Journal of
Water & Climate Change

Journal of Water and Climate Change Vol 13 No 6, 2386 doi: 10.2166/wcc.2022.438

Fate and emission of methyl mercaptan in a full-scale MBBR process by TOXCHEM simulation

Ahmed M. Faris[a], Basim K. Nile[b], Zainab H. Mussa[c], Hasan F. Alesary[d,*], Maad F. Al Juboury[b], Waqed H. Hassan[b], Hussein A. Al-Bahrani[e] and Stephen Barton[f]

[a] Kerbala Sewerage Directorate, Kerbala 56001, Iraq
[b] Engineering College, University of Kerbala, Karbala 56001, Iraq
[c] College of Pharmacy, University of Al-Ameed, P.O. Box 198, Karbala, Iraq
[d] Department of Chemistry, College of Science, University of Kerbala, Karbala, Iraq
[e] College of Nursing, University of Al-Ameed, Karbala, Iraq
[f] School of Life Sciences, Pharmacy and Chemistry, Kingston University London, Kingston-Upon-Thames, Surrey, UK
*Corresponding author. E-mail: hasan.f@uokerbala.edu.iq

HFA, 0000-0002-3116-5145

ABSTRACT

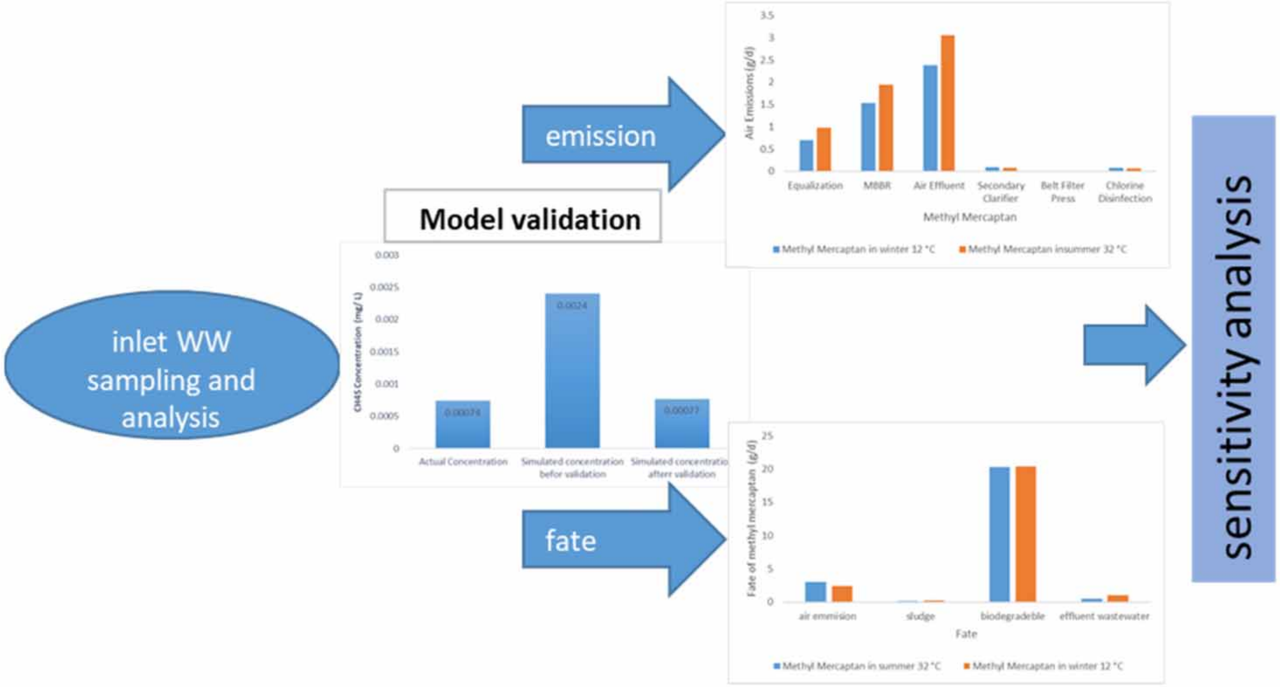
The emission and fate of methyl mercaptan from the residential complex treatment plant (RCTP) moving bed bioreactor (MBBR) process in the city of Al-Hur in Karbala governorate in Iraq were studied using the TOXCHEM 4.1 model. The release of odorous sulfur compounds from treatment plants harms workers and the surrounding area. Methyl mercaptan, in particular, is responsible for odors similar to rotten cabbage. The sensitivity analysis for the methyl compounds in the MBBR system was conducted based on the following factors: a large thick biofilm layer, the specific surface area of media, media fill fraction, and aeration flowrate. The model was validated via *RMSE* and *R*, which showed the model outputs are representatives of real-world observations. Degradation and emission were shown to be the two most important processes in the system. During the summer (32 °C) and winter (12 °C), about 13 and 10%, 2 and 4%, 0.5 and 1%, and 85 and 85% were emitted into the atmosphere, discharged with effluent, sorbed into sludge, and biodegraded, respectively. The overall concentrations of CH_4S emitted in summer and winter were 1.78 and 1.38 ppm, respectively. Operating the MBBR system with a thick biofilm layer, a large specific surface area of media, a greater media fill fraction, and a low aeration rate contributed significantly to the decomposition of methyl mercaptan and thus decreased emission into the atmosphere. Finally, the TOXCHEM simulation accurately predicts the fate of CH_4S and the emissions inherent to the MBBR system. The manipulation of the operating factors led to the improvement of the system and the reduction of methyl mercaptan gas emissions without the need to add units and chemical additives.

Key words: emission, fate, MBBR, methyl mercaptan, sensitivity analysis, TOXCHEM

HIGHLIGHTS

- The methyl mercaptan emitted by a full-scale MBBR WWTP was studied.
- Aeration tank and equalization basin emitted the highest CH_4S concentrations.
- TOXCHEM modeling was used to calculate the distribution of CH_4S around the WWTP.
- CH_4S concentrations exceeded the threshold limit at this plant.
- CH_4S emission was affected by the following three main factors: biodegradation, absorption by the sludge, and stripping.

GRAPHICAL ABSTRACT



1. INTRODUCTION

The biological decomposition of organic materials in sewage treatment plants produces noxious odors due to anaerobic breakdown (Asadi & McPhedran 2021). The odors of a wastewater treatment plant (WWTP) may be the result of sewerage odorants emitted into the air during the plant's operations (Gao *et al.* 2021). Biodegradability in wastewater can also lead to the formation of odorants (Wiśniewska *et al.* 2021). Chemical substances such as hydrogen sulfide, methane, and ammonia, as well as organic chemicals such as mercaptans, amine, indole, and skatole are produced during anaerobic processes (Andraskar *et al.* 2021). Sulfurous chemicals, such as hydrogen sulfide and mercaptans, which include methyl, ethyl, propyl, and butyl mercaptans all have a generally disagreeable odor and are common in WWTPs (Grzelka *et al.* 2019).

Volatile sulfur compounds (VSCs) are potentially the most significant of the odorous compounds emitted by WWTPs as they can create health-related issues such as discomfort and a non-carcinogenic danger. Hydrogen sulfide (H_2S), methyl mercaptan (MT), dimethyl sulfide (DMS), carbon disulfide (CS_2), and dimethyl disulfide (DMDS) are the most common VSCs emitted from WWTPs. Detecting VSCs emitted from WWTP units in the ambient air has been the topic of many earlier investigations examining VSC discharge. For example, a review article considered 24 studies that had examined VSC concentrations in WWTPs' ambient air and found a wide range for H_2S (0.1–20,480 $\mu g/m^3$), MT (0.4–2.4 $\mu g/m^3$), DMS (0.4–5,450 $\mu g/m^3$), CS_2 (3.06–9.82 $\mu g/m^3$), and DMDS (0.62–1,600 $\mu g/m^3$). Direct monitoring at the water–air interface is typically used to determine the concentrations of VSCs emitted from WWTPs. VSC emission fluxes from a main and secondary clarifier, for example, were assessed over an 8-day period using water–air interface sampling and included H_2S (0.004–1.404), MT (0.004–0.684), DMS (0.086–0.612), CS_2 (0.005–0.012), and DMDS (0.002–2.988) (Li *et al.* 2021).

The organic molecule methanethiol (also known as methyl mercaptan or thiolmethane) has the formula CH_3SH or CH_4S (Kleinhenz 2003). Methyl mercaptan is a colorless gas with a distinct dry smell (Zhou *et al.* 2018), and is a naturally occurring substance found in the blood and brains of humans and animals, as well as plant tissues. Animals remove it through their feces. Some foods, such as nuts and cheese, naturally contain CH_4S. It is also one of the key chemicals responsible for bad breath and the smell of flatulence.

Methanethiol, abbreviated as MeSH, is a thiol that is extremely flammable. Food and feed manufacturers use methanethiol to make methionine. Methanethiol is also employed as a free-radical polymerase in the plastics sector, and is also used in the pesticide industry (Vision & Mission 2013). H_2S odor detection thresholds have fluctuated from 0.491 to 0.97 $\mu g/m^3$ over the previous 20 years. Different smell thresholds exist for mercaptans, chemical substances found in wastewater treatment operations (ranging from 0.01 μg/m^3 for butyl mercaptan to 2.16 μg/m^3 for CH_3SH) (Grzelka *et al.* 2019). When methyl mercaptan combines with water, steam, or acids, it creates flammable vapors that are dangerous on inhalation. CH_4S has the potential to cause respiratory paralysis, which can easily result in death. It is irritating to the eyes and respiratory tract, with pneumoedema, hepatic, and renal impairment all being symptoms of exposure.

An OSHA PEL (permissible exposure limit) of 10 ppm (20 mg/m^3) is the standard and guideline for methyl mercaptan, with a NIOSH REL (recommended exposure limit) of 0.5 ppm and NIOSH IDLH (immediately dangerous to life or health) of 150 ppm The AIHA ERPG-2 (where many people might be exposed for up to 1 h without experiencing or developing permanent or other serious health problems or symptoms that could hinder their ability to take protective action) is 25 ppm (Nile 2018; Michaels & Wagner 2020). Methyl mercaptan is a relatively volatile organic compound (Weihua *et al.* 2021). The volatile organic compounds produced in WWTPs are affected by a number of factors, the most significant of which are stripping, decomposition, and sorption by mixed liquid suspended solids (MLSS) or biofilm (Zwain *et al.* 2020a, 2021). The organic and mineral materials represented by the MLSS with the reactor can adsorb and absorb organic materials and heavy elements. Bhatti *et al.* (2020) studied the treatment of arsenic from water by absorbing it with polyacrylonitrile fiber (organic) and iron ore. There are several models used to simulate the emission of volatile organic compounds in WWTPs (Buaisha *et al.* 2020) and TOXCHEM is considered one of the most important tools for determining the fate and emission of volatile organic compounds in sewage treatment plants (Zwain *et al.* 2020b, 2021). The majority of previous studies have focused on eliminating the methyl compound on emission from the treatment plant facilities and thus treating it in the gaseous state, but there are no studies to date about the fate of this compound within the processes of the treatment plant, i.e., while it is still within the wastewater.

TOXCHEM was developed in the early 1990s to replace the EPA's Water8 (Water9) software, which had certain limitations such as lack of enhanced mass transfer methods, sorption of pollutants to solids, and a peer-reviewed compound database of physical, chemical, and biological processes. TOXCHEM is a popular tool for calculating volatile organic carbon (VOC) emissions from sewage intake, storage (preliminary, primary, and secondary), and sludge treatment. Site-specific drainage parameters, pollutant qualities, and process design and operation statistics are used to estimate VOC contamination concentrations. TOXCHEM research centers on mass transfer equations and balances, such as stripping and volatilization reduction methods, and biodegradation and sorption processes. Not all of these processes would be active for all compounds. It would be necessary to use sorption (and/or precipitation, which might be confused with sorption) to remove heavy metals. Removal of VOCs is mostly accomplished utilizing biodegradation and volatilization, with sorption playing only a small part. Some hydrophobic organic molecules can be effectively removed by all three techniques. Photolysis and hydrolysis are difficult to distinguish from biodegradation. Under steady-state or dynamic settings, it may be used to forecast the fate of any chemical species synthesized in WWTPs (Masoomi *et al.* 2021).

The lack of a slope in the sewage network for the residential complex in Al-Hur favors anaerobic conditions and, combined with the high temperatures found in Iraq, this promotes the emission of sulfur compounds. In this study, the fate and emission of methyl mercaptan and the factors affecting its emission will be determined via the TOXCHEM 4.1 model in Al-Hur's moving bed bioreactor (MBBR) treatment plant. The novelty of this study lies in the determination of the plant's strengths and limitations, as well as the identification of areas of concern for methyl mercaptan emission. This risk can be addressed without incurring additional expenditures, but the biological processes can only be regulated by recognizing the system's important processes, as outlined in the preceding section. This is the first time that methyl mercaptan, a sulfur compound with a disagreeable odor, has been evaluated and investigated in the MBBR system and by the TOXCHEM model. The investigation provides precise information on the location of the irritating gas emissions, allowing appropriate precautions and safety procedures for workers to be put in place.

2. MATERIALS AND METHODS

2.1. Site location and description

The residential complex treatment plant (RCTP-MBBR) is located in the city of Al-Hur, about 10 km away from the center of the Karbala governorate and about 110 km from the Iraqi capital, Baghdad, located at coordinates of 32.645454 °N and 43.973323 °E (Figure 1). The plant technique is an MBBR process, as shown in Figure 2. Designed on the basis of a flow rate of 800 m^3/d and a service of 4,000 capita, the station contains the following four stages: the first level is preliminary

Figure 1 | Aerial view of the study site.

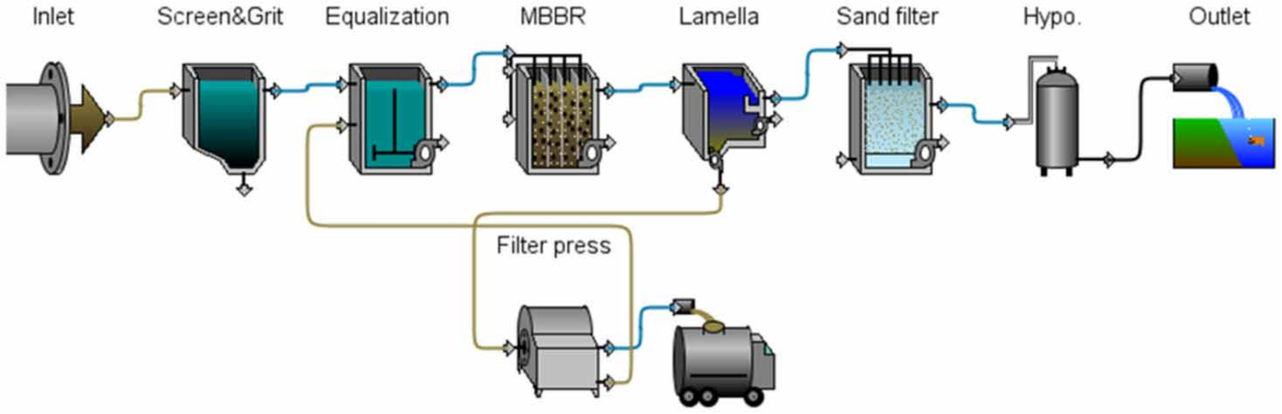


Figure 2 | Schematic diagram of the MBBR system in the RCTP.

treatment, which includes sand removal basins and a balance basin; the second level includes aeration basins; the third is the tertiary treatment, which includes disinfection (by calcium hypochlorite) and filters; and the fourth level includes sludge treatment by filter press and operations according to the data shown in Table 1. The study methodology was conducted according to the procedure shown in Figure 3.

2.2. Sampling and analysis

To assess the performance of the RCTP, laboratory samples were collected and analyzed for a period of 1 year from 1/7/2020 to 1/7/2021, as shown in Table 2. All the tests shown in Schedule 1 were carried out in accordance with standard methods for the examination of water and wastewater (Mohsen *et al.* 2020). These results were compared with the Iraqi Law on Wastewater Determinants treated with the exception of methyl mercaptan, which will be compared to the invasive condition with the determinants in the Acute Exposure Guideline Levels for Selected Airborne Chemicals: Volume 15, National Research Council, shown in Table 3.

Table 1 | RCTP-MBBR operational conditions

No.	Parameter	Value
1	Flow, Q	800 m^3/d
2	SALR for BOD removal	7.5 g/m^2 d
3	SALR for NH_4 removal	0.87 g/m^2 d
4	DO	3 mg/L
5	BOD removal	$\geq$95%
6	NH_4 removal	$\geq$95%
7	Carrier fill	40%
8	HRT for the MBBR	4 h
9	Specific surface area	500 m^2/m^3
10	HLR for lamella	1 m/d
11	HRT for lamella	1.5 h
12	Weir length	2.5 m
13	Angle for lamella plate	60°
14	MBBR volume	144 m^3
15	Equalization tank volume	220 m^3

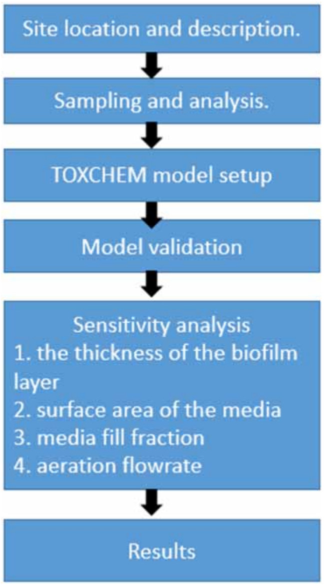


Figure 3 | Basic flow chart of the study methodology.

2.3. TOXCHEM model setup

This work uses TOXCHEM V4.1 to predict the fate of methyl mercaptan at the MBBR-STP in Al-Hur, Iraq. Although the TOXCHEM V4.1 model can predict removal rates via mass transfer, biodegradation, and sorption, each molecule may or may not be subject to all of these processes. Here, the removal of methyl mercaptan via biodegradation, stripping, and sorption in the equalizer; MBBR; and secondary clarifier were of particular interest. Attached and suspended growth biodegradation models were used to allow for the combination of treatment processes in the MBBR system. Biodegradation

Table 2 | Performance characteristics of the Karbala RCTP

Parameter	Inlet concentration	Outlet concentration	Standard Iraq
PH	7.2	7.4	7
COD (mg/L)	500	35	100
BOD_5 (mg/L)	350	10	40
TSS (mg/L)	250	8	60
NO_3 (mg/L)	2	45	50
NH_4^+ (mg/L)	22	0.5	1
PO_4-P (mg/L)	5	2	3
H_2S (mg/L)	35	ND	3
SO_4 (mg/L)	400	450	600
Oil and grease (mg/L)	60	8	10
Methyl mercaptan (mg/L)	0.03	0.00074	–
Methyl mercaptan (ppm_v)	14	0.34	–

Table 3 | Odor intensity of methyl mercaptan

Intensity	Description	Concentration (ppm)
0	No odor	0.003
1	Threshold	0.041
2	Faint	0.57
3	Median, easily noticeable	7.9
4	Strong	110
5	Most intense	1,500

Source: Acute Exposure Guideline Levels for Selected Airborne Chemicals: Volume 15, National Research Council.

of methyl mercaptan in small concentrations during suspended growth processes can be expressed as follows:

$$rb = kb\left(\frac{C}{1 + (C/K_S)}\right)XV \tag{1}$$

As a trace contamination, methyl mercaptan's biodegradation kinetics can be expressed as follows:

$$rb = kb \times f \times CV \tag{2}$$

where rb is the biodegradation rate (mg/h), kb is the first-order biodegradation rate coefficient (L/mg VSS/h), X is the biomass concentration (mg/L), Xf is the biofilm density (mg/L), C is the contaminant concentration (mg/L), K_s is the half saturation constant (mg/L), and V is the vessel volume (L).

Using sorption, pollutants can be transported from the liquid state to a dead mass, and then to the residual suspended solids or into a biofilm layer. A linear isotherm was seen for low concentrations of methyl mercaptan on sludge, as per the expression:

$$q = Kp \times C \tag{3}$$

where q is the concentration of contaminant in the solid phase (μg/g) and Kp is the sorption partition coefficient (L/g).

Volatilization of methyl mercaptan from the surfaces of the equalization tank, MBBR, and final clarifier can be stated as per the mass transfer mechanisms:

$$KL = \left(\frac{1}{kL} + \frac{1}{kGH}\right)^{-1} \tag{4}$$

where KL is the overall mass transfer coefficient, H is the Henry's law coefficient, kL is the liquid phase mass transfer coefficient (m/h), and kG is the gas phase mass transfer coefficient (m/h).

2.4. Model validation

Validation is a necessary process for the purpose of determining how close the real results are to the predicted results. There are many statistical equations for this purpose, such as Nash–Sutcliffe Efficiency, root mean square error ($RMSE$), ratio of standard deviation, mean absolute error, and the determination coefficient (Hussein *et al.* 2015). To assess the quality of data predicted by TOXCHEM V4.1, all actual and forecast data were compared using the Chang and Hanna statistical parameters. To verify the model, mathematical validation according to $RMSE$ and correlation coefficient (R) were tested, as shown in the following equations:

$$RMSE = \frac{\overline{(C_P - C_O)^2}}{\overline{C_O}\;\;\overline{C_P}} \tag{5}$$

$$R = \frac{\overline{(C_O - \overline{C_O})(C_P - \overline{C_P})}}{\sigma_{C_O}\sigma_{C_P}} \tag{6}$$

where C_o (mg/L) is the actual data, C_P (mg/L) is the modeled data, $\overline{C_O}$ (mg/L) is the average of the actual data, $\overline{C_P}$ (mg/L) is the average of the modeled data, and σ is the standard deviation over the dataset. The statistical criteria reasonable limits are $1 \geq R > 0.8$ and $0 \leq RMSE < 1.5$ (Chang & Hanna 2004; Zwain *et al.* 2020a, 2021).

2.5. Sensitivity analysis

Sensitivity analysis is one of several important methods used to understand the impact of various operational parameters on the fate and emission of CH_4S. Using the key factors that influence the treatment process used in MBBR systems, sensitivity analysis was used to understand the fate and emission of CH_4S in this study, which includes the thickness of the biofilm layer, surface area for media, media fill fraction, and aeration flowrate, different thicknesses of the biofilm layer (0.5–7 mm), surface area for media (250–1,250 m^2/m^3), media fill fraction (30–70%), and aeration flowrate (225–900 m^3/h) were considered.

3. RESULTS AND DISCUSSION

3.1. The performance evaluation of RCTP-MBBR

The performance of RCTP-MBBR is shown in Table 2 and Figure 4, which operates very well compared to the Iraqi standard, as it achieved a removal efficiency of 93, 97, 60, 86, 97, 97, and 96% for COD and BOD5, PO_4, oil and grease, NH_4, total suspended solids (TSS), and 97% for methyl mercaptan, respectively, while the plant generated nitrate and sulfate at 95 and 12.5%, respectively. The plant is divided into two parts, the first for the treatment of substrate by heterotrophic bacteria, and the second for the treatment of nutrients by autotrophic bacteria. It was observed that the plant treats both the substrate and nutrients well. Phosphate removal was observed to be 60% due to the growth of phosphorous-accumulating bacteria in the equalization basin due to anaerobic processes, and therefore these bacteria move to the aeration basin for biological complementary processes, to be removed with the generated sludge (Faris *et al.* 2022). The generation of a high concentrations of nitrates was observed due to the absence of the anoxic basin in the plant as well as due to the nitrification process that oxidizes ammonia, proteins, and amino acids in the wastewater, all of which contribute to the increase in nitrate concentrations, reaching a generation rate of 95% (Daims *et al.* 2015). High sulfate concentrations were also observed in the treated wastewater due to the oxidation of sulfur compounds that takes place in the aeration basin, such as for hydrogen sulfide gas and proteins that contain a higher percentage of sulfur in addition to methyl mercaptan, where the generation rate reached more than 12% (Syed *et al.* 2006). High concentrations of methyl compounds were observed in the influent

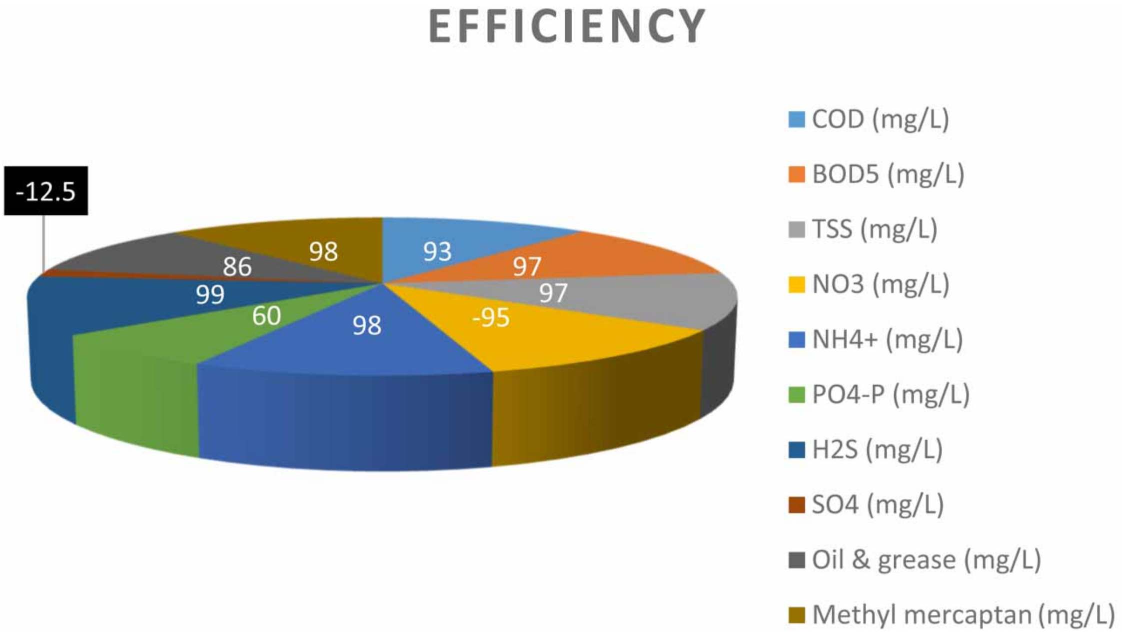


Figure 4 | Plant efficiency performance ratios.

wastewater, which led to the emission of unpleasant odors that negatively affected the workers in this plant and the residents of the residential complex. Processing stages and temperatures greatly affected the emission of these odors (Andraskar *et al.* 2021). It was observed that the concentration of methyl mercaptan compounds in the atmosphere exceeded the threshold limit compared to the parameters in Table 3. Methyl mercaptan concentrations in the plant's atmosphere reached about 14 ppm_v. These concentrations are undesirable as they lead to health problems amongst the workers in the station and people in the surrounding areas. Therefore, the necessary measures must be taken to determine the causes of emission, the factors affecting it, and how to reduce these odors.

3.2. Results validation

The TOXCHEM model is one of the best models to determine the fate and emission of volatile organic compounds (Behnami *et al.* 2019). To gain results as close to the real-world observations as possible, a calibration and validation process must be carried out. Figure 5 compares actual concentration and simulated concentration prior to validation (default), and simulated concentration after validation (predicted). The model was run on the basis of default data, so the exit results for the methyl

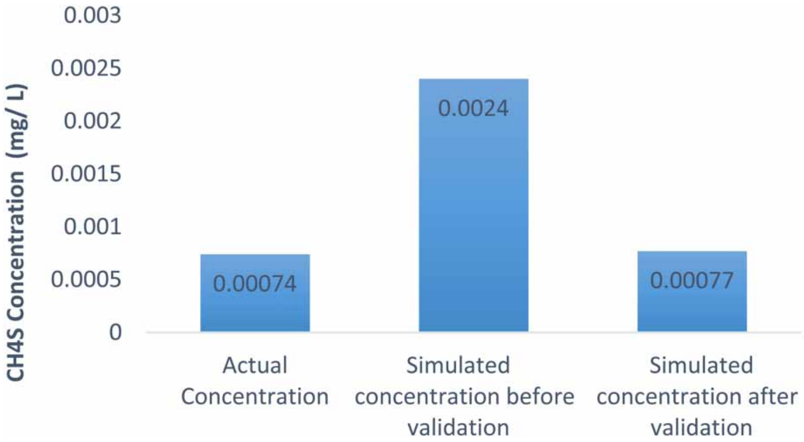


Figure 5 | Validation of the actual, simulated, and default values.

mercaptan pollutant were far from the real-world observations, where the concentration of methyl mercaptan in the treated wastewater was 0.0024 mg/L, and the results validation for *RMSE* and *R* were 1.55 and 0.0003, respectively. To make the predicted results closer to the actual, the following parameters were changed: the volatile suspended solids (VSS)/TSS ratio from 75 to 80%, the oxygen transfer efficiency from 10 to 18%, the thickness of the biofilm layer from 1 to 5 mm, the media volume inside the reactor from 35 to 45%, whilst the concentration of sludge at the bottom of the sedimentation tank was taken to be in the range from 6,000 to 9,000 mg/L and the MLSS concentration from 500 to 800 mg/L (Cao *et al.* 2021). The results were 0.00077 mg/L of methyl mercaptan in the treated wastewater, and the validation result for *RMSE* was 1.2, and for *R* was 0.9.

3.3. CH_4S fate and emission

An average of 24 g/d of methyl mercaptan enters the plant. In Figure 6, it can be observed that this compound was affected by several factors, including temperature, stripping, surface area of the reactor, and depth of liquid in the reactor (Padalkar & Kumar 2018). The temperature affected the emission and fate of this compound during winter and summer. In this study, the average temperature during winter was 12 °C, and during summer was 32 °C. It was observed that in the winter and at an average temperature of 12 °C, the rate of emission of this compound was about 10%, but in the summer, it reached 13% of the total amount entering the plant, so the increase in temperature is considered to represent a negative factor with regard to the emission of these compounds into the atmosphere of the plant. It was also observed that for both winter and summer, the emission concentration exceeded the threshold limit at 1.38 and 1.8 ppm, respectively.

Figure 6 shows the emission of methyl mercaptan compound in the treatment stages during the winter and summer seasons. The highest emissions during both winter and summer were observed in the aeration basin due to the stripping that takes place for this compound and the transition of the mass from the liquid state to the gaseous state (Lv *et al.* 2021). The aeration basin follows the equalization basin, and the reason for the emission of these quantities of methyl compounds is that this basin was affected by the following three important factors, namely the process of stripping by mixing, the large associated surface area, which was 110 m^2, and the height of the water, which was not large at 1.5 m (Wang *et al.* 2021). All of these factors contribute to the emission of this compound from the equalization basin, while in the remaining basins it was only present in very low concentrations, as shown in Figure 7.

As for the fate of this compound, its decomposition during winter and summer was the highest in terms of stripping and absorption. Methyl mercaptan decomposition occurs via two processes, the first being anaerobic in the equalization basin, with the conversion of a part of this compound into methane and hydrogen sulfide gas, while the second, which is predominant, took place in the aeration basin through the reaction of methyl mercaptan with dissolved oxygen, resulting in carbon dioxide, water, and sulfates (Lu *et al.* 2018). Emission follows the decomposition process as shown in Figure 8. The aeration process contributed mainly to the elimination of this compound through its oxidation via dissolved oxygen, but the process of stirring and stripping contributed greatly to the emission of this compound into the atmosphere (Cheng *et al.* 2021).

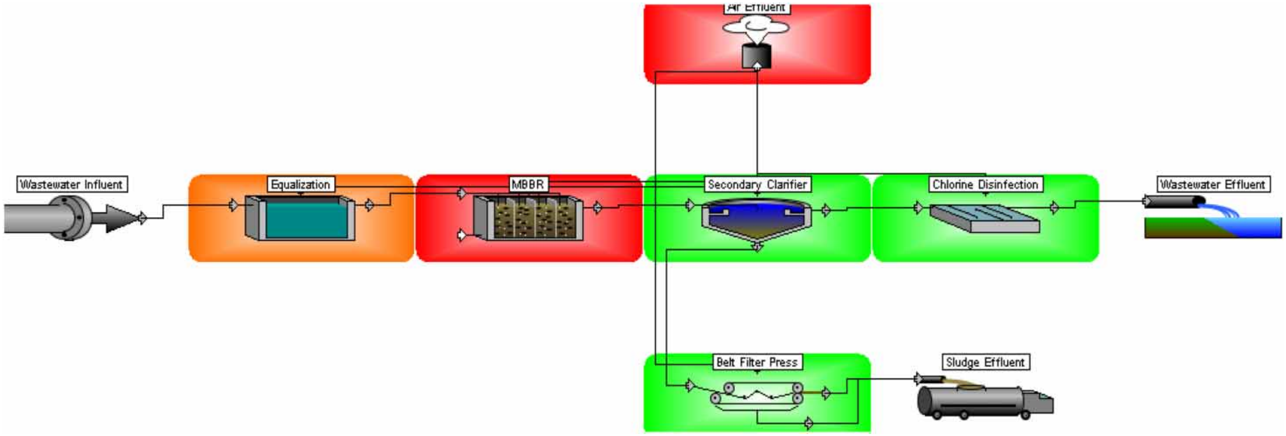


Figure 6 | Critical stages that emit odors.

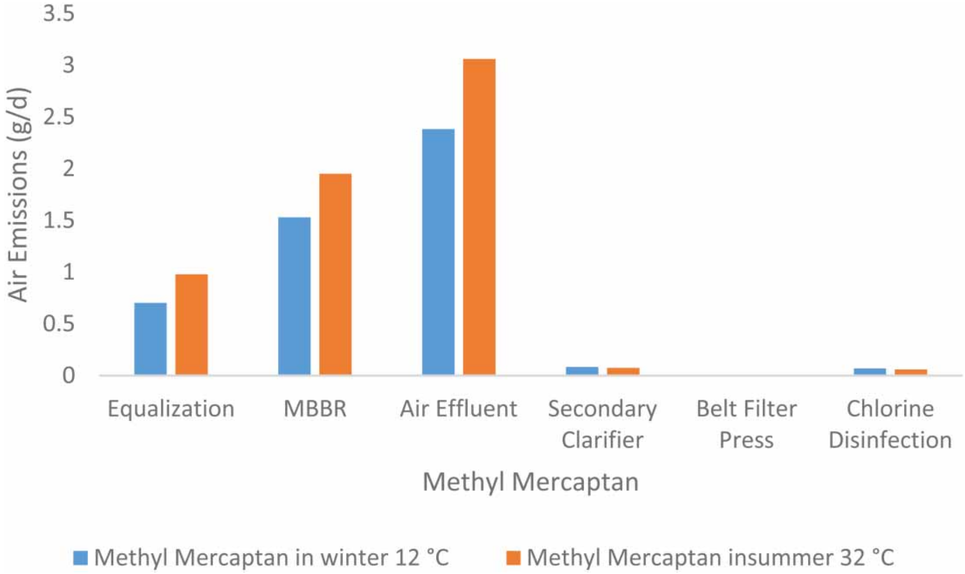


Figure 7 | Emission of H_2S into the atmosphere from each unit (ppm) during summer and winter.

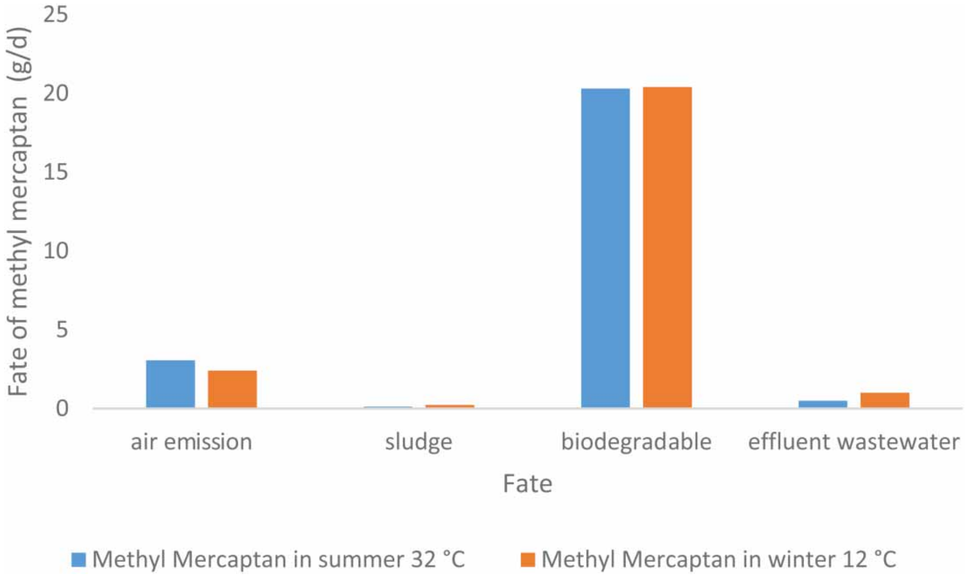


Figure 8 | CH_4S dispersion (g/d) throughout the MBBR system in the RCTP during summer and winter.

3.4. Sensitivity analysis

The MBBR treatment process is affected by several factors, where the most important operational factors that affect the sensitivity of this system are temperature, pH, wind speed, the amount of media and its surface area, the thickness of the biofilm layer on the media, and the concentration of the pollutant, among others (Saidulu *et al.* 2021).

Figure 9(a) shows the effect of the thickness of the biofilm layer on the decomposition and emission of methyl mercaptan. It was observed that when the thickness of the biofilm layer increased from 0.5 to 7 mm, the biodegradation process increased from 74 to 86%. This is logical as the increase in the biofilm layer increases the bacterial population that degrades this compound and eliminates it instead of releasing it into space or expelling it into sludge. It was also observed that when the biofilm layer was increased, the emission rate decreased from 20 to 11%, i.e., there was an inverse relationship between the increase in the biofilm layer thickness and the emission of this compound. By increasing the biofilm layer, the concentrations of the

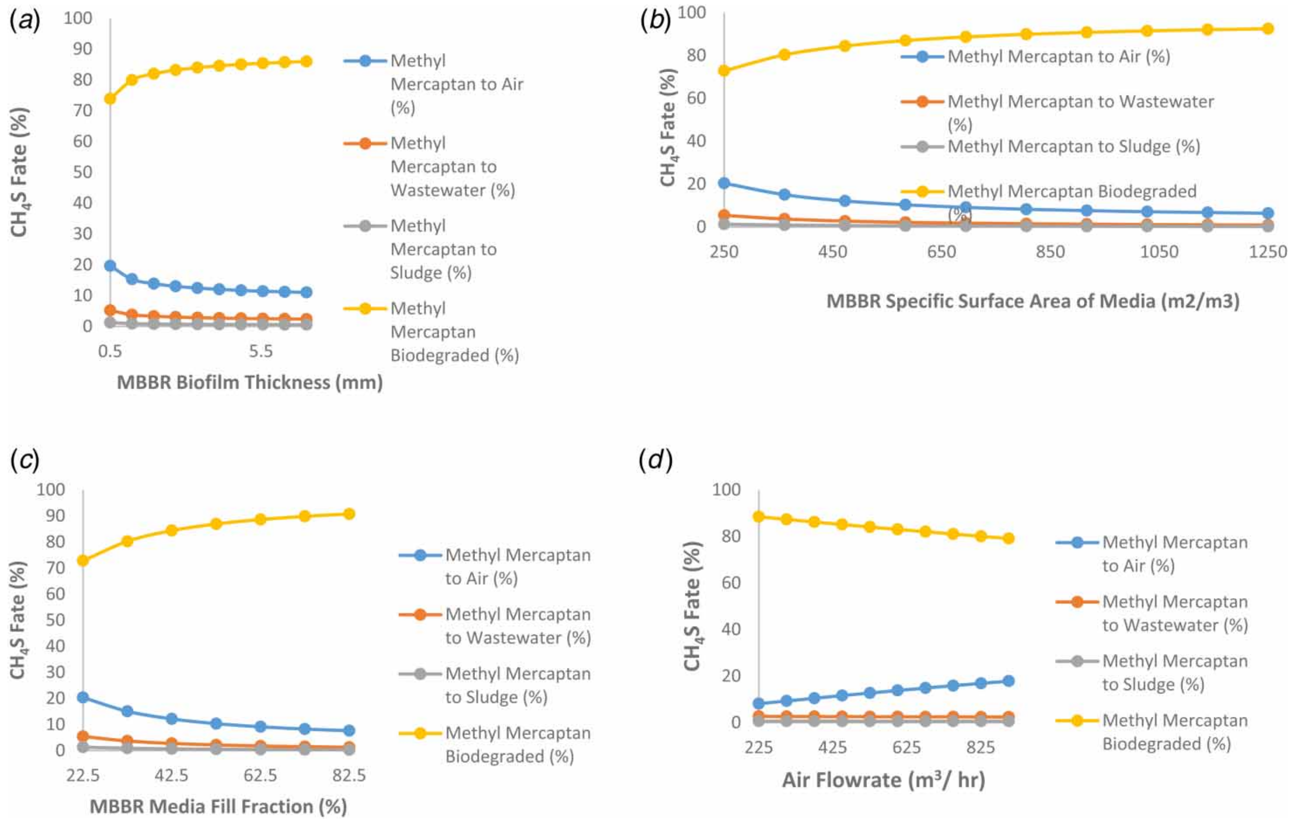


Figure 9 | Sensitivity analysis for different methods of CH_4S dispersion: (a) the thickness of the biofilm layer, (b) surface area of the media, (c) media fill fraction, and (d) aeration flowrate.

methyl mercaptan compound in the effluent wastewater decreased from 5 to 2%. It was also observed that this compound was affected in the process of absorption by the sludge. When the biolayer thickness was increased, the amount of the compound did not decrease in the resulting sludge due to the ability of microorganisms to effect its decomposition (Bhattacharya & Mazumder 2021).

Figure 9(b) shows the extent of the impact of the surface area on the decomposition and emission of methyl mercaptan. As observed when using media with a surface area of 250 m^2/m^3; the process of biodegradation decreased to 73%, resulting in an increase in the emission of the compound into the atmosphere of the plant as well as high concentrations of methyl mercaptan in the effluent wastewater. But when using media with a surface area of 1,250 m^2/m^3, the decomposition process increased to 93%, and odor emissions reached 6.5%. The surface area provided a suitable and sufficient environment for the growth of bacteria that decompose organic compounds, thus good efficiency was achieved in the system. The use of media with a surface area of 1,250 m^2/m^3 also positively affected the effluent wastewater quality, reducing its concentration from 5% to less than 1%, while reducing the proportion of this compound in the resulting sludge to less than 0.2% (Bachari 2021; Sun *et al.* 2021).

Figure 9(c) shows that when the proportion of media inside the reactor was 22.5%, the emissions due to methyl mercaptan were 20% higher, while the degradation rate, which was 72%, reached more than 75% after the increase in media inside the reactor. The decomposition rate of the methyl mercaptan compound increased to more than 90%, while the emission reduction was observed to reach less than 8% (Khan *et al.* 2021).

Figure 9(d) illustrates that increasing the air flow rate from 225 to 900 m^3/h led to an increase in the emission of odors from the plant space from 8 to 18%, and which also caused the rate of biological decomposition to decrease from 89 to 79% with a slight change in the sludge and wastewater lines (Zwain *et al.* 2020a, 2021; Khalid 2021).

The novelty of this study was the determination of the strengths and weaknesses of the plant's operations and the identification of regions of concern regarding the emission of this compound. It is possible to address this issue without incurring additional costs, but the biological processes can only be controlled by identifying the relevant processes of the system as described in the above discussion. This is the first time that one of the sulfur compounds with an unpleasant smell has been comprehensively assessed via the TOXCHEM model in an MBBR. This provides accurate data on the location of the noxious gas emissions, facilitating remedial action by the specialists at this plant.

4. CONCLUSION

The emission of methyl mercaptan from WWTPs presents a hazard risk and odor nuisance to operatives and the local populace. In this study, the biological elimination of methyl mercaptan in a MBBR was modeled using TOXCHEM V4.1. The results show that biological degradation, stripping, compound sorption, and discharge with effluents are the main processes that influence the fate of methyl mercaptan in the MBBR system. It was further shown that operating the MBBR system with (i) a thick biofilm layer, (ii) large specific surface area of media, (iii) greater media fill fraction, and (iv) increased aeration all contribute significantly to the decomposition of methyl mercaptan and decreased emissions into the atmosphere. This demonstrates that a TOXCHEM V4.1 model can be used to estimate the dispersion and fate of methyl mercaptan within a WWTP and hence inform policy regarding this toxin. To summarize, the main findings are as follows:

- biological degradation, stripping, compound sorption, and discharge with effluents are the main processes that influence the fate of methyl mercaptan in the MBBR system.
- operating the MBBR system with (i) a thick biofilm layer, (ii) large specific surface area of media, (iii) greater media fill fraction, and (iv) increased aeration all contribute significantly to the decomposition of methyl mercaptan and decreased emissions into the atmosphere.
- The TOXCHEM V4.1 model can be used to estimate the dispersion and fate of methyl mercaptan within a WWTP.

ACKNOWLEDGEMENT

The authors thank the Kerbala Sewerage Directorate for providing the required materials and instruments for this work.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

REFERENCES

Andraskar, J., Yadav, S. & Kapley, A. 2021 Challenges and control strategies of odor emission from composting operation. *Applied Biochemistry and Biotechnology* **193** (1), 1–26. https://doi.org/10.1007/s12010-021-03490-3.

Asadi, M. & McPhedran, K. 2021 Estimation of greenhouse gas and odour emissions from a cold region municipal biological nutrient removal wastewater treatment plant. *Journal of Environmental Management* **281**, 111864. https://doi.org/10.1016/j.jenvman.2020.111864.

Bachari, Z. 2021 *Influence of Carrier Surface Area and Surface Area Loading Rate on Moving bed Biofilm Reactor Performance in COD Removal From Municipal and Industrial Wastewater*. PhD Thesis, University of Manitoba, Canada.

Behnami, A., Benis, K. Z., Shakerkhatibi, M., Derafshi, S. & Chavoshbashi, M. M. 2019 A systematic approach for selecting an optimal strategy for controlling VOCs emissions in a petrochemical wastewater treatment plant. *Stochastic Environmental Research and Risk Assessment* **33** (1), 13–29. https://doi.org/10.1016/j.jclepro.2019.01.218.

Bhattacharya, R. & Mazumder, D. 2021 Simultaneous nitrification and denitrification in moving bed bioreactor and other biological systems. *Bioprocess and Biosystems Engineering* **44**, 1–18. https://doi.org/10.1007/s00449-020-02475-6.

Bhatti, Z. A., Qureshi, K., Maitlo, G. & Ahmed, S. 2020 Study of PAN fiber and iron ore adsorbents for arsenic removal. *Civil Engineering Journal* **6** (3), 548–562. http://dx.doi.org/10.28991/cej-2020-03091491.

Buaisha, M., Balku, S. & Özalp-Yaman, S. 2020 Heavy metal removal investigation in conventional activated sludge systems. *Civil Engineering Journal* **6** (3), 470–477. http://dx.doi.org/10.28991/cej-2020-03091484.

Cao, J., Yang, E., Xu, C., Zhang, T., Xu, R., Fu, B. & Luo, J. 2021 Model-based strategy for nitrogen removal enhancement in full-scale wastewater treatment plants by GPS-X integrated with response surface methodology. *Science of The Total Environment* **769** (15), 144851. https://doi.org/10.1016/j.scitotenv.2020.144851.

Chang, J. C. & Hanna, S. R. 2004 Air quality model performance evaluation. *Meteorology and Atmospheric Physics* **87** (1), 167–196. https://doi.org/10.1007/s00703-003-0070-7.

Cheng, H. H., Lu, I. C., Huang, P.-W., Wu, Y.-J. & Whang, L.-M. 2021 Biological treatment of volatile organic compounds (VOCs)-containing wastewaters from wet scrubbers in semiconductor industry. *Chemosphere* **282**, 131137. https://doi.org/10.1016/j.chemosphere.2021.131137.

Daims, H., Lebedeva, E. V., Pjevac, P., Han, P., Herbold, C., Albertsen, M. & Bulaev, A. 2015 Complete nitrification by Nitrospira bacteria. *Nature* **528** (7583), 504–509. https://doi.org/10.1038/nature16461.

Faris, A. M., Zwain, H. M., Hosseinzadeh, M. & Siadatmousavi, S. M. 2022 Modeling of novel processes for eliminating sidestreams impacts on full-scale sewage treatment plant using GPS-X7. *Scientific Reports* **12** (1), 1–17. https://doi.org/10.1038/s41598-022-07071-0.

Gao, W., Yang, X., Zhu, X., Jiao, R., Zhao, S., Yu, J. & Wang, D. 2021 Limitations of GC-QTOF-MS technique in identification of odorous compounds from wastewater: the application of GC-IMS as supplement for odor profiling. *Atmosphere* **12** (2), 265. https://doi.org/10.3390/atmos12020265.

Grzelka, A., Romanik, E. & Miller, U. 2019 Odour nuisance assessment of the food industry wastewater treatment plant. In: *E3S Web of Conferences*, Vol. 100, p. 24. https://doi.org/10.1051/e3sconf/201910000024.

Hussein, A., Shamsuddin, S., Kn, B. & Shreeshivadasan, C. 2015 Modelling of sewage quality during rainy season. *Asian Journal of Microbiology, Biotechnology and Environmental Sciences* **17**, 593–601.

Khalid, K. M. 2021 *Correlation Between Air Quality and Wastewater Pollution. Environmental Sustainability: Preparing for Tomorrow*. London, United Kingdom.

Khan, N. A., Ahmed, S., Farooqi, I. H. & Ali, I. 2021 Performance evaluation and parameter optimization of moving bed biofilm reactor (MBBR) along with electrocoagulation for removal of Azithromycin. **11** (2), 3329–3343. https://doi.org/10.33263/LIANBS112.33293343.

Kleinhenz, J. P. 2003 *Medium and Higher Molecular Weight Volatile Thiols in Aged Cheddar Cheese and Their Relation to Flavor*. The Ohio State University, United States.

Li, R., Han, Z., Shen, H., Qi, F. & Sun, D. 2021 Volatile sulfur compound emissions and health risk assessment from an A2/O wastewater treatment plant. *Science of The Total Environment* **749** (10), 148741. https://doi.org/10.1016/j.scitotenv.2021.148741.

Lu, J., Liu, P., Xu, Z., He, S. & Luo, Y. 2018 Investigation of the reaction pathway for synthesizing methyl mercaptan (CH_3SH) from H 2 S-containing syngas over K–Mo-type materials. *RSC Advances* **8** (38), 21340–21353. https://doi.org/10.1039/C8RA03430C.

Lv, Y., Xi, X., Xue, Y., Jiang, F., Zhu, X., Dai, L. & Chen, Z. 2021 A sustainable filtering material for efficient removal of volatile organic compounds from their aqueous mixtures. *Cellulose* **28**, 6353–6360. https://doi.org/10.1007/s10570-021-03938-z.

Masoomi, S. R., Azizi, M., Aghlmand, R., Gheibi, M. & Kian, Z. 2021 Simulating the dispersion of poisonous organic chemical compounds in wastewater treatment process through the active sludge method using the TOXChem model. **5** (1), 025–031. https://dx.doi.org/10.29328/journal.abse.1001014.

Michaels, D. & Wagner, G. R. 2020 Occupational Safety and Health Administration (OSHA) and worker safety during the COVID-19 pandemic. *Jama* **324** (14), 1389–1390. doi:10.1001/jama.2020.16343.

Mohsen, K. A., Nile, B. K. & Hassan, W. H. 2020 Experimental work on improving the efficiency of storm networks using a new galley design filter bucket. *IOP Conference Series: Materials Science and Engineering* 012094. IOP Publishing, Bristol.

Nile, B. K. 2018 Effectiveness of hydraulic and hydrologic parameters in assessing storm system flooding. *Advances in Civil Engineering* **2018**. https://doi.org/10.1155/2018/463917.2.

Padalkar, A. V. & Kumar, R. 2018 Removal mechanisms of volatile organic compounds (VOCs) from effluent of common effluent treatment plant (CETP). *Chemosphere* **199**, 569–584. https://doi.org/10.1016/j.chemosphere.2018.01.059.

Saidulu, D., Majumder, A. & Gupta, A. K. 2021 A systematic review of moving bed biofilm reactor, membrane bioreactor, and moving bed membrane bioreactor for wastewater treatment: comparison of research trends, removal mechanisms, and performance. *Journal of Environmental Chemical Engineering* **9** (5), 106112. https://doi.org/10.1016/j.jece.2021.106112.

Sun, H., Liu, H., Zhang, M. & Liu, Y. 2021 A novel single-stage ceramic membrane moving bed biofilm reactor coupled with reverse osmosis for reclamation of municipal wastewater to NEWater-like product water. *Chemosphere* **268**, 128836. https://doi.org/10.1016/j.chemosphere.2020.128836.

Syed, M., Soreanu, G., Falletta, P. & Béland, M. 2006 Removal of hydrogen sulfide from gas streams using biological processes• a review. *Canadian Biosystems Engineering* **48**, 2.

Vision, N. & Mission, N. 2013 *National Institute for Occupational Safety and Health*.

Wang, Y.-C., Han, M.-F., Jia, T.-P., Hu, X.-R., Zhu, H.-Q., Tong, Z. & Hsi, H.-C. 2021 Emissions, measurement, and control of odor in livestock farms: a review. *Science of The Total Environment* **776**, 145735. https://doi.org/10.1016/j.scitotenv.2021.145735.

Weihua, Y., Xiande, X., Gen, W., Jie, M., Zengxiu, Z. & Jiayin, L. 2021 Emission characteristics of volatile odorous organic compounds in fragrance and flavor industry. *Environmental Chemistry* **4**, 1071–1077. http://dx.doi.org/10.7524/j.issn.0254-6108.2020010705.

Wiśniewska, M., Kulig, A. & Lelicińska-Serafin, K. 2021 The use of chemical sensors to monitor odour emissions at municipal waste biogas plants. *Applied Sciences* **11** (9), 3916. https://doi.org/10.3390/app11093916.

Zhou, J., Jiang, Y. H., Li, W. H. & Liu, X. Y. 2018 Comparison and analysis of several wet scrubbing solutions to remove methyl mercaptan. *Journal of Environmental Science and Health, Part A* **53** (9), 819–824. https://doi.org/10.1080/10934529.2018.1455340.

Zwain, H., Basim, K., Faris, A. M., Vakili, M. & Dahlan, I. 2020a Modelling of hydrogen sulfide fate and emissions in extended aeration sewage treatment plant using TOXCHEM simulations. *Scientific Reports* **10**. https://doi.org/10.1038/s41598-020-79395-8.

Zwain, H., Vakili, M., Faris, A. M. & Dahlan, I. 2020b Modeling the fate of phenol in moving bed biofilm reactor sewage treatment plant. *Proceedings of AICCE* **19** (53), 1643–1653. https://doi.org/10.1007/978-3-030-32816-0_126.

Zwain, H. M., AL-Marzook, F. A., Nile, B. K., Zuhair, M. A. J., Atallah, A. H., Dahlan, I. & Waqed, H. H. 2021 Morphology analysis and microbial diversity in novel anaerobic baffled reactor treating recycled paper mill wastewater. *Archives of Environmental Protection* **47** (4), 9–17.

First received 2 December 2021; accepted in revised form 24 April 2022. Available online 14 May 2022