration techniques are regarded as sustainable and green technologies for air purification (Sarkar et al., 2022). However, their beneficiary application can be expanded by the circular economy approach through valorization of the process final products i.e. treated gas and spent trickling liquid for culturing of plants. Selection of proper plant species may allow to obtain advantageous effects of managing post-biofilter streams. For example, utilization of spent trickling liquid may positively affect the plant growth, owing to the presence of microelements. It may also enhance polluted soil phytoremediation, both due to increased biomass yield and possible symbiosis between soil and biofilter-originating microorganisms for pollutant assimilation and biodegradation. Such an approach of combining air biofiltration and phytoremediation techniques has not been previously described in the literature.

The main aim of this work was to investigate the effects of treated gas composition on the performance of biotrickling filtration of air polluted with cyclohexane. The results are discussed taking into account both gas and liquid phases. An

attempt is made to verify the possibility of utilizing a spent trickling liquid solution as an additive for ryegrass cultivation in pot experiments.

## 2. EXPERIMENTAL

### 2.1. Biotrickling filtration set-up

Investigations were performed in five biotrickling filters (BTFs), treating air containing various VOC compositions: cyclohexane solely (BTF A), cyclohexane and hexane (BTF B), cyclohexane and toluene (BTF C), cyclohexane, hexane and toluene (BTF D), and cyclohexane, hexane, toluene and ethanol (BTF E). Hexane, cyclohexane, toluene and ethanol were purchased from POCH (POCH, Poland) and were of pure analysis grade. Detailed information on the feed gas compositions is given in Table 2. The biofilters used in the research were all identical and were operating in a counter-current mode. Each biotrickling filter was made of a plexiglass column (height of 0.68 m and internal diameter of 0.08 m). Biofilters were packed in a sandwich-type manner with a polyurethane disc (0.015 m in height) and a 0.015 m – high layer of a peat-perlite mixed with ceramic Raschig rings. This alternate layers were packed in a column to a total volume of packing equal to 2.5 dm<sup>3</sup>.

Peat and perlite were purchased as a commercially available substrate for plant cultivation (Compo Sana, Compo Group GmbH, Germany). Peat bulk density, porosity and water capacity were found to be 0.22 g/cm<sup>3</sup>, 0.9, and 65%, respectively. These values are in line with typical literature values (Kormanek et al., 2021). Physical parameters of a mixture of peat, perlite and Raschig rings were determined according to Koppecki and Gracanin methods (Markoska et al., 2018). Ceramic Raschig rings (6 × 6 × 2 mm, BIOWIN, BROWIN, Poland) were added in order to increase the air porosity of the packing material and limit the possible clogging of the biofilter bed due to over wetting of the peat material, resulting in the average values of porosity of 48±6% and bulk density of 0.79±0.05 g/cm<sup>3</sup>.

The applied polyurethane foam (Ultramar, Poland) properties were as follows: PPI 10; porosity: 97%; density 0.025 g/cm<sup>3</sup>.

Biotrickling filter columns were fed with a gas mixture from the bottom. Model gas mixtures used in the experiments were obtained by mixing compressed air with vapors of investigated volatile organic compounds in mixing chambers. VOC vapors were obtained by passing air through liquid layers of hexane, cyclohexane, toluene or ethanol. Compressed air was divided into two streams. One stream of air was supplied to a gas-tight glass cylinder, filled with a mixture of liquid form of VOCs investigated, through a porous ceramic sinter. Air bubbles rising in the liquid layer were saturated

Table 2. Compositions of feed gases supplied to biotrickling filters.

Biotrickling filter abbreviation	VOC	$C_{IN}$ [ppm v/v]	$C_{IN}$ [mg/m <sup>3</sup> ]	$IL$ [g/(m <sup>3</sup> ·h)]	Total inlet loading of VOCs [g/m <sup>3</sup> h]
A	cyclohexane	141–1454	0.49–5.05	29–300	29–300
B	cyclohexane	227–674	0.78–2.32	47–140	76–250
	hexane	141–508	0.49–1.79	29–110	
C	cyclohexane	227–652	0.78–2.25	47–135	81–285
	toluene	147–685	0.55–2.58	34–150	
D	cyclohexane	79–507	0.27–1.75	40–105	84–315
	hexane	79–378	0.28–1.33	15–80	
	toluene	127–577	0.48–2.19	29–130	
E	cyclohexane	79–507	0.27–1.75	40–105	121–630
	hexane	100–410	0.35–1.45	21–87	
	toluene	127–460	0.49–1.74	29–104	
	ethanol	253–2725	0.25–5.57	31–334	

with VOCs. The air flow rate to the glass cylinders was controlled using mass flow controllers (Aalborg GFC17, Aalborg Instruments & Controls, USA). In order to ensure a constant concentration of VOCs in air, levels of liquid VOCs were monitored and refilled each three days. Then, the air stream saturated with VOC vapors was mixed with a clean air stream, before entering the biotrickling filter. Total flow rate of air supplied to the biofilter was controlled and regulated using mass flow controllers (Red-y, GSC-C3SA-BB26, Vögtlin, Switzerland). Total gas flow rate to the biofilter was kept equal to 2.5 dm<sup>3</sup>/min, corresponding to the empty bed residence time (EBRT) of 1 min. The experiments were run at room temperature of 24±2°C.

Biotrickling filter packing was intermittently sprayed with a trickling solution of mineral salt medium (MSM) with following salts dissolved in 1 dm<sup>3</sup> of distilled water: Na<sub>2</sub>HPO<sub>4</sub> · 2H<sub>2</sub>O (7.39 g; POL-AURA, Poland, pure for analysis), KH<sub>2</sub>PO<sub>4</sub> (3 g; POL-AURA, Poland, pure for analysis), NH<sub>4</sub>Cl (1 g; POCH, Poland, pure for analysis), NaCl (0.5 g; POCH, Poland, pure for analysis). The spraying of the packing was done using a peristaltic pump (VMA447, Velleman, Belgium) with a frequency set at 0.5 minute of trickling each 30 minutes, corresponding to MSM circulation flow rate of 0.2 dm<sup>3</sup>/h.

## 2.2. Determination of VOC concentrations

Concentrations of cyclohexane, hexane, toluene and ethanol were determined using a gas chromatograph equipped with a flame ionization detector (Varian CP-3800, Varian Analytical Instruments, USA). DB-WAX column (30 m × 0.53 mm × 1 μm, Agilent Technologies, USA) was applied. The following parameters of chromatographic analysis were set: oven temperature 100°C (isothermal conditions), detector temperature 200°C, carrier gas flow rate 3 cm<sup>3</sup>/min, split ratio

10. Nitrogen was used as a carrier gas. Concentrations of investigated VOCs in the head-space of trickling liquid samples were determined using the same method.

For head-space analysis, 5 mL samples of trickling liquid were taken to head-space vials and thermostated for 10 minutes at 65°C (WHLL-30BE Drying oven, Chemland, Poland) prior to GC analysis.

## 2.3. Determination of physico-chemical parameters of biotrickling filtration systems

The pH of a trickling liquid was determined using a PH-100ATC pH meter (Voltcraft, Germany) and a DJ113 pH electrode (VWR, Germany).

Pressure drop of treated air flowing through a biotrickling filter packing was monitored using a U-tube manometer.

Surface tension of trickling liquid samples was determined using a Krüss K11 tensiometer (Krüss, Germany) with Wilhelmy method using a rolled PL22 plate. The measurements were performed at 24±2°C.

## 2.4. Assessment of microbial activity in a biotrickling filter

To estimate the activity of microorganisms in the biotrickling filters, trickling liquid (leachate) samples were introduced into Petri plates as surface and submerged cultivation preparations. The solid minimum medium feed with the following composition was used: 15.2 g of Na<sub>2</sub>HPO<sub>4</sub> · 12H<sub>2</sub>O (CHEMPUR, Poland, pure for analysis); 3 g of KH<sub>2</sub>PO<sub>4</sub> (POLAURA, Poland, pure for analysis); 0.5 g of NaCl (POCH, Poland, pure for analysis); 1 g of NH<sub>4</sub>Cl (POCH, Poland, pure for analysis); 1 cm<sup>3</sup> of 1M MgSO<sub>4</sub> · 7H<sub>2</sub>O (POCH,



Poland, pure for analysis); 1 cm<sup>3</sup> of 0,1M CaCl<sub>2</sub> (POCH, Poland, pure for analysis); 1 cm<sup>3</sup> of 20% glucose (POL-AURA, Poland, pure for analysis); and 1.5% agar (BTL, Poland) per 1000 dm<sup>3</sup> of feed medium, pH = 7.0. The number and variety of cultures were determined and compared using colony counter A03492 (Chemland, Poland).

## 2.5. Utilization of spent trickling liquid to plant cultivation

A trickling liquid was renewed with a fresh MSM solution each 7 days. Single turfs of ryegrass, taken from the open-space mown in Pomeranian region, Poland, were placed in 500 cm<sup>3</sup> pots and were daily watered with 10 cm<sup>3</sup> of spent trickling liquid. Ryegrass turfs were cultivated in clay loam soil (Marcinek and Komisarek, 2011). The experiment was conducted in triplicate for 21 days at room conditions with poor natural light conditions (winter season).

A control sample irrigated with distilled water was set as a basis for comparison of the experimental results for samples watered with spent trickling liquid from biofilters A–E.

The pH of soil samples was measured using the same apparatus as described in p. 2.3. Soil samples (20 g) were taken after 21-day cultivation period and placed in a beaker with 20 cm<sup>3</sup> of distilled water. The pH was measured after 24 hours for freshly agitated suspensions (Antonkiewicz, 2021).

## 2.6. Evaluation of biotrickling filtration performance and plant-based experiments

Concentrations of volatile organic compounds fed with air to the biotrickling filter were expressed using inlet loading (*IL*) (Chuang et al., 2018):

$$IL = \frac{Q_G C_{IN}}{V} \quad (1)$$

Performance of biotrickling filtration process was described using values of removal efficiency (*RE*) and elimination capacity (*EC*) (Dobrzyniewski et al., 2023; Nagendranatha Reddy et al., 2019):

$$RE = \left( \frac{C_{IN} - C_{OUT}}{C_{IN}} \right) \cdot 100\% \quad (2)$$

$$EC = \frac{Q_G (C_{IN} - C_{OUT})}{V} \quad (3)$$

Results of plant-based experiments were evaluated by measuring the weight of biomass collected from each pot culture (*Y*, g). Biomass was weighed (RADWAG AS 220.R2, Radom, Poland) as a fresh, wet biomass just after cutting and as a dry biomass after drying at 50 °C for 24 h (WHLL-30BE Drying oven, Chemland, Poland).

## 3. RESULTS AND DISCUSSION

### 3.1. Effects of gas composition on the performance of biotrickling filters

The results of air treatment using biotrickling filters are discussed depending on the gas phase composition and are presented in Figures 1–5. 70-day treatment period is reported and the results indicate that the start-up phase lasted for about 30 days from the process initiation (Rodriguez et al., 2014). Then the steady-state conditions with respect to biofilm activity were reached. Removal performance of cyclohexane from air (cyclohexane was a single VOC in the gas phase) in biotrickling filter A is presented in Figure 1. During the start-up phase, an increase of removal efficiency during the first 3 days may be due to sorption capacity of the packing, because after 3<sup>rd</sup> day of the process a drop in *RE* values is observed for similar *IL* values. Increase of cyclohexane inlet loading results in the decrease of its removal performance, which may be due to incomplete formation of biofilm in the start-up phase (days 8–12). BTF performance increases with decreasing *IL* and after about 30 days stabilizes at the level of *RE* of about 30–40%, irrespective of the changes in inlet loading, indicating stable biofiltration performance.

Removal of cyclohexane solely from air using biotrickling filtration has rarely been investigated so far. Salamanca and co-workers, using polyurethane foam inoculated with *Acivodorax* sp. CHX100 species (Salamanca et al., 2017), reached the elimination capacity of about 38 g/(m<sup>3</sup>·h) for inlet loading of about 46 g/(m<sup>3</sup>·h) at EBRT equal to 37 s. Rybarczyk and co-workers, for inlet loading of cyclohexane of about 45 g/(m<sup>3</sup>·h) at EBRT of 60s, obtained *EC* values of about 9 and 13.5 g/(m<sup>3</sup>·h), respectively when *C. subhashii* and *C. albicans* were used as inoculum (Rybarczyk et al., 2021). In this work, elimination capacity of about 19.5 g/(m<sup>3</sup>·h) was reached for *IL* of about 45 g/(m<sup>3</sup>·h) with EBRT equal to 60 s and a maximum *EC* of 75 g/(m<sup>3</sup>·h) was reached for *IL* equal to 300 g/(m<sup>3</sup>·h) when cyclohexane was solely removed from air (Fig. 1).

Biotrickling filtration performance when treating a mixture of hexane and cyclohexane is presented in Figure 2. For both investigated VOCs, similar trends during the start-up phase are observed as it was for cyclohexane solely (Fig. 1). The *RE* values of cyclohexane are however lower than in the BTF A due to co-existence of hexane. *RE* values for hexane are higher than for cyclohexane (Figs. 2a and 2b), probably due to slightly higher inlet concentrations of cyclohexane than hexane. It may be stated that the presence of hydrophobic hexane decreases the removal efficiency of cyclohexane, but the system presents overall treatment performance similar to BTF A for comparable inlet loadings of VOCs. Thus, results of hydrophobic VOCs mixture co-treatment VOCs reveals neutral to negative interaction behavior between the target pollutants to undergo biodegradation (Cheng et al., 2020; Wu et al., 2023).

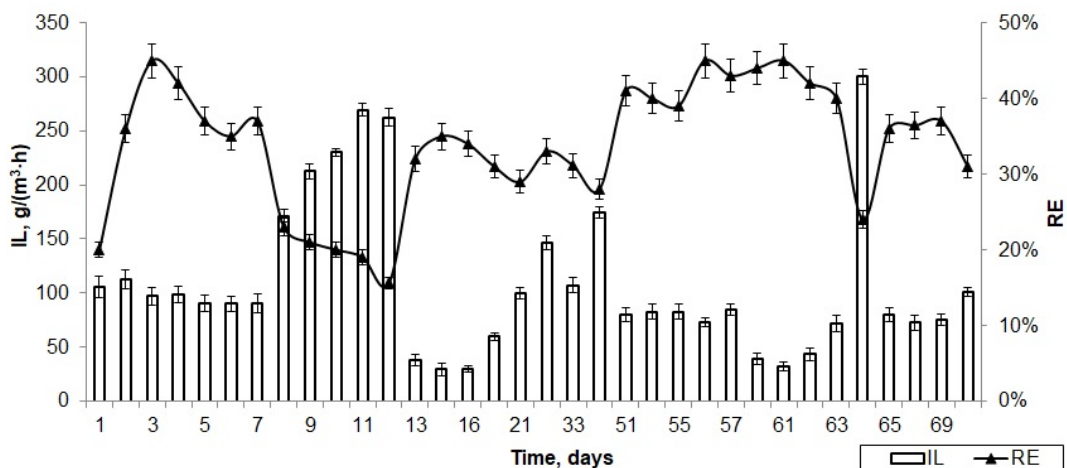


Figure 1. Performance of a biotrickling filter A, treating solely cyclohexane vapors in air.

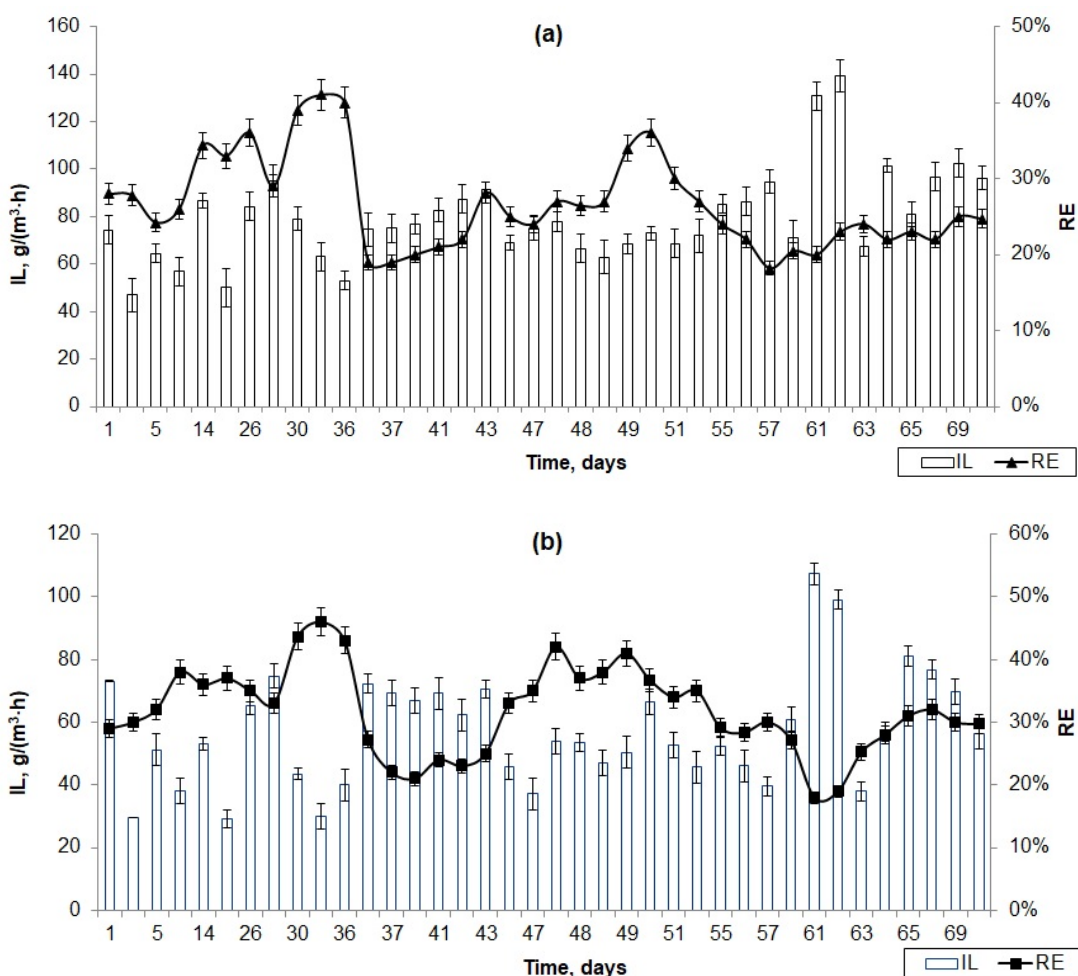


Figure 2. Performance of biotrickling filter B, treating a mixture of hexane and cyclohexane vapors in air: results for cyclohexane (a) and hexane (b).

Biotrickling filtration performance for treatment of air containing cyclohexane and toluene is presented in Figure 3. The results for the discussed system C are different compared to the performance of systems A and B. Firstly, the removal

efficiency of cyclohexane is higher than in systems A and B. Secondly, the removal efficiency of toluene is very high, reaching  $RE$  values exceeding 90%, irrespective of the inlet loading values.

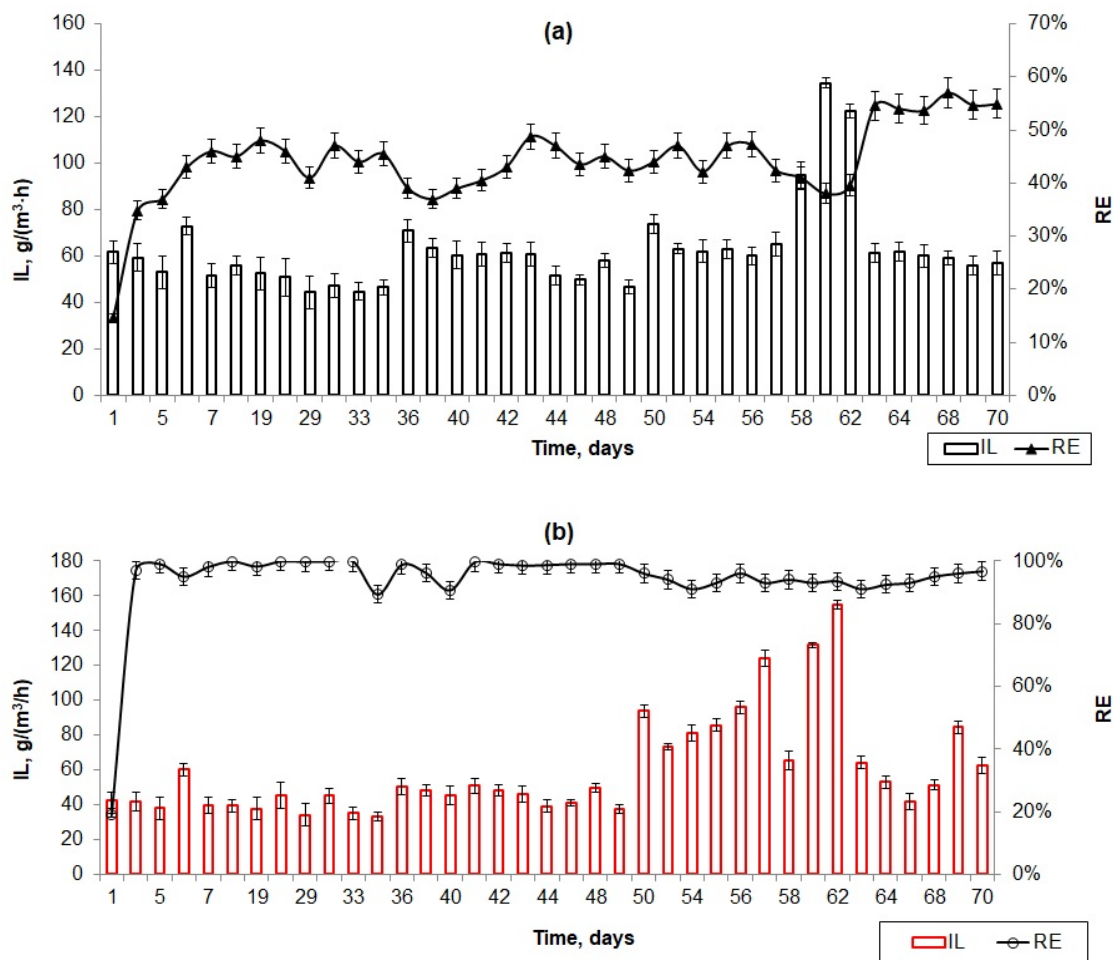


Figure 3. Performance of biotrickling filter C, treating a mixture of cyclohexane and toluene vapors in air: results for cyclohexane (a) and toluene (b).

The results on simultaneous treatment of hexane, cyclohexane and toluene are given in Figure 4. Depending on the inlet loading of hexane and cyclohexane (in the range between 20–80 and 40 to 100 g/(m<sup>3</sup>·h), respectively), their removal efficiency in the steady-state conditions (i.e. after 30 days from the process start-up) is about 35–40% for cyclohexane and 40–50% for hexane. At the same time, toluene removal efficiency is between 80 to 95% for its inlet loading from 30 to 120 g/(m<sup>3</sup>·h). The total VOC loading is thus higher in biofilter D than in biofilter C (Fig. 3) and higher RE values are reached for system D. It may be concluded that toluene has a positive effect on the removal efficiency of hydrophobic hexane and cyclohexane and synergistic effects on the removal of co-treated hydrophobic VOCs can be observed. This is related to physicochemical properties of toluene which is regarded as less hydrophobic and better water-soluble VOC than cyclohexane or hexane (Table 1). Additionally, it also more easily undergoes biodegradation. It has already been proven that toluene enhances the removal performance of other co-treated hydrophobic VOCs (Cox et al., 1998; Dou et al., 2022; Sun et al., 2017), which is supported by the results presented in this work.

Biotrickling filtration performance for simultaneous treatment of a mixture of cyclohexane, hexane, toluene and ethanol is presented in Figure 5. This system represents the co-treatment results for VOC mixture components which differ greatly in terms of physicochemical process (Table 1) i.e. hydrophobic hexane and cyclohexane are treated with medium-hydrophobic toluene and hydrophilic ethanol. The reported values of removal efficiency are the highest compared to biofilters A–D. For days between 50 and 70 from the process initiation, the removal efficiency is about 80% for cyclohexane (Fig. 5a), about 85% for hexane (Fig. 5b), about 90% for toluene (Fig. 5c) and about 95% for ethanol (Fig. 5d).

In this work, mixtures of VOCs were treated in biotrickling filtration systems with intentionally variable values of inlet loading. This was done to mimic the possible variations in VOC concentrations in waste gases like in real industrial applications (San-Valero et al., 2015). Nevertheless, the average values of IL were kept between 30–50 g/(m<sup>3</sup>·h) for each investigated VOC. Because the results for the same composition of VOCs have not been reported previously, the out-

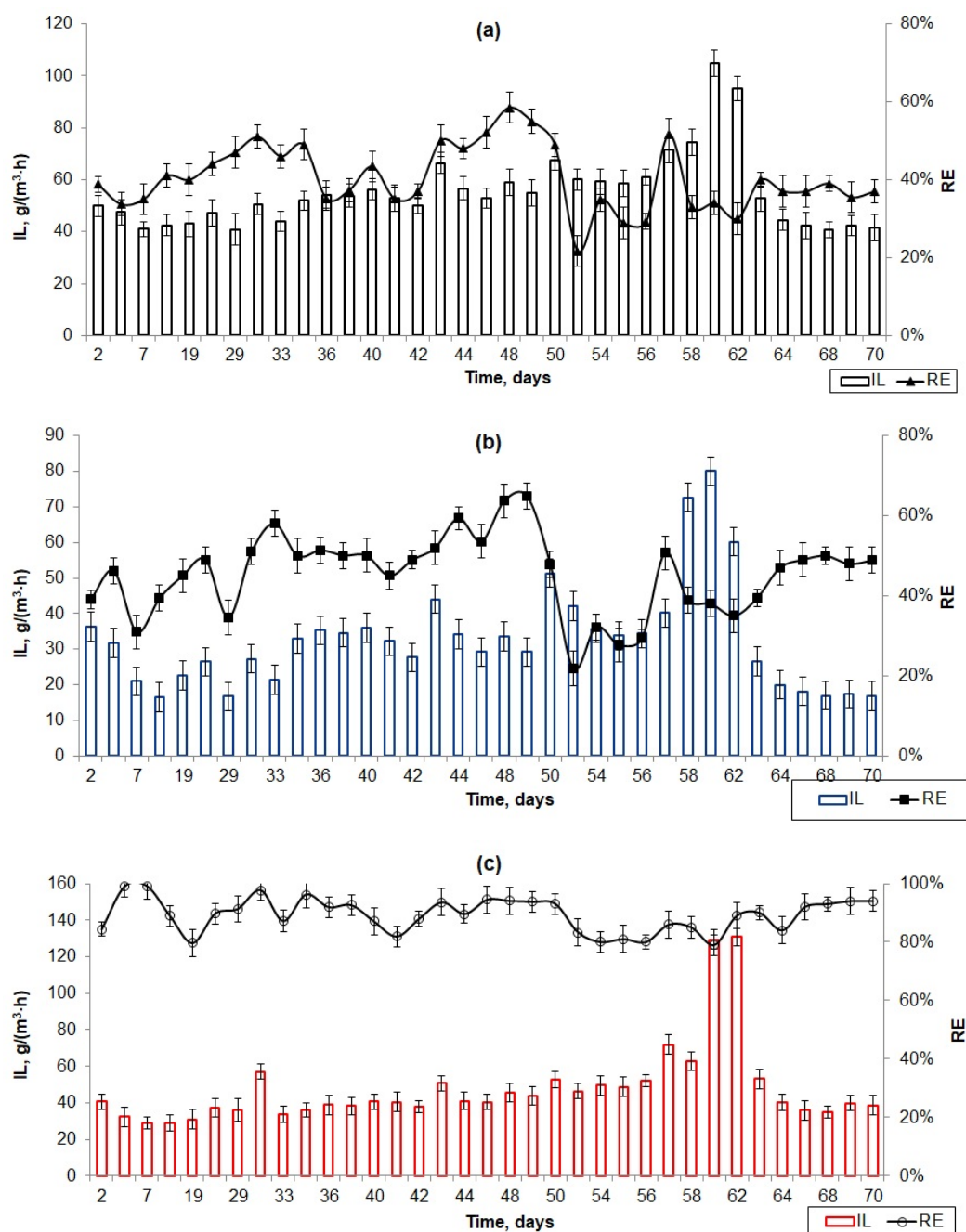


Figure 4. Performance of biotrickling filter D, treating a mixture of cyclohexane, hexane and toluene vapors: results for cyclohexane (a), hexane (b) and toluene (c).

comes of this work can be compared to other works only for similar VOC mixtures. Maximum elimination capacities of 32 and 117  $\text{g}/(\text{m}^3\cdot\text{h})$  were reached for hexane and toluene, respectively, when treated simultaneously with cyclohexane (Figs. 4b and 4c). These values corresponded to inlet loading of 80 and 130  $\text{g}/(\text{m}^3\cdot\text{h})$  for hexane and toluene, respectively. Elimination capacity of hexane increased to about 64  $\text{g}/(\text{m}^3\cdot\text{h})$  when it was co-treated with a mixture of cyclohexane, toluene and ethanol (Fig. 5a). Marycz and co-workers obtained elimination capacities for hexane and toluene of about 5 and 15 for inlet loadings of 12 and 20  $\text{g}/(\text{m}^3\cdot\text{h})$  for

EBRT of 77 s using a consortium of *Candida subhashii* and *Fusarium solani* (Marycz et al., 2023).

The presence of ethanol in the treated gas mixture increases the process performance with respect to all other VOCs treated (system E, Fig. 5) compared to other investigated systems (biotrickling filters B–D, Figs. 2–4). In general, ethanol enhances the removal of other co-treated VOCs, similarly as previously reported for e.g. co-treatment of ethanol with cyclohexane or hexane (Rybarczyk et al., 2021; 2020). The synergistic effect of other aliphatic alcohols



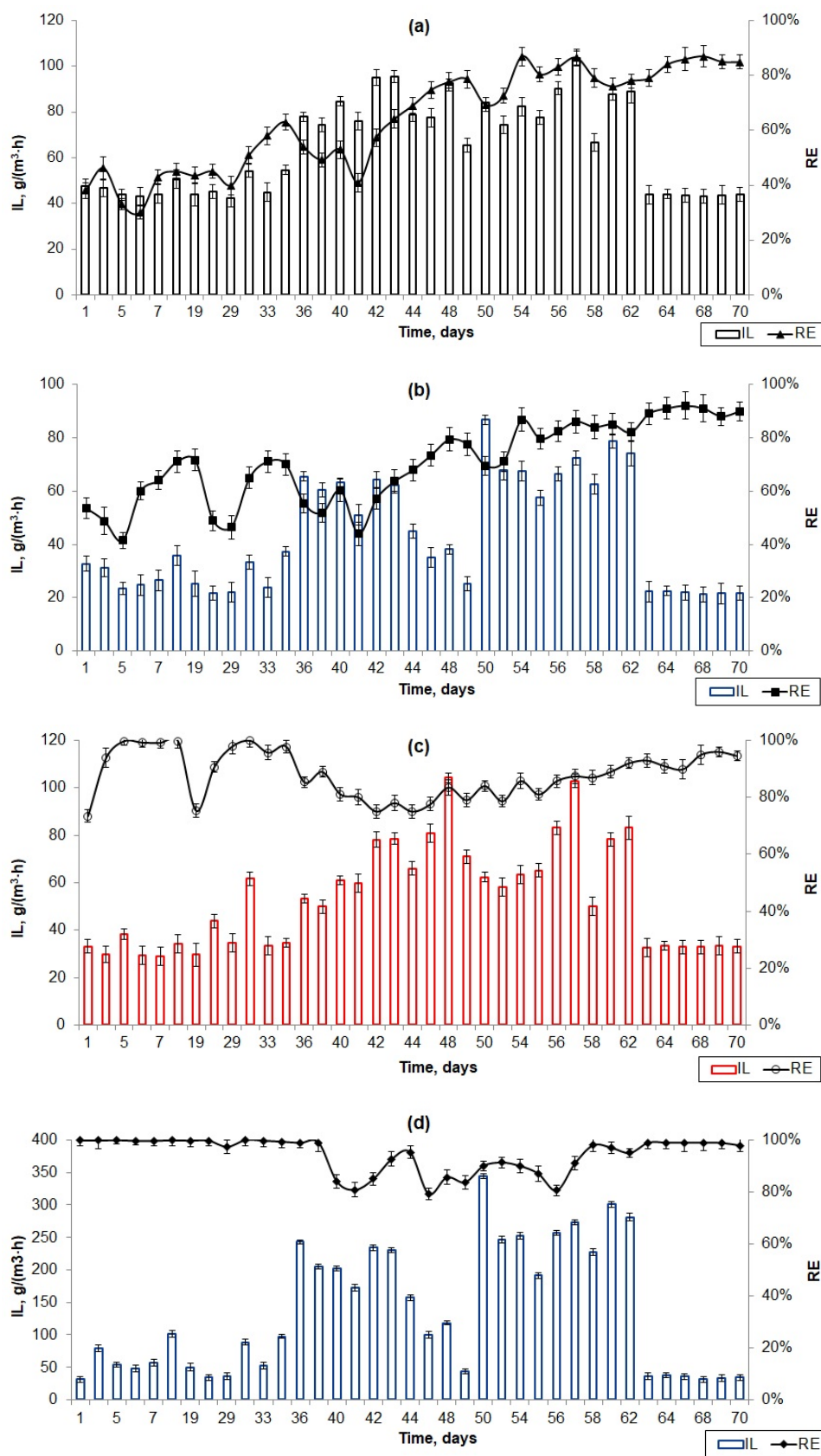


Figure 5. Performance of biotrickling filter E, treating a mixture of cyclohexane, hexane, toluene and ethanol vapors: results for cyclohexane (a), hexane (b), toluene (c) and ethanol (d).

on the removal performance of biotrickling filters has also been identified (Lamprea Pineda et al., 2021; Yang et al., 2018). For example, methanol has been proven to enhance the biotrickling filtration of n-hexane (Zehraoui et al., 2012). Methanol aided the removal of trichloroethylene and toluene, but only at low inlet loadings of methanol to other treated VOCs. At such conditions, methanol served as a co-metabolite and enhanced the removal performance of co-treated VOCs, while at higher inlet loadings inhibition effects were observed (Chheda and Sorial, 2016).

Synergistic effect of ethanol addition to the VOC mixture treated in a biotrickling filter results from increased biomass growth and increased water solubility of hydrophobic VOCs due to presence of ethanol. The presence of ethanol in the treated gas stream may therefore decrease the mass transfer limitation for hydrophobic VOCs to be transferred from gas to liquid phase (Lamprea Pineda et al., 2021; Rybarczyk, 2022; San-Valero et al., 2014).

### 3.2. Effects of gas composition on physicochemical aspects of biotrickling filtration systems

Effects of gas phase composition on the liquid phase were investigated with the following parameters: VOCs concentrations in the liquid phase (Fig. 6), changes of liquid phase surface tension (Fig. 7) as well as liquid phase pH and pressure drop for the gas phase across the biofilter packings (Fig. 9). In this section, variations in above given physicochemical parameters are discussed in terms of elimination capacities of investigated VOCs (Fig. 8). The results are presented for the steady-state conditions and were collected between 50<sup>th</sup> and 60<sup>th</sup> day of biotrickling filtration processes.

Variations in VOCs concentrations in the liquid phase for biofilters A–E are given in Figure 6. Concentrations are compared for the 2<sup>nd</sup> and 7<sup>th</sup> day after the MSM (i.e.

trickling liquid) renewal. Determined concentrations of VOCs in the liquid phase were below 10 ppm for all VOCs except for ethanol which were 81 and 149 ppm v/v for 2<sup>nd</sup> and 7<sup>th</sup> day, respectively. For biofilters A, B and C, concentrations of VOCs decrease from 2<sup>nd</sup> to 7<sup>th</sup> day after MSM renewal. Concentrations of cyclohexane in systems A and B are similar, while they are higher for system C (2<sup>nd</sup> day), probably due to the increase of cyclohexane solubility in the trickling liquid due to toluene presence. For biofilter D, concentration of toluene increases in the liquid between 2<sup>nd</sup> and 7<sup>th</sup> day after MSM renewal, probably due to longer contact time between liquid and gas containing moderately hydrophobic toluene. Similarly, but for all investigated VOCs, it is in the case of biofilter E. In the system E, however, increasing concentrations of VOCs in the liquid phase with time may also be related to their increased water solubility in the presence of ethanol. Additionally, as reported above, easily-soluble ethanol concentrations are also increasing in the trickling liquid with time (Fig. 6).

The mechanism of biotrickling filtration assumes absorption of VOCs to liquid and biofilm phases prior to their biodegradation (Barbusinski et al., 2017; Rybarczyk et al., 2019). It is favorable for high biofiltration performance if VOCs undergo biodegradation in the biofilm, rather than get absorbed by the liquid phase. It was found previously (Rybarczyk et al., 2021) that VOC concentrations in the liquid phase may either increase or decrease with time counted from the MSM renewal, depending on the stage of biofiltration (start-up or steady-state conditions), gas phase composition (increased concentrations when easily water-soluble VOCs are treated) and the system performance efficiency. In a well-operating biotrickling filter, the concentrations of VOCs in the liquid phase should be low and rather constant with time. Intensive increase of VOC concentrations in liquid phase with time after MSM renewal indicates that these compounds tend to be absorbed in the liquid rather than undergo biodegradation in

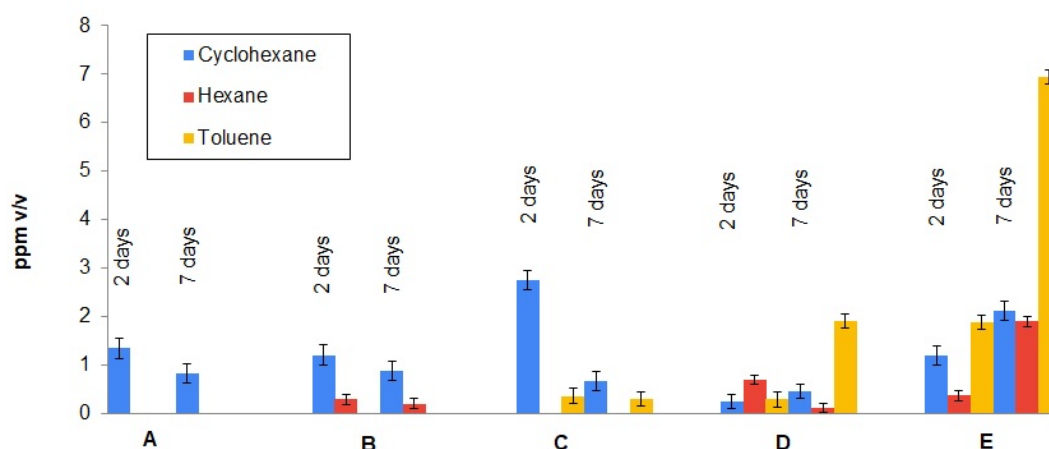


Figure 6. Head-space concentrations of VOCs in the trickling liquid for biofilters A – E (time after MSM renewal at steady-state process conditions).

the biofilter. The results presented in Figure 6 are in line with the above discussion.

A new approach of discussing the experimental BTF performance results is proposed based on trickling liquid surface tension measurements (Fig. 7). Surface tension changes (i.e. its decrease) of aqueous solutions can be a measure of increasing concentrations in the solution of substances with surface active properties, like surfactants or biosurfactants. Lower values of surface tension (i.e. lower than that of clean water, which is about 72 mN/m) can indicate higher affinity of liquid phase to dissolve hydrophobic compounds. Higher solubility of hydrophobic VOCs can decrease their mass transfer resistance from gas to liquid/biofilm phase and results in increased absorption of these compounds in the liquid phase. Consequently, their bioavailability to biodegradation is increased, and thus their removal rate from air is higher.

Decreased surface tension can lead to the increase of gas-liquid mass transfer coefficient (Lamprea Pineda et al., 2021), thus constituting favorable conditions for enhanced removal of hydrophobic VOCs.

It has been observed (Fig. 7) that surface tension decreases with time after renewal of MSM in all investigated systems. However, the extent of the decrease varies depending on the gas-phase composition. Based on the above discussion it may be stated that the lower the surface tension of the trickling liquid solution, the higher the affinity of the biofiltration system towards hydrophobic VOCs. It has been already proven that e.g. toluene increases the hydrophobicity of biofilm in BTF and enhances the mass transfer of hydrophobic VOCs towards both liquid phase and biofilm (Dou et al., 2022). This corresponds to the lowest values of surface tension for biofilters C, D and E, where toluene was present in the treated gas stream. The highest decrease of surface tension may thus be related to the presence of well water-soluble VOCs, which in turn favors increased solubility of hydrophobic VOCs. Additionally, systems C, D and E revealed better performance of

VOC removal from air than systems A and B (Figs. 1–5 and Fig. 8). Similarly, for systems C–E, increased biomass growth was observed (see discussion in Section 3.3). Increased biomass growth may result in both increased concentrations of organic matter washed out from the biofilm to trickling liquid as well as increased secretion of biosurfactants, resulting in decrease of surface tension of the liquid phase.

It may be concluded that the presence of toluene (biofilters C, D and E) and especially the presence of ethanol (biofilter E) decreases the mass transfer barrier for hydrophobic hexane and cyclohexane, increasing their availability for degradation in the biofilm and thus enhancing biofiltration performance. Determination of surface tension of the trickling liquid may therefore aid both identification of the biofilter capacity to treat hydrophobic VOCs and developing models for predicting biotrickling filtration performance.

The pH of trickling liquid decreases with time after the renewal of MSM solution (Fig. 9a). Slight decrease of the pH from 7 to about 6.8 (BTF A) and 6.6 (BTFs B – E) was observed which is typical for such biofiltration systems (Rybarczyk et al., 2021). This is related e.g. to the production of CO<sub>2</sub> and acid decomposition products during the biodegradation process. The lowest pH of about 6.6 was noted for biofilter E, which may also be related to the highest concentrations of VOCs identified in the trickling liquid solution. This results from the highest inlet loading of a biotrickling filter E and its highest performance efficiency compared to other investigated systems.

Similar observations on the relation between trickling liquid pH value and process performance (i.e. the higher the removal performance, the higher the pH drop) was observed by Marycz and co-workers (Marycz et al., 2022).

In this work, a mixed natural – synthetic biofilter packing was used. A typical problem of natural packings for biofiltration is their degradation with time and biofilter clogging issues.

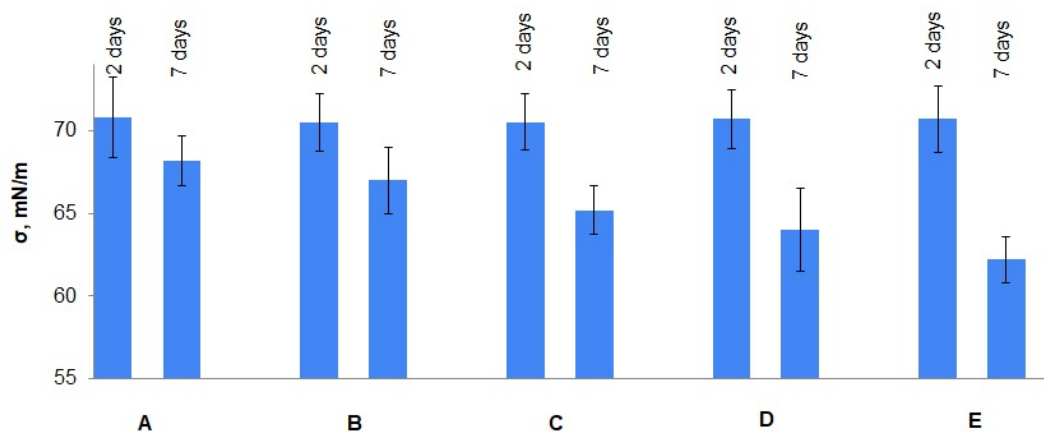


Figure 7. Changes in the surface tension of trickling liquid for biofilters A–E (time after MSM renewal at steady-state process conditions).

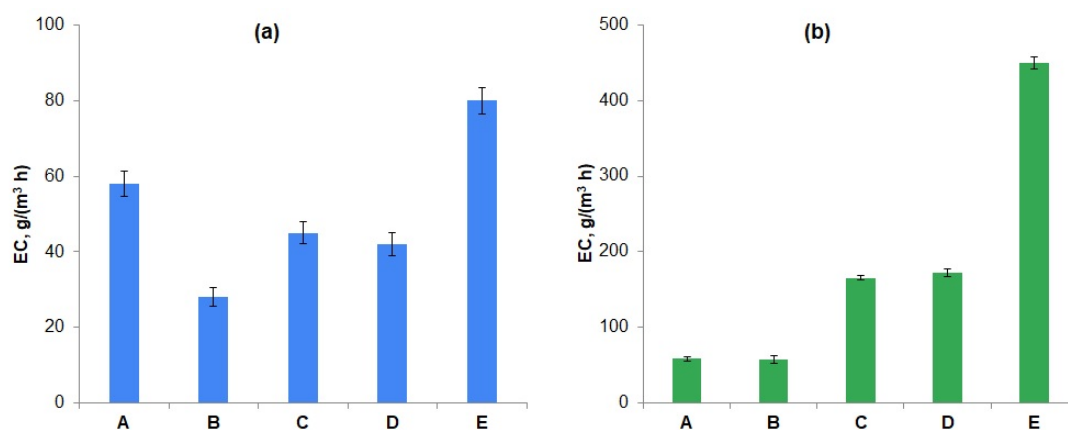


Figure 8. Maximum values of elimination capacities for biofilters A – E: with respect to cyclohexane (a); with respect to the sum of VOCs treated (b).

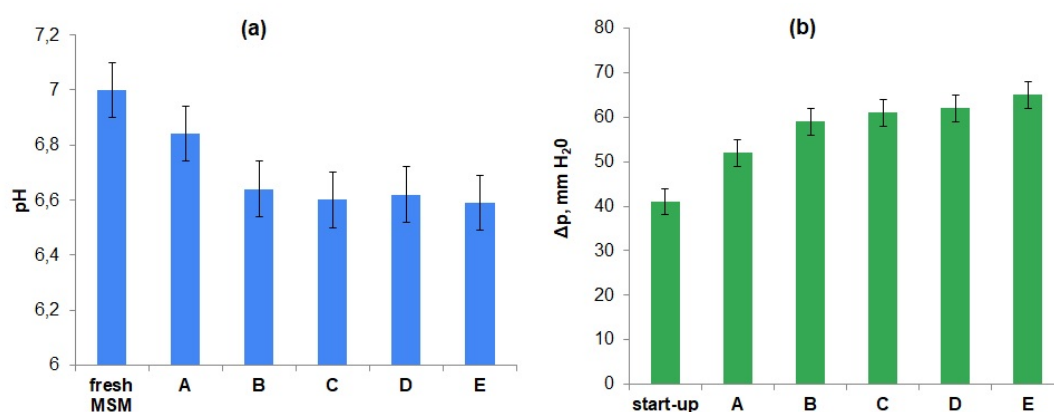


Figure 9. Physicochemical parameters for biotrickling filters A–E: pH of trickling solution after 7 days from MSM renewal at steady-state conditions (a); pressure drop across the biofilter packing after 70 days of biofiltration process (b).

However, in the reported studies, the problem of bed clogging did not arise during biofiltration processes. Pressure drop across the packing increased from about 40 to about 50–60 mm H<sub>2</sub>O, depending on the system (Fig. 9b). The highest pressure drop was noted for biofilter E which corresponded to the highest visually observed biomass growth. Values of a pressure drop are similar to other reported ones, indicating  $\Delta p$  values for well-operating systems at steady-state conditions i.e. within the order of a few to hundreds of Pa, equivalent to a few to tens of mm of H<sub>2</sub>O (Jiménez et al., 2017; Lebrero et al., 2021). The pressure drop for a given system is dependent on the size and material of a packing. The lower the size of packing elements, the higher the pressure drop (Zhang et al., 2021). Additionally, higher pressure drop is associated with natural rather than synthetic packing materials (Dobslaw et al., 2018).

### 3.3. Evaluation of biological activity of biotrickling filtration systems

Reliable assessment of the quality of peat can be achieved by testing the activity of enzymes, measuring the number of selected groups of microorganisms or the content of forms

of organic matter (carbon and nitrogen). In this paper, the microbial species in the biofilm were assessed with respect to the number and quality of colonies observed in the leachate from each biotrickling filter. Microorganisms were introduced to the biofilter with peat. Even though the polluted air flowing through the biofilter is recognized as the main carbon source, nitrogen, phosphorus and sulfur are required for microbial growth and these were supplied with the peat during the biofilter start-up. Wild peat microorganisms release various enzymes into the biofilter environment, but the most important for the changes taking place in the cultivated environment are those involved in the degradation of cellulose and other components of plant cells and in the transformation of nitrogen, phosphorus and sulfur. Therefore, highly diversified cultures of microorganisms in biofilter promote the degradation of carbohydrate, nitrogen and other polymers, as it requires multi-component enzyme systems produced by different groups of microorganisms. Application of peat as a material naturally colonized by microorganisms capable of degrading various air pollutant impurities is widely reported in the literature (Gospodarek et al., 2019; Khoramfar et al., 2018; López et al., 2019). Microbial characterization of peat highlights the fact that peat is able to provide sulfide-oxidizing bacteria and improve H<sub>2</sub>S removal (Dumont et al., 2012). Ac-



According to Lopez et al., during enhanced biological phosphorus removal process, CO<sub>2</sub> is continuously produced from the oxidation of organic matter and stripped due to process aeration (López et al., 2019). Guisasola et al. (2007) describes this problem as a non-biological reaction which affects the pH in a bioreactor or biofilter system. Similarly to peat, also compost is believed to improve soil quality and contribute to carbon sequestration, as differentiated microbial systems may be found in different stages of their growth, which allows to use a wide range of chemical carbon sources as feed material (Tambone et al., 2013). Therefore, the presence of diversified microorganisms allows a wide range of nutritional materials to act as carbon, nitrogen, phosphorus and sulfur sources.

The natural sequence of species developing in the biofilter is a consequence of the presence of nutrients in the peat, the composition of contaminated gas treating the biofilter, and the process conditions. As the presence of nutrients in the peat is considered, the sources of organic matter, sulfur, phosphorus and nitrogen need to be discussed. A high activity of dehydrogenases occurs as the content of organic matter, soil fertility and the number of soil microorganisms change throughout the experiment and with respect to the composition of gas introduced to the biofiltration columns. The presence of these enzymes is typical for the presence of bacteria and *Actinomycetes* and should be considered as an indicator of the intensity of respiratory metabolism of peat microorganisms. The assimilation of organic phosphorus from the peat by microorganisms takes place with the participation of phosphatases. Since microbial growth has been visually observed, also the activity of phosphatases in the soil environment occurred and reflected the activity of enzymes related to soil colloids and humic substances, free phosphatases in soil solution and phosphatases associated with alive and dead microorganisms. In the research, the source of phosphorus from peat needed to be supplemented. Cyclical introduction of a fresh portion of nutrient solution containing phosphate buffers allows to rejuvenate the microbiological system and related increase in VOC removal efficiency observed respectively on the third and fifth day introducing fresh MSM solution, for cyclohexane (Figs. 1–5), with no effects on removal of toluene (Figs. 2–5) and ethanol (Fig. 5) and increasing *RE* for all VOCs when ethanol was added to the gas mix-

tures (Fig. 5). The effect of surface tension decrease (Fig. 7) can be recognized and BTFs D and E (Figs. 4, 5) achieve higher *RE* values when the gas mixture is more complex than compared to biofilters B and C (Figs. 2, 3). The overall VOC consumption, measured as *RE* of pure cyclohexane (biofilter A), cyclohexane in the presence of hexane (biofilter B), and cyclohexane in the presence of toluene (biofilter C) is comparable. The course of the consumption of both cyclohexane and hexane does not significantly change when toluene is added in the mixture (biofilter D). The addition of both toluene and ethanol to the gas mixture (biofilter E) indicates changes in cyclohexane and hexane *RE*. It should be assumed that the presence of ethanol affects the microorganisms present in the biofilm structure, limiting the growth of those that are sensitive to the presence of ethanol in the environment. Moreover, despite the fact that in Petri plates with preparations from trickling solution taken from BTF E, less diversity of microorganisms was found, the number of colonies was greater than for preparations from biofilters A, B, C and D (Fig. 10). Also the surface tension drops to the lowest value for BTF E (Fig. 7).

As reported (Gribbins and Loehr, 1998), at high VOC loading rates, the mineralization of organic nitrogen may not be high enough to balance the effect of soluble nitrogen loss in the biofilter media. Therefore, the addition of nitrogen or decomposition of nitrogen bonded in the microbial remnants occurring throughout the biofiltration may be periodically required to obtain satisfying removal of VOCs from air. Among the bacteria that take free nitrogen from the peat and air, *Rhizobium* plays the greatest role (in the presence of oxygen). *Actinomycetes* contribute to the degradation of plant and animal residues, as well as hardly degradable compounds such as: chitin, lignin, higher fatty acids, steroids, cellulose or humic acids and therefore play an important role in the fertilization and mineralization of peat and in the degradation of resistant compounds. *Rhodococcus*, *Arthrobacter* and *Micrococcus* are highly active in the decomposition and mineralization of organic substances. Peat *Actinomycetes* have the ability to carry out reduction of sulphates to hydrogen sulphide, nitrates to nitrites, decomposing pectins and numerous organic compounds, as well as proteins with the release of nitrogen into the substrate.

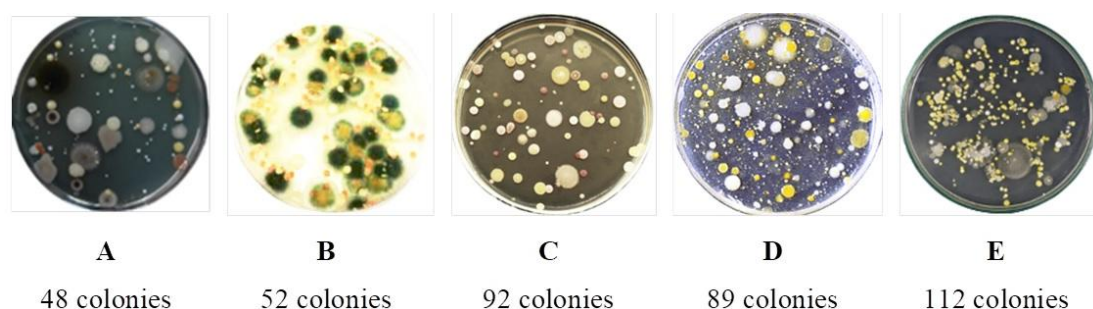


Figure 10. The diversification of microorganisms on Petri plates and number of colonies for preparations from the trickling liquid samples collected from BTFs during MSM renewal.

Another group of microorganisms occurring in peat are filamentous fungi of the genus *Trichoderma* sp. *Trichoderma*. These fungi produce lytic enzymes, which cause modifications in the environmental conditions, i.e. by creating unfavorable conditions for the development of other fungi. On the other hand, lignin peroxidase isolated from *Phanerochaete chrysosporium* takes part in the decomposition of lignins, exhibits low substrate specificity and catalyzes the oxidation of lignin and other structurally diverse compounds known to be resistant to biodegradation. Amongst this group, aromatic and aliphatic hydrocarbons, chlorinated organic compounds, pesticides and dyes can be mentioned and considered as VOCs. Therefore, cooperation between fungi and bacteria is advantageous, since different oxygen routes are adopted. Enhancement of biodegradation of pollutants can be achieved by adjusting the parameters that have the primary influence on the growth of microorganisms, thus increasing not only their number, but also their degradation activity. Ethanol decreases the diversity of colonies and therefore significantly affects the process efficiency. The review paper by Hammes et al. (2011) summarizes that the main purpose of biofiltration is the removal of biodegradable organic carbon, which can be enhanced in all biofilters, when biological component comprises indigenous bacteria that proliferate in biofilms at low nutrient concentrations or when the diversity of microbes is promoted by addition of a porous material. Since the layer of a biofilm formed in the biofilter has a certain thickness, also air and oxygen distribution may affect the system. Cabrera et al., (2019) reported that predominant microorganisms used in biofiltration are aerobic and require oxygen to metabolize substrates. The proportion of oxygen required for biological survival on the surface of the biofilm depends on the microbial culture present in the biofilter. Aerobic heterotrophic bacteria require at least 5%–15% oxygen in the inlet gas, while the facultative anaerobic bacteria and fungi in the depth of the biofilm require lower concentration of oxygen. Anoxic conditions of the biofiltration in the depth of the biofilm may occur only when the final electron acceptor is nitrate and/or nitrite (Cabrera et al., 2019).

Microbes capable to use hydrocarbons (i.e. cyclohexane, hexane) and organic compounds (i.e. ethanol and toluene) as sources of carbon and energy are also capable of producing biological surfactants (BS), lowering the surface tension of aqueous solutions and emulsifying organic pollutants. This type of micro-emulsions promotes the association of hydrocarbon droplets and facilitates their transport through hydrophobic channels of the cytoplasmic membrane. Moreover, by lowering the surface tension, BSs increase interfacial surface occupied by hydrophobic ingredients, as well as reduce tension allowing hydrophobic substances to be mixed with water soluble compounds. The lipophilic part of the stream is not capable of forming hydrogen bonds in the water phase and therefore the reduction of free energy occurs through adsorption of the hydrophobic part on the organic matrix or by the formation of micelles. The reduction of surface ten-

sion in the effluents with a more complex matrix should be seen not only in relation to the gas mixture composition, but also in relation with the composition related to additional substances secreted by microorganisms functioning in the biofilm. On the basis of the performed tests, however, there is no knowledge whether the reduction of surface tension in ethanol-containing matrices is associated with the emergence of larger amounts of BS under ethanol conditions, or with the death of microorganisms and the release of the cytoplasmic content from cellular debris. This part of investigations shall be expanded in the further planned experiments. To the best knowledge of the authors, this issue has not yet been elucidated in the literature.

In a biotrickling filtration system, microorganisms able to use hydrocarbons and organic compounds as sole carbon sources need to develop biofilm structures on an enhanced interfacial area to reveal carbon reservoir from the hydrophobic components, despite possible toxic effects due to the presence of high VOC concentrations. Abubacker et al. (2019) reported that both physical and chemical conditions of the packing material and the composition of the waste gas have a great influence on the survival of microbial groups or the dominance of certain microbial species in biofilms. A natural sequence of microbial growth occurs in the biofilter system during the operational time (Abubacker et al., 2019). With respect to the obtained results, it can be concluded that both the biodegradability kinetics and mass transfer affect the biofiltration process in biotrickling filters. As each part of this balance is considered taking into account the limitations of carbon, nitrogen, sulfur and phosphorus availability, the mass transfer and kinetics of degradation may change along the height of the biofilter and depend on the thickness of the biofilm. Therefore, it should be assumed that a consortium of microorganisms occurs in the BTF packing and on the surface of the biofilm, microbes capable of working in the presence of oxygen that metabolize organic and nitrogen compounds. The limitations in this area are related to the kinetics of biotransformation. On the other hand, removal of hydrophobic substances may be carried out in deeper sections of the biofilm and then the mass transfer of the compounds may have a limiting effect. Since the biomass grows and accumulates, the mass transfer may be hampered and the interfacial area reduced. Therefore, the conditions in the biotrickling filtration promote the development or at least decrease the mass transfer limitations at the interfacial area (especially BTF E), since the inner layer of the biofilm is continuously rejuvenated.

### 3.4. Evaluation of plat-based experiments

The authors of this paper are convinced that in the current situation of environmental pollution on one side, and economic crisis on the other, new strategies for managing environmental issues are urgently needed, especially for waste management. In this perspective, coupling of air biofiltration

process (regarded as sustainable and environmentally-friendly technology) with plant cultivation was proposed, including the utilization of post-biofilter liquid stream. The assumption is that the composition of trickling liquid solution may be favorable for the plant growth, which may in the future be used e.g. for soil phytoremediation or production of biomass for energetic purposes. In such a way, circular economy ideas can be developed for technological processes.

Waste solution of MSM was used for watering of ryegrass in pot cultures. Weights of biomass for freshly cut (wet) and over-night dried ryegrass samples are given in Figure 11. It was found that utilization of a spent trickling liquid increased the ryegrass biomass weight compared to the control sample which was irrigated with distilled water. Obtained biomass weight is related to the BTF system from which the spent MSM solution was taken. The lowest biomass yield was noted for systems A and B while the highest for system E. This may be a result of the highest washing out effect of organic components from BTF E, due to the most intensive biomass growth within the biofilter, which may be favorable for the plant growth. The pH determined for control sample was about 6.10, while for biofilters A, B, C, D and E these were 6.65, 6.62, 6.55, 6.45 and 6.40, respectively.

The results of plant-based experiments are promising and require more in-depth studies. It is probable that the biomass yield could be higher when e.g. better growth conditions would have been secured (the experiment was carried out at room conditions in winter season with little light available). What is more, coupling air biofiltration with plant cultivation may be also focused on polishing of biofilter-treated air by means of its passing through above-ground parts of plants (leaves). This requires proper selection of plant species, allowing the uptake of possible minor concentrations of VOCs that can still be present in the treated air. At the same time, CO<sub>2</sub> from post-biofilter air can be captured by plants since as a result of biodegradation, CO<sub>2</sub> concentrations in the outlet gas from biofilter are higher than in the inlet stream. This aspect requires further investigations.

## 4. CONCLUSIONS

In this work, biotrickling filtration of cyclohexane from air containing two-, three- or four-component VOC mixtures with different hydrophobicity were studied. Investigations of biofiltration performance of gas mixtures is a valuable piece of work because it mimics real gas effluents and is increasingly more popular in BTF research. It was found that the removal of cyclohexane from gas mixture depended on the physicochemical properties of the co-treated VOCs and the lower the hydrophobicity of the co-treated VOC, the higher the removal efficiency of cyclohexane. The performance of biotrickling filtration of cyclohexane was discussed in terms of changes of physicochemical parameters of the trickling liquid (pH, absorption of VOCs in the liquid phase, surface tension). To the best knowledge of the authors, the evaluation of surface tension of liquid phase for the assessment of enhanced biofiltration performance of hydrophobic VOCs has not been reported in the literature previously. It was found that the highest decrease of the trickling liquid surface tension was achieved for biofilter treating a mixture of cyclohexane, hexane, toluene and ethanol. What is more, for this biotrickling filtration system, the process performance was the highest, which may due to the most intensive biomass growth within the biofilter as well as synergistic effect of ethanol and toluene presence with respect to the removal of hydrophobic hexane and cyclohexane. Maximum elimination capacity of 95 g/(m<sup>3</sup>·h) for cyclohexane was reached corresponding to the total inlet loading of VOC mixture equal to 450 g/(m<sup>3</sup>·h).

A practical approach of utilizing a mixed natural/synthetic packing for a biotrickling filter, presenting promising performance and limited maintenance requirements is proposed.

Additionally, utilization of a spent trickling liquid for ryegrass cultivation was proposed. The resulting biomass yield was higher for the plant samples watered with the post-biofilter liquid compared to the control sample irrigated with distilled water. The possibility of coupling air biofiltration with other

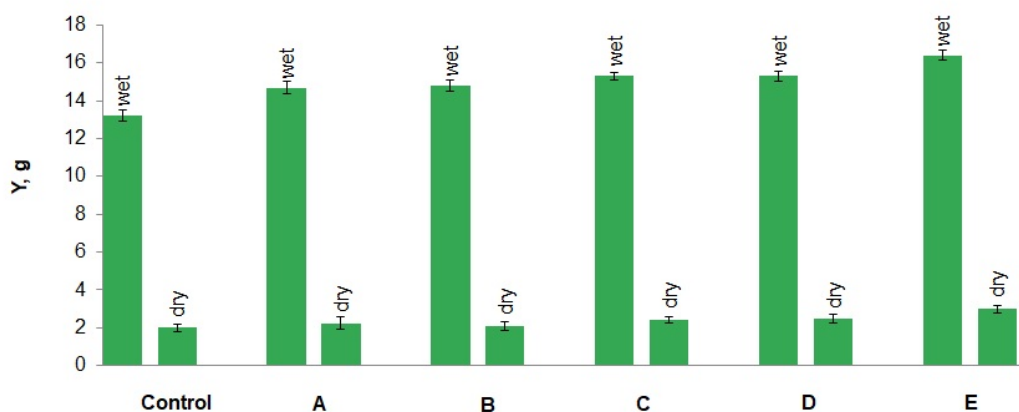


Figure 11. Biomass weights from ryegrass: control sample watered with distilled water vs. plants watered with spent trickling liquid.

bio-based treatment technologies lies within a circular economy assumptions and requires further studies to maximize the economic, technical and environmental benefits of this approach.

## ACKNOWLEDGMENTS

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## SYMBOLS

BS	biosurfactants
BTF	biotrickling filter
C	concentration of volatile organic compound, g/m <sup>3</sup>
EBRT	empty bed residence time, s
EC	elimination capacity, g/(m <sup>3</sup> ·h)
H	Henry's law constant, mol/(m <sup>3</sup> ·Pa)
IL	inlet loading, g/(m <sup>3</sup> ·h)
log P <sub>ow</sub>	octanol/water partitioning coefficient, -
MSM	mineral salt medium
ppm v/v	parts per million, volume fraction
Q <sub>G</sub>	gas volumetric flow rate, m <sup>3</sup> /h
RE	removal efficiency, %
V	volume of a biofilter packing, m <sup>3</sup>
VIC	volatile inorganic compound
VOC	volatile organic compound

Y biomass yield, g

### Greek symbols

Δp	pressure drop, mm H <sub>2</sub> O
σ	surface tension, mN/m

### Subscripts

IN	inlet
OUT	outlet

## REFERENCES

- Abubackar H.N., Veiga M.C., Kennes C., Das J., Rene E.R., van Hullebusch E.D., 2019. 2.31 – Gas-phase bioreactors, In: Moo-Young M. (Ed.), *Comprehensive Biotechnology (Third edition)*. Pergamon, 2, 446–463. DOI: [10.1016/B978-0-444-64046-8.00142-7](https://doi.org/10.1016/B978-0-444-64046-8.00142-7).
- Antonkiewicz J. (Ed.), 2021. *Przewodnik do ćwiczeń z chemii rolnej*. Publishing House of the University of Agriculture in Krakow.
- Barbusinski K., Kalemba K., Kasperczyk D., Urbaniec K., Kozik V., 2017. Biological methods for odor treatment – a review. *J. Clean. Prod.*, 152, 223–241. DOI: [10.1016/J.JCLEPRO.2017.03.093](https://doi.org/10.1016/J.JCLEPRO.2017.03.093).
- Botros M.M., Hassan A.A., Sorial G.A., Botros M.M., 2017. Role of fungal biomass in n-hexane biofiltration. *Adv. Microbiol.*, 7, 673–688. DOI: [10.4236/AIM.2017.710053](https://doi.org/10.4236/AIM.2017.710053).
- Cabrera G., Almenglo F., Ramírez M., Cantero D., 2019. 2.30 – Biofilters, In: Moo-Young M. (Ed.), *Comprehensive Biotechnology (Third Edition)*. Pergamon, 428–445. DOI: [10.1016/B978-0-444-64046-8.00082-3](https://doi.org/10.1016/B978-0-444-64046-8.00082-3).
- Cheng Y., He H., Yang C., Zeng G., Li X., Chen H., Yu G., 2016. Challenges and solutions for biofiltration of hydrophobic volatile organic compounds. *Biotechnol. Adv.*, 34, 1091–1102. DOI: [10.1016/j.biotechadv.2016.06.007](https://doi.org/10.1016/j.biotechadv.2016.06.007).
- Cheng Y., Li X., Liu H., Yang C., Wu S., Du C., Nie L., Zhong Y., 2020. Effect of presence of hydrophilic volatile organic compounds on removal of hydrophobic n-hexane in biotrickling filters. *Chemosphere*, 252, 126490. DOI: [10.1016/j.chemosphere.2020.126490](https://doi.org/10.1016/j.chemosphere.2020.126490).
- Chheda D., Sorial G.A., 2016. Effect of a ternary mixture of volatile organic compounds on degradation of TCE in biotrickling filter systems. *Water Air Soil Pollut.*, 227, 246. DOI: [10.1007/s11270-016-2950-8](https://doi.org/10.1007/s11270-016-2950-8).
- Chuang F.-J., Chou M.-S., Chang H.-Y., 2018. Biotrickling filtration of airborne styrene: a comparison of filtration media. *J. Air Waste Manage. Assoc.*, 68, 369–376. DOI: [10.1080/10962247.2017.1416002](https://doi.org/10.1080/10962247.2017.1416002).
- Cox C.D., Woo H.-J., Robinson K.G., 1998. Cometabolic biodegradation of trichloroethylene (TCE) in the gas phase. *Water Sci. Technol.*, 37, 97–104. DOI: [10.1016/S0273-1223\(98\)00239-X](https://doi.org/10.1016/S0273-1223(98)00239-X).
- Dobrzyniewski D., Szulczyński B., Rybarczyk P., Gębicki J., 2023. Process control of air stream deodorization from vapors of VOCs using a gas sensor matrix conducted in the biotrickling filter (BTF). *Arch. Environ. Prot.*, 49, 85–94. DOI: [10.24425/AEP.2023.145900](https://doi.org/10.24425/AEP.2023.145900).
- Dobslaw D., Woiski C., WinkleK.-H., Dobslaw C., 2018. Prevention of clogging in a polyurethane foam packed biotrickling filter treating emissions of 2-butoxyethanol. *J. Cleaner Prod.*, 200, 609–621. DOI: [10.1016/J.JCLEPRO.2018.07.248](https://doi.org/10.1016/J.JCLEPRO.2018.07.248).
- Dou X., Liu J., Qi H., Li P., Lu S., Li J., 2022. Synergistic removal of m-xylene and its corresponding mechanism in a biotrickling filter. *Process Biochem.*, 118, 404–412. DOI: [10.1016/J.PROCBIO.2022.05.010](https://doi.org/10.1016/J.PROCBIO.2022.05.010).
- Dumont E., Da Silva Cabral F., Le Cloirec P., Andrès Y., 2013. Biofiltration using peat and a nutritional synthetic packing material: influence of the packing configuration on H<sub>2</sub>S removal. *Environ. Technol.*, 34, 1123–1129. DOI: [10.1080/09593330.2012.736691](https://doi.org/10.1080/09593330.2012.736691).
- González-Martín J., Cantera S., Lebrero R., Muñoz R., 2023. Biofiltration based on bioactive coatings for the abatement of indoor air VOCs. *Sustainable Chem. Pharm.*, 31, 100960. DOI: [10.1016/j.scp.2022.100960](https://doi.org/10.1016/j.scp.2022.100960).
- Gospodarek M., Rybarczyk P., Szulczyński B., Gębicki J., 2019. Comparative evaluation of selected biological methods for the removal of hydrophilic and hydrophobic odorous VOCs from air. *Processes*, 7, 187. DOI: [10.3390/pr7040187](https://doi.org/10.3390/pr7040187).
- Gribbins M.J., Loehr R.C., 1998. Effect of media nitrogen concentration on biofilter performance. *J. Air Waste Manage. Assoc.*, 48, 216–226. DOI: [10.1080/10473289.1998.10463676](https://doi.org/10.1080/10473289.1998.10463676).



- Guisasola A., Vargas M., Marcelino M., Lafuente J., Casas C., Baeza J.A., 2007. On-line monitoring of the enhanced biological phosphorus removal process using respirometry and titrimetry. *Biochem. Eng. J.*, 35, 371–379. DOI: [10.1016/J.BEJ.2007.02.001](https://doi.org/10.1016/J.BEJ.2007.02.001).
- Hammes F., Velten S., Egli T., Juhna T., 2011. 6.36 – Biotreatment of drinking water, In: Moo-Young M. (Ed.), *Comprehensive Biotechnology (Third edition)*. Pergamon, 6, 463–476. DOI: [10.1016/B978-0-444-64046-8.00374-8](https://doi.org/10.1016/B978-0-444-64046-8.00374-8).
- He S., Ni Y., Lu L., Chai Q., Liu H., Yang C., 2019. Enhanced biodegradation of n-hexane by *Pseudomonas* sp. strain NEE2. *Sci. Rep.*, 9, 16615. DOI: [10.1038/s41598-019-52661-0](https://doi.org/10.1038/s41598-019-52661-0).
- Jiménez L., Arriaga S., Muñoz R., Aizpuru A., 2017. Effect of extended and daily short-term starvation/shut-down events on the performance of a biofilter treating toluene vapors. *J. Environ. Manage.*, 203, 68–75. DOI: [10.1016/j.jenvman.2017.07.057](https://doi.org/10.1016/j.jenvman.2017.07.057).
- Khoramfar S., Jones K.D., Boswell J., Ghobadi J., Paca J., 2018. Evaluation of a sequential biotrickling–biofiltration unit for removal of VOCs from the headspace of crude oil storage tanks. *J. Chem. Technol. Biotechnol.*, 93, 1778–1789. DOI: [10.1002/JCTB.5556](https://doi.org/10.1002/JCTB.5556).
- Kormanek M., Małek S., Banach J., Durło G., Jagiełło-Leńczuk K., Dudek K., 2021. Seasonal changes of perlite-peat substrate properties in seedlings grown in different sized container trays. *New For.*, 52, 271–283. DOI: [10.1007/s11056-020-09793-3](https://doi.org/10.1007/s11056-020-09793-3).
- Lamprea Pineda P.A., Demeestere K., Toledo M., Van Langenhove H., Walgraeve C., 2021. Enhanced removal of hydrophobic volatile organic compounds in biofilters and biotrickling filters: a review on the use of surfactants and the addition of hydrophilic compounds. *Chemosphere*, 279, 130757. DOI: [10.1016/j.chemosphere.2021.130757](https://doi.org/10.1016/j.chemosphere.2021.130757).
- Lebrero R., Rodríguez E., Collantes M., De Juan Alvarez C., Norden G., Rosenbom K., Muñoz R., 2021. Comparative performance evaluation of commercial packing materials for malodorants abatement in biofiltration. *Appl. Sci.*, 11, 2966. DOI: [10.3390/APP11072966](https://doi.org/10.3390/APP11072966).
- Lee S.-H., Kurade M.B., Jeon B.-H., Kim J., Zheng Y., Salama E.-S., 2021. Water condition in biotrickling filtration for the efficient removal of gaseous contaminants. *Crit. Rev. Biotechnol.*, 41, 1279–1296. DOI: [10.1080/07388551.2021.1917506](https://doi.org/10.1080/07388551.2021.1917506).
- Li K., Zhou J., Wang L., Mao Z., Xu R., 2019. The styrene purification performance of biotrickling filter with toluene-styrene acclimatization under acidic conditions. *J. Air Waste Manage. Assoc.*, 69, 944–955. DOI: [10.1080/10962247.2019.1604450](https://doi.org/10.1080/10962247.2019.1604450).
- López L.R., Mora M., Baeza J.A., Lafuente J., Gabriel D., 2019. Titrimetry as a tool for the on-line monitoring of biological activity in a desulfurizing biotrickling filter under aerobic conditions. *Process Saf. Environ. Prot.*, 124, 151–157. DOI: [10.1016/J.PSEP.2019.02.010](https://doi.org/10.1016/J.PSEP.2019.02.010).
- Marcinek J., Komisarek J. (Eds.), 2011. *Roczniki Gleboznawcze. Soil Science Annual*. 62(3). Wydawnictwo "Więś Jutra", Warszawa.
- Markoska V., Spalevic V., Gulaboski R., 2018. A research on the influence of porosity on perlite substrate and its interaction on porosity of two types of soil and peat substrate. *Agric. For.*, 64, 15–29. DOI: [10.17707/agricultforest.64.3.02](https://doi.org/10.17707/agricultforest.64.3.02).
- Marycz M., Brillowska-Dąbrowska A., Cantera S., Gębicki J., Muñoz R., 2023. Fungal co-culture improves the biodegradation of hydrophobic VOCs gas mixtures in conventional biofilters and biotrickling filters. *Chemosphere*, 313, 137609. DOI: [10.1016/j.chemosphere.2022.137609](https://doi.org/10.1016/j.chemosphere.2022.137609).
- Marycz M., Rodríguez Y., Gębicki J., Muñoz R., 2022. Systematic comparison of a biotrickling filter and a conventional filter for the removal of a mixture of hydrophobic VOCs by *Candida subhashii*. *Chemosphere*, 306, 135608. DOI: [10.1016/j.chemosphere.2022.135608](https://doi.org/10.1016/j.chemosphere.2022.135608).
- Meena V., Rajendran L., Kumar S., Jansi Rani P.G., 2016. Mathematical modeling of gas phase and biofilm phase biofilter performance. *Egypt. J. Basic Appl. Sci.*, 3, 94–105. DOI: [10.1016/j.ejbas.2015.09.007](https://doi.org/10.1016/j.ejbas.2015.09.007).
- Mudliar S., Giri B., Padoley K., Satpute D., Dixit R., Bhatt P., Pandey R., Juwarkar A., Vaidya A., 2010. Bioreactors for treatment of VOCs and odours – a review. *J. Environ. Manage.*, 91, 1039–1054. DOI: [10.1016/j.jenvman.2010.01.006](https://doi.org/10.1016/j.jenvman.2010.01.006).
- Nagendranatha Reddy C., Bae S., Min B., 2019. Biological removal of H<sub>2</sub>S gas in a semi-pilot scale biotrickling filter: optimization of various parameters for efficient removal at high loading rates and low pH conditions. *Bioresour. Technol.*, 285, 121328. DOI: [10.1016/j.biortech.2019.121328](https://doi.org/10.1016/j.biortech.2019.121328).
- Pachaiappan R., Cornejo-Ponce L., Rajendran R., Manavalan K., Femilaa Rajan V., Awad F., 2022. A review on biofiltration techniques: recent advancements in the removal of volatile organic compounds and heavy metals in the treatment of polluted water. *Bioengineered*, 13, 8432–8477. DOI: [10.1080/21655979.2022.2050538](https://doi.org/10.1080/21655979.2022.2050538).
- Revah S., Morgan-Sagastume J.M., 2005. Methods of odor and VOC control, In: Shareefdeen Z., Singh A. (Eds), *Biotechnology for Odor and Air Pollution Control*. Springer, Berlin, Heidelberg, 29–63. DOI: [10.1007/3-540-27007-8\\_3](https://doi.org/10.1007/3-540-27007-8_3).
- Rodríguez G., Dorado A.D., Fortuny M., Gabriel D., Gamišans X., 2014. Biotrickling filters for biogas sweetening: oxygen transfer improvement for a reliable operation. *Process Saf. Environ. Prot.*, 92, 261–268. DOI: [10.1016/j.psep.2013.02.002](https://doi.org/10.1016/j.psep.2013.02.002).
- Rybarczyk P., 2022. Removal of volatile organic compounds (VOCs) from air: focus on biotrickling filtration and process modeling. *Processes*, 10, 2531. DOI: [10.3390/PR10122531](https://doi.org/10.3390/PR10122531).
- Rybarczyk P., Marycz M., Szulczyński B., Brillowska-Dąbrowska A., Rybarczyk A., Gębicki J., 2021. Removal of cyclohexane and ethanol from air in biotrickling filters inoculated with *Candida albicans* and *Candida subhashii*. *Arch. Environ. Prot.*, 47, 26–34. DOI: [10.24425/aep.2021.136445](https://doi.org/10.24425/aep.2021.136445).
- Rybarczyk P., Szulczyński B., Gębicki J., 2020. Simultaneous removal of hexane and ethanol from air in a biotrickling filter–process performance and monitoring using electronic nose. *Sustainability*, 12, 387. DOI: [10.3390/su12010387](https://doi.org/10.3390/su12010387).
- Rybarczyk P., Szulczyński B., Gębicki J., Hupka J., 2019. Treatment of malodorous air in biotrickling filters: a review. *Biochem. Eng. J.*, 141, 146–162. DOI: [10.1016/j.bej.2018.10.014](https://doi.org/10.1016/j.bej.2018.10.014).
- Salamanca D., Dobslaw D., Engesser K.-H., 2017. Removal of cyclohexane gaseous emissions using a biotrickling filter system. *Chemosphere*, 176, 97–107. DOI: [10.1016/j.chemosphere.2017.02.078](https://doi.org/10.1016/j.chemosphere.2017.02.078).
- Sander R., 2015. Compilation of Henry's law constants (version 4.0) for water as solvent. *Atmos. Chem. Phys.*, 15, 4399–4981. DOI: [10.5194/acp-15-4399-2015](https://doi.org/10.5194/acp-15-4399-2015).

- San-Valero P., Peña-Roja J.M., Álvarez-Hornos F.J., Gabaldón C., 2014. Modelling mass transfer properties in a biotrickling filter for the removal of isopropanol. *Chem. Eng. Sci.*, 108, 47–56. DOI: [10.1016/J.CES.2013.12.033](https://doi.org/10.1016/J.CES.2013.12.033).
- San-Valero P., Peña-Roja J.M., Álvarez-Hornos F.J., Marzal P., Gabaldón C., 2015. Dynamic mathematical modelling of the removal of hydrophilic VOCs by biotrickling filters. *Int. J. Environ. Res. Public Health*, 12, 746–766. DOI: [10.3390/ijerph120100746](https://doi.org/10.3390/ijerph120100746).
- Sarkar P., Tiwari H., Garkoti P., Neogi S., Biswas J.K., Dey A., 2022. Chapter 24 – Biofiltration as a green technology for abatement of volatile organic compounds (VOCs): A synoptic review, In: Shah M., Rodriguez-Couto S., Biswas J. (Eds.), *An innovative role of biofiltration in wastewater treatment plants (WWTPs)*. Elsevier, 477–496. DOI: [10.1016/B978-0-12-823946-9.00019-X](https://doi.org/10.1016/B978-0-12-823946-9.00019-X).
- Schlegelmilch M., Streese J., Stegmann R., 2005. Odour management and treatment technologies: an overview. *Waste Manage.*, 25, 928–939. DOI: [10.1016/j.wasman.2005.07.006](https://doi.org/10.1016/j.wasman.2005.07.006).
- Sheoran K., Siwal S.S., Kapoor D., Singh N., Saini A.K., Alsanie W.F., Thakur V.K., 2022. Air pollutants removal using biofiltration technique: a challenge at the frontiers of sustainable environment. *ACS Eng.*, 2, 378–396. DOI: [10.1021/acsengineeringau.2c00020](https://doi.org/10.1021/acsengineeringau.2c00020).
- Sun Z., Yang B., Wang L., Ding C., Li Z., 2017. Toluene-styrene secondary acclimation improved the styrene removal ability of biotrickling filter. *Chem. Speciation Bioavailability*, 29, 54–59. DOI: [10.1080/09542299.2017.1301219](https://doi.org/10.1080/09542299.2017.1301219).
- Tambone F., Genevini P., Adani F., 2013. The effects of short-term compost application on soil chemical properties and on nutritional status of maize plant. *Compost Sci. Util.*, 15, 176–183. DOI: [10.1080/1065657x.2007.10702330](https://doi.org/10.1080/1065657x.2007.10702330).
- Vikrant K., Kim K.-H., Szulejko J.E., Pandey S.K., Singh R.S., Giri B.S., Brown R.J.C., Lee S.-H., 2017. Bio-filters for the treatment of VOCs and odors – A review. *Asian J. Atmos. Environ.*, 11, 139–152. DOI: [10.5572/AJAE.2017.11.3.139](https://doi.org/10.5572/AJAE.2017.11.3.139).
- Wu X., Lin Y., Wang Y., Wu S., Li X., Yang C., 2022. Enhanced removal of hydrophobic short-chain *n*-alkanes from gas streams in biotrickling filters in presence of surfactant. *Environ. Sci. Technol.*, 56, 10349–10360. DOI: [10.1021/acs.est.2c02022](https://doi.org/10.1021/acs.est.2c02022).
- Wu X., Lin Y., Wang Y., Yang C., 2023. Interactive effects of dual short-chain *n*-alkanes on removal performances and microbial responses of biotrickling filters. *Chem. Eng. J.*, 461, 141747. DOI: [10.1016/J.CEJ.2023.141747](https://doi.org/10.1016/J.CEJ.2023.141747).
- Yang C., Qian H., Li X., Cheng Y., He H., Zeng G., Xi J., 2018. Simultaneous removal of multicomponent VOCs in biofilters. *Trends Biotechnol.*, 36, 673–685. DOI: [10.1016/j.tibtech.2018.02.004](https://doi.org/10.1016/j.tibtech.2018.02.004).
- Yoshikawa M., Zhang M., Toyota K., 2017. Biodegradation of volatile organic compounds and their effects on biodegradability under co-existing conditions. *Microbes Environ.*, 32, 188–200. DOI: [10.1264/JSME2.ME16188](https://doi.org/10.1264/JSME2.ME16188).
- Zehraoui A., Hassan A.A., Sorial G.A., 2012. Effect of methanol on the biofiltration of *n*-hexane. *J. Hazard. Mater.*, 219–220, 176–182. DOI: [10.1016/j.jhazmat.2012.03.075](https://doi.org/10.1016/j.jhazmat.2012.03.075).
- Zhang Y., Liu J., Li J., Yue T., 2021. Effects of filler voidage on pressure drop and microbial community evolution in fungal bio-trickling filters. *Chemosphere*, 273, 129710. DOI: [10.1016/j.chemosphere.2021.129710](https://doi.org/10.1016/j.chemosphere.2021.129710).
- Zhang Y., Denga W., Qina Y., Yanga Z., Liua J., Lia J., 2018. Research on simultaneous removal of cyclohexane and methyl acetate in biotrickling filters. *Proceedings of the 2nd International Conference of Recent Trends in Environmental Science and Engineering (RTESE'18)*, Niagara Falls, Canada, 10–12 June 2018, 107. DOI: [10.11159/rtese408.107](https://doi.org/10.11159/rtese408.107).