Ambiente & Água - An Interdisciplinary Journal of Applied Science
ISSN 1980-993X – doi:10.4136/1980-993X
www.ambi-agua.net
E-mail: ambi.agua@gmail.com

Fate and emission of methyl mercaptan in a full-scale A2/O plant using TOXCHEM Simulation

ARTICLES doi:10.4136/ambi-agua.3160

Received: 07 Mar. 2026; Accepted: 12 Jul. 2026

Rabab Riyadh[1]; Khabeer Al-Awad[1];
Najah M. L. Al Maimuri[2]; Basim K. Nile[1];
Ahmed N. Al-Dujaili[3*]; Layth Abdulameer[1]

[1]Department of Civil Engineering. College of Engineering. University of Kerbala, Al Mozafeen District Complex, Karbala 56001, Iraq. E-mail: rabab.r@s.uokerbala.edu.iq, khabeera@uokerbala.edu.iq, dr.basimnile@uokerbala.edu.iq, laith.saeed@uokerbala.edu.iq
[2]Building and Construction Technologies Engineering Department. College of Engineering and Engineering Technologies. Al-Mustaqbal University, 51001, Babylon, Hillah, Iraq. E-mail: najahml@yahoo.com
[3]Petroleum Engineering Department. Amirkabir University of Technology, Hafez Ave, n° 350, 1591634311, Valiasr Square, Tehran, Iran.
[*]Corresponding author. E-mail: ahmed.noori203@aut.ac.ir

Editor-in-Chief: Nelson Wellausen Dias

ABSTRACT

Methyl mercaptan (methanethiol) is one of the essential volatile, repugnant compounds released from wastewater treatment plants. This work uses a TOXCHEM simulator to model emission production and dispersal of odorous methyl mercaptan gas in full-scale A2/O plants. The sewage treatment plant (STP) in Karbala served as the basis for the case study, which showed that the two most significant processes in the system were emissions and degradation. Models were calibrated and validated to ensure that all data were within predefined limits. The root means square error (RMSE) and correlation coefficient (R) showed that the model was close to an ideal fit. 30.4% and 27.1% of all such gas were released into the atmosphere at 37°C in the summer and 12°C in the winter, respectively; 0.0096 and 0.45% were released with wastewater; 0.0.32 and 0.19% were absorbed by sludge; and 69.31% and 71.9% were degraded. To gain a better understanding of the production and dispersal of CH_4S emissions, a sensitivity analysis was also conducted. This was done by looking at the main influencing factors in the treatment process of the A2/O system, such as wind speed, wastewater temperature, flowrate and MLSS concentration in aeration reactors. Regarding the forecasting generation and dispersion of CH4S gas in an A2/O system, the TOXCHEM simulation is the best choice for the plant's decision-makers.

Keywords: biodegradation, Karbala STP, sewage treatment, TOXCHEM model.

Destino e emissão de metilmercaptana em uma estação A2/O em escala real utilizando a simulação TOXCHEM

RESUMO

O metilmercaptano (metanotiol) é um dos principais compostos voláteis de odor desagradável liberados por estações de tratamento de águas residuais. Este trabalho utiliza o

This is an Open Access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

simulador TOXCHEM para modelar a produção e a dispersão das emissões do gás odorífero metilmercaptano em estações de tratamento de grande porte que utilizam o processo A2/O. A estação de tratamento de esgoto (ETE) de Karbala serviu de base para o estudo de caso que demonstrou que os dois processos mais significativos no sistema eram emissão e degradação. Os modelos foram calibrados e validados para garantir que todos os dados estivessem dentro dos limites predefinidos. A raiz do erro quadrático médio (RMSE) e o coeficiente de correlação (R) indicaram que o modelo apresentou um ajuste próximo ao ideal. As frações do gás liberadas para a atmosfera foram de 30,4% no verão (a 37°C) e 27,1% no inverno (a 12°C); 0,0096% e 0,45% foram liberados juntamente com o efluente; 0,032% e 0,19% foram absorvidos pelo lodo; e 69,31% e 71,9% foram degradados. Para compreender melhor a produção e a dispersão das emissões de CH4S, também foi realizada uma análise de sensibilidade. Essa análise considerou os principais fatores de influência no processo de tratamento do sistema A2/O, tais como velocidade do vento, temperatura do efluente, vazão e concentração de sólidos em suspensão no licor misto (MLSS) nos reatores de aeração. No que diz respeito à previsão da geração e dispersão do gás CH4S em um sistema A2/O, a simulação via TOXCHEM representa a melhor opção para os tomadores de decisão da estação.

Palavras-chave: biodegradação, ETE de Karbala, modelo TOXCHEM, tratamento de esgoto.

1. INTRODUCTION

Human activity has significantly raised air pollution emissions at the local, regional, and global levels (Al-Shammari *et al.*, 2026). Understanding the source and concentration of pollutants is essential for more efficient pollution control and for assessing any possible adverse effects on human health (Godoi *et al.*, 2018; Rahi and Faisal, 2019; Hassan *et al.*, 2024). A persistent environmental problem brought on by urbanization and population growth is the discharge of odors from sewage treatment facilities (STPs) (Zwain *et al.*, 2020; Abdulameer *et al.*, 2025). Anaerobic breakdown during the biological breakdown of organic compounds in sewage treatment facilities results in offensive odors (Asadi and McPhedran, 2021). Sewage odorants released into the atmosphere while a wastewater treatment plant (WWTP) is operating may be the cause of the plant's smells (Faris *et al.*, 2022). Odorants may also develop as a result of wastewater's biodegradability (Wiśniewska *et al.*, 2021).

Anaerobic reactions generate chemicals including hydrogen sulfide, methane, and ammonia as well as organic compounds like mercaptans, amine, indole, and skatole (Andraskar *et al.*, 2021).The pH, temperature, and hydraulic parameters of the water phase all have an impact on the behavior of methyl mercaptan (fate and emission), a physicochemical process that impacts the WWTP's air and wastewater phases (Rathnayake *et al.*, 2021; Hassan *et al.*, 2024). Even though odors from municipal wastewater treatment plants (WWTPs) are common in urbanized areas, their emissions can cause serious ecological and social issues due to their negative impacts on the environment and the quality of life for those who live nearby (Jung *et al.*, 2020; Fan *et al.*, 2021; Riyadh *et al.*, 2024). Microbial processes use the biological sulfur cycle to eliminate sulfur compounds. The sulfur cycle has two components: reduction and oxidation. In the metabolic activities of certain microorganisms, sulfate acts as an electron acceptor on the reduction side and is transformed into sulfide. Phototrophic or chemolithothrophic bacteria use reduced sulfur compounds, including sulphides, as electron suppliers. On the oxidation side, these bacteria transform the reduced sulfur compounds into elemental sulfur or sulphate (Barbusiński and Kalemba, 2016).

Methanethiol, also called methyl mercaptan, is an organic compound with the formula CH_3SH or CH_4S (Faris *et al.*, 2022) Methyl mercaptan is a moderately volatile organic compound. It is a naturally occurring chemical that can be found in plant tissues, animal and human blood, and brains. It is a colorless gas with a characteristic dry smell. It is eliminated by animals through their excrement. Certain foods, like cheese and nuts, naturally contain CH_4S. It is also one of the main substances that cause flatulence and bad breath (Zhou *et al.*, 2018). Mercaptans, which are chemicals present in wastewater treatment operations, have varying smell thresholds (from 0.01 µg/m3 for butyl mercaptan to 2.16 µg/m3 for CH_3SH) (Faris *et al.*, 2022). Methyl mercaptan has an OSHA PEL (permissible exposure limit) of 10 ppm (20 mg/m3), an NIOSH REL (recommended exposure limit) of 0.5 ppm, and an NIOSH IDLH (immediately harmful to life or health) of 150 ppm. Many individuals may be exposed to the AIHA ERPG-2 for up to one hour without feeling any effects or developing long-term or other severe health issues (or symptoms that would make it difficult for them to adopt preventative measures) is 25 ppm.

Waste gas streams with high flow and pollutant concentrations are treated with physical technology. The ability to carry out biological activities at ambient temperature and air pressure is the primary benefit of biological treatment techniques over physical and chemical technology. Biological techniques are inexpensive and simple to use (Barbusiński and Kalemba, 2016). The final products of biological treatment are carbon dioxide, water, sulfate, and nitrate, making them environmentally cleaner than physicochemical treatments (Kennes *et al.*, 2009). While all reactors use similar basic pollutant removal techniques, the primary distinctions are caused by the type of packing media used, the concentration of pollutants, the usage of microorganisms (suspended in liquid or immobilized on biofilm), etc. (Mudliar *et al.*, 2010; Barbusiński and Kalemba, 2016).

The behavior of pollutants in sewage networks and wastewater treatment facilities has been simulated using a variety of models, many of which rely on empirical mass transfer coefficient derivations in the liquid phase (KL) or gas phase (KG). These include Gostelow, BASTE, CINCI, WATER9, and TOXCHEM. The most popular model is TOXCHEM (Zwain *et al.*, 2020; Masoomi *et al.*, 2021). The control of CH3S can benefit from mathematical models that explain its fate and emission. In these models, the methods for eliminating pollutants are volatilization, sorption, and degradation from different processes. These processes require biological interactions in addition to mass transfer in the liquid and gas phases (Carrera-Chapela *et al.*, 2014). It is based on the mass balance of many compounds in WWTPs, taking into consideration a range of physical, biological, and chemical procedures such volatilization, biodegradation, stripping and sorption.

Estimating the VOC air emissions from wastewater collecting systems, disposal sites, and WWTPs is its main application. Using project planning, design, and optimization to reduce air emissions is another aspect of this (Zwain *et al.*, 2020; Hassan *et al.*, 2024). This technique can also be used to forecast the loads and concentrations of contaminants in the residual solids and water effluent streams.

The model in this study is the Karbala wastewater treatment plant project. The residential developments are not far from the station that was modeled in this study. Karbala Sewerage Directorate received complaints from certain residents regarding offensive odors, particularly during the summer. methyl mercaptan and other compound sulfate in the sewage are the cause of the odors coming from this plant. Sulfates are where methyl mercaptan and another compound sulfate originates. Karbala's geology is recognized by its high groundwater levels and gypsum soil. Because of this, the groundwater contains high concentrations of sulfide (SO_4^{-2}) compounds. Because of the gypsum terrain in this area and the high groundwater levels there, sulfates are the source of methyl mercaptan and other compounds enter the network through leaching. The objective of this study is to estimate the amounts of volatilization, absorption, decomposition, and emission for the summer and winter seasons by modelling the behavior of methyl mercaptan using a TOXCHEM simulation, while being aware of the most significant sensitive variables on the A2\O system, including the pH level, temperature, and flow rate of wastewater influent (m^3/ d), for example.

2. MATERIAL AND METHODS

2.1. Karbala sewage treatment plant.

Karbala sewage treatment plant is located on the main road between Karbala and Najaf, about 20 kilometers from Karbala's center and nearly 110 kilometers south of Baghdad, coordinates 32°32'15.2" N and 44°04'31.7" E, as shown in Figure 1. The plant serves the residents of Kerbala city, with a design capacity of 400000 m 3 /d, giving it the capacity to serve 2 million people. The biological treatment process at this plant uses A2/O (anaerobic, anoxic, and oxic) activated sludge. The plant was designed according to the data in Table 1.

This plant includes stages of treatment as follows and as illustrated in:

- The coarse and fine screen units as well as the API separator (oil and grease) unit are part of the preliminary stage.
- The biological stage includes a primary clarifier unit, a biological treatment reactor (anaerobic, anoxic, oxic) and a secondary clarifier.
- a tertiary stage (chlorine disinfection unit)
- Sludge treatment stage (thickener, anaerobic digester, and drying beds), as shown in Figure 2 Karbala STP A2/O system designs using the TOXCHEM simulation.

Figure 1. Aerial view of the study site.

2.2. Taking samples and analyzing

From January to December 2024, monthly influent and effluent samples were collected in order to assess the Karbala STP's effectiveness. Following standard procedures for water and waste water analysis, measurements were made from three samples in each case including pH, COD, BOD5, TSS, NO_3, NO_2, NH_4^+, SO_4^{-2}, H2S, oil and grease, $PO_4^{-3}$and CH_4S. All influent and effluent properties reported in Table 2 were compared to Iraqi standards, and only average values are given. The operational conditions of the Karbala STP are described in Table 1, and the average laboratory test results for the Karbala STP in 2025 are displayed in Table 2. The wind speed varied from 5 to 25 km/h throughout the year, with the north-west (305°) direction being the most common.

Table 1. Karbala WWTP's design and operational parameters.

Parameters of A2/O system	design Value	Operation value
(MLSS) (mg/l)	2000- 4000	3000
F/M (kg BOD/kg MLVSS day)	0.16	0.16
SLR (kg MLSS/m2 h)	3.6	3.6
Hydraulic Loading Rate (m3/m2 day) (m3/m2 day)	15.5	15.5
Hydraulic retention time (h)	4	4
DO (mg/l)	2-3	2
SRT (day)	3-10	10
Return activated sludge %	60	60
SVI (ml/g)	85	85
Mainstream flowrate (m3/day)	400000	100000

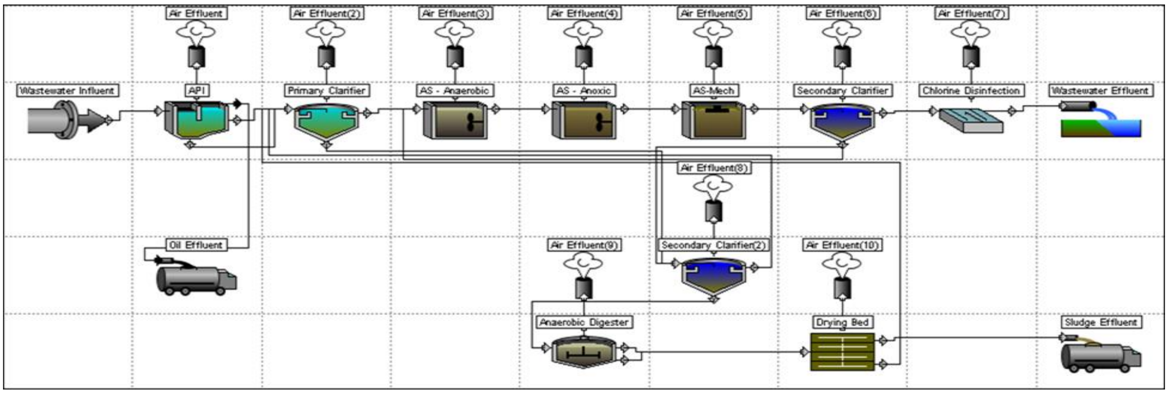


Figure 2. Karbala STP A2/O system designs using the TOXCHEM simulation.

Table 2. Laboratory test of Kerbala sewage treatment plant.

Parameter	Influent concentrate	Outlet concentrate	Iraqi standard
pH	7.2 – 7.4	7.1 – 7.2	6 – 9
COD	200 – 300	28 – 34	100
BOD	120 – 160	10 – 16	40
TSS	190 – 210	10 – 18	60
NO_3	0 – 1	20 – 80	50
NO_2	0	ND	---
NH_4	16 – 20	0.3 – 0.8	10
SO_4^{-2}	600 – 800	650 – 850	400
H_2S	20 – 40	0.5	3
Oil & grease	40	2	10
Po_4^{-3}	14 – 15	2 – 3	3
CH_4S	0.98	0.002	-

2.3. Setup of the TOXCHEM simulation

The emission and dispersion of methyl mercaptan odorous gas from various Karbala STP units were simulated using a dispersion model in TOXCHEM. This model assumed that methyl mercaptan and volatile organic molecules shared the same properties. TOXCHEM combines the sorb, mass transfer, and degradation processes to model elimination. Biodegradation and volatilization are the main methods of removal; sorption is less significant.

2.3.1. Biodegradation

In an aerobic biodegradation process, oxidation facilitates the elimination of methyl mercaptan. Since the biological treatment procedures in the Karbala STP system depend on suspended growth, the methyl mercaptan biodegradation rate (rb) in TOXCHEM can be determined using Equation 1:

$$rb = kb\left(\frac{C}{1+(C\backslash ks)}\right)XV \quad (1)$$

Where rb is the rate of degradation (mg/h), V is the reactor volume, kb is the coefficient of the first order rate of degradation (L/mg VSS/h), X is the amount of biomass (mg/L), ks is the half-saturated constant (mg/L), and C is the volume of volatile compound contaminants in the water (mg/m^3).

2.3.2. Liquid- gas mass transfer

The TOXCHEM simulation includes both surface volatilization and air stripping as mass transfer mechanisms. Surface volatilization is the process by which compounds are expelled from the open surfaces of tanks such as clarifiers. However, air stripping, which often occurs in aerated turbulent process vessels, accounts for the majority of mass transfer losses (Melcer *et al.*, 1994), Volatilization in Karbala STP occurs from various sources, including tank tops, air stripping during aeration, weirs, and sewer reaches. TOXCHEM accounts for the varying rates of stripping and volatilization from a range of surfaces by applying Equations 2 and 3, respectively (Melcer *et al.*, 1994):

$$rd = kd\ C\ fnon\ V \quad (2)$$

Where *rd* is the Diffused aeration stripping rate (mg/h), kd is the aeration diffused stripping constant, C is the concentration of volatile contaminants in liquid (mg/m^3), f non is the pH dependent part of non-dissociated contaminant, and V is the volume of the aeration reactor (m^3).

$$rv = kv\ C\ fnon\ V \quad (3)$$

Where *rv* is the rate of volatilization (mg/h) and kv is the volatilization average constant (l/h).

2.3.3. Sorption

Methyl mercaptan sorption by particles in sewage treatment plants has been observed to be a reasonably quick process. TOXCHEM simulation models assume that such systems are in continuous equilibrium, with sorption equilibrium reached quickly (Melcer *et al.*, 1994). Methyl mercaptan can be reduced from wastewater in Karbala STP's activated sludge process by focusing sorption on primary and secondary clarifier solids. Equation 4 represents the concentration of H2S on a solid sorbent in an equilibrium liquid-solid system.

$$q = kp\ C \quad (4)$$

Where q is the pollutant concentration in solid state (µg/g), and kp is the sorption fraction coefficient (L/g). This connection is a benchmark for the lowest pollutant concentrations that occur in both municipal and some industrial STPs (Melcer *et al.*, 1994).

2.4. TOXCHEM simulation 's calibration and validation

A TOXCHEM model was created to simulate the emission and distribution of toxic pollutants in sewage treatment plants, which required review once completed. Validation and calibration are required methods for such evaluations.

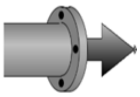
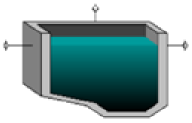
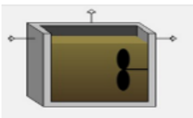
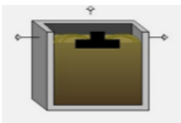
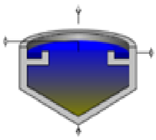
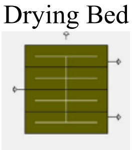
Calibration is the process of measuring a sample with results that are within an acceptable range when compared to actual data, such as that received from the Karbala STP in this case. A calibration process was performed for the average of the winter season, and a validation method was conducted for the average of the summer season, following the input of all required data into the model, as indicated in Table 3. Results that are extremely close to reality were achieved after adjusting the model's default parameters. The correlation coefficient (R) and root mean square error (RMSE) will be used to statistically verify that the projected values are acceptable when compared to the actual results. Their Equations 5 and 6 are displayed below:

$$R = \frac{(Ca - Ca|)(Cp - Cp|)}{\sigma\, Ca\, \sigma\, Cp} \quad (5)$$

$$RMSE = \frac{(Ca - Cp)2}{CaCp} \quad (6)$$

Where σ is the standard deviation across the data set, Ca is the measured CH_4S data, Cp is the simulated CH_4S data, Ca| is the mean over the measured CH_4S data, and Cp| is the mean over the simulated CH_4S data (Augusto *et al.*, 2020), Reasonable limitations according to the statistical criterion are $0 \leq RMSE < 1.5$ and $1 \geq R > 0.8$.

Table 3. Validation and calibration in summer and winter at Karbala WWTP.

Nit Process	Parameter	Unit	Default	Calibration	Validation
wastewater influent 	Flowrate	m^3\d	50000	1500000	1500000
	SS	mg\l	200	250	220
	Vss to ss ratio	%	75	78	77
	Oil\ grease concentration	mg\l	0	30	20
	Temperature	^{0}C	15	12	37
Apl 	SS removal efficiency	%	50	15	20
	Oil removal efficiency	%	80	92	98
	Sludge SS conc. (mg/L)	mg\l	10000	400	400
	Flowrate of recovered oil	m^3\d	500	100	100
AS- anaerobic\ anoxic  AS- Mech  Secondary clarifier 	MLSS (mg/L)	mg\l	3000	3000	3500
	VSS/SS ratio (%)	%	75	78	77
	SRT		10	10	10
	Standard oxygen transfer rate	kgO_2/kWh	1.8	1.8	2.5
	Sludge SS concentration	mg\l	6000	7000	10000
	Local pH		7	7.3	6.9
	Liquid depth	m	5	6	6
	Effluent SS concentration	mg\l	10	7	14
	Total aerator Power	KW	300	280	450
Drying Bed 	Final solid concentration	%	50	50	50
	Filtrate/centrate SS conc.	mg/l	200	200	200

2.5. Sensitivity analysis.

One of the most crucial techniques required to comprehend how sensitive parameters inside the treatment plant affect emissions and the destiny of the gas methyl mercaptan is the sensitivity analysis. In the treatment of methyl mercaptan gas, one of the most hazardous pollutants in wastewater, the most significant factors influencing suspended and attached growth processes and their susceptibility to variable factors were found in this study. Sensitivity analysis was utilized to discover which parameters or plant operating conditions had the largest and lowest impact on the emission and dispersal of methyl mercaptan odorous gas in A2/O systems. The factors and operational circumstances evaluated in this study included MLSS concentrations in mechanically aerated activated sludge basins, wastewater temperature, and wind speed. ranged MLSS content 2,500 to 6,000 mg/l, temperature 10 to 40°C, and wind speed 10 to 35 km/h.

3. RESULTS AND DISCUSSION

3.1. Operating parameter for Kerbala STP

The data provided in Table 2 show that the Karbala STP effluent concentration of pollutants is highly variable, though typically acceptable for parameters such as COD, BOD5, and Po_4^{-3}, and very good for specific parameters such as NH_4, H_2S, oil, and grease, according to Iraqi requirements (Al-Iraqiya, 2012). In this investigation, Table 2 also reveals that the concentration of SO_4^{-2} in the plant is comparatively high, but most likely owing to the oxidation of Sulphur compounds, such as CH_4S and those proteins that contain bigger amounts of Sulphur in the aeration basin, resulting to higher sulphate concentrations in the treated effluent (Faris *et al.*, 2022).

3.2. Methyl mercaptan gas behavior in Karbala STP

Several odorants associated with sewage that are discharged into the atmosphere when the plant is operating may be the source of the odors coming from a sewage treatment plant (Gao *et al.*, 2021). Every day, the Karbala STP's A2/O system receives about 98 kg of CH_4S, which is processed by a number of treatment facilities. According to the TOXCHEM simulation, Figure 4 displays the percentage dispersion of CH_4S gas for Karbala STP in the summer (37C) and winter (12°C), which are (30.4% and 27.1% emission to air, 0.0096% and 0.45% discharged with effluent, 0.19% and 0.32% sorbed to sludge, and 69.3% and 71.9% subject to biodegradation, respectively (Figure 3). These mechanisms are therefore summarized up below in light of the previously discussed results:

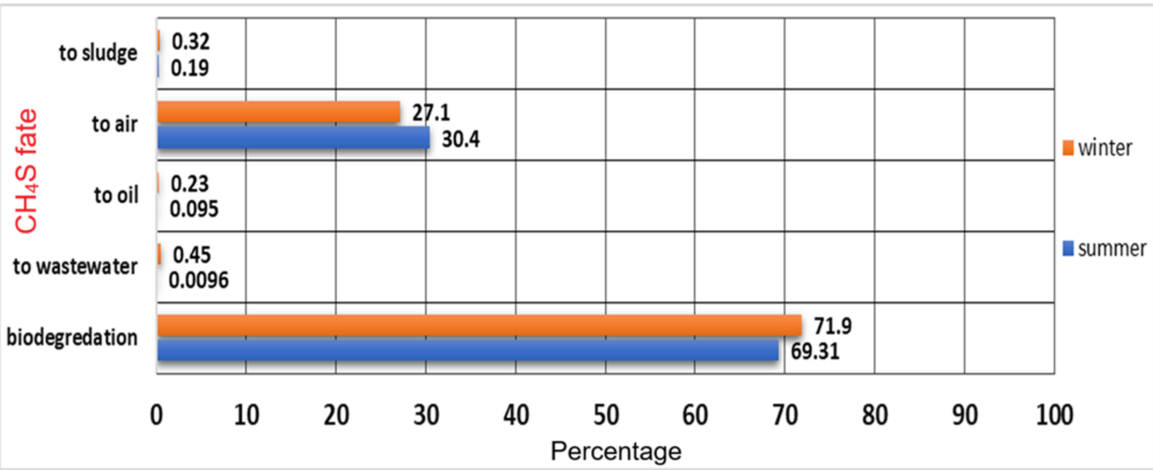


Figure 3. CH_4S fate (%) in the summer and winter.

3.2.1. Degradation, with aerobic processes oxidizing methyl mercaptan

The most popular physical, chemical, and biological techniques for clarifying freshwater include sorption, chemical oxidation and reduction, and biological treatment (Gao *et al.*, 2021). When the right conditions are naturally available, the process of biodegradation using activated sludge for STP operation is very prevalent (Mozo *et al.*, 2012). The biological sulfur cycle, which consists of oxidative and reductive reactions, is the foundation for biodegradation procedures used to eliminate sulfur compounds. On the reductive side, sulfate is transformed into sulphide in the metabolic pathways of some bacteria by acting as an electron acceptor. Following their use as electron donors, the reduced sulfur compounds—such as sulphides-oxidize to produce elemental sulfur or sulphates by phototrophic or chemolithotrophic bacteria (Tansel and Eyma, 1999). While chemolithotrophic SOB get their energy from metabolic processes involving oxygen (aerobic species) or nitrates and nitrites (anaerobic species), photoautotrophic SOBs get their energy from light in anaerobic environments. The desulphurization of CH_4S in activated sludge systems is more technically feasible with chemolithotroph SOB because of their high sulphide tolerance and adaptability to various environmental conditions.

3.2.2. Stripping from open surfaces into the atmosphere through mechanical aeration and volatilization

The most significant mechanism causing air emissions is frequently volatilization, which happens when the molecules of a dissolved substance escape to a nearby gas layer (Zwain *et al.*, 2020). The most pungent substances produced by STP are volatile sulfur compounds (VSCs), which can also lead to pain and a higher risk of non-carcinogenic diseases, among other health issues. Since hydrogen sulfide, methyl mercaptan are the most common VSC released from WWTPs (Faris *et al.*, 2022), improving biodegradation and lowering non-biotic transfer to the atmosphere is now a key objective of volatilization and stripping development (Mozo *et al.*, 2012). According to Figure 3, the Karbala STP releases about 98 kg of CH_4S into the atmosphere every day. Based on the TOXCHEM simulation and as a percentage of total emissions. Figure 4 provides an additional classification of the CH_4S emissions from each unit. This demonstrates that the plant emits more ch4s during the summer than during the winter, with the AS-Mecha counting for the majority of these emissions (> 50%), followed by primary clarifiers (25 to 50%). The drying beds had the lowest emissions, which varied between 10% and 25%.

Aerobic treatment can lower liquid-phase odorant concentrations because of biological oxidation. However, these may operate as big odor generators, particularly if overloaded, because they expose large amounts of sewage to the air and accelerate the stripping of odorants. One common way to address this is to recycle settled activated sludge

with sulfur compounds like H_2S and methyl mercaptan from secondary clarifiers or from aerated aeration tanks to the WWTP entrance. This allows for a higher consumption of odorous compounds before they volatilize from the liquid (Barbusiński and Kalemba, 2016).

Volatilization from an open surface is the most common source of VOC and H2S and CH4s emissions. The quantity of volatile compounds in the water, the volatility of individual compounds, the surface area of the water exposed to the gas phase, the level of turbulence of the water surface, and the water's settling period in the basin all influence the rate of emissions (Tansel and Eyma, 1999). Figure 5 illustrates the release of methyl mercaptan gas to the atmosphere from each unit in the Karbala treatment facility. The greatest emissions occurred in the AS-Mechunit, which had a concentration of 7 ppm in summer and 4ppm in winter, followed by the primary clarifier unit, where the emissions reached 3.27ppm in summer and 1.67ppm in winter.

According to these numbers, which puts people at risk for headaches, nausea, dizziness, and irritation of mucous membranes. More precisely, even at low quantities, CH_4S can have a very disagreeable odor. The World Health Organization (WHO, 2000) states that it is detectable at concentrations as low as 0.0005 parts per million. Good operating practices in WWTPs, such as regular cleaning of grit chambers or screening facilities, shortening the time that sludge is retained in thickeners or dewatering units, and operating with adequate aeration and blending, are therefore all thought to be crucial elements in assisting in the reduction of odor production and the minimization of the inconvenience that such odors cause to nearby residents.

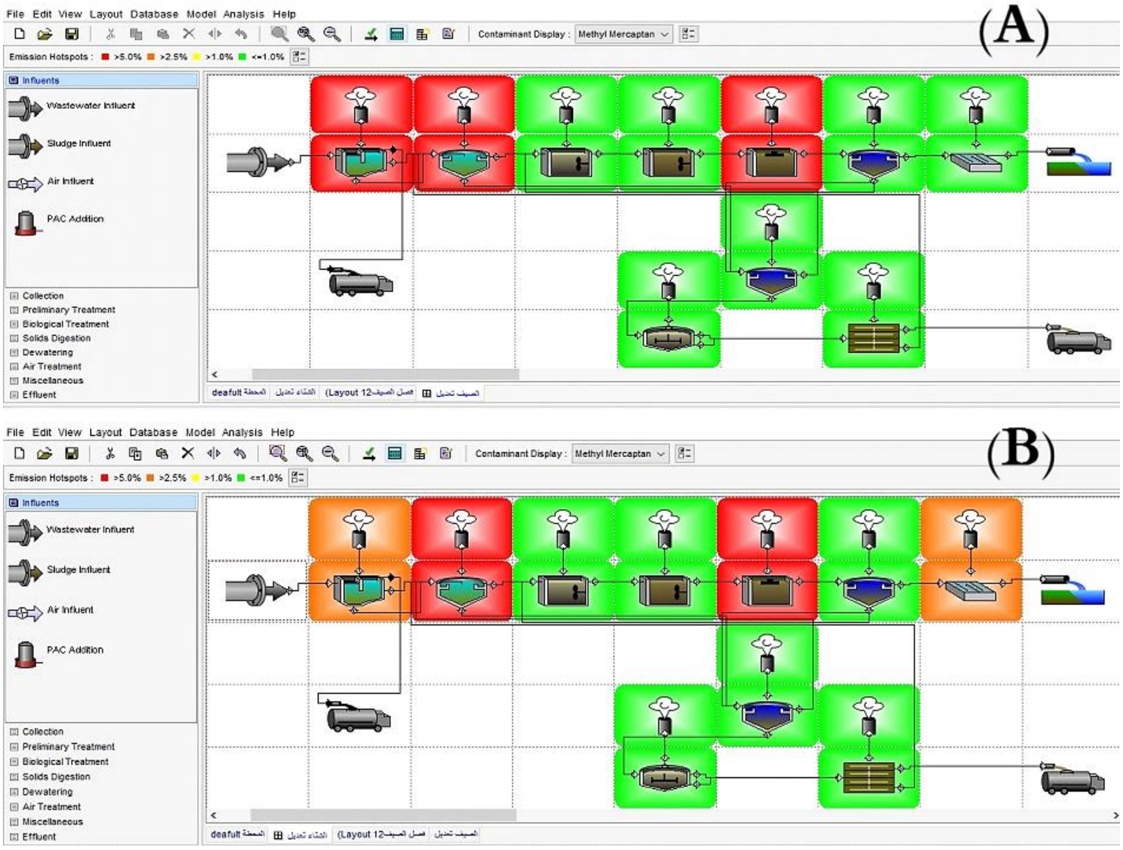


Figure 4. CH_4S emissions to the atmosphere per unit (as a percentage of total emissions): (A) summer and (B) winter.

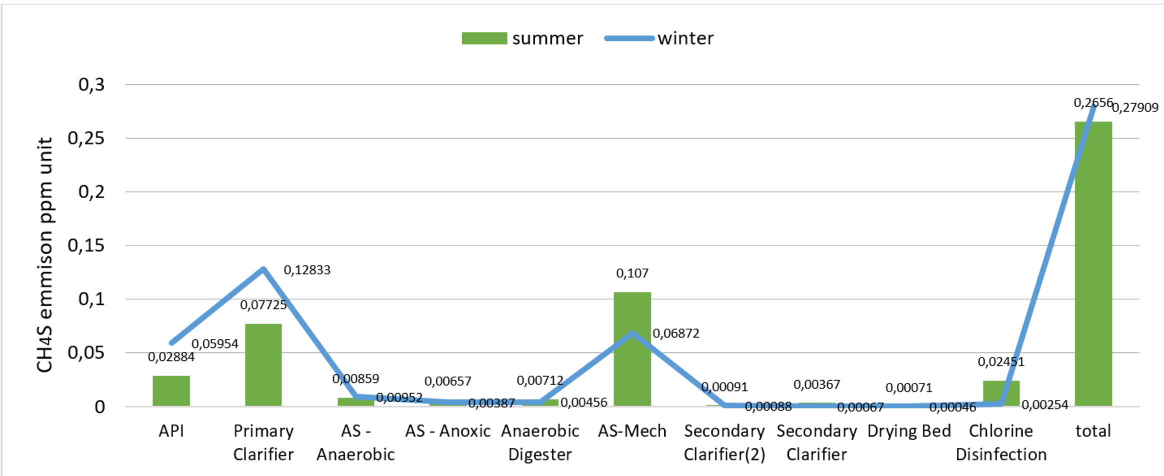


Figure 5. CH_4S emissions to the atmosphere per unit (ppm) in the summer and winter.

3.3. Calibration and validation of results

General information has been integrated into the TOXCHEM simulation, including the plant's dimensions and volumes, daily discharge, and hydrogen sulfide gas concentration. R and RMSE were not applicable to the methyl mercaptan gas outlet results in the treated wastewater, which were far from realistic. The calibration of the model's default variables have been modified, as indicated in Table 3. Figure 6 illustrates the good results of the calibration of methyl mercaptan gas in the treated water, which matched the R and RMSE limitations of 0.95 and 0.06, respectively.

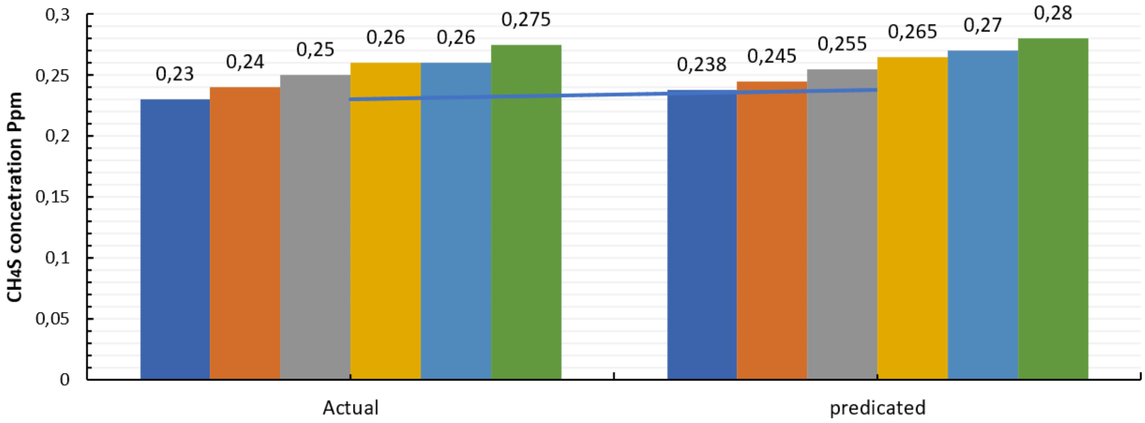


Figure 6. Methyl mercaptan gas results for winter and autumn (calibration).

Following proper calibration of the plant, validation was the following stage. To get the best fit between the model and reality, a number of parameters were changed throughout the validation phase, as indicated in Table 3, which involves determining the degree of validity of the findings simulated by the TOXCHEM simulation. The validation results are shown in Figure 7 and were identical to R and RMSE. It is necessary to modify three crucial and sensitive TOXCHEM simulation parameters before starting the calibration and validation procedure. These parameters are pH, VSS to SS ratio, and Mixed liquor suspended solids (MLSS). The parameters mentioned were changed as shown in Table 3.

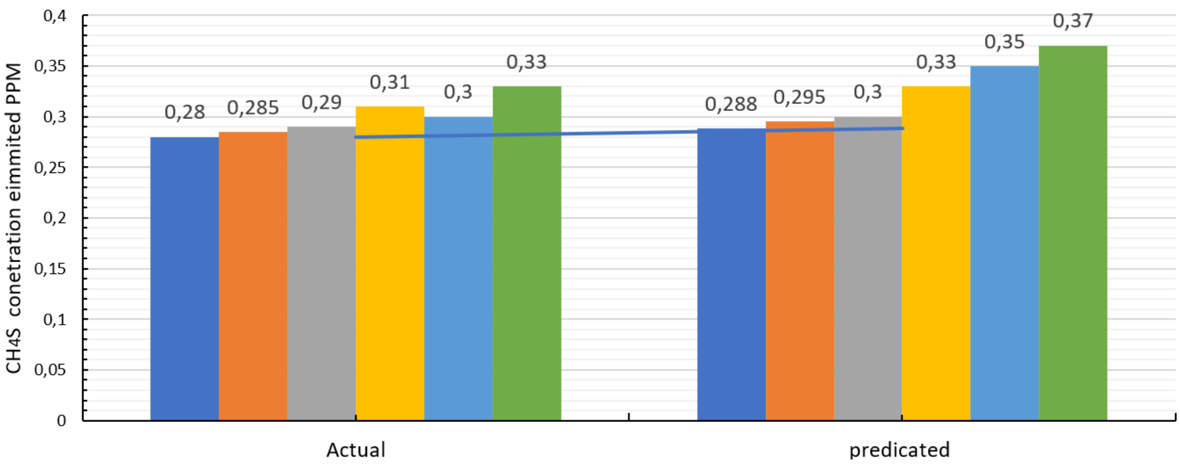


Figure 7. Methyl mercaptan gas results for spring and summer (validation).

3.4. Sensitivity analysis

Many variables, such as wastewater influent flowrate, wastewater influent temperature (°C), MLSS, wastewater pH level, wind speed, and VSS to SS ratio, influence the fate and emission of hydrogen sulfide gas at the Karbala sewage treatment plant.

3.4.1. MLSS

Figure 8(a) illustrates how MLSS concentration affects CH_4S dispersion. The ratios of absorption to sludge and discharge to effluents did not significantly alter, but when the MLSS concentration was raised to 6,500, the biodegradation rates decreased from 70to 50% and the emission rates increased from 28 to 44%. According to (Moussavi *et al.*, 2007) the efficiency of hydrogen sulfide removal decreased as MLSS concentration increased. They observed an inverse relationship between MLSS concentration and removal efficiency, with higher MLSS concentrations leading to decreased biodegradation, lower CH_4S removal efficiency, and higher aqueous CH_4S concentrations, which facilitate CH_4S emission to the atmosphere.

3.4.2. Wind Speed

The impact of wind speed on CH_4S dispersion and release from STP into the atmosphere is shown in Figure 8(b). While the sorption to sludge and discharge to wastewater processes were unchanged, the CH_4S volatilization rate increased from 30% to 40% and biodegradation decreased from 65% to 60% when the average wind speed was increased from 5 to 25 km/h. As demonstrated by different volatilization models (Santos *et al.*, 2012), under quiescent meteorological conditions (calm winds and low concentrations of atmospheric blending), methyl mercaptan volatilization can be considered nearly constant at low wind speeds with a friction velocity less than 0.3 m/s. However, volatilization of CH_4S may vary depending on higher wind speeds. However, depending on the weather, some odors can be detected at undiluted concentrations far from their source (Metcalf & Eddy, 2014). Since this study focuses on odorous compound emissions from the passive liquid surfaces of wastewater treatment plants, wind speed significantly impacted every chemical that was tested.

3.4.3. Temperature

Temperature affects the physical and chemical properties of gases in addition to biological reaction mechanisms and the Henry Gas Law. Figure 8(c) shows the influence of wastewater temperatures ranging from 6 to 40°C on CH_4S dispersion because it has been demonstrated that temperature significantly affects the mass transfer of CH_4S, regardless of whether it is dissolved in wastewater or vitalized into the air. Along with more modest delaying effects on sorption processes and effluent to wastewater, the amount of CH_4S released increased from 25 to 40% as the temperature increased from 6 to 40°C, whereas CH_4S degradation decreased from 70% to 60%. Based on a full-scale sequencing batch reactor (SBR) sewage treatment plant studied over a full year, another study by Calvo *et al.* (2018) demonstrated that emissions of volatile sulfur compounds at the air-liquid layer are significantly impacted by increased atmospheric temperature and aeration, with the highest emissions taking place during the summer. Increases in CH_4S emissions during the last month of the study confirmed the impact of air temperature on CH_4S emissions, which has previously been observed in other investigations. The CH_4S emissions from the screening building ranged from 0.4 to 2.3 parts per million, which is an order of magnitude more than what was seen in the pre-aeration basin (Baawain *et al.*, 2017).

3.4.4. Flowrate

Figure 8 (D) demonstrates how the destiny and emission of methyl mercaptan gas are affected by the wastewater influent flow rate (50000–300000 m3/d). At the lowest flow, it was found that the emission rate was 20% and the biodegradation rate was 80%. This is because the basins' increased hydraulic retention time (HRT) causes the gas to biodegrade more quickly. The emission process rises to 47% at the flow's maximal condition, while the biodegradation processes start to decline (50%). According to previous studies, HRT has an impact on the destiny and emission of methyl mercaptan gas, but the increased flow also speeds up turbulence in the WWTP basins, which additionally contributes to the gas's release. The concentrations of methyl mercaptan that are created in the network and released as it enters the plant's open channels also rise with increased flow. The process of removing methyl mercaptan gas improves when the flow is normal since it was found that when the flow reduces, it allows adequate time for the gas to break down and oxidize into sulfate (Sherief and Aly Hassan, 2022; Hassan *et al.*, 2024).

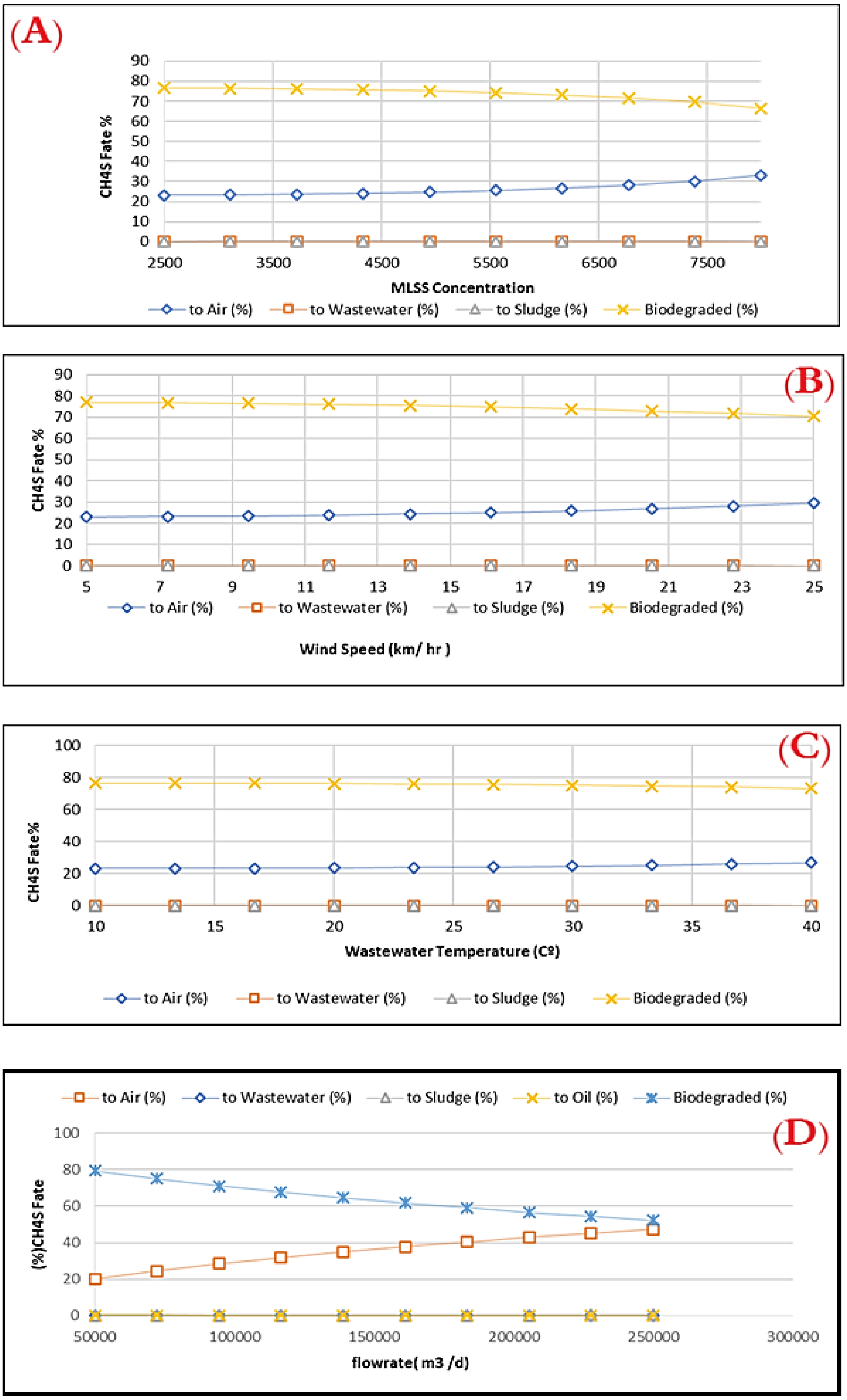


Figure 8. Sensitivity Analysis for the TOXCHEM simulation of Various CH_4S Desperation.
A) MLSS Concentration, B) Wind Speed, C) Wastewater Temperature, and D) Wastewater Flowrate.

4. CONCLUSIONS

In this study, a TOXCHEM V4.1 simulation of a full-scale plant of type A2/O was utilized to predict the emissions and distribution of CH_4S from the Karbala STP. In order to provide well-fitted data that accurately reflected the simulation, the system was used to mimic biological treatment for the elimination of CH_4S. Model calibration and validation were then applied.

1. The STP units' CH_4S emissions to the environment were arranged as follows: Pretreatment is greater than Advanced Treatment, which is greater than Biological Treatment.

2. Degradation was the primary mechanism in the system, with aerobic processes oxidizing the greatest amount of methyl mercaptan in summer and mechanical aeration and volatilization from open surfaces into the environment at a maximum effect in winter.

3. In addition to being annoying due to excessive odor, CH_4S frequently has a detrimental effect on human health. Thus, an accurate TOXCHEM simulation could help academics and decision-makers estimate emissions under different situations and guide operators in managing and decreasing sewage odor.

4. Model calibration and validation by the root mean square error (RMSE) and correlation coefficient (R) showed that the model was close to an ideal fit.

5. DATA AVAILABILITY STATEMENT

Data availability not informed.

6. REFERENCES

ABDULAMEER, L. S.; ABDALRAHEM, M. K.; AL MAIMURI, N. M.; AL-DUJAILI, A. N.; AL-SHAMMARI, M. Artificial Intelligence in Sustainable Drainage Water Reuse: A Comprehensive Review. **Water Conservation Science and Engineering**, v. 10, n. 3, p. 107, 2025. https://dx.doi.org/10.1007/s41101-025-00430-8

AL-IRAQIYA. **Iraqi regulation number 3: national limits for the use of secondary treated effluents in agricultural irrigation**. Baghdad: Ministry of Justice of Iraq, 2012. p. 4223-4231.

AL-SHAMMARI, M.; ABDULAMEER, L.; AL JOUBOURY, M. F.; AL MAIMURI, N. M. L.; AL-DUJAILI, A. N. Precipitation Influence on Air Quality: Unraveling the Air Quality Index-Rainfall Dynamics. **Journal of Renewable Energy and Environment (JREE)**, v. 13, n. 3, p. 1-7, 2026. https://dx.doi.org/10.30501/jree.2026.553575.2677

ANDRASKAR, J.; YADAV, S.; KAPLEY, A. Challenges and control strategies of odor emission from composting operation. **Applied Biochemistry and Biotechnology**, v. 193, n. 7, p. 2331-2356, 2021. https://dx.doi.org/10.1007/s12010-021-03490-3

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

AUGUSTO, M. R. *et al.* Modeling of H_2S dispersion in Brazil with AERMOD: Case study of water resource recovery facility in south of Brazil. **Revista Brasileira de Meteorologia**, v. 34, n. 4, p. 497-504, 2020. https://dx.doi.org/10.1590/0102-7786344063

BAAWAIN, M. *et al.* Assessment of hydrogen sulfide emission from a sewage treatment plant using AERMOD. **Environmental Monitoring and Assessment**, v. 189, n. 6, p. 263, 2017. https://dx.doi.org/10.1007/s10661-017-5983-6

BARBUSIŃSKI, K.; KALEMBA, K. Use of biological methods for removal of H_2S from biogas in wastewater treatment plants: a review. **Architecture Civil Engineering Environment**, v. 9, n. 1, p. 103-112, 2016. https://dx.doi.org/10.21307/acee-2016-011

CALVO, M. J. *et al.* Sensitivity analysis of the WATER9 model: emissions of odorous compounds from passive liquid surfaces present in wastewater treatment plants. **Water Science and Technology**, v. 77, n. 3, p. 903-912, 2018. https://dx.doi.org/10.2166/wst.2018.271

CARRERA-CHAPELA, F. *et al.* Modeling the odor generation in WWTP: an integrated approach review. **Water, Air, & Soil Pollution**, v. 225, n. 6, p. 1932, 2014. https://dx.doi.org/10.1007/s11270-014-1932-y

FAN, F. *et al.* Activated sludge diffusion for efficient simultaneous treatment of municipal wastewater and odor in a membrane bioreactor. **Chemical Engineering Journal**, v. 415, p. 128765, 2021. https://dx.doi.org/10.1016/j.cej.2021.128765

FARIS, A. M. *et al.* Fate and emission of methyl mercaptan in a full-scale MBBR process by TOXCHEM simulation. **Journal of Water and Climate Change**, v. 13, n. 6, p. 2386-2398, 2022. https://dx.doi.org/10.2166/wcc.2022.438

GAO, W. *et al.* Limitations of GC-QTOF-MS technique in identification of odorous compounds from wastewater: the application of GC-IMS as supplement for odor profiling. **Atmosphere**, v. 12, n. 2, p. 265, 2021. https://dx.doi.org/10.3390/atmos12020265

GODOI, A. F. L. *et al.* Human exposure to hydrogen sulphide concentrations near wastewater treatment plants. **Science of the Total Environment**, v. 610, p. 583-590, 2018. https://dx.doi.org/10.1016/j.scitotenv.2017.07.209

HASSAN, W. H.; FARIS, A. M.; FAISAL, A. A. Using TOXCHEM model for simulation the hydrogen sulfide behavior in a full-scale MBBR process. **Desalination and Water Treatment**, v. 317, p. 100244, 2024. https://dx.doi.org/10.1016/j.dwt.2024.100244

JUNG, H.; BAEK, G.; LEE, C. Magnetite-assisted *in situ* microbial oxidation of H_2S to S^o during anaerobic digestion: a new potential for sulfide control. **Chemical Engineering Journal**, v. 397, p. 124982, 2020. https://dx.doi.org/10.1016/j.cej.2020.124982

KENNES, C.; RENE, E. R.; VEIGA, M. C. Bioprocesses for air pollution control. **Journal of Chemical Technology & Biotechnology**, v. 84, n. 10, p. 1419-1436, 2009. https://dx.doi.org/10.1002/jctb.2216

MASOOMI, S. R. *et al.* Simulating the dispersion of poisonous organic chemical compounds in wastewater treatment process through the active sludge method using the TOXChem model. **Annals of Biomedical Science and Engineering**, v. 5, p. 25-31, 2021. https://dx.doi.org/10.29328/journal.abse.1001014

MELCER, H. *et al.* Modeling volatile organic contaminants' fate in wastewater treatment plants. **Journal of Environmental Engineering**, v. 120, n. 3, p. 588-609, 1994. https://dx.doi.org/10.1061/(ASCE)0733-9372(1994)120:3(588)

METCALF & EDDY. **Wastewater engineering: treatment and resource recovery**. New York: McGraw-Hill Education, 2014.

MOUSSAVI, G. *et al.* The removal of H_2S from process air by diffusion into activated sludge. **Environmental Technology**, v. 28, n. 9, p. 987-993, 2007. https://dx.doi.org/10.1080/09593332808618856

MOZO, I. *et al.* Dynamic modeling of biodegradation and volatilization of hazardous aromatic substances in aerobic bioreactor. **Water Research**, v. 46, n. 16, p. 5327-5342, 2012. https://dx.doi.org/10.1016/j.watres.2012.07.014

MUDLIAR, S. *et al.* Bioreactors for treatment of VOCs and odours: a review. **Journal of Environmental Management**, v. 91, n. 5, p. 1039-1054, 2010. https://dx.doi.org/10.1016/j.jenvman.2010.01.006

RAHI, M.; FAISAL, A. Using horizontal subsurface flow constructed wetland system in the treatment of municipal wastewater for agriculture purposes. **The Iraqi Journal of Agricultural Science**, v. 50, n. 3, p. 1208-1217, 2019. https://dx.doi.org/10.36103/ijas.v50i4.765

RATHNAYAKE, D. *et al.* The role of pH on sewer corrosion processes and control methods: a review. **Science of the Total Environment**, v. 782, p. 146616, 2021. https://dx.doi.org/10.1016/j.scitotenv.2021.146616

RIYADH, R.; NILE, B. K.; ZUHAIRY, M. S. A. Assessment of hydrogen sulfide fate and emission in a full-scale plant type A2/O: Karbala STP as case study. *In*: **AIP Conference Proceedings**. Melville: AIP Publishing, 2024. https://dx.doi.org/10.1063/5.0203164

SANTOS, J. M. *et al.* An experimental determination of the H_2S overall mass transfer coefficient from quiescent surfaces at wastewater treatment plants. **Atmospheric Environment**, v. 60, p. 18-24, 2012. https://dx.doi.org/10.1016/j.atmosenv.2012.06.014

SHERIEF, M.; HASSAN, A. A. The impact of wastewater quality and flow characteristics on H_2S emissions generation: statistical correlations and an artificial neural network model. **Water**, v. 14, n. 5, p. 791, 2022. https://dx.doi.org/10.3390/w14050791

TANSEL, B.; EYMA, R. R. Volatile organic contaminant emissions from wastewater treatment plants during secondary treatment. **Water, Air, and Soil Pollution**, v. 112, n. 3, p. 315-325, 1999. https://dx.doi.org/10.1023/A:1005019630120

WIŚNIEWSKA, M.; KULIG, A.; LELICIŃSKA-SERAFIN, K. The use of chemical sensors to monitor odour emissions at municipal waste biogas plants. **Applied Sciences**, v. 11, n. 9, p. 3916, 2021. https://dx.doi.org/10.3390/app11093916

WHO. **Air quality guidelines for Europe**. 2. ed. Copenhagen: WHO Regional Publications, 2000. (European Series, n. 91).

ZHOU, J. *et al.* Comparison and analysis of several wet scrubbing solutions to remove methyl mercaptan. **Journal of Environmental Science and Health, Part A**, v. 53, n. 9, p. 819-824, 2018. https://dx.doi.org/10.1080/10934529.2018.1455340

ZWAIN, H. M. *et al.* Modelling of hydrogen sulfide fate and emissions in extended aeration sewage treatment plant using TOXCHEM simulations. **Scientific Reports**, v. 10, n. 1, p. 22209, 2020. https://dx.doi.org/10.1038/s41598-020-79395-8