TALLINN UNIVERSITY OF TECHNOLOGY
SCHOOL OF ENGINEERING
Environmental Engineering and Management

CORROSION AND ODOR MANAGEMENT IN SEWER NETWORKS

KORROSIOON JA HAISUHÄIRING KANALISATSIOONIS

MASTER THESIS

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(*On the reverse side of title page*)

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THESIS TASK

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Study programme: EABM03/18 - Environmental Engineering and Management

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Thesis main objectives:

1. To explain the major odor and corrosion producing compounds and their sources.
2. Providing different methods and technologies to control odor and corrosion from the sewer system.
3. To recommend some sustainable and cost-effective new approaches regarding hydrogen sulphide and microbial induced concrete corrosion removable for future research.

Thesis tasks and time schedule:

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1.	Major odor and corrosion producing compounds in sewer system and gas phase odor alleviation	20.03.2021
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CONTENTS

PREFACE

When I started my master's Study at Tallinn university of Technology, I was delighted, motivated, and determined. After two years of my master study in Taltech, I am pleased how I struggled with many difficulties, feelings and how I adored the cheerful moments.

This thesis paper would never be completed without the great contribution of some individuals. At first, I would like to express my gratitude to Professor Karin Pachel who always motivated, guided and supervised me to conduct this study. At the initial stage of this study, when I faced a lot of difficulties to finalize the thesis structure, she raised my confidence by providing proper guidelines and direction. Thereafter, I would like to thank to Md Saifur Rahman and Hemant Pandey who are my beloved friends, for their valuable comments, advices, and criticisms on this study. Finally, I am really indebted to my family members particularly to my mother who has been providing both financial and mental supports in continuing my study since my father died when I was still a child. She deserves maximum credit for the position I am now in. This study is dedicated to my mother who spends her whole life to shape my life.

The main aims of this study are to provide different methods and technologies to control corrosion and odor from the sewer system, to explain the major odor and corrosion producing compounds and their sources. This study has included two models to introduce the practical knowledge about odor formation, mitigation, and further development of hydrogen sulphide and volatile organic compounds removal process. Furthermore, some sustainable and cost-effective new approaches have been recommended in this paper regarding hydrogen sulphide and microbial induced concrete corrosion removable for future research.

Key words: Hydrogen sulphide, methane, odor, corrosion, sewer system, master thesis.

LIST OF ABBREVIATIONS AND SYMBOLS

SRB: Sulfate-Reducing Bacteria
SOB: Sulfide-Oxidizing Bacteria
ORP: Oxidation Reduction Potential
DO: Dissolved Oxygen
WWTP : Wastewater Treatment Plant
MA: Methanogenic Archaea
COD: Chemical Oxygen Demand
CTBB: Compact Trickle Bed Bioreactor
GC: Gas Chromatography
FID: Flame Ionization Detector
RH: Relative Humidity
AC: Activated Carbon
BISM: Biofilm Initiated Sewer process Model
SCOD: Soluble Chemical Oxygen Demand
TCOD: Total Chemical Oxygen Demand
VFA : Volatile Fatty Acid
VSS: Volatile Suspended Solids
VSCs: Volatile Sulfur Compounds
TSS: Total Suspended Solids
HKDSD: Hong Kong Drainage Services Department
HRT: Hydraulic Retention Times
FNA: Free Nitrous Acid
ppm: parts per million

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1 INTRODUCTION

To maintain the maximum quality of water is very important for human being, animals, waterbodies, social and economic prospects and for whole ecosystem. With the rapid growth of population, industries, infrastructures, urbanisation ang agricultural activities, the amount of wastewater is increasing throughout the world. The under-road drainage system that transports the wastewater from all sources to the water treatment plant is known as sewer networks.

Corrosion and odors are the common phenomenon in sewer networks. Sewer pipes are usually made from cast iron or concrete materials and these sewer pipes are highly vulnerable to moisture condensation and different acidic gases. The corrosion of sewer system occurs mainly due to presence of hydrogen sulphide gas. The formation of H_2S from sulfates is very common in both wastewater and WWTPs. Under anerobic condition, sulfates convert into sulphide and finally get the corrosive sulfuric acid form by bacterial activity and occurs corrosion in sewer pipes. When the sewage pipe gets contact with H_2SO4, then it corrodes the pipe. Bacteria grows in high acidity and the inside of sewer pipes is corroded by bacteria from genera acidiphilium and mycobacterium [51].

The odor from sewer system smells like rotten eggs, garlic or among other things. It is usually originated from the anaerobic decomposition of organic components. Hydrogen sulphide from anaerobic digestion gives a nauseous smell and releases into the surrounding environment [52]. Along with hydrogen sulphide, Methane, Nitrous oxide, and Volatile organic compounds (VOCs) are also responsible for generating odor and corrosion in sewer system.

Corrosion from hydrogen sulphide can lead to extensive damage to concrete and metal used in sewage transport system. Furthermore, pumping stations, electrical infrastructure, equipment, ventilation process are also affected by corrosion. At times, sewer system designed to last 70 to 100 years may collapse due to H_2S corrosion [53].

Odor producing gases effect different organs of human body and animals. Sewage workers and surrounding people often suffer by severe diseases. H_2S emission in open air causes eye irritation, sore throat and cough, appetite loss, headaches, short memory, dizziness, breath problem, lungs damage and other diseases. Breathing with high concentration of H_2S can cause an immediate death [54].

This thesis is based on mainly scientific literature and the newest published literature in the field is used. The main objectives of this study research are:

- To explain the major odor and corrosion producing compounds and their sources.
- Providing different methods and technologies to control odor and corrosion from the sewer system.
- To recommend some sustainable and cost-effective new approaches regarding hydrogen sulphide and microbial induced concrete corrosion removable for future research.

2 MAJOR ODOR AND CORROSION PRODUCING COMPOUNDS IN SEWER SYSTEM

This chapter is mainly based on how major odor and corrosion producing compounds like hydrogen sulphide, methane, niitrous oxide and volatile organic compounds emitted from the sewer system and causing corrosion and odors. Moreover, this chapter includes different methods and technologies to remove hydrogen sulphide, and methane measurement systems with different factors related to methane formation.

2.1 Hydrogen sulphide emission in sewer systems

Hydrogen sulphide emission in sewer systems has many complications related to biogenic corrosion of concrete, extrication of annoying odors to the environment and effect of sulphide toxicity to sewer laborers. There are no significant effects when the concentration of total sulphide in the sewer water is between the range of 0.1–0.5 $mgSL^{-1}$. When the sulphide concentration is above 2.0 mg S L^{-1}, violent concrete corrosion may happen [2]. To curve the biogenic corrosion effects, some experiments have been taken, i.e. (1) most effective sewer hydraulic design, (2) controlling the sources of sulfate by urine separation technology (3) developing the inhibition of sewer pipes to biogenic corrosion and (4) minimizing the hydrogen sulphide emersion from sewers [3]. Different chemical and biological technologies to mitigate H_2S emersion in sewers in presented in Figure 2.1.1.

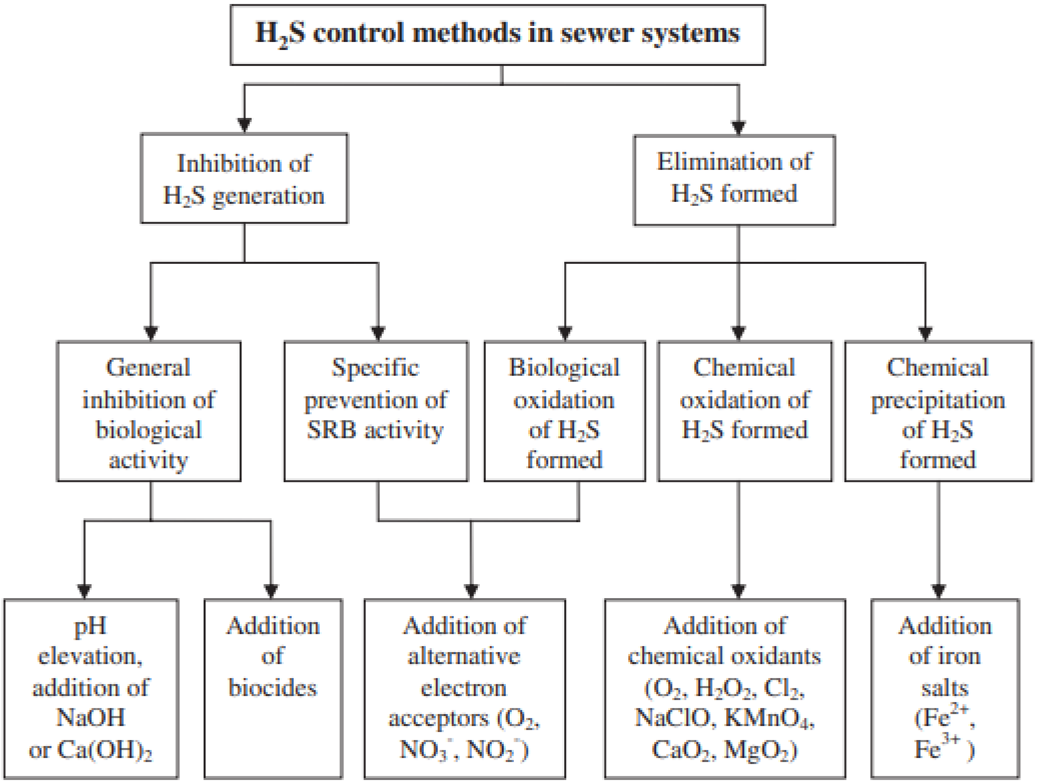

Figure 2.1.1 Controlling of H_2S emission in sewer process (chemical and biological technology) [2].

2.1.1 Biogenic corrosion of sewers

Biogenic corrosion of sewers is a bacterial process of forming H_2S conversion to H_2SO_4 that attacks sewer pipes in the presence of moisture. The key operations and environmental parameters linked with the sulphide cycle in sewer process together with heavy wastewater, biofilms, slits, air, and surface blooming to the environment (Figure. 2.1.1.1). All these processes include composition of sulphide, evaporation of hydrogen sulphide, chemical and biological sulphide oxidation and sedimentation of metal sulphides [4,5].

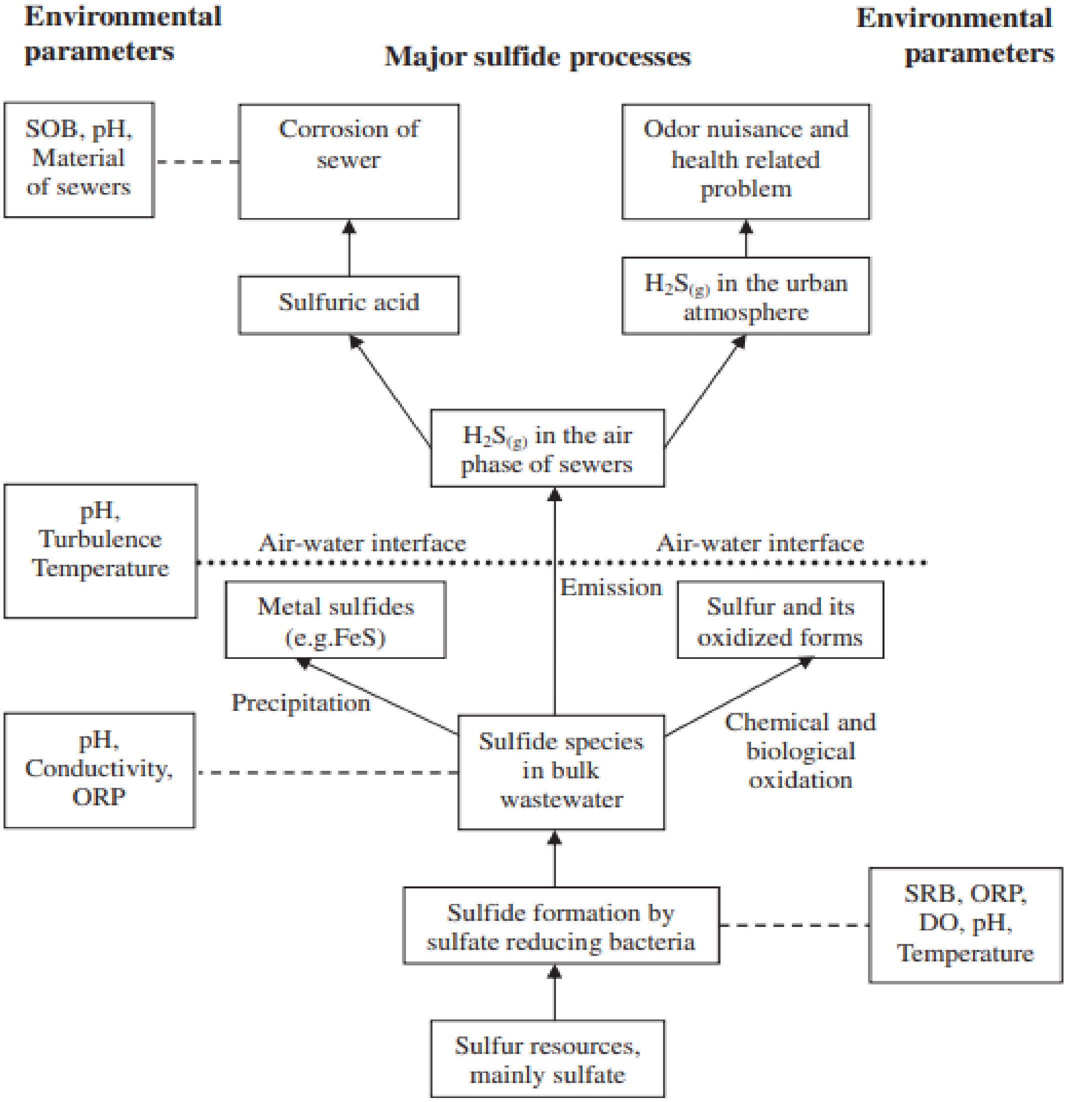

Figure 2.1.1.1 Key sulphide operations and their real causes linked with the sulfur cycle in the sewer system [2].

Sulfate ($SO4^{2-}$) is the main origin of sulfur in domestic wastewater with the range between 40–200 mgL^{-1}. Sulfate can be minimized to sulphide by using sulfate-reducing bacteria (SRB). Under anaerobic state, this biological process takes place in biofilms and sediments in the plunged part of sewers. The physicochemical function of hydrogen sulphide is available in both water and air conditions of sewer system. It mainly depends on temperature, pH, hydraulic conditions of the water state and airspace. The existence of metals as iron, zinc, lead, and copper in the sewage conducts to sedimentation of metal sulfides to reduce sulphide emission. Sulphide Oxidation of wastewater can rise both chemically and biologically and makes the total oxidation operations more complicated [1,2].

Hydrogen sulphide in sewer system disperses into the thin liquid film appeared at sewer surfaces. Chemoautotrophic bacteria oxidize sulfide to sulfuric acid at the surface. Corrosion takes place by biogenic sulfuric acid reaction with cementitious components causes ultimate structural decay of sewers [6]. It is conducted by production of a corroding layer on the surface concrete and the layer contains gypsum and moisture. The formation of concrete to gypsum and the formation of ettringite deteriorates the structural rectitude of the concrete pipe. This curbs the load-bearing capacity of the concrete and causes ultimate failure of the sewer [7]. After investigating of 34 cities in USA, US Environmental Protection Agency (1991) reported, the corrosion rate of sewer pipes is 2.5–10 mm per year, where the lifetime is 20-70 years [2]. An example of lifetime of sewer pipes according to corrosion rates has been presented in Table 2.1.1.1.

Table 2.1.1.1 Lifetime of sewer pipes according to corrosion rates [2].

Corrosion Rate (mm per year)	Lifetime (year)
2.5-10	20-70
2.7	65
4.3-4.7	35-45
2.4	45-90
3.1	55
1.0-1.3	130-170
1.1-1.8	90-160

2.1.2 Rising redox potential to reduce sulphide production

- **Air injection**

Sulphide can be grown from 1mm slime layer depth and more from sewers aerobic wastewater. When dissolved oxygen (DO) is available around the slime layer, chemical and biological oxidation of the sulfide will get place since it goes into the aerobic atmosphere [8,9]. Dissolved sulfide enters the bulk wastewater as a dissolved hydrogen sulphide gas (H_2S) in the absence of DO. Air injection is mostly used in strength mains and wet wells. The main advantage of air injection is it decreases BOD and non-toxicity in sewage. The limitation of air injection is limited oxygen transfer. As pure oxygen works five times more concentrated than air, then injecting pure oxygen in the replacement of air (DO levels: 3–5 mg L^{-1}) can achieve higher DO levels (5-7 mg L^{-1}) [10]. In a pressurized sewer system, using pure oxygen as a sulfide control process is very convenient as dissolution of oxygen is higher at maximum pressure. The only negative thing is it is useable only for high-pressure force mains which may have fire risks [50].

- **Addition of nitrate**

Sodium nitrate was used to minimize odor nuisance and according to oxygen deficient systems, nitrate was curtailed preferentially over sulfate to diminish H_2S production. Addition of 1.0 g L^{-1} of nitrate in wastewater prevents sulfide production for minimum 29 days [2]. This prevention assigned to grow in redox potential due to the presence of nitrate. Addition of nitrate could monitor sulfide generation in a wastewater stream if enough nitrate was put initially to increase the redox potential of the stream above 300mV [2].

2.1.3 Inhibiting sulfate reducing bacteria activity

According to inhibition of biological activity, pH elevation method is used most cases and other inhibitors including biocides and molybdate are also considered [12]. When pH is above 9.0, the amount of $H_2S(aq)$ in solution is ignorable as the presence of sulfide in its completely ionic form. However, ongoing adding of sodium hydroxide (NaOH) to monitor elevated pH (more than 9) is costly and can break up downstream treatment operations. The most efficient application of sodium hydroxide is shock treatment to generate pH between 12.5–13.0 in wastewater for 20–30 minutes duration. Due to this high pH, it inhibits SRB in the slime layer for a time from 3 or 4 days to 14 days. The high pH section of sewage water has to be separated at the WWTP and added gradually into the process when it is not diluted in the accumulation process [13].

2.1.4 Chemically sulphide removal

- **Metal salts precipitation**

Insoluble metal sulphide in wastewater

Dissolved sulphide from the sewer water is removed by metal sulphide precipitation and it decreases the amount of sulphide availability for going out to the sewer environment. An actual fraction of the total amount of sulfide can be available as insoluble metal sulfide at low or moderate sulfide concentration condition in sewage water. A study by Brisbane City Council, 1980 showed that dissolved sulfide is absent when the entire sulfide concentration is around 0.12 mg SL^{-1}. The availability of metal salts (e.g. ferrous, zinc and copper) precipitation in the wastewater play an important role to control dissolved sulfide concentration and other related problems [2].

- **Addition of iron salts**

Iron is one of the principal metals that is always available in municipal wastewater. Formation of iron sulfide is one of the key processes of the sulfur cycle in sewer water as the concentration level of iron is normally between 0.4–1.5 mg L^{-1}. Iron has been extensively used to control sulfide growing in sewer system due to its usefulness in controlling the dissolved sulphide concentration. Chloride iron salts or nitrate can be added to wastewater either in ferric or ferrous forms. According to equation (1) Fe (II) removes sulphide by precipitation as ferrous sulphide (FeS). According to equation (1) and (2), Fe (III) removes sulphide by oxidizing it chemically to physical sulfur while being decreased to Fe (II), which subsequently produces FeS [12].

Fe^{2+} HS^{-} → FeS + H^{+}, ΔG: -21.0 KJ mol^{-1}(HS-) ……………………………………. (1)

$2Fe^{+3}$ + HS^{-} → $2Fe^{2+}$+S^{0} +H^{+}, ΔG: -160.9 KJ mol^{-1}(HS-) ……………………. (2)

Ferrous or ferric ion is more useful in regulating the dissolved sulphide concentration, sometimes ferrous chloride can be effective more than twice compared to ferric chloride [2,12].

- **Addition of oxidizing chemicals**

Hydrogen peroxide (H_2O_2)

Addition of hydrogen peroxide (H_2O_2) in wastewater oxidizes dissolved sulphide and melts to water and oxygen which makes aerobic conditions. The standard ratio of hydrogen peroxide is 1.3–4.0 $mgH_2O_2L^{-1}$ to $1mgSL^{-1}$ and average removal of sulfide is 85–100%. The only limitation of using hydrogen peroxide is its short time duration (less than 90 min) [2].

Chlorine

Chlorine can oxidize sulphide to sulfate or to physical sulfur and it depends on the ph. The working ability of chlorine is frequently low as its reactions with other elements in sewage. It can be added as an aqueous solution (example: sodium hypochlorite) or direct form of gas. The reaction of chemical oxidation is gradual at lower sulfide concentrations which is especially below $1mgL^{-1}$. When chlorine is added directly as a gas, a suggested standard ratio is 9.0–15.0:1 (w/w) and for aqueous solution (NaClO or $Ca(ClO)_2$), the standard ratio of chemicals to sulfide is 1.8–2.0:1 (w/w) [15].

Potassium permanganate

Potassium permanganate (KMnO4) works as a strong oxidizing agent that changes sulfide to sulfate. It is usually found in a dry condition, but it is compiled as a 6% solution in water. The only problem is its high cost [2].

2.2 Methane emission from sewers

A significant amount of methane is produced and emitted from sewer systems. Methane is produced from methanogens within anaerobic conditions in sewer system biofilms and slits. Methane is emitted at the interface between sewage and ambience in gravity sewers system, pumping stations, and outlets of wastewater treatment plants (WWTPs).

2.2.1. Potential sources and sinks of methane formation in sewers

Sewer systems are crucial elements of urban and suburban water infrastructure which collect and transport wastewater from residential and industrial areas to wastewater treatment plants (WWTPs). In case of transporting wastewater, sewers work as a biological reactor with different microbial operations. A sewer pipe has five major stages, named as the ceased wastewater stage, wet sewer biofilms, the slits, the sewer air stage, and the biofilm of pipe area disclosed to sewer environment [17].

- **CH_4 formulation in anaerobic sewer biofilms**

In anaerobic conditions, methanogenic archaea (MA) produce CH_4 from acetate or hydrogen through methanogenesis by applying the products of anaerobic fermentation in sewer biofilms. Generally, sewers have regulable sulfate (around 10–30 mg/L) and adequate carbonaceous substrates (around 200–500 mg/L, COD) to aid both SRB and MA for allowing methane and sulfide production simultaneously [18]. When the sulfate concentration is comparatively high, SRB lead the top layers of biofilms. Methanogenic archaea (MA) need low-sulfate condition. Thus, the deeper state of biofilms is the ideal environment for MA, where the sulfate value is limited or unavailable. There are three categories of wastewater COD: (1) fermented COD (example: volatile fatty acids), (2) Readily fermentable COD (example: carbohydrates) (3) slowly biodegradable COD (example: proteins, polysaccharides) [16]. Slowly biodegradable COD contributes to sulfate deduction and methane formation through hydrolysis and fermentation operations in sewer system. Methanogenic archaea are very sensitive regarding pH and temperature and they grow usually at temperatures above 28 °C and pH between 5.5–9.0 [19].

- **CH_4 formation from sewer sediments**

A significant amount of CH_4 is originated from gravity sewer sediment. The highest methane production area is located near the sediment surface but expanded deeper than the sulfide production area. The lowest methane production in the deeper layer of the sediment caused by provable penetration of fermentable COD [16,20].

2.2.2 Methane measurement of sewer system

- **Off-line CH_4 measurement**

The key method of methane measurement in sewer system is manual sampling with regular intervals over several hours through off-line gas chromatography. Some specific sampling preparations are needed to measure gas phase CH_4 concentration. The samples of gas can be taken by gas bags or evacuated exetainer tubes (Figure 2.2.2.1: A) from the ventilation point or from a sampling chamber linked with the sewer headspace. Samples are then experimented for methane using a gas chromatography equipped with FID. Dissolved methane gas samples are taken by a hypodermic needle including pipe and plastic syringe (Figure 2.2.2.1: B). This process confines disclosure of sampled wastewater to the environment. Wastewater samples are generally taken in a sampling device including an open-head cylindrical container for sampling dissolved methane in sewer system. The container is inclined and loaded below the water level, and then reclaimed carefully. From the container, the sample aliquots are taken out by a plastic syringe at around 5 cm below the water surface without air contact. A submersible pump is an alternative use to take sample from below-ground at lower speed to ignore turbulence [16, 20].

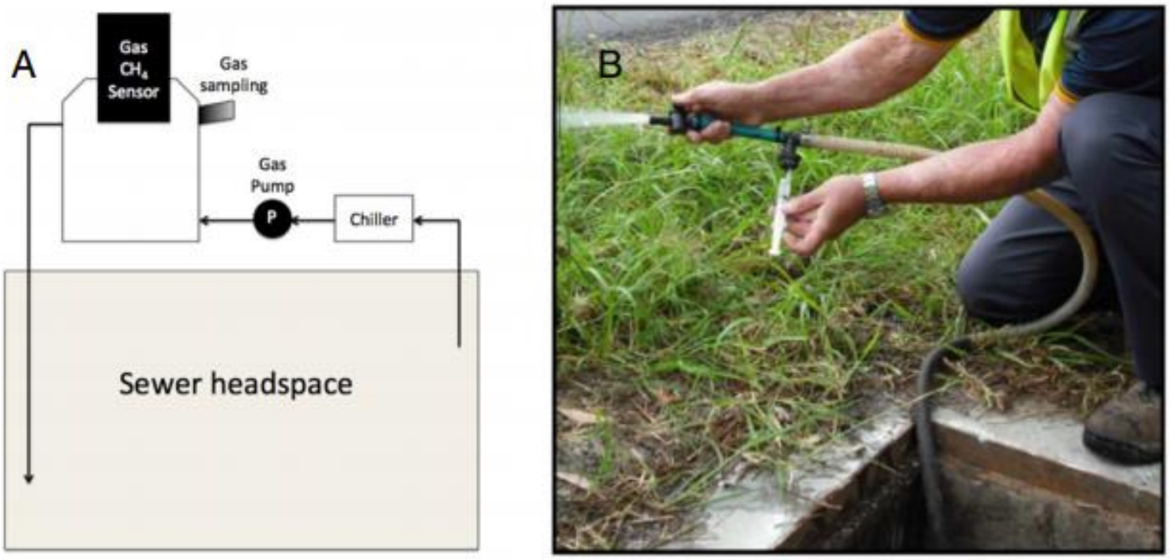

Figure 2.2.2.1 Gas sampling or infrared gas sensor using in sewer headspace (A), collecting dissolved methane sample (B) [16].

Sub-samples are then evicted within an evacuated exetainer tube and the mixture contents then placed overnight to get gas–liquid equilibrium. Finally, the dissolved methane is measured by gas chromatography, and the concentration of sample is measured by Henry's Law and mass balance [20].

- **Online measurement**

There are many online sensors for gas phase methane monitoring, among all of them infrared (IR) spectroscopy is the most effective method for online methane measurement in sewer system. The key characteristic of sewer air is the high humidity and the usual range is between 80–100% RH that could intervene with IR methane measurement. IR spectroscopy-based online sensors were vastly powerful in changeable and high humidity. A battery-driven IR sensor is very sensorial to change in humidity. The limitation was determined by maintaining the humidity at 50–70% RH by rising the surface temperature (Figure 2.2.2.1: A). Both sensors have excellent working power and very suitable for factory calibration [16]. Around 1 month of sensor with external power supply confirms precision and long life in sewer system application. Infrared spectroscopy is going to be a powerful instrument in coming future to ensure maximum accuracy for measuring methane emission in sewers. There are limited number of commercial sensors are available for measuring online dissolved methane and they are developed for measuring methane specially in clean water but not suitable sludge and high sulfide containing sewage water. A recent online dissolved methane sensor has been designed and its gas phase methane sensor is used to measure methane under equilibrium conditions after releasing from the sewage system [21].

2.2.3. Factors related to methane formation and emission

Some key factors play an important role for controlling methane production and emission in sewer system.

- **HRT**

Dissolved methane concentration has positive correlation with HRT in sewer system. Methane concentration increases with the increase of retention time and the length of the sewer. Dissolved CH_4 concentration is higher at night and lower concentration is during daytime. A higher methane concentration occurs in both liquid and gas state in sewer system during the long HRT period. [16,[20]

- **A/V ratio**

Dissolved methane concentration depends on the A/V ratio of the sewer pipe. More higher A/V ratio gives a higher methane production rate [20].

- **Temperature**

Temperature has a great influence on methane production. During summer methane production is higher compared to winter [16]

- **COD**

Methane production in sewer sediments is mainly involved with fermentable COD concentrations. Industrial wastewater contains high COD and thus methane production increases [20].

2.3 Nitrous oxide emission from sewers

Nitrous oxide (N_2O) is an elemental ozone consuming matter and strong greenhouse gas. N_2O plays a crucial role in different aspects of environmental chemistry and climate and its emission from sewer system is comparatively well. It contributes to total anthropogenic global warming is almost 10%. Global N_2O emission rate in sewer water in the years 2005 and 2006 was calculated at around some 95 and 145 Mt CO_2^{-e} y^{-1} respectively. Nitrous oxide emission rate is going to increase in coming days with the rapid growth of population, economic prosperity, urbanisation and industrialization [22].

2.4 Volatile organic compounds (VOCs) emitted from sewers

The volatile organic compounds (benzene, toluene, ethylbenzene, total xylenes, and tetrachloroethene etc.) are available in sewer system and generated from the discharges of residential, industrial, commercial incorporations, and public settlings. They can also be found in wastewater flow as organic substance fester form. Furthermore, groundwater effluents remediation, industrial treatment methods and other illegal sources of discharge are contributing to proximity of VOC in sewer system when discharged directly to the sewer networks. Many studies have been focused on VOC emissions from WWTPs and processes but only few studies trace the VOC emissions from sewer system [23].

3 GAS PHASE ODOR ALLEVIATION IN SEWER NETWORKS

A rapid growth of urbanization and industrialization have led to rise in public allegations against odors from sewer system. Humans and beasts perceive the emergence of chemical contaminants through warmth of their organs. Odor from like perfumes and fresh foods is pleasant and odor from rotten egg and sewage is unpleasant. Some of the major odor containing substances and their related information are presented in Table 3.1. Many approaches can be applied for odor alleviation in sewer networks. In this chapter, two different biological systems, one adsorption-based system and a short summary of other odor alleviation technology have been addressed.

Biological systems are:

- ✓ Biofilters (open topped and closed topped)
- ✓ Bio trickling filters (BTFs)

Adsorption-based system:

- ✓ Activated Carbon (AC)

Table 3.1 Major odorous substances [24].

No.	Compound	Chemical formula	Odor	Threshold value (ppm)	Molecular weight (g/mole)
1	2-propene - 1 thiol	$CH_2=CH-H_2-SH$	Smell of garlic, hot coffee	0.00005	47.15
2	1-thiol-pentane	$CH_3-(CH_2)_3-CH_2-SH$	Stench, goo	0.0003	104.22
3	Benzyl mercaptan	$C_6H_5CH_2SH$	Leek- or garlic	0.00019	124.21
4	2-butene-1-thiol	$CH_3-CH=CH-CH_2-SH$	Smell of skunk	0.000029	90.19
5	Dimethyl sulfide	$(CH_3)_2S$	Cabbage, sulfurous	0.0001	62.13
6	Ethyl mercaptan	C_2H_6S	Rotten cabbage	0.00019	62.10
7	Hydrogen sulfide	H_2S	Rotten egg	0.00047	34.10

8	Methyl mercaptan	CH_4S	Rotten cabbage	0.0011	48.10
9	Propyl mercaptan	C_3H_8S	Cabbage-like	0.000015	76.16
10	Sulfur dioxide	SO_2	Pungent	0.009	64.07
11	Tert-Butylthiol	$C_4H_{10}S$	Smell of skunk	0.00008	90.10
12	Thiocresol	$CH_3\text{-}C_6H_4\text{-}SH$	Smell of rancidity	0.000062	124.21
13	Ammonia	NH_4	Pungent odor	1	18.014
14	Thiophenol	C_6H_6S	Smell of garlic	0.000064	110.18
15	Geosmin	$C_{12}H_{22}O$	Musty odor	0.004	182.3
16	Methylisoborneol	$C_{11}H_{20}O$	Musty odor	0.015	162.28
17	2-Isopropyl-3-methoxypyrazine	$C_8H_{12}N_2O$	Rotten vegetables	0.0002	152.19
18	2-Isobutyl-3-methoxypyrazine	$C_9H_{14}N_2O$	Wood smell	0.001	122.66
19	β-Ionone	$C_{13}H_{20}O$	Smell of violets	0.007	192.3
20	β-Cyclocitral	$C_{10}H_{16}O$	Smell of fruit	19	152.23
21	cis-3-hexen-1-ol	$C_6H_{12}O$	Smell of grass	70	100.16
22	1-Penten-3-one	C_5H_8O	Rotten fish	1.25	82.11
23	Dimethyl trisulfide	$C_2H_6S_3$	Rotten vegetables	0.1	126.26
24	3-Methyl-1-butanal	$C_5H_{12}O$	Smell of oil	0.15	88.14
25	Trans, cis-2,6-nonadienal	$C_9H_{14}O$	Cucumber	0.02	183.2
26	Trans-2, trans-4-decadienal	$C_{10}H_{16}O$	Cucumber, fish, oil	3	152.23
27	Trans-2, trans-4-heptadienal	$C_7H_{10}O$	Vegetables, fish	25	110.15
28	2,4,6-Trichloroanisole	$C_7H_5Cl_3O$	Smell of mold	0.00003	211.47
29	2,4,6-Tribromoanisole	$C_7H_5Br_3O$	Rot, soil	0.00003	344.83
30	Benzothiazole	C_7H_5NS	Smell of chemicals	0.08	135.18

3.1 Biological systems (Biofilters and bio trickling filters)

Biofilters (Figure 3.1.1) and bio trickling filters (Figure 3.1.2) are referred as a biological system. Biofilters work as bioreactors and a humid foul air stream is introduced by an organic media as compost or wood chips. The organic media delivers a surface for mass-transfer from gas stage to liquid stage and introduces an environmental fitting for micro biological cultures to succeed. Organic media is the source of inorganic nutrients to ensure microbiological progress. Media should be replaced in a periodic manner to confirm the availability of inorganic nutrients since media is the origin of nutrients. Media replacement is also important to develop the packing structural stability to minimize bed compaction and air channeling risks. The media is placed with humid by the humidification of oncoming flow and through periodic sprinkling of water to the bed. Biofilters depth is usually controlled by allowable pressure losses [26]. It drives biofilters with extensive surface area to reduce pressure loss. The involvement of extensive surface area makes it hard to fill the unit to diffuse treated air by a stack. Due to this, biofilters are usually open topped with diffusion of treated air occurs from the top of bed [25].

Bio trickling filters are also same as closed-top biofilters in an order that they apply biological culture to eject contaminants. BTF with a mobile liquid stream controls pH and nutrient supply and recirculates unreacted dissolved contaminants for next processes throughout the media. Media is mainly inorganic and usually made of plastic and ceramics. Impure air can be fed from either the top or the bottom though bottom fed is usually used. BTFs are usually performed as towers that delivers the treated air flow to be scattered at elevation or delivered to oncoming polishing treatment with a maximum easement than an open topped biofilter. Diffusing the treated air at elevation, then it is less risky to ground level impact when a biofilter is applied [27].

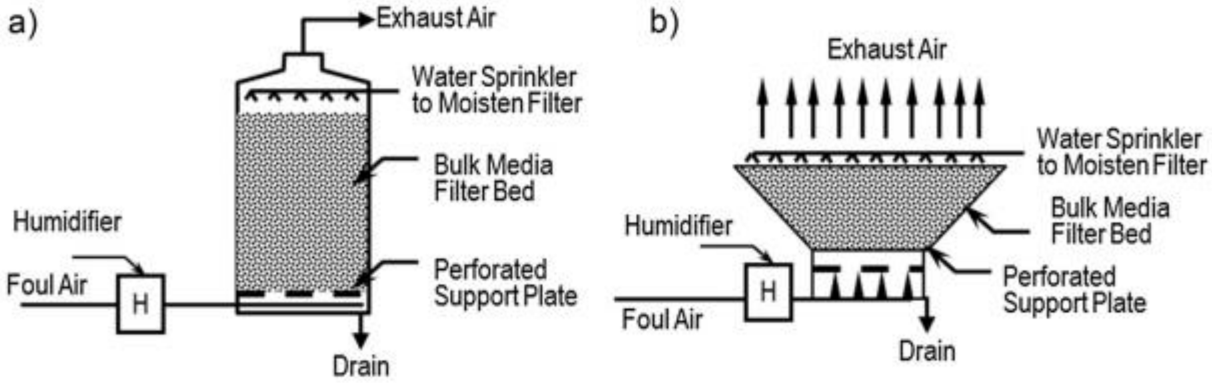

Figure 3.1.1 Closed topped biofilters (a) and open topped biofilters (b) [25].

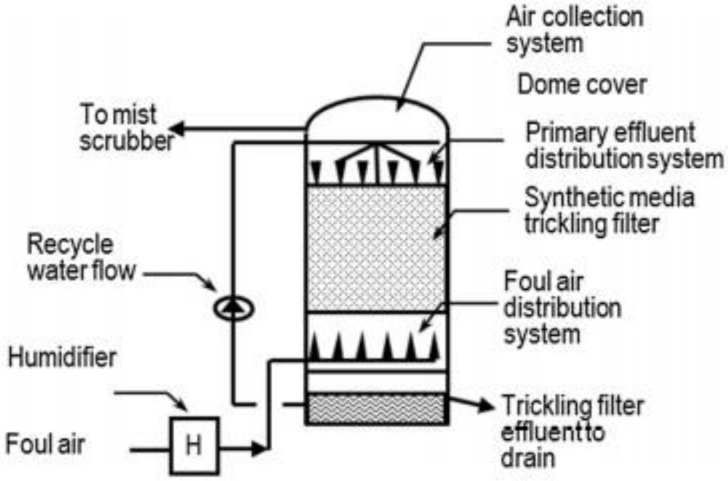

Figure 3.1.2 Bio trickling filters (BTF) [25].

- **Reaction mechanism of biological systems**

In biological system, contaminants are eliminated by two processes: mass transfer and bioreaction.

Mass transfer

At first, contaminants are eliminated from gas stage into the liquid stage and contaminants then visit with a liquid layer to attain biomass and react biologically to get odor free or less odorous by products while biomass produced. Sometimes, fungal biomass removes contaminant substances directly from the gas stream. Fungal biomass then looks to get a greater pressure loss. Mass transfer from the gas stage to the liquid stage is conducted by a concentration differential to get balance. The attainable liquid concentration is ruled with the solubility of the pollutant and gas stage concentration that stated by Henry's formula as $H_{cp} = C_a/p$ [28]. The working ability of an odor control method depends on how contaminants transfer from the gas to the liquid stage. It is mostly associated with Henry's Law solubility constant that provides an indication of readily soluble ability of a particular contaminant. When the Henry's Law solubility constant is lower, then the compound is more hydrophilic /soluble to enter easily into the liquid film (Figure 3.1.3). After the absorption of the contaminant into the liquid stage, then it sprinkles to the liquid-biofilm interface. Then it is adsorbed into the biofilm surface area and biologically degraded by bioreaction [29].

Bioreaction

Most sewer system contaminants including foul air are biodegraded by bacteria or fungi. Microbial populations that observe in a bioreactor depend on contaminants level [28]. If known recalcitrant composites are available in some cases, then it proves favorable to inoculate a bioreactor with a microbial tribe sample to demote xenobiotic pollutant. But this method is not very common for treatment in sewer system foul air. The total rate of biodegradation depends on every single operation reaction value. Gas to liquid mass transfer value has been indicated as speedy than other operations. But the contaminants with higher Henry's Law solubility, mass transfer can be the bounding step and the dispersion to the liquid-biofilm interface is faster than to the biological reactions [30].

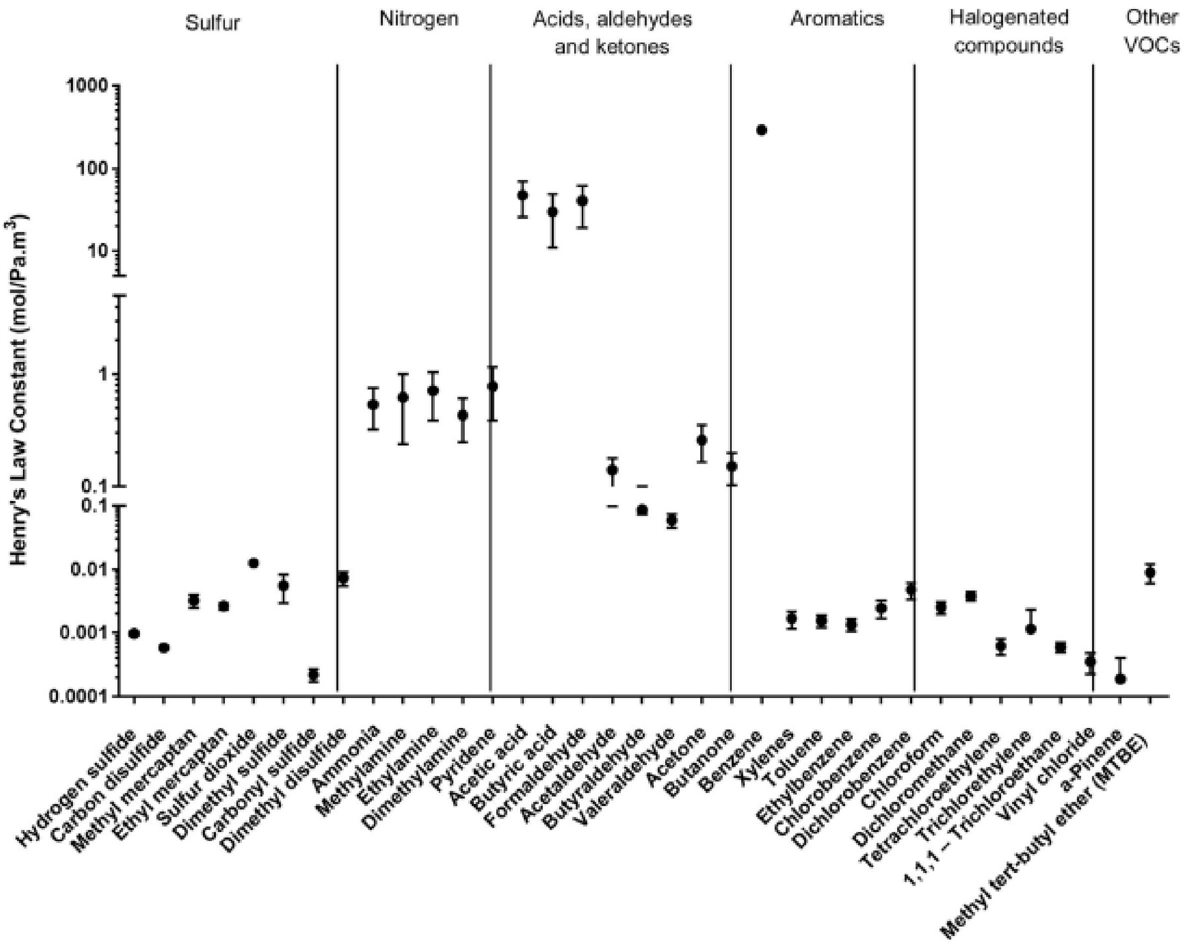

Figure 3.1.3 Henry's law solubility constants with different odorants linked with sewerage treatment [28].

- **Design and operation of biological systems**

The design of biofilters depends on the removal target efficiency with maximum elimination rates. The most usual design is based on hydrophilic substances that can bring crucial breakthrough on VOC. Biological treatment in biofilters has many limitations including the presence of proper constants as diffusion, growth values, knowledge of the structural features of biofilm distribution on media ground. The current models are not well considered to the industry due to lack of high reliability and poor complexity. Therefore, the design of biofilters is mainly based on past perception and typical design standard for working parameters. The major operational thing in a biofilter is to confirm the media is adequately humid. Incoming stream humidification ensures the inlet place like mostly the bottom of the biofilter resides moist. Farther sprinkling which is available on the peak of the bed assures sufficient bed moisture. Different water distribution of the sprinklers leads to short-circuiting that mainly causes biofilter failure [37]. Over-watering causes different types of media which lead to anaerobic conditions and rises in pressure loss. Pressure loss is mostly operated as a test of biofilm thickness and growth of bed compaction.

The standard pressure loss of biofilters and bio trickling filters is 1000–1500 P_a/m, 200–250 P_a/m respectively. Contaminants like H_2S can be removed easily through autotrophic microorganisms. Various steps are housed in single vessels / different vessels. Autotrophic phases are pursued by heterotrophic phases. It is usually available to get autotrophic phases with different steps in a single vessel at base induced from the bottom. This design delivers dynamic extraction of low pH resulting compounds entire the vessel that confines low pH liquor getting into a heterotrophic bed [38]. BTF media moisture is also crucial to manage good biological operation like biofilter. In BTF, the media is always supplied by recycled liquor and proper media moisture is always easy to operate [37].

Media

The longevity and performance of a biofilter or bio trickling filters depend on selection of media. Different types of materials including clay, peat, bark, wood chips, compost and inert additives like perlite, lava rock, and plastics are used as a biofilter media [39]. An ideal media should have following features.

- ✓ Can assist a massive different microbial population.
- ✓ Delivering pH buffering efficiency.
- ✓ Have the capacity to keep microbes.
- ✓ Should be stable physically.
- ✓ Have a lower pressure loss
- ✓ Ability to produce clean leachate water.
- ✓ can release excess moisture.

3.2 Adsorption system (Activated Carbon)

Physical removal of odorous contaminants is mainly by adsorption (Figure 3.2.1). Activated carbon is the most conventional adsorbent in wastewater plants. Zeolite material is used for controlling vent-top odor. Activated carbon has high surface area that allows various active sites for adsorbing contaminant substances.

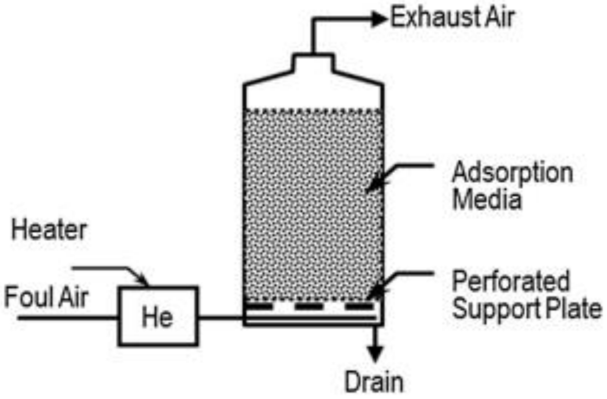

Figure 3.2.1 Adsorption unit [25].

There are mainly two types of activated carbon used for gas treatment in the wastewater industry named impregnated activated carbon and virgin activated carbon. Different types of impregnated carbon are intended to remove certain compounds mainly hydrogen sulphide. Impregnated activated carbon is usually saturated with potassium or sodium hydroxide and potassium iodide as a high-pH chemical also used [31].

Virgin activated carbon is evolved from solid carbonaceous related materials like coal and peat. The carbonaceous materials then carbonized with average to maximum temperature treatment. Due to heat treatment, the temperature of carbonaceous product is between 280 to 800°C to generate the early phases of the nano porous AC structure. Then the carbon is oxidized to eject contaminants and the development of activated carbon. There are different chemicals including alkaline hydroxides, metal oxides, oxidizing agents, and salts which work for impregnating virgin AC to raise the ability for lifting H_2S and other VSCs [32].

- **Reaction mechanism of activated carbon**

Adsorption can be done by both physical and chemical methods.

Physical adsorption of impurities into activated carbon rises during 3 phases –

1. Impure molecules visit to the end of the activated carbon. The contrary can be seen in the same stage when desorption happens.
2. Impurities sprinkle into the porous formation of the adsorbent. The rate totally depends on the size of the molecule and behavior of the pore.
3. Impure molecules cling to the pore ground by weak van der Waals forces and release energy.

The adhesion capacity increases by polar and nonpolar interactions between the impure molecule and the activated carbon. Activated carbon is usually non-polar and polar functional groups invent on the pore ground. Nonpolar molecules are usually linked to the nonpolar AC positions, whereas polar molecules like water attached to the polar positions. The existence of oxygen containing groups can attack the surface chemistry of the activated carbon and change the efficiency of some professions for adsorbing and the total adsorption ability of AC [33].

Chemical adsorption includes a chemical reaction within the adsorbate and the adsorbent through the consequence structure of a chemical bond. More energy is needed to deliver a chemically adsorbed molecule than to a physically adsorbed molecule because of the capacity of the chemical bond than to the power of the van der Waal's forces. Chemical adsorption involves the oxidation of the adsorbent with the assistance of catalytic activity of the functional categories on the surface of activated carbon literally with catalytic or other impregnated carbons. Chemical adsorption molecules can form only single layer, though multilayer molecule often form physical adsorption period [34].

- **Design and operation of activated carbon**

The important thing to design activated carbon system is to confirm sufficient contact time for the contaminant and sufficient bed life for extraction of all impurities. Inlet and outlet conditions should be taken great care to minimize the risk of short-circuiting and low distraction of treated air. Caring is very important in desorption of flammable VOCs from activated carbon system. Impregnated carbons undergo a low auto-ignition temperature than others, however still they are in well over ambient states. Reaction with water and free impregnate is exothermic and conduct to above the auto-ignition temperatures [40]. The availability of other adsorbents raises or decrease of adsorption of target contaminants because of the finite number of active sites. Vapor molecules of polar water fight for adsorption sites to reduce total adsorption ability for other contaminants when the humidity of environment is high. Some of the activated carbon have continuous or sometimes semi-batch attached regeneration advantages. Regeneration is not fully active on chemisorbed impurities and the regenerative operation is not regenerated to all effective sites. VOC like ketones can bind strongly bind to adsorption sites that needs high energy to eliminate them and exempt the effective site for adsorption through other materials. Reproduction of activated carbon consumed some VOCs which are less effective than activated carbon consumed by others [41].

3.3 Comparison in biofilters, bio trickling filters and activated carbon

Difference of three odor elevation technologies including biofilters, bio trickling filters (BTFs) and activated carbon (AC) are presented in Table 3.3.1.

Table 3.3.1 Difference of three different odor elevation technologies [25].

Abatement technology	Advantages	Disadvantages
Biofilters	- Simple operating technology - Low operating cost - Very effective to remove low concentrations - Pressure loss is very lower - Further waste streams are not produced	- Requires large footprint - Media is replaced by every 2–4 years - Not very effective for high concentrations comparatively to bio trickling filters. - Cannot eliminate intermittent peak concentrations in an effective way - Difficult for controlling Moisture and pH - Particulate matter sometimes clogs the bed
Bio trickling filters	- Simple operating technology - Low operating costs with medium capital - Removal is very effective - Can treat acid-producing contaminants perfectly - Pressure loss is very low - Removes intermittent peak concentrations greatly than biofilters	- More complicated for constructing than biofilters - Clogging by rising biomass when too much nutrient is introduced and high pollutant concentrations like VOCs are treated - Waste stream is generated that needs treatment

Activated carbon	- Retention time is short - Consistent and reliable to remove major odorants - Low operating cost - Can fossil intermittent gas flows - Have well dealing capacity by different inlet concentrations	- Operating cost is high because of annual media changing - Carbon lifetime is minimized by moisture - Pressure loss is medium

3.4 Other technologies

Still many other technologies that included in Table 3.4.1 are not proven on large industrial application and only acceptable in appropriate areas or have not been considered economically stable for using in sewer systems.

Table 3.4.1 Key features of other gas phase technologies [35, 36].

Abatement Technology	Principle	Advantages	Disadvantages
Ventilation only	Collection of impure air and diffusing by a stack at elevation.	- Simple and Cheap - Low operating cost	- May not decrease the level of impurities - May rise odor allegation
Bio scrubbers	Two-stage system through scrubbing pursued by biological treatment	- Low cost for implementing in biological treatment areas.	- Needs bioreactor with related aeration system - Expensive in sewer system

			• Removal capacity is too low
Ionization Systems	UV treatment of eradicated impure air	• Simple and cheap • Can treat a variety of impurities with numerous power • Short footprint	• Still not a proven technology, however, study continuing for development • High operating cost
Wet Chemical Scrubbers	Chemically oxidizes impurities though repeat circulating sump liquor and caustic acid	• Can manage larger peaking factors • Can treat a variety of impurities • Quick feedback to changing situations	• High chemical costs • Involved with storing and handling of hazardous chemical substances
Catalytic Iron Filters	Hydrogen sulphide reaction in the existence of iron to grow primary sulfur where iron works as catalyst	• Can decrease load to following treatment operations. • Comparatively cheap	• Effective only for pre-filter • Ejects 50–80% of odorous substances. • Effective only for high concentration streams

			• Treats Hydrogen sulphide only

4 MODELLING OF ODOR FORMATION AND MITIGATION IN SEWERS

Two different model studies have been included in this chapter to explain different practical knowledge about odor formation, mitigation, and further development of H_2S and VOCs removal process.

4.1 A dynamic sewer process model in sewers system in Hong Kong

To control and prevent odor formation and emission, different sewer process models are developing with the rolling of time. In this study, a dynamic sewer process model has been developed and calibrated with the required data collection from two pressurized mains (TCS and MH17) in practical operation in Hong Kong. The result of this study shows that this sewer process model can forecast the progressive sulfide and ammonium concentrations. MH17 collects wastewater from the nearby domestic sources and airport area and TCS stores wastewater from MH17 and the area of Tung Chung. The main characteristics of sewer systems (MH17 and TCS) are shown in Table 4.1.1.

Table 4.1.1 Key features of sewer systems (MH17 and TCS) [42]

Sewer systems	Pipe diameter (mm)	Pipe material	Pipe length (m)	A/V (m^2 /m^3)	Daily average flow (m^3 /day)	Velocity (m/s)	HRT (h)
MH17	700	HDPE (High-density polyethylene)	700	5.71	9600	0.28	0.63
TCS	1100	Cement	6280	3.64	35500	0.43	3.5

4.1.1 Materials and methods of dynamic sewer process model

A biofilm-initiated sewer process model (BISM) was introduced for simulating dynamically the odor formation and emergence in sewer system. The whole BISM has three sub-designs named a sewage quality design, a modified biofilm design and a gas exchange design (Figure 4.1.1.1). The whole pipe is separated into n segments and every single segment works as a biofilm reactor. According to every sewer segment, the effect of the heterogeneous biofilm processes on sulfur and nitrogen conversions pretended to predict the variable concentration of sulfide, sulfate, nitrate, ammonia, and organic substances in sewars [42].

- **Sewage quality design**

The following equation describes how the water quality changes in a sewer segment. The exchanged substates from segment upstream, biofilms, atmosphere, and transfigurations within biochemical reactions in sewage segment all are in consideration.

$$\frac{\partial C}{\partial t} = -u\frac{\partial C}{\partial x} + \frac{\partial M_D}{\partial x} + \frac{\partial M_{gas}}{\partial x} + \sum r \quad \text{...} \ (3)$$

Where, *C,* substrate concentration (g/m^3); t, time interval (s); *u,* sewage flow value (m/s; *x,* sewer segment length (m); M_D, mass exchange value (g/(m^2.s)); M_{gas}, is the mass transfer of gaseous substances within water and sewer atmosphere (g/(m^2.s)); and *r*, wastewater conversion with biochemical reactions in water phase (g/m^3 -s). An updated activated sludge design No. 3 was worked to simulate $\sum r$ [42].

- **Modified biofilm design**

In this study, a vertically layered biofilm design was used that has the capacity to simulate sewer biofilm dynamics within the presence of different hydraulic and wastewater. In this design, the biofilm is divided into different thin layers (Figure 4.1.1.1) as a vertical direction. The biofilm model can simulate 22 biochemical processes to forecast the variable concentration of seven soluble and seven particulate variations in every single biofilm layer. This biofilm design was modified by more considering the anoxic sulfide oxidation operations to ensure better simulation of sulfur and nitrogen transformations [43]. Methanogenesis was not occurred in the sewer biofilm design. The high sulfate value in sewage (500 to 1000 mg/L) due to toilet-flushing water in Hong Kong could curve the production of methanogenic archaea [42,44].

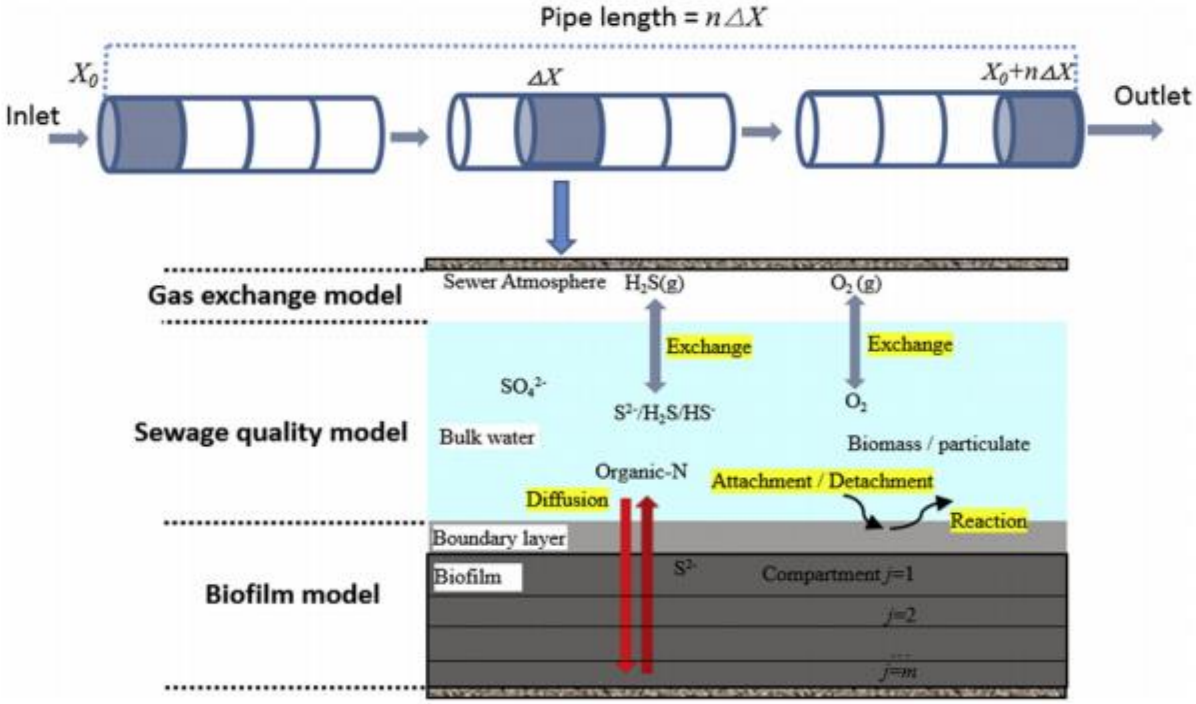

Figure 4.1.1.1 Sewer process model design [42]

- **Gas exchange design**

Intersections, H_2S emission and O_2 reaeration can occur at sewer manhole. At first, H_2S in sewage calculated with this following equation:

$$H_2S \leftrightarrow H^+ + HS^- \qquad PKa_1 = 6.97 \text{ (at } 25^\circ \text{ C)} \ldots\ldots\ldots\ldots\ldots \text{(4)}$$

Where, the pH variation in sewer system was not pretended and pH at sewer outlet was employed for input parameter to determine the concertation of unionized H_2S with further determination of H_2S exemption [42].

4.1.2 Field information on large-scale sewer

According to Hong Kong Drainage Services Department (HKDSD), calcium nitrate is used as a daily operation in sewer system MH17 to control sulfide. The amount of using calcium nitrate is 4.02 kg N/h of 40% (w/w) for everyday from 7:00 to 23:00 and for the remaining time

5.74 kg N/d of 40% calcium nitrate used. In sewer system TCS, 16.73 kg N/h of 40% calcium nitrate is used to minimize sulfide emission. To identify the effectiveness of the proposed sewer biofilm model in different sewer system, all relevant data were collected from TCS and MH17. The sampling campaign duration in TCS was 3 days (07/02/2010-10/02/2010) and it started from 11:00 and during this period, water samples were taken every two hours to determine the water parameters. In MH17, it started from 17:00 and the duration is two days (11/07/2012-13/07/2012). During this period, water samples were observed to determine concentrations of the inlet and outlet of pH, temperature, DO, sulfate, sulfide, SCOD, TCOD, VFAs, alkalinity, ammonia, volatile suspended solids VSS and TSS [42].

To determine the effectiveness of the proposed sewer process model for pretending the effects of different odor control measures in sewer system, scenarios including nitrate addition, biocide addition and hydraulic flushing were pretended in TCS or MH17. Calcium nitrate was dosed constantly in TCS after evaluating the long-term effects of nitrate adding on sulfide production. In hydraulic flushing, different flow rates from lower to high (1000 m3 /h, 2000 m3 /h and 4000 m3 /h) for 1 h were employed in MH17 for pretending their impacts on biofilm transformation and sulfide control within 14 days. In case of simulating of biocide inclusion in MH17, it assumed that 50% or 90% of the bacteria in biofilms were killed and pretended the lifting process and sulfide rebound [42].

4.1.3 Results and discussion

- **Dynamics of sulphide production in sewer system MH17 and TCS**

The HRTs of wastewater in both sewer system (TCS and MH17) were determined by the flow rates (Figure 4.1.3.1: a and b). In TCS, the variation of in flow rate is from 483 to 4026 m^3/h and where the average flow rate is 1573 m^3/h) and HRT value is from 2.2 h to 11 h. The same standard was also performed in the sewer system MH17, Where the fluctuation of flow rate is from 90 to 1300 m^3/h and the average value is 695 m^3/h. Consequently, a dramatic change in HRT value from 0.2 h to 3 h. The highest value of HRT observed from midnight and it lasted till morning in both TCS and MH17 sewer system. The inlet and outlet values of both sewers regarding TCOD and ammonium concentrations and pH levels were not observed a significant difference (Figure 4.1.3.1: c, d and Figure 4.1.3.2: a to d). In case of sulphide production, outlet sulfate concentration was lower than inlet in both TCS and MH17 (Figure 4.1.3.2: e and f). Though nitrate was added to reduce sulphide production in TCS, but higher outlet sulphide concentration was observed than that inlet (Figure 4.1.3.2: e), but sulphide production in MH17 was controlled effectively with the addition of nitrate where, lower 0utlet sulfide concentration than inlet (Figure 4.1.3.2: f). It observed that HRT had a great role in sulfide production, though it did not show a significant correlation between TCS and MH17.They did not also find any correlation significantly within sulfide concentration and TCOD, sulfate and VFA concentrations. The production of sulphide production in sewers does not depend on single water quality parameter, it totally depends on the combination of all parameters [45].

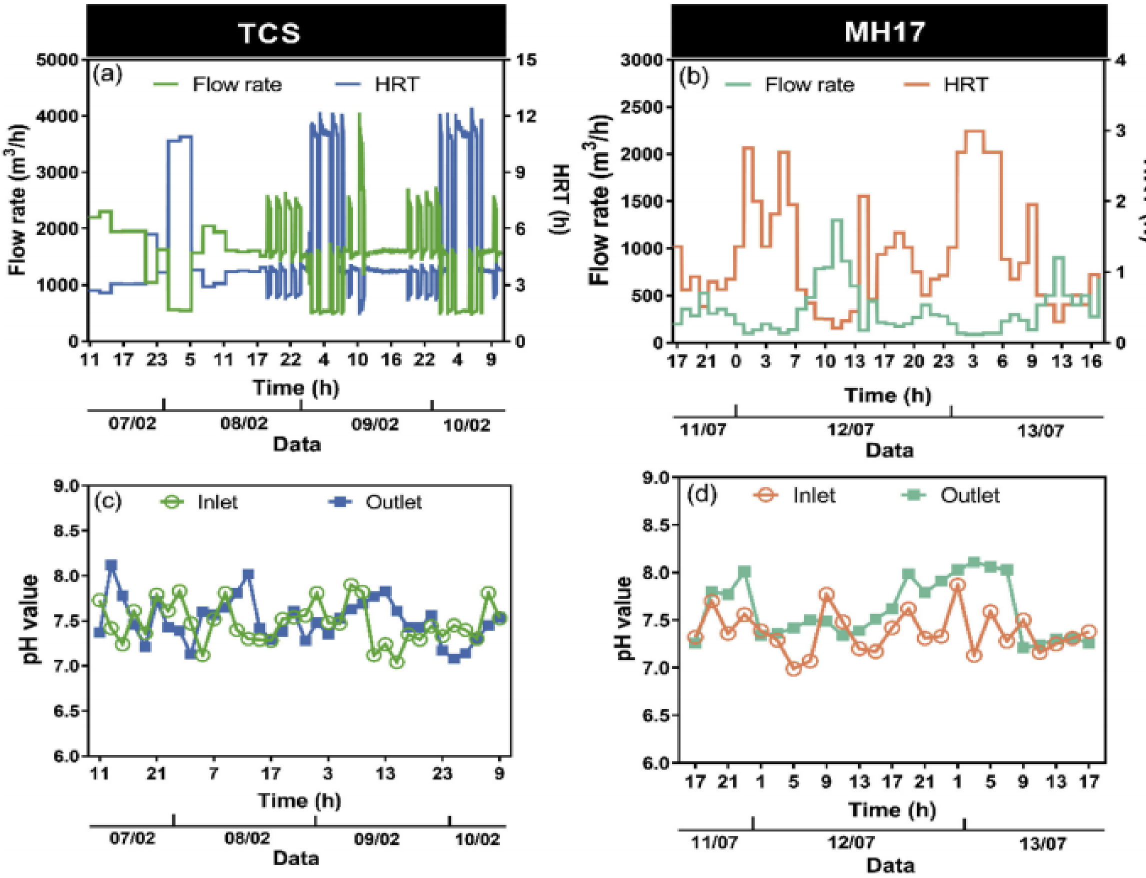

Figure 4 .1.3.1 Different flow rate and HRT, inlet and outlet pH values in sewer systems TCS (a and c) and MH17 (b and d). The sampling campaign duration in TCS is 3 days (07/02/2010-10/02/2010) and it started from 11:00. In MH17, it started from 17:00 and the duration is two days (11/07/2012-13/07/2012) [42].

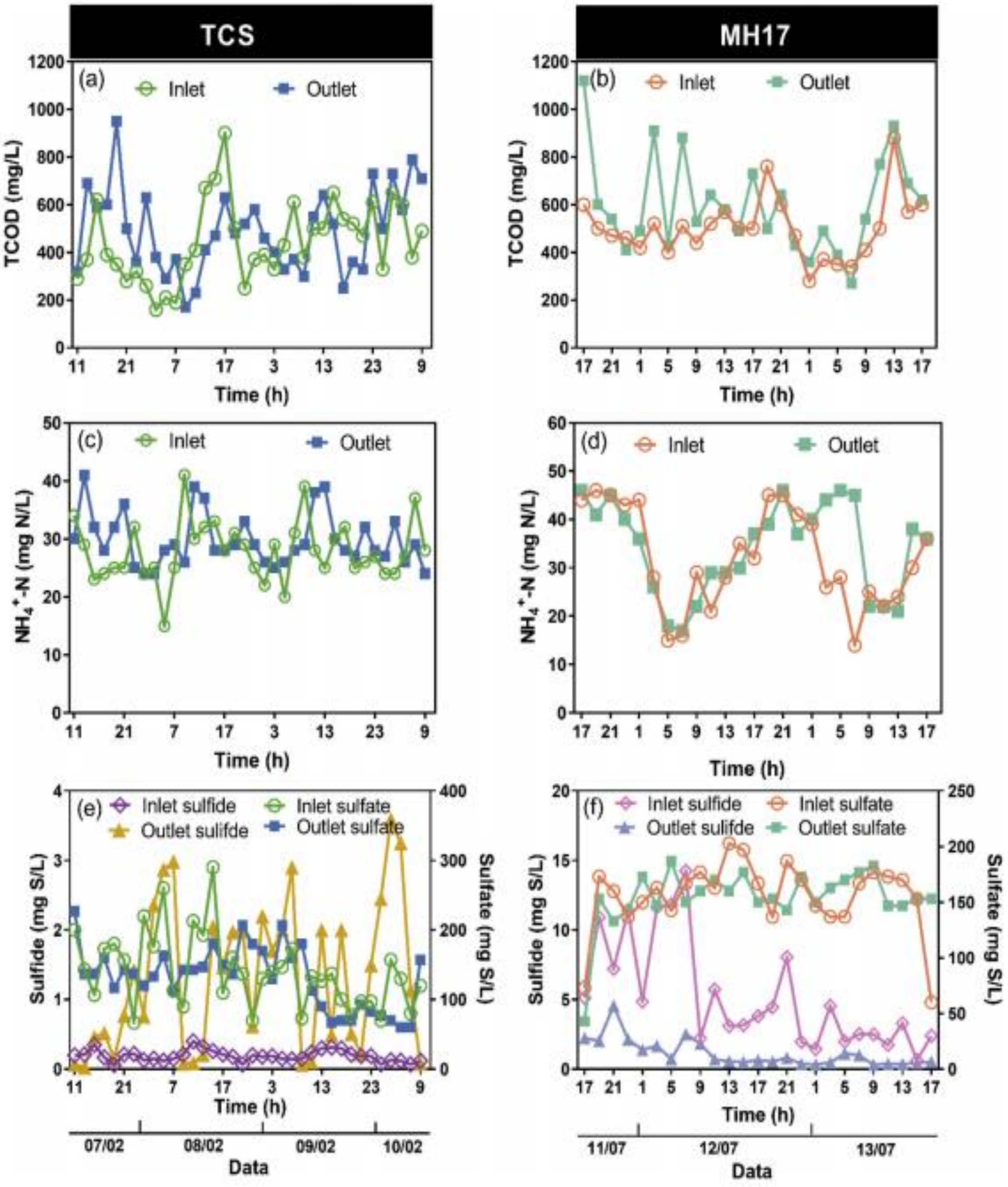

Figure 4.1.3.2 Different variation concentration of inlet and outlet TCOD, ammonium, sulfate and sulphide in TCS (a, c, and e) and MH17 (b, d, and f). The sampling campaign duration in TCS is 3 days (07/02/2010-10/02/2010) and it started from 11:00. In MH17, it started from 17:00 and the duration is two days (11/07/2012-13/07/2012) [42].

- **Model calibration of TCS**

The collective data of 3 days sampling period from TCS (Figure 4.1.3.1: a, c, Figure 4.1.3.2: a, c and e) were applied to calibrate BISM. After model calibration in TCS (Figure 4.1.3.3) shows the fit within the measured and simulated ammonium and sulfide concentrations. The deviating movement within the measured and simulated average ammonium and sulfide concentrations was less than 5%, that exposes BISM can narrate the differences in ammonium and sulfide outlines satisfactorily. From the present result, BISM can simulate nitrogen transformation operations adequately in sewer biofilms and sewage. Then it can forecast sulfide and ammonia concentrations in the sewer gate [42].

- **Model validation of MH17**

In MH17, the biofilm model validated more with the measured ammonium, sulphide and H_2S gas concentrations for 2 days sampling time. The simulated outcomes showed a well match with the measured ammonium, sulphide and H_2S gas concentrations (Figure 4.1.3.4). The present result shows that biofilm model can predict the sulfide production in an efficient way. Moreover, the gaseous emission of H_2S also simulated in MH17 outlet manhole and the concentration level was similar to the measured data (Figure 4.1.3.4: c). The biofilm model can even reproduce the measured data nearly to indicate that advanced sewer model can portend the dynamics of ammonia and sulfide concentrations practically municipal in sewers systems though sewer circumstances of TCS and MH17 were fully different [42].

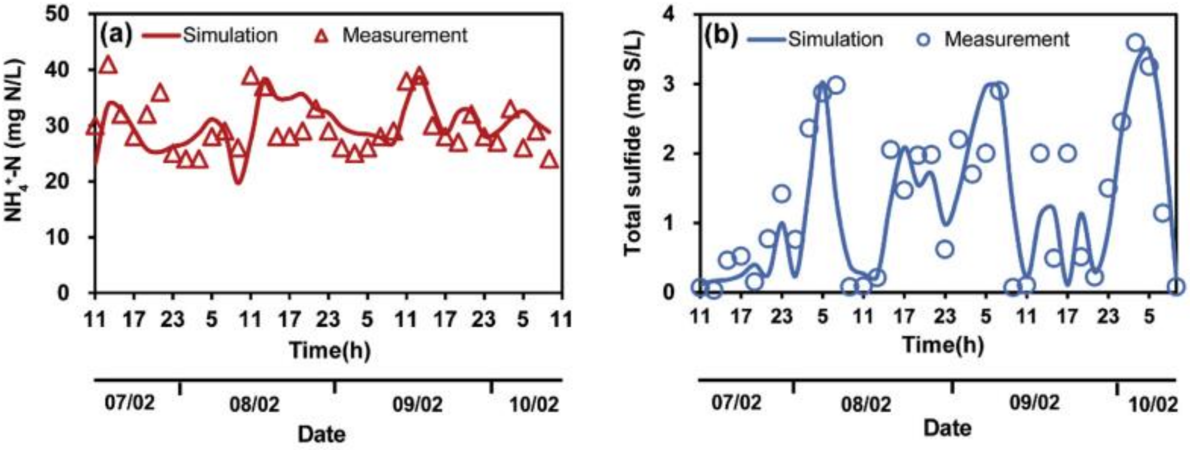

Figure 4.1.3.3 Differences of measured with simulated ammonium (a) and sulfide (b) levels in sewer system TCS. The sampling campaign duration in TCS is 3 days (07/02/2010-10/02/2010) and it started from 11:00 [42].

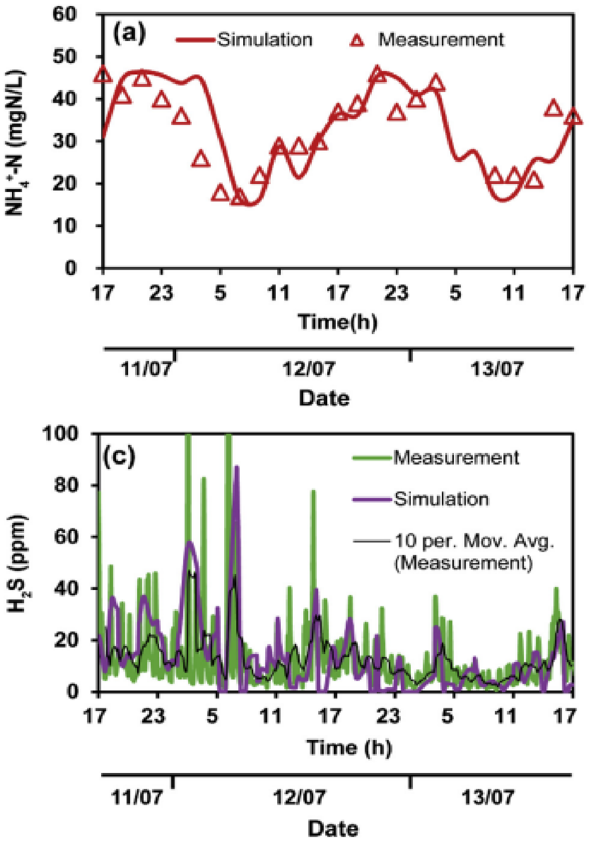

Figure 4.1.3.4 Differences of measured with simulated ammonium (a), sulfide (b) and H_2S gas (c) concentrations in sewer system MH17. The sampling campaign started from 17:00 and its duration is two days (11/07/2012-13/07/2012) [42].

4.1.4 Model application of TCS and MH17

- **Nitrate addition**

The validated sewer system model worked for simulating the longer effects of adding nitrate in TCS. There is an extensive use of nitrate salts to control sulfide effectively in sewers system, but long-term addition of nitrate brings unsatisfying result [46]. For the long-term addition of nitrate in sewer system TCS, the efficiency of sulfide controlling was not satisfactory. From the simulation result in TCS, it shows that only short-term nitrate addition can control effectively in sulfide production [42].

- **Hydraulic flushing**

The efficiency of hydraulic flushing to reduce sulfide production and detach sewer biofilms is very high [47]. A model work was conducted at the outlet of MH17 to observe the effectiveness of hydraulic flushing with three different flow rates (1000, 2000 and 4000 m^3 /h) for 1 h durations to curve the H_2S emission and dissolved sulfide. From the modeling results, it found that when the flow rate is extremely high (4000 m^3 /h) only then hydraulic flushing can significantly detach sewer biofilms and control sulfide formation, though the impact lasted for only 10 days after flushing activity [42].

- **Biocide addition**

The inclusion of biocides such as FNA or caustic solution can significantly suppress the sulfide production in sewer system. The effect of biocide addition to reduce H_2S emission and dissolved sulfide at the outlet of MH17 were simulated by employing BISM. Addition of excessive biocides may spoil more bacteria in biofilms, and it can prolong the effective period of sulfide controlling. From the result of biocide addition, it found that sulfate-reducing activity revolved to actual levels approximately after five days of FNA addition [42].

4.1.5 Summary of dynamic sewer process model

According to this study, a dynamic sewer process model (BISM) was developed from a sewer biofilm model for simulating the setting and emission of sulfide and ammonium in sewer system. Biofilm initiated sewer process model was applied in two pressurized mains (TCS and MH17) for the real operation. This model can forecast the differences of sulfide and ammonium concentrations within variable sewage and hydraulic conditions. It can also predict the long-term effects of different sulfide control strategies including nitrate and biocide addition and hydraulic flushing to suppress the sulfide production in sewer system. According to the final results, long-term addition of nitrate addition in a pressurized main was not sustainable. Hydraulic flushing or biocide addition could be the fundamental factor for the long-term effect of sulfide controlling though for large-scale pressurized sewers, chemical dosing or hydraulic flushing will be very expensive [42].

4.2 A compact trickle-bed bioreactor (CTBB) model to remove odor and Voc$_s$

To reduce the amount of hydrogen sulphide and volatile organic compounds, a compact trickle-bed bioreactor (CTBB) was installed in a wastewater treatment plant in Poland with the efficiency rate of around 95% to 97%. The trickle-bed bioreactor was designed for 200 ppm range for maximum hydrogen sulphide concentration and 25–240 ppm$_V$ for VOC concentrations. The main objective of this study focused on designing, testing, and applying a semi-industrial scale bioreactor to remove odor and VOC [48].

4.2.1 Materials and methods of CTBB model

The vessel height and inner diameter of CTBB are 2.2 m and 0.8 m respectively. The bio-trickling filter includes 3 sections which are made of 304 stainless steel to stick up in any bad working conditions in practical wastewater treatment plants. The schematic design of the compact trickle-bed bioreactor is presented in Figure 4.2.1.1 and the actual view is presented in Figure 4.2.1.2. The bioreactor is introduced with the treatment plant's ventilator process (Figure 4.2.1.3). The operating capacity of the Plant was 2000 m^3 daily during the experimental period. The maximum concentrations of volatile organic compounds and hydrogen sulphide observed during daytime and negligible at night. The implementation of CTBB at WWTP for the biodegradation of VOC and hydrogen sulphide contained polluted air ejected from the fermentation pond. Ekoinwentyka Ltd. Worked for the development of bacterial co-culture during experiments [48].

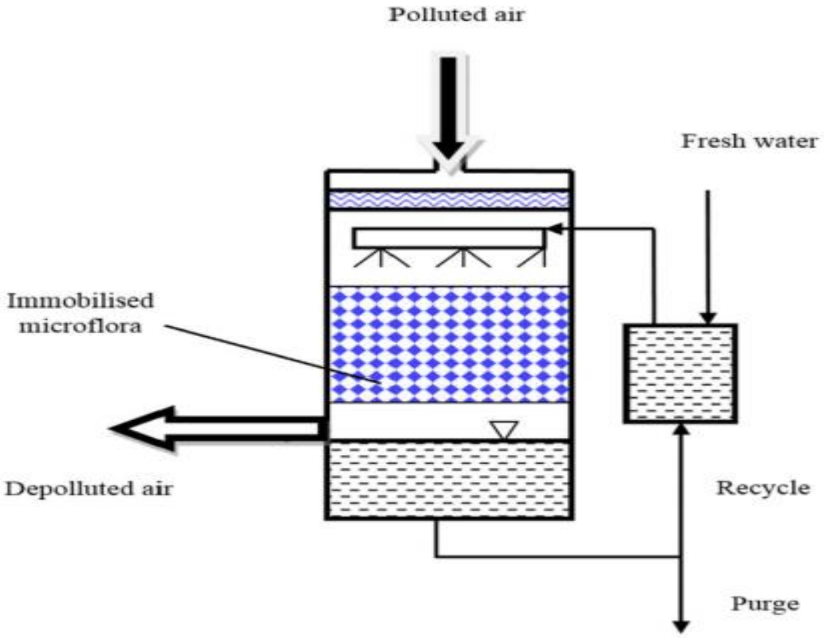

Figure 4.2.1.1 Schematic design of CTBB [49]

Figure 4.2.1.2 Installation of CTBB in laboratory (left) and in a cabin at wastewater treatment plant (right) in Poland [48].

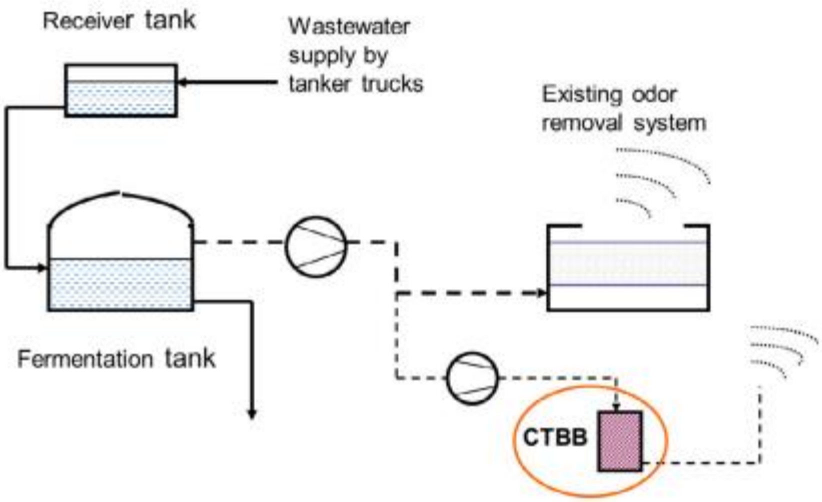

Figure 4.2.1.3 Connection of CTBB with WWTP ventilation system [48]

4.2.2 Results and discussion of CTBB model

- **Laboratory test**

At the beginning stage, CTBB started its work in the laboratory with wastewater sample from real wastewater treatment plant. The initial result from laboratory experiments helped Ekoinwentyka Ltd.to use CTBB for the removal of VOCs, mercaptans and hydrogen sulphide contained polluted air from the fermentation pond of real wastewater treatment plant [48].

- **Initial performance of CTBB at wastewater treatment plant**

The variable concentration of VOC and H_2S was observed in a particular day for two hours test period (Figure 4.2.2.1). In case of VOC, the highest temporary concentration was almost 55 ppm and the maximum average concentration was around 28 ppm. Regarding H_2S, the highest temporary concentration was just above 100 ppm and maximum average value was just below 100 ppm. However, the remarkable point is that the H_2S removal capability of CTBB was more than 90% during this short time test period and concentration level is less than 80 ppm [48].

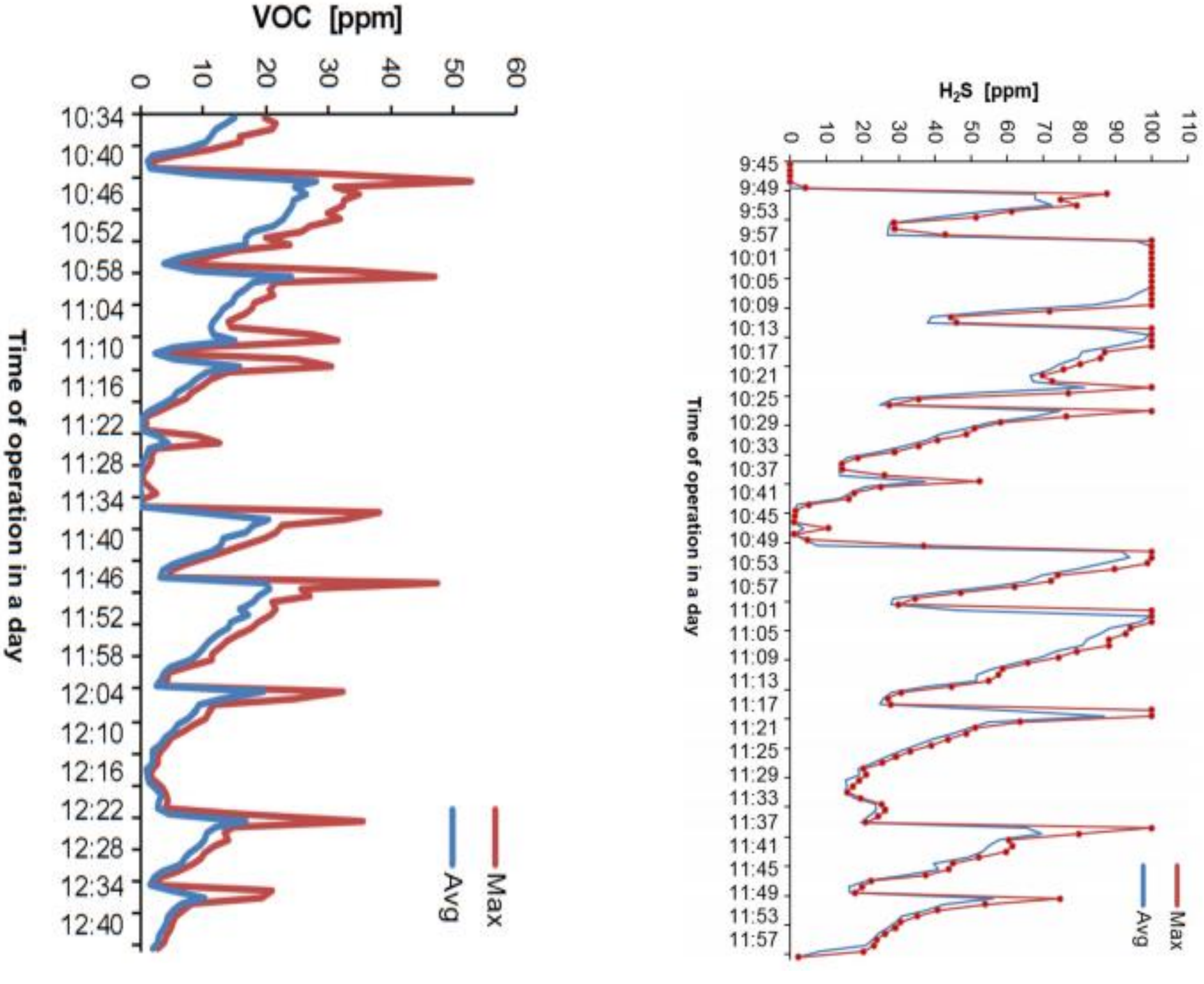

Figure 4.2.2.1 Variations of VOC and H_2S concentration [48]

- **Start-up of long-term CTBB trial at the wastewater treatment plant**

An industrial trial was preceded for a 7 days period in CTBB (Figure 4.2.2.2). According to the trial experiment, the fluctuation of conversion factor of removing H_2S was 10–70% on first day. The conversion factor was going to increase on second day from 70 to 95% and highest ranged recorded on third day (above 97%). The maximum H_2S removal was also observed during CTBB operation for remaining days [48].

- **Long-term CTBB experience at the wastewater treatment plant**

After getting the satisffactory result from 7 days trial period, CTBB was carried out for 60 days experiment. The ambient temperature, the concentration of air pollutants of plant's ventilation air of the WWTP are higher than the previous test. The concentration of H_2S was observed at CTBB inlet within the range from 2.0 ppm - 660 ppm. According to Figure 4.2.2.3, the range of inlet H_2S concentration was between 50–440 ppm, though sometimes H_2S concentration increased to 660 ppm which was not seen in graph.

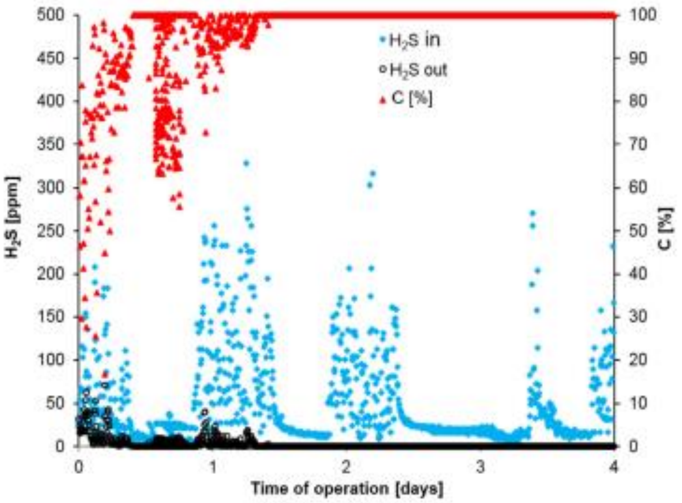

Figure 4.2.2.2 H_2S concentration and conversion factor (C) in CTBB for 7 days trial period [48].

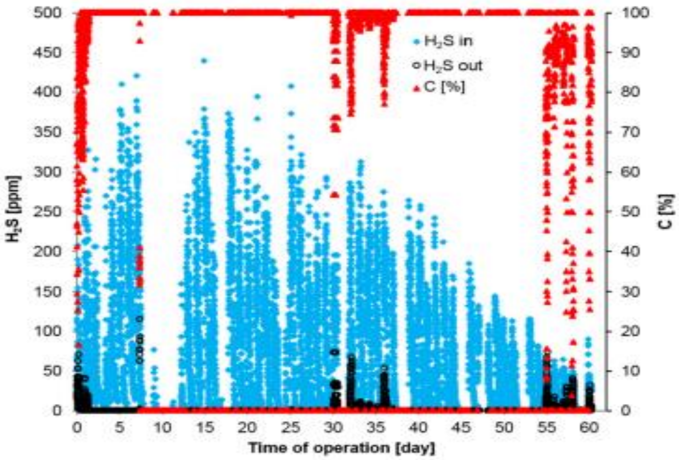

Figure 4.2.2.3 H_2S concentration and conversion factor (C) in CTBB for 60 days long-term period [48].

The value of the H_2S conversion factor was observed more than 97% during whole period just except the fluctuation for two or three days due to malfunction of some sensors [48].

- **The daily fluctuations experience of CTBB in H_2S and VOC concentrations**

After a long-term good working performance of removing H_2S, CTBB was employed for daily observation of inlet pollutant concentrations (Figure 4.2.2.4). The usual H_2S concentration varied from 0 to 2 ppm at early morning till 6:30 a.m., raised rapidly from 300–440 ppm until evening and after evening 8:00 p.m., it returned to 0 to 2 ppm. It is very remarkable that the system was working successfully to notify any sudden variation of pollutant concentration. With the similar way of H_2S biodegradation, the conversion factor of VOC observed the range from 35 to 65% during the beginning hours (12 hours) of CTBB operation. From 13th to 24th hour, the conversion factor raised within 50 to 85%. The measured first day performance of VOC are presented in Figure 4.2.2.5 and the conversion factor of VOC after acclimation are shown in Figure 4.2.2.6 [48].

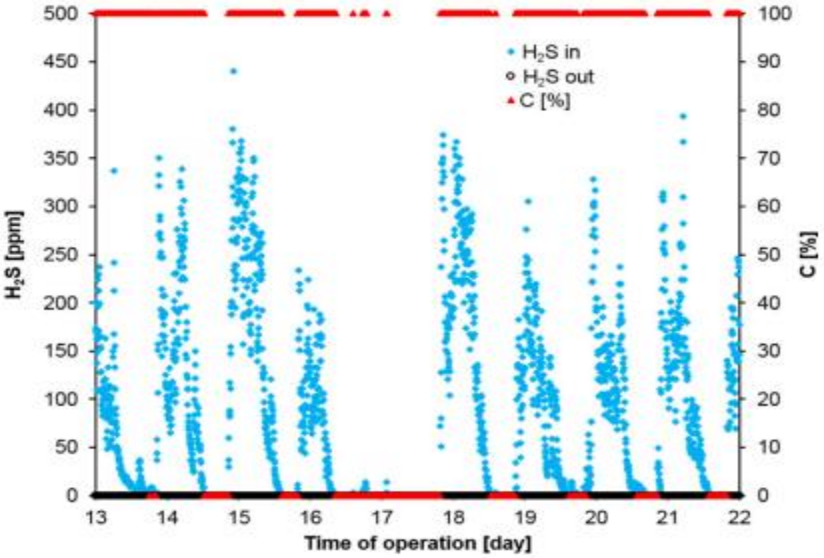

Figure 4.2.2.4 The conversion factor of daily observation of inlet H_2S concentrations [48].

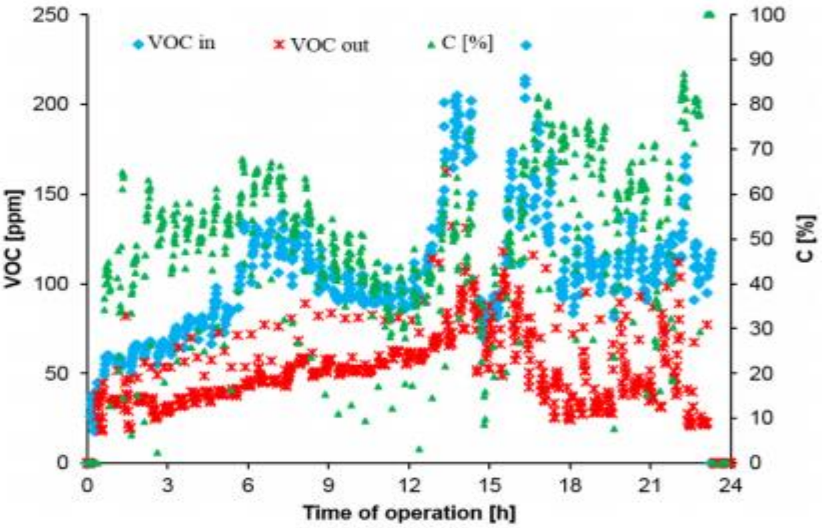

Figure 4.2.2.5 VOC concentration and conversion factor (C) in CTBB for 0–24 h [48].

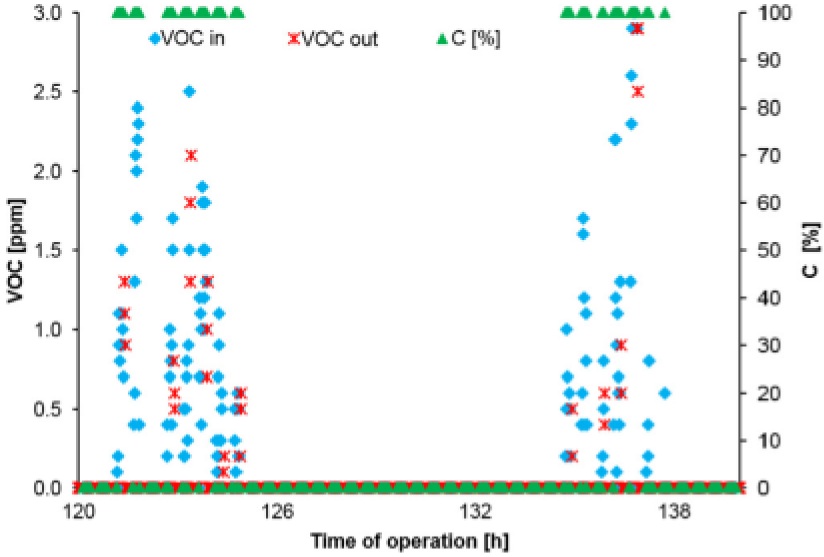

Figure 4.2.2.6. VOC concentration and conversion factor (C) in CTBB after initial period [48].

4.2.3 Summary of CTBB model

The field trial of compact trickle bed bioreactor (CTBB) model in a wastewater treatment plant in Poland showed maximum performance for the removal of H_2S and VOC concentrations in a sustainable manner. In CTBB, the removal rate of H_2S and VOC concentrations observed more than 90%. The concentrations of H_2S and VOC was less than 440 ppm and 200 ppm respectively. The practical data and information from this trial period in the wastewater treatment plant will be patronizing for future intensification and further development of the process.

5 POSSIBLE ACTIVITIES AND SOLUTIONS TO MITIGATE ODOR AND CORROSSION PROBLEM

The new sewer system are building rapidly with the fast growth of population, urbanisation and industrialization. If some possible activities and mathods are applied in newly and existing sewer systems, it may bring maximum positive outcomes to control odor and corrosion occurrences.

5.1 Future outlooks of hydrogen sulphide removal

There are some new applications which might be more cost effective and sustainable for future research to control hydrogen sulphide emission. The new applications are:

- ✓ Application of formaldehyde and paraformaldehyde
- ✓ Slow releasing of solid-phase oxygen
- ✓ Application of Microbial fuel cells (MFCs)

- **Application of formaldehyde and paraformaldehyde**

To control H_2S emission in sewer systems, inhibitors like molybdate can be applied [55]. There is an extensive use of formaldehyde in microbial growth, mainly in food factories. Microbial growth can be suspended by formaldehyde and it is fully biodegradable in wastewater treatment plants [56]. The inexpensive chemical paraformaldehyde is an ideal alternative for formaldehyde in wide range of industrial uses. Paraformaldehyde can be transformed to formaldehyde in neutral pH and aqueous environment conditions. To control H_2S formation in sewer system, the sufficient formaldehyde concentration is 10–20 mgL^{-1}. Easily water-soluble formaldehyde reacts with water in a reversible way to get methanediol [$CH_2(OH)_2$] form [57]. The exchange rate of urban environment and gas phase in sewers is negligible due to closed sewer system. The application of formaldehyde or paraformaldehyde as an inhibitor is a big concern for treatment plants' workers due to its toxicity. Therefore, adequate protection facilities should be ensured for sewer workers and further necessary study should be conducted about the effect of formaldehyde application to the environment and sewer workers. The cost of formaldehyde treatment is approximately US$1.63 to 2.00/kg of sulfur in sewer water [2, 24].

- **Slow releasing of solid-phase oxygen**

To control the production of hydrogen sulphide in oil wells and river sediments, many technologies have been used and they are rarely applied in case of wastewater [58]. The slow release of oxygen from solid catalyst compounds like MgO_2 and CaO_2 react with water to produce $Mg(OH)_2$ and $Ca(OH)_2$ respectively. The injection of $Mg(OH)_2$ and $Ca(OH)_2$ into lakes or rivers suppress anaerobic biological movement for a long run. Elimination of H_2S by magnesium peroxide and calcium peroxide is because of chemical oxidation of H_2S and toxicity to SRB. A series of lab tests showed that 0.4% magnesium peroxide can inhibit H_2S formation for 40 days or more. [59]. Slow release of oxygen in solid phase is the best way to eliminate the hydrogen sulphide formation for a long time. The only problem is to ensure solid-phase oxygen in sewer system being washed off. Dry weather can only bring maximum result under this method [2].

- **Application of Microbial fuel cells (MFCs)**

Microbial fuel cell is an electrochemical apparatus that transforms chemical energy to electrical energy in a continuous order. Many research specialists found that H_2S is used as a fuel in a solid oxide fuel cell [60]. Microbial fuel cells are the appliances to transform chemical to electrical energy directly via electrochemical reactions with biochemical process. Dissolved sulphide can be transformed into elemental sulfur with the presence of a fuel cell. H_2S oxidation in the anodic section of fuel cell can produce electrical energy up to 101 mW. An up flow anaerobic sludge reactor connected with microbial fuel cell can eliminate 98% of sulfate and 46% of acetate from sewer water. Controlling H_2S emission by MFC might be interesting in coming future (Figure 5.1.1). Along with the removal of H_2S, odor, and corrosion, MFC application can also produce some electricity. When electron transfers from bacteria to electron acceptors, H_2S removal occurs in fuel cells. Microbial fuel cell might be a more sustainable and cost-effective device if the device can be developed in a productive way with an advantage of electricity generation [2, 24].

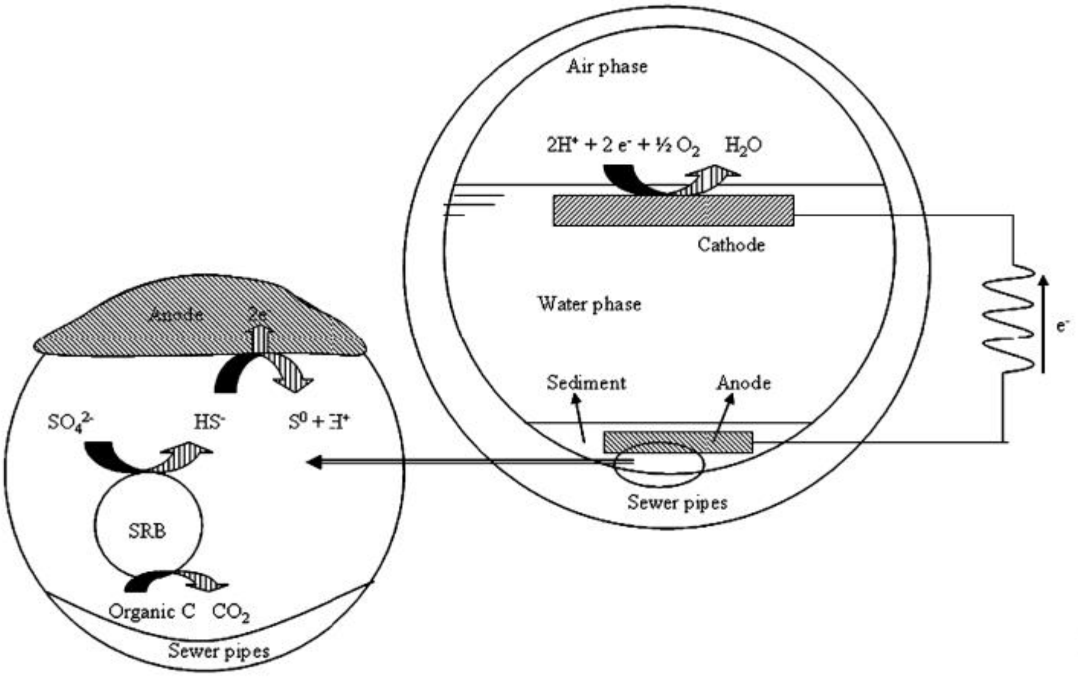

Figure 5.1.1 Schematic possible design of a microbial fuel cell [2].

5.2 Future outlooks to control and mitigate the microbial induced concrete corrosion

The application of latest developed corrosion-proof concrete in new sewer system can highly protect the corrosion occurrence. This new application involves the use of admixtures, acid-resistant cement, protective coatings, and biofilms to solve the sulfuric acid attack. Recently many research experts, packing and coating industries have found that antimicrobial substances like silver/copper zeolites are more safe and inexpensive materials to control the microbial growth and activity in sewer system. A study of chemical exposure test shows that epoxy coating and polyuria lining result higher corrosion protection. Therefore, the application of epoxy coating and polyuria lining in sewer system can ensure maximum protection of corrosion occurrence in near future [61,62].

6 DISCUSSION

The whole study shows an overview of corrosion and odor management in sewer system. This study has mainly focused on hydrogen sulphide as it is the main phenomenon of corrosion and odor formation in sewer networks. Along with the hydrogen sulphide, methane, nitrous oxide and volatile organic compounds are also responsible for corrosion and odor generation. The discussion part has been divided into four sections: identification of major odor and corrosion producing compounds, gas phase odor alleviation, odor removing models and future outlooks of hydrogen sulphide and corrosion prevention.

Hydrogen sulphide, methane, nitrous oxide, volatile organic compounds emission in sewer networks have been explained in chapter 2. H_2S emission in Chapter 2.1 gives information that sulfur cycle is very complicated, and it involves many factors including the volume of wastewater, biofilms, concentration of microorganisms and the amount of slits in sewer pipes. The processes of sulfur cycle are production of sulphide, transformation of sulphide from the liquid state to the gas state, chemical and biological sulphide oxidation. The transformation of hydrogen sulphide from one phase to another depends on temperature, pH, wastewater flow, hydraulic condition of water state and air space. Rising redox potential (pure air injection, nitrate addition) is very effective to control sulphide production. Using pure oxygen as a sulfide control process is very convenient as dissolution of oxygen is higher at maximum pressure. The only negative thing is it is useable only for high-pressure force mains which may have fire risks. Addition of 1.0 g L-1 nitrate in wastewater prevents sulfide production for minimum 29 days.

To inhibit the SRB activity, pH elevation method is the most effective way. For chemical removal of H_2S - metal salts precipitation, addition of iron salts and addition of oxidizing chemicals have been mentioned. Metal salts (e.g. ferrous, zinc and copper) precipitation in the wastewater play an important role to control dissolved sulfide concentration and other related problems. Ferrous or ferric ion is more useful in regulating the dissolved sulphide concentration, sometimes ferrous chloride can be effective more than twice compared to ferric chloride. Oxidizing chemicals include hydrogen peroxide, chlorine and potassium permanganate can oxidize sulphide to sulfate or to physical sulfur.

Chapter 2.2 describes how methane is originated from anaerobic condition and sewer sediments. Sewer methane can be measured by off-line and online CH_4 measurement. The key method of off-line methane measurement in sewer system is manual sampling with regular intervals over several hours through off-line gas chromatography. For online CH_4 measurement infrared (IR) spectroscopy is the most efficient system. There was not sufficient information in the sources regarding the emission of nitrous oxide and volatile organic compounds.

The gas phase odor alleviation chapter (3) explains two different biological systems (Biofilters, Bio trickling filters), one adsorption-based system (Activated Carbon) and a short summary of other odor alleviation technology.

In odor removal model section, a dynamic sewer process model and a compact trickle-bed bioreactor model are included for odor formation and mitigation. Two pressurized mains (TCS and MH17) are used for the operation dynamic sewer process model. This model can forecast the differences of sulfide and ammonium concentrations within variable sewage and hydraulic conditions. It can also predict the long-term effects of different sulfide control strategies including nitrate and biocide addition and hydraulic flushing to suppress the sulfide production in sewer system. According to the final results of this model, long-term addition of nitrate addition in a pressurized main was not sustainable. Hydraulic flushing or biocide addition could be the fundamental factor for the long-term effect of sulfide controlling though for large-scale pressurized sewers, chemical dosing or hydraulic flushing will be very expensive.

In case of compact trickle-bed bioreactor model, it was installed in a wastewater treatment plant in Poland to reduce the amount of hydrogen sulphide and volatile organic compounds with the efficiency rate of around 95% to 97%. The practical data and information from this trial period in the wastewater treatment plant will be patronizing for future intensification and further development of H_2S and VOCs removal process.

Finally, in future outlooks section - some sustainable and cost-effective new applications are recommended for future research to control hydrogen sulphide emission and microbial induced concrete corrosion. The recommended approaches to control hydrogen sulphide are application of formaldehyde and paraformaldehyde, slow releasing of solid-phase oxygen and application of microbial fuel cells (MFCs). The remarkable additional advantage of microbial fuel cell application is its electricity generation. To mitigate the microbial induced concrete corrosion, the application of epoxy coating and corrosion-proof concrete like use of admixtures, acid-resistant cement, protective coatings, and biofilms can bring maximum positive result.

7 SUMMARY

Corrosion and odor problem are one of the biggest concerns in sewer network. This study has introduced different methods to control the emissions of various odorous compounds. The main priority of this study is the prevention of hydrogen sulfide production as it is mainly responsible for corrosion and odor formation. To prevent the growth of sulfur reducing bacteria, pH increasing is very effective. Moreover, pure air injection, nitrate addition, and addition of oxidizing chemicals are the most important methods to control hydrogen sulphide formation. Along with hydrogen sulphide, methane is another dominant source of odor production. Generally, methane is generated by methanogens in the sediment surface but expanded deeper than the sulfide production area. The factors like HRT, A/V ratio, temperature, and COD have significant effects on methane production. Methane can be measured by both offline and online measurement, but online measurement is very suitable.

Apart from these, there are various technologies for gas phase odor alleviation. Among all the gaseous treatment methods, biological systems and activated carbon remove H_2S 80% and 79% respectively. Activated carbon systems are very cost effective with shorter start up time and sporadic flow capacity than biological systems. Furthermore, two model studies illustrate the practical knowledge about odor formation, mitigation, and further development of H_2S and VOCs removal process. In addition, some new approaches like application of formaldehyde and paraformaldehyde, slow releasing of solid-phase oxygen and application of microbial fuel cells are recommended strongly to ensure more sustainable and cost-effective method for the removal of hydrogen sulphide emission. In case of microbial induced concrete corrosion, the application of epoxy coating and corrosion-proof concrete may bring maximum positive outcomes.

Finally, future technologies should perform network-wide corrosion and odor control with the collaboration of advanced sewer system and water industries should invent new materials to ensure long lasting corrosion resistant sewers.

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