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Removal of volatile organic compounds and hydrogen sulfide in biological wastewater treatment plant using the compact trickle-bed bioreactor

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A B S T R A C T

Odours emitted by biological wastewater treatment plants (WWTPs) may cause a nuisance and negatively impact people's health. It is possible to tackle this issue using known deodorization technologies such as adsorption, absorption, combustion, catalytic oxidation, and biofiltration. However, applying some of these may lead to secondary pollution, high operating and investment costs, periodic replacing, utilising or regenerating reactor or filter bed, or using expensive catalysts. It is possible to avoid problems of this kind using the compact trickle-bed bioreactor (CTBB) technology to biodegrade odours emitted from WWTPs. A pilot-scale CTBB reactor, with a total volume of 1.07 m^3, diameter of 0.8 m and height of 2.13 m, was installed on the premises of a municipal WWTP. At variable parameters of the biodegradation process, odour reduction was investigated using mobile measuring devices to detect hydrogen sulfide (H_2S) and volatile organic compounds (VOCs). The factor of H_2S conversion was 71%–97%, and that of VOC conversion was 82%–94% when the gaseous-phase flow rate ranged from 7–30 m^3 h^{-1}, at pH = 7 in the liquid-phase. The research results confirm the significant potential of CTBB technology for application in the municipal sector.

Keywords: Air purification; Biodegradation; Hydrogen sulfide; Odour removal; Biotrickling filter; Trickle bed bioreactor; Volatile organic compound

1. Introduction

One of the consequences of the population tending to concentrate in urban areas or settlements scattered in rural areas is people's exposure to odours. Recent decades have seen increasing public awareness of the associated adverse health effects. Driven by the pertinent regulations and social image concerns of the operators of odour-emitting facilities, it is becoming increasingly common to make such facilities airtight or apply odour mitigation measures.

The established technologies for degrading odours in gas streams are physicochemical, for example, chemical scrubbing, combustion, catalytic oxidation, activated-carbon adsorption, and biological ones, for example biofiltration and biotrickling filtration [1]. Some literature sources discussed the suitability of different technologies for treating gases emitted from wastewater treatment plants, for example, Barbusiński and Kalemba [2] focused on biological methods, and Liang et al. [3] reviewed Chinese odour-reducing practices. Among novel ideas on the degradation of gaseous odorants, the study Fan et al. [4] reported on the application of membrane technology, and Kim et al. [5] investigated a deodorization device combining catalytic and adsorption technologies.

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Biological treatment technologies appear to outcompete physicochemical technologies in terms of environmental friendliness. It is possible to avoid using hazardous chemicals or disposal of waste in landfills while reaching the odour removal efficiency of 98% for biofilters and 99% for biotrickling filters. These results were pointed out by the study of Alfonsin et al. [6] and supported by the study of Wu et al. [7] who reviewed applications of the said technologies. It is worth noting that biological air purification processes are carried out in mild conditions – under atmospheric pressure and moderate temperature up to 40°C [8].

Odours and volatile organic compound (VOCs) emitted from wastewater treatment plants can be removed using well-known biofilters. The pollutant degradation occurs in a moist bed of particles covered by an active biofilm. Despite their disadvantage due to the need for regular replacement of the used bed, biofilters are economical and satisfactory solutions in many cases. However, they are sometimes ineffective in degrading odours [9]. They may also generate additional problems, such as difficulty maintaining the filter bed's proper humidity and pH and corrosion damage to biofilter components or foundations caused by hydrogen sulfide (H_2S) [10].

Biotrickling filters (BTFs, also known as trickle bed bioreactors) are an increasingly studied alternative technology. It combines the pollutant absorption from the gas mixture into the liquid, pollutant degradation in the biofilm maintained on filter bed particles, and liquid recirculation in a single apparatus. The biofilm contains microorganisms selected for their ability to degrade the pollutant and introduced by inoculation to the bioreactor bed. Schiavon et al. [11] noted that more precise process control and a much smaller footprint of the odour-removal equipment put the BTFs in a more favourable light than biofiltration technologies. More recently, Rybarczyk et al. [12] gave a similar evaluation of biotrickling filtration. The present authors share this view observing that BTFs' advantages make them particularly well suited for retrofitting biofilter-based odour removal systems of the wastewater treatment plants (WWTPs).

In the recent decade, there has been a steady stream of new research papers on biotrickling filters showing their potential for implementation. Lopez et al. [13] investigated the biodegradation of a mixture of volatile pollutants (including H_2S) from the air using lab-scale BTFs. The pollutant mixture consisted of methanol, α-pinene, and H_2S at concentrations of 0.05–3.3, 0.05–2.7, and 0.01–1.4 g m^{-3}. The microbial consortium for the inoculation of the filter bed included an autotrophic H_2S-degrading culture and pure strains of *Candida boidinii*, *Rhodococcus erythropolis*, and *Ophiostoma stenoceras*. When maintaining the pH range of 6.0 ± 0.4 in the liquid-phase and empty bed retention time (EBRT) values up to 38 s, the maximum removal efficiency of H_2S was 99%, methanol was 100%, and α-pinene – 67%; notably, the presence of H_2S did not affect the degradation of methanol and α-pinene.

Dorado et al. [14] studied a BTF for reducing emissions from a WWTP sludge composting plant. They investigated the effects of EBRT, pH control, and water make-up flow rate during a test period of eight months. The bioreactor bed was inoculated using sludge from the nitrifying reactor of the same WWTP. At EBRT values below 10 s and pH range 7.4–7.6, the achieved maximum elimination capacity (EC) was 13 g $N\cdot m^{-3}\cdot h$ and 3.3 g $C\cdot m^{-3}\cdot h$ for NH_3 and VOCs, respectively. The authors identified liquid renewal as a decisive factor for avoiding substrate inhibition by nitrite formation or NH_3 accumulation in the filter bed.

Bąk et al. [15] successfully applied the biotrickling filter technology to remove VOC mixture from the air. They maintained a pH level of around 7 in the liquid-phase. *Cedecea davisae* and *Pseudomonas* species were the dominant bacterial components of the biofilm. The range of EBRT values was 19.2–57.6 s. The research results indicated a 95% removal efficiency for a VOC mixture containing styrene, ethanol, and dimethyl sulfide.

Wu et al. [16] reviewed the design, mechanism, and standard analytical methods of recent BTF advances aimed at VOCs and odour removal. In addition, they evaluated and discussed operating conditions, mass transfer, packing materials, microorganisms, and their potential for improving the removal performance of BTFs.

Bu et al. [17] studied, in a lab-scale BTF, the possibility of improving H_2S removal performance through the intermittent liquid supply to the filter bed. At a pH level of 1–2, *Acidithiobacillus* was the dominant microorganism in the collected biofilm samples. Maintaining short EBRT values of up to 6 s, a biodegradation efficiency of 100% was achieved at low pollutant concentration at the filter inlet (below 100 ppmv) for continuous and intermittent liquid supply. The intermittent supply ensured better biodegradation efficiency at inlet H_2S above 120 ppmv.

Researchers used laboratory or pilot-scale BTFs to investigate the biodegradation of diverse gaseous pollutants emitted from industrial wastewater treatment plants. Nitrogenous compounds were the primary pollutants in the fishmeal industry [18]. The emissions in the chemical fibre industry mainly contain alcohol, aromatic compounds, acetate, alkanes, and odorous gases, including NH_3 and H_2S [19]. San-Valero et al. [20] investigated VOC (mainly acetone) biodegradation in a BTF applied in a wood finishing and painting shop.

Most of the analyses performed have built on studies conducted under laboratory conditions that usually are far from the actual ones in a wastewater treatment plant. Laboratory investigations cannot simulate sudden fluctuations of pollutant concentration, filter bed overload, or process disturbances resulting from random events or extreme weather conditions. Therefore, it seems essential to investigate the performance of odour biodegradation under actual wastewater treatment plant conditions [21].

Kasperczyk et al. [22] studied applying a pilot-scale biotrickling filter (called compact trickle-bed bioreactor − CTBB, a proprietary product of Ekoinwentyka Ltd.) to remove H_2S and volatile organic compounds from the air discharged from a small WWTP. During the study period, the plant capacity was around the population equivalent of PE = 10,000. The bioreactor bed was inoculated with a bacterial consortium including *Pseudomonas fluorescens* selected from Ekoinwentyka's collection of microorganisms and other strains (*Thiobacillus* sp.) isolated from the plant's activated sludge. The pH level was between 5.5 and 7.5, and EBRT ranged from 1.2 to 18 min. The measurements indicated 97% H_2S degradation occurring at pollutant concentrations around 200 ppm and 85%–99% VOC degradation in the 25–240 ppm concentration range. However, the considered plant was not fully representative of the municipal WWTPs. Apart from its small size, it was characterized by specific fluctuations in pollutant concentrations resulting from the intermittent supply of wastewater transported by tanker cars on working days only.

The novelty of the present research is that, contrary to most studies conducted so far, the test site is a representative medium-sized municipal WWTP. Its capacity expressed as population equivalent is PE = 218,950. It is continuously supplied with wastewater streams coming mainly from the cities of Chorzów and Świętochłowice in the Silesia Region of Poland. Due to its size and supply mode, it is representative in terms of daily, weekly and seasonal cycles of variable wastewater flow and pollutant load.

The research objective is to evaluate the efficiency of odour and VOC biotreatment in pilot-scale CTBB and the possibility of upscaling this technology to a full industrial scale. The effects of process control parameters on odor biodegradation efficiency are studied to optimise and maximise the performance of the CTBB biopurification technology. The studied parameters include variable gas-phase flow rates and different pH levels in the circulating liquid. At a fixed volume of the bioreactor bed, the gas flow rate determines the EBRT, that is, the duration of the time interval available for pollutant absorption from the gas mixture into the liquid and pollutant degradation in the biofilm.

The expected results will enable assessing the studied parameters' impact on the efficiency of the biodegradation of odours and VOCs, providing valuable knowledge on biopurification processes under real conditions of a municipal WWTP. The results will also provide the basis for further studies, for example, on the influence of liquid-phase flow on the efficiency of pollutant removal or biodegradation of specific groups of odorous gases, such as sulfur- or nitrogen-containing compounds.

2. Materials and methods

This section summarises the information specific to the experimental study on the efficiency of biodegradation of odours (including H_2S and VOCs) carried out using a pilot CTBB reactor that processed off-gases from the municipal wastewater treatment plant "Klimzowiec" located within the administrative area of the city of Chorzów. In performing the research, Ekoinwentyka Ltd. relied on the approach developed and experience gathered during previous projects on CTBB application for odour mitigation [22,23].

2.1. Test site

Fig. 1 shows the pilot CTBB installed on the "Klimzowiec" WWTP premises. The plant applies an integrated process of nitrogen, carbon and phosphorus removal from the wastewater.

The off-gases supplied to the CTBB reactor consisted of polluted air discharged from the hermetic tanks that contained excess sludge, thickened sludge, and digested sludge. These tanks constitute the most challenging part of the concerned WWTP regarding odour emissions. The primary pollutants were H_2S and VOCs.

During regular WWTP operation, the polluted air is cleaned in a biofilter 8 m long and 4 m wide, filled with ground pine bark where active microorganisms form a biofilm on the bark particles. The nominal biofilter capacity is 2,800 $m^3\ h^{-1}$ (m^3 of polluted air/h); however, biofilter efficiency has proved insufficient in everyday use leading to incidents of excessive odour emissions from the WWTP area. The pilot bioreactor was deliberately placed at the described site to see if one could cope with the biodegradation of the nuisance pollutants using CTBB technology. The maximum throughput of the pilot unit was 30 $m^3\ h^{-1}$, that is, slightly more than 1% of the biofilter capacity. The experience proves that pilot-test results obtained at this capacity level may be sufficient for technology upscaling to the industrial level [23].

During the tests, the CTBB was continuously supplied with an air stream drawn from the biofilter supply line. The volumetric air flow and pH value in the circulating liquid-phase in the CTBB were the parameters that the researchers could control. The concentrations of pollutants varied depending on the variable WWTP load.

2.2. Experimental set-up

The heart of the experimental setup was a pilot CTBB reactor made of 304 stainless steel with a tank diameter d = 0.8 m and height h = 2.13 m. The reactor bed includes a packing made of polypropylene rings that is 1.2 m high and has a working volume of V_{bed} = 0.6 m^3. The microflora used for pollutant degradation originated from a mixture of microorganisms from two sources: the biofilter currently operated in the "Klimzowiec" WWTP and the Ekoinwentyka-owned collection of microorganisms that include *P. fluorescens* strain. The mixed culture was first adapted to the odours emitted from the WWTP at a temperature of 302 ± 5 K (~29°C) in laboratory conditions. After completing the adaptation, the microorganisms were used to inoculate the bioreactor bed, creating the active biofilm on the surfaces of packing elements.

The liquid and gas-phases flow in co-current downwards through the CTBB bed. While the gas-phase consists of polluted air, the liquid-phase is a suspension of microorganisms in a water solution of mineral salts, including ones that contain micro-nutrients necessary for microorganism growth.

Fig. 1. Pilot-scale compact trickle-bed bioreactor in the wastewater treatment plant.

A distributor positioned above the bioreactor bed disperses the liquid uniformly over the packing surface to ensure constant wetting and micro-nutrient supply to the active biofilm immobilized on the packing elements. Pollutant biodegradation occurs in the bed. The purified air flows through a condenser and is discharged to the ambient, so the bioreactor tank is kept at near-atmospheric pressure. CTBB operation is fully automated, making it possible to maintain stable pH and temperature levels. The pH value was adjusted during the experiments by dosing appropriate amounts of buffer solutions (10% solution of KH_2PO_4 or 10% solution of KOH). A temperature sensor in the circulation loop and an electric heater inside the bioreactor tank ensured the liquid-phase temperature stabilization.

More information on CTBB details and the procedures for selecting and adapting microorganisms to degrade the pollutants is available in the work by the study of Kasperczyk et al. [23].

2.3. Sampling and measurement methods

The presence and activity of the microorganisms were controlled by spectrophotometric analysis. The relevant instruments included Hach Lange DR2800 spectrophotometer (from Mettler Toledo) and MBL 180T laboratory optical microscope with an integrated camera (from mikroLAB, Poland).

Determining the indices to characterize the efficiency of odour and VOC biotreatment in the CTBB necessitates measuring pollutant concentration in the gas streams at the bioreactor inlet and outlet. The measuring instruments used in the tests included mobile gas detectors:

- Industrial Scientific Ventis MX4 (electrochemical sensor – H_2S measurement in the concentration range 0–500 ppm in 0.1 ppm increments, data logging in 10 s intervals). More information is available at: https://www.indsci.com/en/products/gas-detectors/ventis-mx4/ventis-mx4-monitor/
- Honeywell MiniRAE 3000 (VOC analyser with PID detector – the standard of the measured gas: isobutylene, M = 56.106 g mol^{-1}, enables VOCs reading in ppm by volume). More information is available at: https://sps.honeywell.com/us/en/products/safety/gas-and-flame-detection
- Honeywell MultiRAE (VOC analyser with PID detector – the standard of the measured gas: isobutylene, M = 56.106 g mol^{-1}; VOC measurement in the concentration range 0–5,000 ppm). It can also detect H_2S (0–200 ppm), CO (0–2,000 ppm), and O_2 (0%–30% vol.). More information is available at: https://sps.honeywell.com/us/en/products/safety/gas-and-flame-detection

The evaluation of the operating efficiency of the CTBB pilot reactor included calculating pollutant load Ms, gas retention time t_g, pollutant EC, and pollutant removal efficiency (conversion factor) K according to the following formulas:

$$\text{Ms} = \frac{C_{\text{gin}}}{t_g} \tag{1}$$

$$t_g = \frac{V_{\text{bed}}}{V_g} \tag{2}$$

$$\text{EC} = \frac{C_{\text{gin}} - C_{\text{gout}}}{t_g} \tag{3}$$

$$K = \frac{C_{\text{gin}} - C_{\text{gout}}}{C_{\text{gin}}} \times 100\% \tag{4}$$

where C_g denotes pollutant concentration and subscripts in, out indicate bioreactor inlet and outlet. V_{bed} – empty bed volume, V_g – volumetric gas flow rate.

3. Results and discussion

The research was carried out from June to August when the highest temperatures occur in Poland – up to 30°C. It is a period when the emissions of pollutants from the WWTPs reach their highest levels leading to the most significant odour nuisance risk for the neighbouring houses and recreational areas.

A stable biofilm was present throughout the test period in the bioreactor bed. A detailed analysis of the bacterial flora of biomass samples enabled the identification of *Thiobacillus novellus* and *P. fluorescens* as the dominant bacteria strains.

The efficiency of pollutant degradation was investigated for H_2S and VOCs. The range of gas-phase flow rate was V_g = 7–30 m^3 h^{-1}, equivalent to the EBRT range of t_g = 1.2–5.1 min, and the flow rate of the liquid-phase was V_l = 7 m^3 h^{-1} (±5%). Investigating the impact of variable gas-phase flow rate on the air biopurification efficiency was aimed at selecting the optimum EBRT range to scale up the CTBB reactor for applications in municipal WWTPs.

The tests included bioreactor operation at two different pH values in the liquid-phase, namely 5 and 7. The latter value is regarded as a reference because neutral and alkaline pH intensifies the mass transfer, thus promoting a higher H_2S removal rate [24]. Furthermore, as studied by Kim and Deshusses [25] and Cheng et al. [24], maintaining a slightly alkaline pH in the liquid-phase facilitates the growth of sulfur-oxidizing bacteria. Consequently, a pH of 7.0–8.0 is recommended, especially during the start-up period [26]. On the other hand, as H_2S absorption decreases the liquid's pH level, pollutant solubility drops [27]. Therefore, repetitive control actions (injecting buffer solutions into the liquid) to stabilize pH are required to prevent absorption from slowing down and reducing the H_2S degradation rate. The higher the pH set point value, the more buffer solutions are consumed, thus increasing bioreactor operation cost. Investigating biopurification efficiency at a slightly acidic pH of 5 enables exploring the potential for satisfactory bioreactor operation at a pH setpoint below the pH range recommended in the literature.

The gas detectors performed concentration measurements in 10-s cycles, and the computer-aided data acquisition system recorded 1-min averages of the measured values. The averaged values were then processed to determine the indices characterizing the biodegradation effects: pollutant load Ms, pollutant EC, and pollutant removal efficiency (the conversion factor) *K*.

3.1. Biodegradation of hydrogen sulfide

During the bioreactor tests, the average concentration of H_2S in the gas stream supplied to the CTBB inlet was 20.2 mg m^{-3}. Frequent concentration jumps to 140–160 mg m^{-3} were observed (Figs. 2 and 3), and the maximum recorded concentration value was 297.4 mg m^{-3}. High values of H_2S removal efficiency were achieved for most of the test period, with variations depending on the process parameters. Fig. 2 illustrates pollutant concentrations and removal efficiency recorded for the gas-phase flow of V_g = 25 m^3 h^{-1} during a representative 7-d time interval when maintaining the pH value of 7. Temporary drops in efficiency values occurred at relatively low and fluctuating concentration levels and after sudden jumps in H_2S concentration to 130–140 mg m^{-3} at the bioreactor inlet. Low pollutant concentration recorded on 20 June 2020 caused starvation conditions for the filter-bed microflora leading to reduced H_2S removal efficiency; however, H_2S concentration at the CTBB outlet was insignificant anyway. Two examples of pollutant concentration jumps that resulted in temporary poisoning of the microflora and subsequent efficiency reduction were observed on 24 and 25 June 2020.

When the gas-phase flow was V_g = 7 m^3 h^{-1} (Fig. 3), at comparable average concentrations of H_2S, concentration jumps to around 130–140 mg m^{-3} in the air entering the CTBB, did not affect the efficiency of pollutant removal. Due to the smaller gas-phase flow, the pollutant loads were lower and did not cause microflora poisoning. This observation was exemplified by the measurement data recorded on 6 July 2020.

Fig. 4a and b depict the relationships between H_2S specific EC and specific pollutant load (Ms) at different pH values. These graphs illustrate the cumulative results of bioreactor investigation in the flow rate range from 7–30 m^3 h^{-1}, thus characterizing CTBB operation when both H_2S concentration and gas-phase flow rate may vary. The specific elimination capacity is the mass of pollutant removed per unit time and unit volume of the bioreactor bed. When polluted air flows through the CTBB reactor, H_2S is transferred from the gas-phase by diffusion into the liquid-phase and the biofilm on the surfaces of bed-packing elements; then, H_2S is metabolized by the microorganisms. The elimination capacity in the CTBB is one of the most critical operation indices. When EC equals Ms, the technology works perfectly well [28]. Indeed, in some parts of the presented results, the linear relationship EC = Ms is visible, which indicates the complete degradation of the pollutants introduced into the CTBB.

By comparing Fig. 4a and b, one can conclude that regarding elimination capacity, the difference between H_2S degradation results at pH = 5 and pH = 7 is insignificant except for gas flow rate range 25–30 m^3 h^{-1} where at pH = 7, short-lived jumps of pollutant concentration may impair the removal efficiency (Fig. 2).

The bioreactor achieved the highest factor of H_2S conversion at the gas-phase flow of 7 m^3 h^{-1} for both pH values of 7 and 5 and a gas-phase flow rate of 25 m^3 h^{-1} for pH equal to 5. On the other hand, the lowest H_2S removal efficiency occurs at gas-phase flow rate V_g = 30 m^3 h^{-1}. For V_g = 7 m^3 h^{-1}, the specific elimination capacity is linearly related to the specific pollutant load implying that the mass transfer rate from gas to liquid, not microbial metabolism, limits H_2S removal [29]. The same is true for flows of 15 and 25 m^3 h^{-1}, as the relationship between EC and Ms is linear. On the other hand, when approaching the flow rate of 30 m^3 h^{-1}, the deviations from the linear relationship between EC and Ms become more significant, especially for pH = 7. The conclusion can be that the flow rate of 30 m^3 h^{-1} is too large because higher values of H_2S concentration in the polluted air entering the bioreactor

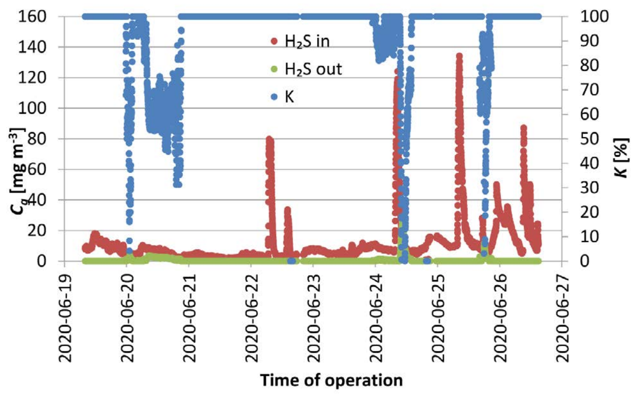

Fig. 2. Hydrogen sulfide removal efficiency for gas-phase flow rate V_g = 25 m^3 h^{-1} and liquid-phase pH = 7.

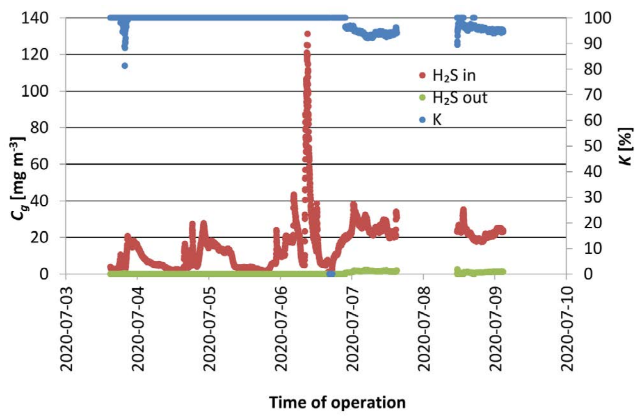

Fig. 3. Hydrogen sulfide removal efficiency for gas-phase flow rate V_g = 7 m^3 h^{-1} and liquid-phase pH = 7 (no data were available on 8 July 2020 due to the malfunction of measuring instruments).

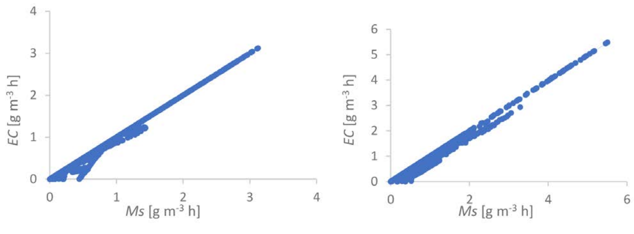

Fig. 4. Hydrogen sulfide elimination capacity as a function of pollutant load at the gas-phase flow rate range of 7–30 m^3 h^{-1}: (a) liquid-phase pH = 7 and (b) liquid-phase pH = 5.

lead to excessive pollutant load for which the CTBB reactor is not adequately dimensioned. This conclusion agrees with the results of research on H_2S biodegradation done by the study of Yang and Allen [30], who tested a lab-scale biofilter. They found that satisfactory elimination of H_2S is achievable at higher pollutant concentration values at reduced gas flow rates only.

Fig. 5 depicts the cumulative results of the determination of H_2S elimination capacity at various gas-phase flow rates and two different pH values in the liquid-phase. The highest EC values observed for the flow rates of 20 and 25 m³ h⁻¹ indicate efficient mass exchange between the gas and liquid-phases due to their adequate mixing and, thus, increased gas/liquid contact surface in the bioreactor bed. In the studied range of gas-phase flow rates 7–30 m³ h⁻¹, the interval 20–25 m³ h⁻¹ is preferable for H_2S elimination in the tested CTBB reactor. Fig. 5 for a gas-phase flow of 20 m³ h⁻¹ shows only the EC results obtained for pH = 5. No data for pH = 7 and that flow rate were available during the initial period of conducting the study due to the failure of the H_2S sensor.

3.2. Biodegradation of VOCs

During the bioreactor tests, VOC concentration in the polluted air supplied to the CTBB was usually below 1,000 mg m⁻³. Temporary concentration jumps occurred, typically to 2,200–2,600 mg m⁻³ (Figs. 6 and 7), and the maximum recorded value was around 4,000 mg m⁻³. VOC measurements focused on their total content in air streams at the bioreactor inlet and outlet. No qualitative analyses on the composition of the VOCs mixture were performed; however, air quality measurements in the WWTP area indicated the presence of ethyl and butyl mercaptans (according to an internal report of WWTP "Klimzowiec"). The mixture also included dimethyl sulfide and dimethyl disulfide judging from the measurement results obtained at the Aquanet WWTP [22].

The highest VOC removal efficiency values were recorded when maintaining pH = 5 in the liquid-phase for the flow rate of V_g = 25 m³ h⁻¹ (Fig. 6) and V_g = 7 m³ h⁻¹. VOC conversion was close to 100% at both flow rates despite temporarily increased VOC concentration in the gases at the CTBB inlet to over 3,000 mg m⁻³. Apparently, the resulting short-lived jumps in the values of VOC loads did not affect pollutant removal efficiency.

In the case of pH = 7, the highest average value of VOC removal efficiency of C = 94.9% was observed at V_g = 25 m³ h⁻¹ (Fig. 7). Compared to pH = 5, similar jumps in pollutant concentration caused significant drops in the removal efficiency's temporary values, thus reducing its average value.

Fig. 8a and b illustrate VOC EC as functions of the mass pollutant load Ms at different process conditions. The graphs indicate how EC values change at constant gas flow rates (7 and 15 m³ h⁻¹, respectively) when the pollutant loads Ms may vary due to variable VOC concentration in air at the bioreactor inlet. Both relationships are linear, indicating that the diffusion of pollutants into the liquid-phase, not microbial metabolism limits VOC removal. The cumulative

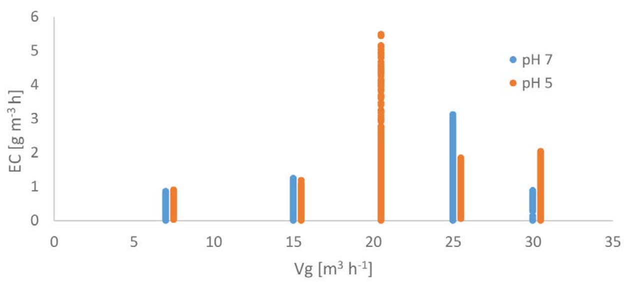

Fig. 5. Hydrogen sulfide elimination capacities determined at different values of gas-phase flow rate and two different liquid-phase pH values.

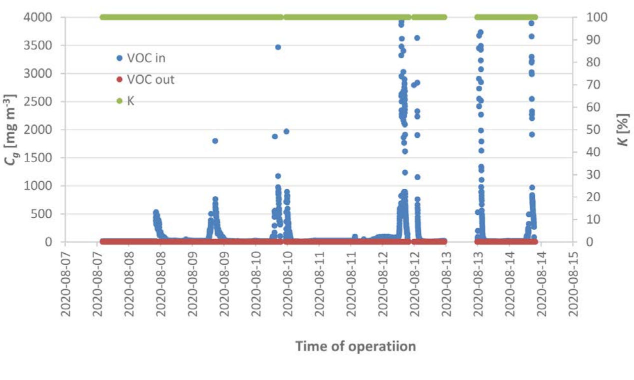

Fig. 6. Volatile organic compound removal efficiency for gas-phase flow rate of 25 m³ h⁻¹ and liquid-phase pH = 5 (no data were available on 13 August 2020 due to the malfunction of measuring instruments).

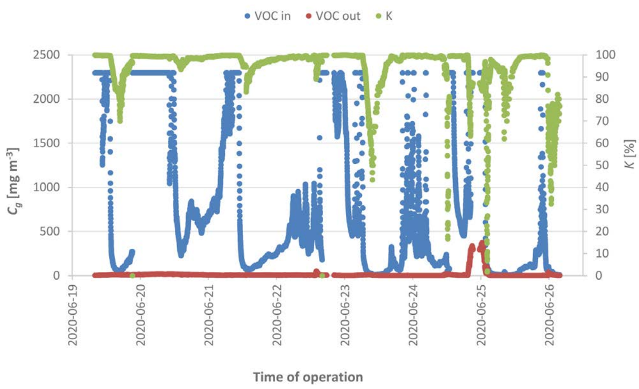

Fig. 7. Volatile organic compound removal efficiency for the gas-phase flow rate of 25 m³ h⁻¹ and liquid-phase pH = 7.

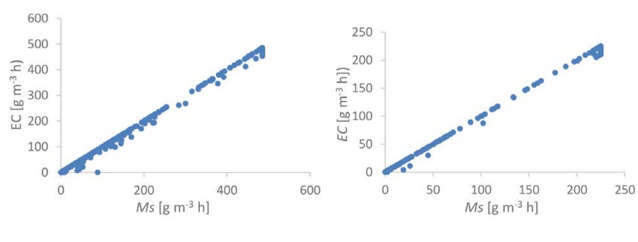

Fig. 8. Volatile organic compound elimination capacities as a function of pollutant load: (a) at gas-phase flow rate 7 m³ h⁻¹ and liquid-phase pH = 5 and (b) at gas-phase flow rate 15 m³ h⁻¹ and liquid-phase pH = 5.

investigation results on the relationships between EC and Ms, that is, when accounting for Ms variability due to changes in VOC concentration and air flow rate, also prove linearity. The efficiency of VOC biodegradation is high at both tested pH levels; the conversion factor for pH = 7 is close to *K* = 95%, and for pH = 5 − to *K* = 100% (Figs. 6 and 7). High EC values indicate efficient mass exchange between the gas and liquid-phases due to their adequate mixing that increases the gas/liquid contact surface in the bioreactor bed. The rate of VOCs transported by diffusion from the gas-phase to the liquid-phase equals the rate of VOC metabolization by the microorganisms. In other words, the pollutant diffusion rate is a factor limiting biodegradation efficiency.

Fig. 9 provides more information by depicting the cumulative results of determining VOC elimination capacity at various gas-phase flow rates and two different pH values in the liquid-phase. The upper limit of 30 $m^3 h^{-1}$ is the preferred flow rate for eliminating VOCs in the studied range of gas-phase flow rates because the EC was highest for both pH values in the tested CTBB, in the range of 950–1,000 $g m^{-3}·h$.

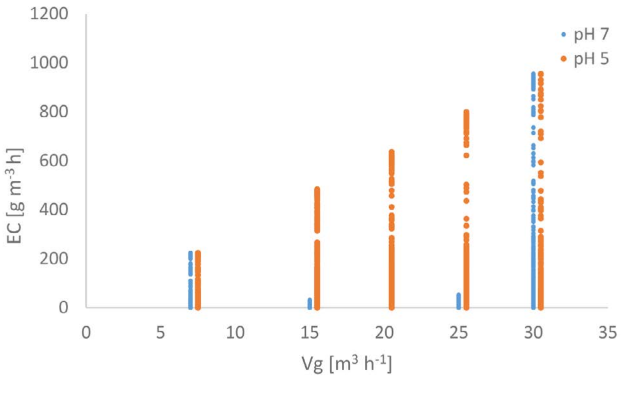

Fig. 9. Volatile organic compound elimination capacities determined at different values of gas-phase flow rate and two different liquid-phase pH values.

3.3. Discussion

The selection of a suitable range of pH values for H_2S biodegradation is a complex issue that requires considering various factors, including H_2S concentration and solubility in water, presence of other pollutants, type of microorganisms involved, and favourable conditions for their growth [26]. Jin et al. [31] experimented with an autotrophic H_2S degrading microbial consortium isolated from the activated sludge of a WWTP. They found that the effectiveness of H_2S removal was highest in the pH range between 4 and 7. H_2S biodegradation efficiency decreased when the pH dropped to below 4. Aroca et al. [32] compared H_2S degradation in BTFs inoculated with sulfur-oxidizing bacteria, including *Thiobacillus thioparus* (filter operated in pH range 5.5–7.0) and *Acidithiobacillus thiooxidans* (pH range 1.8–2.5). Both bacterial strains ensured satisfactory biodegradation results at low H_2S concentrations in the supplied gas, but *A. thiooxidans* proved more effective at higher H_2S concentrations above 300 ppmv. Zhuo et al. [33] studied the desulfurization of low H_2S concentration biogas in a lab-scale BTF at pH values between 7 and 9. Removal efficiency values in the 82%–100% range were achieved using the inoculum obtained from the anoxic tank of a WWTP.

In the present study concerned with the biotreatment of air polluted by low-concentration H_2S and VOCs, the pH range was between 5 and 7. Higher pH facilitates faster H_2S dissolution in the liquid and consequently increases the mass transfer efficiency of H_2S. However, a lower pH is easier and cheaper to stabilize. Furthermore, higher pH is more suitable for the growth of microorganisms needed for VOC degradation and sulfur-oxidizing bacteria. Based on the results, no significant variations of the conversion factor *K* were observed between pH = 7 and 5. The conversion factor observed at pH = 7 was more sensitive to and temporarily decreased after short-lived pollutant concentration jumps at the CTBB inlet. However, no significant differences in the average EC were noted when the gas-phase flow rate varied at the two pH values.

Cox and Deshusses [34] came to similar conclusions after investigating the biodegradation efficiency of toluene and odours at acidic pH = 4.5 and neutral pH = 7. They found that pH value had no significant impact on H_2S and toluene removal efficiency, although the start-up phase of toluene degradation at pH = 4.5 was longer. In addition, the microorganisms developed at pH = 7 had limited tolerance to low pH, while the population of microorganisms that developed at acidic pH showed a broader tolerance to changes in pH. Fortuny et al. [35] investigated the effects of short-term pH changes in a lab-scale biotrickling filter used to treat high-H_2S-loaded gases. Biodegradation efficiency was insensitive to pH drop, but a pH increase significantly affected biological activity and H_2S removal.

In the present research on H_2S removal, comparable EC values were found for pH = 5 and 7 at lower gas-phase flows of 7 and 15 $m^3 h^{-1}$. At an increased gas-phase flow rate of 25 $m^3 h^{-1}$, higher EC was for pH = 7, while for the flow rate of 30 $m^3 h^{-1}$, higher EC was for pH = 5. Regarding VOC removal, there were no significant differences between the different pH values at gas-phase flows of 7 and 30 $m^3 h^{-1}$. In contrast, significantly higher EC values were observed for pH = 5 at gas flows in the 15–25 $m^3 h^{-1}$ range.

Many scientific reports describe the results of applications of biotrickling filters in wastewater treatment plants. However, few studies focused on filter performance under variable liquid-phase pH and gas-phase flow rate. Montebello et al. [36] investigated H_2S removal in the BTF and the development of a bacterial community at neutral pH and the transition range from neutral to acid pH. The transition to acid pH drastically reduced the microbial diversity and led to the dominance of the sulfur-oxidizing bacteria without affecting the pollutant removal efficiency of the reactor. However, an elemental sulfur accumulation occurred during acidic pH operation, indicating a risk of bed clogging. Zhang et al. [37] conducted research in a real-life WWTP, the efficiency of simultaneous degradation of H_2S and siloxanes from biogas was determined. The bioreactor bed was inoculated with acidophilic microorganisms. The study results showed that pH value was a critical parameter affecting the BTF performance. After investigating pollutant removal at pH values of 0.9–4.0, pH = 1.2 was found to ensure the most effective removal of H_2S and siloxanes from the biogas.

The CTBB technology considered in this paper has been studied before in applications other than wastewater treatment. Kasperczyk and K. Urbaniec [38] used pilot-scale CTBB for the biopurification of ventilation air from a copper ore mine. The measurements performed 1,000 m underground demonstrated high bioreactor efficiency except for incidents of short-lived increase in H_2S concentration up to 1,000 ppm, which caused temporary poisoning of the CTBB reactor. Kasperczyk et al. [23] was devoted to CTBB's effectiveness in removing VOCs from ventilation air in the automotive paint industry. VOC biodegradation factors of 85%–99% were achieved in a full-scale bioreactor, thus confirming the success of scaling up CTBB technology from pilot to full industrial scale.

Overall, the present research provided complementing information to the studies cited above, thus enabling a realistic evaluation of the potential for implementing CTBB technology in various industries, including wastewater treatment plants. The results shown in Section 3 – Results and discussion may facilitate the selection of operating parameters for new applications of biotrickling filters to maximize the efficiency of VOC and odour biodegradation. By conducting CTBB tests under actual conditions of a biological treatment plant, knowledge was gathered on the fluctuations of odour and VOC concentrations during their peak emission period and bioreactor responses to process disturbances and sudden changes in pollutant concentrations. Based on the accumulated experience, one can evaluate the possibility of expanding this technology to the full industrial scale needed for broader applications in biological wastewater treatment plants.

4. Conclusions

The results of this study on the application of CTBB technology indicate that it is capable of nearly complete degradation of H_2S and VOCs in the polluted air discharged from around 200,000 PE biological wastewater treatment plants. The pollutant-degrading culture was obtained from the existing biofilter working on the WWTP and enriched with *P. fluorescens* strain. After adapting to the application conditions, the microorganisms were used to inoculate the pilot-scale bioreactor. At the average H_2S concentration of 20 g m^{-3} and VOC concentration below 1,000 g m^{-3}, when maintaining pH = 5 or 7 in the circulating liquid-phase, the removal efficiency ranged between 95% and 100% for both pollutants.

Regarding optimization of the effective gas-phase flow rate, the highest capacity of H_2S elimination, around 5 g $H_2S{\cdot}m^{-3}{\cdot}h$, was recorded at a gas-phase flow rate ranging from 20 to 25 $m^3\ h^{-1}$, equivalent to EBRT of 3.3–4.2 min. The highest VOC elimination capacity, around 1,000 g $VOC{\cdot}m^{-3}{\cdot}h$, occurred at a gas-phase flow rate of 30 $m^3\ h^{-1}$, equivalent to EBRT of around 5 min. The EBRT values in the 4–5 min range can be regarded as a guideline for bioreactor upscaling when applying the same type of bed packing.

No significant variations in the pollutant conversion factor occurred at pH = 5 or 7 in the circulating liquid-phase. One can safely operate CTBB reactors at pH values lower than the recommended range of 7.0–8.0, providing the level of H_2S concentration in the incoming air is similar to that measured during the test period (around 20 mg m^{-3} on average, with jumps to 140–160 mg m^{-3}). However, CTBB operation at higher H_2S concentrations remains an open question. It may risk clogging the bioreactor bed through elemental sulfur accumulation if an excessive pH drop in the liquid-phase occurs.

The studied technology of air biopurification from odours and VOCs in CTBB reactors shows the implementation potential for its upscaling to a full scale for municipal WWTPs. This study may serve as a prelude to further investigations of the impact of liquid-phase flow or other compositions of odorous contaminants undergoing biotreatment on pollutant removal efficiency. The research question will be if CTBB technology is suitable for use in wastewater treatment plants with different characteristics of emitted odours. With the proper adaptation of process parameters and microorganism strains to specific application conditions, one can expect that CTBB technology will also be suitable for removing other types of odour emitted from anaerobic processes in the municipal sector.

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Symbols

C_g	—	Pollutant concentration in the gas-phase, g m^{-3}
EC	—	Specific elimination capacity $EC = (C_{gin} - C_{gout})/t_g$, g $m^{-3}{\cdot}h$
K	—	Removal efficiency (conversion factor) $100(C_{gin} - C_{gout})/C_{gin}$, %
Ms	—	Specific pollutant load $Ms = C_{gin}/t_g$, g $m^{-3}{\cdot}h$
t	—	Time, h
t_g	—	Empty bed retention time $t_g = V_{bed}/V_g$, h
T	—	Temperature, K
V_g	—	Volumetric gas flow rate, $m^3\ h^{-1}$
V_{bed}	—	Empty bed volume, m^3

Subscripts

g	—	Gas
in	—	Inlet
out	—	Outlet

Abbreviations

BTF	—	Biotrickling filter
CTBB	—	Compact trickle-bed bioreactor
EBRT	—	Empty bed retention time
H_2S	—	Hydrogen sulfide
VOC	—	Volatile organic compound
WWTP	—	Wastewater treatment plant

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