Liquid Phase Adsorption of Volatile Organo Sulphur Compounds in presence of a Cationic Surfactant: Process Innovations towards Dearomatization of Sewage Waste Water

Thesis submitted by

Shyamal Jana

Under the guidance of

Prof. Ujjaini Sarkar

for the degree of

Doctor of Philosophy (Engineering)

Submitted to

Department of Chemical Engineering

Faculty Council of Engineering & Technology

Jadavpur University

Kolkata, India

July 2018

In the name of God, the compassionate, the merciful

DEDICATED TO

MY

PARENTS

JADAVPUR UNIVERSITY

KOLKATA - 700032

INDEX NO. 27/12/E

1. **Title of thesis:** Liquid Phase Adsorption of Volatile Organo Sulphur Compounds in presence of a Cationic Surfactant: Process Innovations towards Dearomatization of Sewage Waste Water.

2. **Name, Designation & Institution of the Supervisor:**

   Dr. Ujjaini Sarkar

   Professor

   Department of Chemical Engineering

   Jadavpur University

3. **List of publication(Journals):**

   - Alkaline functionalization of granular activated carbon for the removal of Volatile Organo Sulphur Compounds (VOSCs) generated in Sewage Treatment Plants, *Shyamal Jana* and *Ujjaini Sarkar*, ***Journal of Environmental Chemical Engineering*, 6 (2018) 3510–3519.**
   - Application of an Alkali Functionalized Material for Treating Pharmaceutical Wastewater Containing Chlorohexidine Gluconate and Cetrimide, Debasree Banerjee, *Shyamal Jana, Ujjaini Sarkar and Debasri Roy,* ***Clean-Soil, Air, Water*, 2016, 44(2), 169-179**.

4. **List of Patents:** None

5. **List of Presentations in National/International:**

   National

   - **Shyamal Jana** and U. Sarkar, Poster presentation entitled ‘Alkali Functionalization of Granular Activated carbon for adsorption of Volatile Organo Sulphur Compound’, National Seminar on *Innovative Process Technology for sustainable Development* dated 23rd - 24th Feb, 2018 at IIChE Auditorium & K.P. Bose Auditorium, Jadavpur University Campus.

   International

   - **Jana S.,** and Sarkar U. Synthesis and characterisation of a novel alkali functionalised super-microporous material: Performance with respect to an expensive mesoporous aluminosilicate (MCM-41). *Fourth International Conference on Multifunctional, Hybrid and Nanomaterials (HYMA, 2015)*; 9-13 March, 2015.

CERTIFICATE FROM THE SUPERVISOR(S)

This is to certify that the thesis entitled ***"Liquid Phase Adsorption of Volatile Organo Sulphur Compounds in presence of a Cationic Surfactant: Process Innovations towards Dearomatization of Sewage Waste Water"*** *submitted by* ***Mr. Shyamal Jana****, who got his name registered on 04/07/2012 for the award of Ph.D. (Engineering) degree of Jadavpur University is absolutely based upon his own work under the supervision of* ***Dr. Ujjaini Sarkar*** *and that neither his thesis nor ay part of the thesis has been submitted for any degree/diploma or any other academic award anywhere before.*

Signature of the Supervisor
&date with Office Seal

Acknowledgement

I would like to express my sincere thanks to all those who contributed in many ways towards the success of this piece of research work and made it an unforgettable experience for me.

First and foremost, I owe my deepest gratitude to my supervisor Prof Ujjaini Sarkar for her excellent supervision and valuable advice throughout the course of my study. Without her encouragement, continuous guidance and the loving care for me at the Laboratory, I could not have finished this work. She was always there to meet and talk about my ideas, to proofread and mark up my works and to ask me good questions to help me think through my problems (whether philosophical, analytical or computational). She also made the laboratory a wonderful workplace with different valuable and necessary equipment for this kind of research. Her experience in issues related to odour nuisance in and around waste management facilities has been indispensable in the evolution of this work.

I would like to convey my sincere thanks to Prof. Kajari Kargupta, Prof. Chandan Guha, Prof. Avijit Bhowal, Dr (Mrs) Sudeshna Saha and Dr (Mrs)Ratna Dutta of Department of Chemical Engineering, Jadavpur University. I always got invaluable advice from them whenever needed. I am also grateful to Mr. Ashim Bhattacharya, Mr. Lakhindar Bhandari, Mr. Jyotis Das and Mr. Debu Ari for their kind cooperation in several occasions.

I wish to convey my earnest gratitude to Thermo Fisher India Limited, Nasik Factory, for allowing me to carry out GC-MS analysis at their industrial facility using PFPD (Pulse Flame Photometric Detector). I am especially thankful to Mr Smriti

Ranjan Maji, technician of The Bose Institute, Kolkata (Centenary Campus) for his kind co-operation for conducting all the analytical tests of samples by GCMS in their laboratory. I am grateful to Mr. Vivek Bharadwaj, Executive Engineer, Mr. Asim Nag and Staff of Baranagar-Kamarhati sewage treatment plant, Kolkata Municipal Development Authority (KMDA), West Bengal, India, for their kind co-operation during collection of sewage waste water and sampling. I am also grateful to the Indian Association for the Cultivation of Science, Raja S.C. Mullik Road, Kolkata-700032, for carrying out some characterization tests of various types of functionalized adsorbents at their central facility.

I am thankful to the group of trained Sniffers for their kind help and perseverance during the olfactometry tests carried out based on panel method. My friends in the laboratory and my wife, who spent time for sniffing the odorous sewage samples without any remuneration need a 'thank-you' from me. I would also acknowledge invaluable support and immense help received from my colleagues and would like to express my earnest thanks to Mr Pabitra Kumar Baidya, Mr Sibasis Baksi, Mr Dipanjan Ghosh, Ms Baisali Rajbansi, Ms Suvra Sadhukhan, Mr Somdutta Singha,Mr Rajib Kumar Das and Ms Debreka Ghosh for their kind co-operation during collection of sewage samples and Olfactometriy tests. I am also thankful to Mr Rakesh Dey for extending his help during my experimental work.

Lastly I am indebted to my parents (Mr. Sachindra Nath Jana and Mrs. Arati Jana) and my family for providing me strength and support in every moment of my life.

Shyamal Jana

Abstract

Odorous emissions from sewers and sewage wastewater treatment plants are a complex mixture of volatile organic compounds that can cause a nuisance to adjacent populations and contribute significantly to atmospheric pollution. Odour abatement and control is thus a major issue for Sewage Treatment Plants. A quantitative Odour Assessment and Control Scheme (OACS) describing various methods for the assessment and control of odour have been developed. Assessment of odour intensity is carried out by panel based olfactometry method, with the help of trained human sniffers. Psychophysical laws are applied and validated to evaluate odour concentration in the semi solid, liquid and gas phases. For raw sewage, Beidler's equation represents the intensity-concentration relationship best. Odours from waste water treatment plant have been traditionally treated using physicochemical processes, such as scrubbing, adsorption, condensation and oxidation, Adsorption is the most effective technique to control the odour of raw sewage. Granular Activated Carbon (GAC) is a common adsorbent material for the adsorption of Volatile Organo-Sulphur Compounds (VOSCs). Waste water contains so many cationic surfactants, coming from household cleaners, soap, shampoo, saving cream etc. In presence of cationic surfactants removal of VOSCs decreases with GAC. Adsorption capacity of GAC was enhanced by functionalization with different alkaline solutions such as NaOH , KOH, NH_3 *etc. The alkali Functionalized Activated Carbons (FACs) have higher surface area and pore volume, and reduction of oxygen containing functional groups than precursor GAC. Analytical methods characterize odours in terms of their chemical composition and attempt to quantify the odorants present by Gas Chromatography Mass Spectrometer (GC-MS) equipped*

with Pulse Flame Photometric (PFPD) Detector The time variant odour concentration profile (Olfactometry based) goes at per with the time variant VOSCs concentration (GCMS outputs) for all the four components like Methyl Mercaptan (CH_3SH), Ethyl Mercaptan (C_2H_5SH), Dimethyl di-sulphide (CH_3SCH_3) and Carbon di-sulphide (CS_2), having low enough odour threshold values. Successful field use of physical adsorption using GAC and different FACs will require measurements which would account for the extreme variations in sewage composition, sewage age, sewage conditions and type of secondary treatment provided. It is important to determine the magnitude and distribution of such variability and the impact on emission of the VOCs in order to design an accurate emission monitoring and control programme.

VOSCs undergo physical and chemical adsorption through film and pore-diffusion. They form surface complexes with the functional groups of GAC and FACs sample. An increase in the adsorption capacity of FACs is primarily due to chemisorption, ensured by the 'good-fits' in the pseudo kinetics and Boyd's film diffusion models.

TABLE OF CONTENTS

Chapter 2

Chapter 3

Chapter 4

Chapter 5

Chapter 6

List of Figures

Chapter 5

Chapter 6

List of Tables

Chapter 5

Chapter 6

Nomenclature

Symbol	Description	Unit
q	Amount adsorbed	mg/lit/g
$q_{\max}$	Maximum amount adsorbed	mg/lit/g
C	Equilibrium concentration	mg/lit
R	Gas constant	8.314 J/mol K
T	Absolute temperature	K
C_e	Equilibrium concentration	mg/lit
S	Surface area of the adsorbent per solution volume	m^{-1}
C_s	Concentration at the surface	mg/L
A_0	Initial peak area of solutes adsorbed per unit weight of the adsorbent	-
A_t	peak area of solutes adsorbed per unit weight of the adsorbent at different time	-
OU	Odor unit	-
C_{eqv}	equilibrium concentration of solute	mg/lit
Xm	maximum amount adsorbed for solute	mg/lit/g
q_e	Amount adsorbed at equilibrium	mg/lit/g
q_t	Amount adsorbed at time *t*	mg/lit/g
k_1	Pseudo first-order rate constant	min^{-1}
k_2	Pseudo second-order rate constant	mg/L/ g. min
k_i	Intraparticle diffusion rate constant	mg/L/ g.$min^{1/2}$
I	Constant which indicates the boundary layer thickness	mg/L/ g
$F(t)$	Fractional attainment of equilibrium, at different times	-
Bt	Mathematical function of F(t)	-
C_0	Initial concentration	g/L
C_t	Solute concentration in effluent at any time*t*	g/L
M	Mass of the adsorbent	g
t	Time or Service time	min

Chapter I

Introduction

With growing population, industrialization and urbanization, odour problem has become an objectionable issue. Urbanization, without proper sanitation facilities, is the major cause of odour nuisance. Rapid growth of industrialization has aggravated the problem of odour nuisance due to generation of obnoxious odour caused by mostly volatile organo-sulphur compounds. These compounds are mostly generated through industrial operations. Nowadays, people in and around the sewage treatment plants (STPs) are quite concerned about the effects of malodorous gases on human life. The same is primarily caused by emission of volatile organo-sulphur compounds (VOSCs), which have very low odour threshold[1] values and a high negative hedonic tone[2] (Ras et al. 2009).

Odours in sewer systems is produced by anaerobic microbial decomposition of sewage waste water containing high levels of organic matter, nutrients, toxic compounds and chemicals. Most of the odours generated within the sewer systems are sulphur based compounds, the predominant compound often being hydrogen sulphide **(**A. Vincent, 2001**)**. Organo-sulphur based volatile compounds like carbon disulphide, methyl mercaptan, dimethyl sulphide, ethyl mercaptan, dimethyl disulphide etc., though found in lower concentration, are the key compounds behind most of the

---

[1] **Odour Threshold:** The lowest physical intensity at which an odour stimulus is correctly identified for a specified percentage of time.

[2] **Hedonic Tone:** Odours of equal intensity may differ in character. Hedonic tone is a character of odour that identifies its place on a scale of pleasantness and unpleasantness. However, a pleasant odour may be considered objectionable by the exposed population in the context of industrial emission and pollution hazards.

odour complaints. These are detectable at very low levels of concentrations (Hinokiyama et al. 1991; Patterson et al. 1993; Patterson et al. 1985) and tend to disperse relatively slowly till a concentration level is reached which is far below a concentration that corresponds to a nuisance level. These VOSCs are primarily produced due to anaerobic microbial decomposition of proteins (A.G. Boon, 1995).

Undesirable odour contributes to air quality concerns and affect human lifestyles. Odour is undoubtedly the most complex of all the air pollution problems. In addition to odour, VOSCs, while present in the gas phase, may affect human health and create corrosion problem (Gostelow *et al.,* 2001). However, high risks are associated with either a long-term exposer to low concentrations of mercaptans or the combined effect of mixture of volatile organic compounds. Assessment of risk to human health due to these kinds of exposures needs to be developed. On the economic front, loss of property value near odour causing operations/ industries and odorous environment is partly a consequence of offensive odour.

1.1 Wastewater: sewage waste water in particular

Wastewater is a mixture of constituents from domestic and industrial sources, often diluted with groundwater from infiltration and run-off water where the system is partially combined. Sewage is a water carried waste, in solution or suspension that is intended to be removed from a community. This is also known as waste water; it is more than 99% water and is characterized by volume or rate of flow, physical condition, chemical constituents and the bacteriological organisms that it contains. Classes of sewage water include sanitary, commercial, industrial, agricultural and surface runoff. The spent water from residences and institutions, carrying body wastes, washing water, food preparation wastes, laundry wastes and other waste products of normal living are called '*domestic*' or '*sanitary*' sewage. Liquid carried wastes from stores and service establishments serving the immediate community, known as *'commercial waste'*. Waste those results from an industrial process or the production of goods are classed as *'industrial waste water'*. Their flows and strengths are usually more varied, intense and concentrated than those of *'sanitary sewage'*. Surface runoff, also known as '*storm flow'* or *'overland flow'*, is that portion of precipitation that runs rapidly over the ground surface into a defined channel. All categories of sewage are likely to carry '*pathogenic organisms'* that can transmit disease to humans and other animals. All forms of sewage waste water contain organic matter that can cause malodorous emissions, which contaminate with the atmosphere. Increasing urban growth and lifestyle expectation have led to an increase in public complaints against odours from sewer systems (Frechen, 1994**)**. Odour problem have been increasing around sewer networks, predominantly around manholes, sewer pumping stations, drop shafts and siphon vents. In recent times sewage treatment plants have been upgraded with treatment processes that would remove odour emitting contaminants.

1.2 *Sewag7e treatment in developing countries*

In many developing countries the bulk of domestic and industrial wastewater is discharged without any treatment or after primary treatment only. In Latin America about 15% of collected waste water passes through treatment plants (with varying levels of treatment). In Venezuela (a country in South America with a below average outlook and practice on wastewater treatment), 97% of the countries sewage is discharged raw into the environment. In a relatively developed Middle East country such as Iran, the majority of Tehran's population discharges totally untreated sewage into the city's groundwater. However, in Tehran, the construction of sewage system, collection and treatment, is fully completed by the end of 2012. However, in Isfahan, Iran's third largest city, sewage treatment started more than100 years ago. In Israel, about 50% of agricultural water usage (total use was 1 billion cubic metres in 2008) is provided through reclaimed sewer water. Future plans call for increased use of treated sewer water as well as more desalination plants. Most of sub- Saharan Africa is also without any kind of waste water treatment

1.3 Sources of odorous pollutants

Most of the odorous compounds derived from anaerobic decomposition of organic matter contain sulphur and nitrogen. Most of the odorous substances are gaseous under normal atmospheric conditions or at least have a significant volatility. Usually lower the molecular weight of a compound, higher is its vapour pressure and potential for emission into the atmosphere. Substances of high molecular weight are normally less volatile and thus normally contribute much less towards odour. Reduced sulphur compounds, such as the mercaptans and organic sulphides, tend to be the most odorous, based on their relatively low odour threshold concentrations. Most commonly reported odour producing compounds are hydrogen sulphide and ammonia. Volatile organic compounds (VOCs) include reduced sulphur, nitrogen compounds, aldehydes, mono-aromatics, heterocyclic compounds, halogenated organic compounds, carbon disulphide, mercaptans, product of decomposition of proteins, phenols and some petroleum hydrocarbons etc. are other common odorants. Most offensive odour is created by the anaerobic decomposition of wet organic matter such as flesh, manure etc. For example, odour originating from livestock manure is a result of a broad range of over 168 odour producing compounds (Ania et al. 2007). Warm temperature enhances anaerobic decay and thus foul odour production. Different stages in a treatment works (Primary, Secondary and Tertiary) have different odour nuisances due to physical and biological characteristics of sewage.

There are also many other factors that affect the emissions of malodorous VOCs such as the contents of solid, which can adsorbs the dissolve gasses, turbulences, ventilation and the area of exposed liquid surfaces. Odour sources can be classified as-

i) Point Sources- Point sources are confirmed emissions from vents, stacks and exhausts**.**

ii) Area Sources- Area sources may be unconfined like a sewage treatment plant, a waste water treatment plant, a municipal solid waste landfill, composting facilities, household manure spreading, settling lagoons etc.

iii) Building Sources- Building sources of odour are like pig sheds, hog confinement, chicken confinement etc..

iv) Fugitive Sources- In these sources of odour, emissions are of fugitive nature like odour emissions from soil bed or bio-filter surface.

Most of these sources are manmade. Garbage/improper dumping on vacant land are a common phenomenon. It leads to foul smell due to putrefaction of dumped garbage, which lies uncollected for days together. In urban areas, improper handling of public amenities like toilets of cinema halls, bus/railway stations, hospitals, shopping complex etc. generate pungent odour, which affects the users as well as neighbourhood residents. Congested markets do not allow the escape of odour from markets, thus causing problems to shop-owners as well as to customers. Industries such as pulp and paper, fertilizer, pesticides, tanneries, sugar and distillery chemical, dye and dye intermediates, bulk drugs and pharmaceuticals etc., large livestock operations, poultry farms, slaughter houses, food and meat processing industries and bone mills are among the major contributors to odour pollution. Agricultural activities like decaying of vegetation, production and application of compost etc. also contribute to odour pollution.

Table 1 Important sources of odour pollution and concerned odorous compounds *[Guidelines on odour pollution and its control, May 2008, CPCB, New Delhi]*

Sources	***Sections***	***Odorous Compounds***
Waste Water Treatment Plant	Anaerobic decomposition	H_2S and Mercaptans
Municipal Solid Waste	Anaerobic decomposition	H_2S and Mercaptans
Slaughter Houses	By product/ Waste Storage/ Effluent Treatment plants	CH_4,H_2S and Mercaptans
Chemical	-	NH_3, SO_2,H_2S and phenols
Pesticides	-	CH_3CHO, NH_3, H_2S
Fertilizers	Nitrogenous and Phosphatic	NH_3,SO_2, F_2
Pulp and Paper	Digester	CH_3SH
	Black Liquor Storage Tank	CH_3SH, $(CH_3)_2S$
	Evaporator	$(CH_3)_2S$, $(CH_3)_2S_2$, H_2S
	Recovery Boiler	CH_3SH, $(CH_3)_2S$
	Smelt Dissolving Tank	CH_3SH, H_2S
	Lime Kiln	CH_3SH, SO_2
Dye and Dye Intermediates	-	NH_3, SO_2,H_2S and Mercaptans
Bulk Drug and Pharmaceuticals	Biological extracts and wastes spent termination liquors	SO_2,H_2S and Mercaptans
Tanneries	Raw hides & skin storage	Putrification of hides & skins
	Beam house operation	NH_3, H_2S

Sources	***Sections***	***Odorous Compounds***
	Finishing operation	Volatile organic compounds
	ETP: Collection tank	H_2S
	ETP: Preliminary treatment unit	H_2S
	ETP: Sludge dewatering system	H_2S
	ETP: Anaerobic lagoons	H_2S, CH_4
Sugar and Distillery	Bio-methanation	H_2S
	Aeration Tank	NH_3

Vehicular sector also has its share in odour pollution. Rapidly growing vehicular population as well as pollutants emitted by them generate harmful and pungent odour that have marked effects on pedestrians as well as near-by residents.

Some of the important sources of odour pollution, the specific section/ sources in the process and odorous compounds emitted are listed in Table 1.1.

1.3.1 *Odorous components in sewage wastewaters*

Odours that humans perceive are not due to a single compound but are rather a combined impact of mixture of separate compounds. This impact can vary with time because the volatility and diffusivity of different compounds also vary (Gardner and Bartlett, 1999). The mixtures of odorous chemicals typically contain:

i a wide range of aliphatic, aromatic and chlorinated hydrocarbons derived from cleaning agents used in the home (such as toluene, limonene, aromatic benzene derivatives, saturated aliphatic hydrocarbons C_9 to C_{14}, xylene, phenol etc.),

ii solvents (such as chlorinated hydrocarbons), iii petrol derivatives (such as benzene),

iv Odours associated with human waste such as urea and ammonia from urine and skatole and indole (breakdown products of tryptophan) from faeces.

Most volatile organic compounds originating from discharges of solvents or petrochemicals have relatively low solubility and therefore are partially stripped from solution in the sewerage system. Odours associated with wastewater emissions are made of a number of compounds (*see* Table 1.2). Hydrogen sulphide is the most important of these compounds, however the interactions of H_2S with other compounds (particularly those derived from industrial discharges into the sewer) can lead to odour problems that produce even more unpleasant odours (Vincent and Hobson 1998). Owing to the complexity of odour mixtures and the subjectivity of perceived intensity of odours, the development of techniques for magnitude matching[3] has assisted in making comparison between groups of subjects (Gardner and Bartlett 1999). There are two types of thresholds that can be identified: i) the threshold orf detection[4] and ii) the threshold for recognition. These threshold values are dependent on the solvents used to present the samples and the methodology for assessment; consequently tabulated values of odour thresholds vary widely (Gardner and Bartlett 1999). Some typical examples for threshold values of compounds associated with wastewater treatment are shown in Table 1.2.

---

[3] whereby the judgement of a sensory magnitude is made by reference to a known stimulus.

[4] the minimum concentration at which the assessor can detect a difference between a sample and a blank.

Table1.2 Odorous pollutants at waste water treatment plants (WWTP) and odour threshold concentration (OTC) ppm (v/v). [*Source: Journal of Indian Association for Environmental Management, Vol. 29, Feb, 2002*].

Pollutants	Formulae	OTC (ppm)	Odor Description
Allylmercaptan	C_2H_3SH	0.0015	Garlic
Amyl mercaptan	$C_5H_{11}SH$	0.0003	Unpleasant, Putrid
Benzyl mercaptan	C_7H_7SH	0.0002	Unpleasant, strong
Phenyl mercaptan	C_6H_5SH	0.0003	Putrid, garlic
Propyl mercaptan	C_3H_7SH	0.0005	Unpleasant
Methyl mercaptan	CH_3SH	0.0005	Rotten Cabbage
Ethyl mercaptan	C_2H_5SH	0.0003	Decayed Cabbage
Hydrogensulphide	H_2S	0.00047	Rotten eggs
Dimethyl sulphide	CH_3SCH_3	0.001	Decayed Cabbage
Carbon disulphide	CS_2	0.21	Decayed Vegetable
Diethyl sulphide	$C_2H_5SC_2H_5$	0.02	Ether
Diphenyl sulphide	$C_6H_5SC_6H_5$	0.0001	Unpleasant
Dimethyl disulphide	CH_3SSCH_3	0.0076	Putrid
Indole	C_8H_9N	0.0001	Faecal, nauseating
Pyridine	C_5H_5N	0.0001	Pungent, irritating
Skatole	C_9H_9N	0.001	Faecal,nauseating
Methyl amine	CH_3NH_2	4.7	Putrid, Fishy
Dimethyl amine	CH_3NHCH_3	0.34	Putrid, Fishy
Trimethyl amine	$(CH_3)_3N$	0.0004	Putrid, Fishy
Ethyl amine	$C_2H_5NH_2$	0.27	Ammoniacal
Diethyl amine	$C_2H_5NHC_2H_5$	0.02	Ammoniacal
Di-isopropyl amine	$(CH_3)_2CHNHCH(CH_3)_2$	0.13	Fishy
Dibutyl amine	$C_4H_9NHC_4H_9$	0.016	Fishy
n-butyl amine	$CH_3CH_2CH_2CH_2NH_2$	0.08	Sour, ammonia
Acrolein	C_2H_3CHO	0.21	Burnt sweet, Pungent
Acetaldehyde	CH_3CHO	0.067	Fruit
Butanal	$CH_3CH_2CH_2CHO$	0.0046	Rancid, sweety
Crotonaldehyde	C_3H_5CHO	0.034	Burnt sweet, Pungent
Acetone	CH_3COCH_3	100	sweet, pungent
Acetic acid	CH_3COOH	1.0	Vinegar
Butyric acid	$CH_3CH_2CH_2COOH$	0.12	Rancid butter
Benzene	C_6H_6	4.68	Solvent
Nitrobenzene	$C_6H_6NO_2$	0.0047	Shoe polish, pungent

Pollutants	Formulae	OTC (ppm)	Odor Description
Toluene	$C_6H_5CH_3$	2.14	Pungent, solventy
p-Xylene	$C_6H_4(CH_3)_2$	0.47	Sweet
Styrene	$C_6H_5CH{=}CH_2$	0.047	Rubbery, solventy
Phenol	C_6H_5OH	0.047	Medicinal
Thiocresol	$C_6H_4(CH_3)SH$	0.0001	Skunk, rancid
Paracresol	$C_6H_4(CH_3)SH$	0.001	Pungent

1.3.2 Toxicological Information of some malodorous compounds

Chemicals can have a wide range of effects on our health. Depending on how the chemical will be used, many kinds of toxicity tests may be required. Since different chemicals have different toxic effects, it is difficult to compare the toxicity of one with another. We could measure the amount of a chemical that causes kidney damage, for example, but not all chemicals will damage the kidney. We could say that nerve damage is observed when 10gram of chemical A is administered and kidney damage is observed when 10gram of chemical B is administered. However, this information does not tell us if A or B is more toxic because we do not know which damage is more critical or harmful. Therefore, in order to compare the toxic potency or intensity of different chemicals, researchers must measure the same effect. One way is to carry out lethality testing (the LD_{50} tests) by measuring how much of chemicals is required to cause death. This type of test is also referred to as a ‘quantal-’ test because it measures an effect that occurs or does not occur. LD_{50} stands for *‘Lethal Dose’*, is the amount of a material given all at once. This causes the death of 50% (one half) of a group of test animals. The LD_{50} is one way to measure the short term poisoning potential (acute toxicity) of a material.

Toxicologists can use many kinds of animals but most often testing is done with rats and mice. It is usually expressed as the amount of chemical administered (milligram) per 100grams (for smaller animals) or per kg (for bigger test subjects) of the body weight of the test animals. The LD_{50} can be found for any route of entry or administration but dermal (applied to the skin) and oral (given through mouth) administration methods are the most common.

Similarly LC_{50} is the standard measure of the toxicity of the surrounding medium that will kill half of the sample population of a specific test-animal in a specified period through exposure via inhalation (respiration). It is measured in microgram (or milligram) of the material per litre or parts per million (ppm) of air or water. Lower the value of LC_{50}, more toxic is the material. Used in the comparison of toxicities, LC_{50} values cannot be directly extrapolated from one species to the other or to humans. It is also called *median lethal concentration* or *population critical concentration 50*, written also as LC_{50}. Toxicity values of some aliphatic and aromatic mercaptans are shown in Table 1.3 and Table 1.4 (*E.J. Fairchild and H.E. Stokinger, Toxicological studies on organic sulphur compounds*).

Table 1.3 LD_{50} toxicity values of aliphatic and aromatic mercaptan. compounds (*E.J. Fairchild and H.E. Stokinger, Toxicological studies on organic sulphur compounds*).

Compounds	**IP LD_{50} mg/kg (rats)**	**Oral LD_{50} mg/kg (rats)**	**Skin LD_{50} mg/kg**		**Toxicity Class**
			Rats	Rabbits	
Ethanethiol	226	682	_	_	Slightly
Propanethiol	515	1790	_	_	Slightly
2-methyl 1-propanethiol	917	7168	_	_	Nontoxic
2-methyl 2-propanethiol	590	4729	_	_	Nontoxic
Butanethiol	399	1500	_	_	Slightly

Compounds	**IP LD_{50} mg/kg (rats)**	**Oral LD_{50} mg/kg (rats)**	**Skin LD_{50} mg/kg**		**Toxicity Class**
			Rats	Rabbits	
Hexanethiol	396	1254	–	–	Slightly
Methyl heptanethiol	12.9	83.5	1594	600	Highly
Benzenethiol	9.8	46.2	300	134	Highly
α-toluenethiol	373	493	–	–	Moderately

Table 1.4 LC_{50} toxicity values of aliphatic and aromatic mercaptan compounds *(E.J. Fairchild and H.E. Stokinger, Toxicological studies on organic sulphur compounds).*

Compounds	**Inhale LC_{50} (ppm)**			**Toxicity Class**
	Mice	**Rats**	**Eye Irritation (Rabbits)**	
Ethanethiol	2770	4420	Moderate	Slightly
Propanethiol	4010	7300	Very Slight	Slightly
2-methyl 1-propanethiol	>25000	>25000	Slight	Nontoxic
2-methyl 2-propanethiol	16500	22200	Slight	Nontoxic
Butanethiol	2500	4020	None	Slightly
Hexanethiol	528	1080	Slight	Slightly
Methyl heptanethiol	47	51	Severe	Highly
Benzenethiol	28	33	Severe	Highly
α-toluenethiol	178	>235	Slight	Moderately

1.4 Methods of sewage wastewater treatment: *Primary, Secondary and Tertiary*

With explosive population and industrial growth, the need of cost-effective water purification and wastewater treatment technologies has become more urgent than ever. Chemical engineering principles are used to remove harmful pollutants from both raw source water and contaminated wastewater. Specifically, chemical engineers developed cost-effective methods to –

i Purify water from subsurface aquifers and surface sources, such as rivers and lakes, to produce potable drinking water.

ii Produce purified water that meets the increasingly strict requirements for industrial use.

iii Treat contaminated industrial and municipal wastewater and sewage to make them suitable either for discharge to public waterways or for reuse.

Engineers and scientists develop collection and treatment processes to carry out this waste material away from where people live and produce the waste and discharge it into the environment. In developed countries, substantial resources are applied for the treatment and detoxification of this waste before it is discharged into a river, lake or ocean system. Developing nations are striving to obtain the resources to develop such systems so that they can improve water quality in their surface waters and reduce the risk of water born infectious disease.

Usually wastewater treatment involves first collecting the wastewater in a Waste Water Treatment Plant (WWTP) and then subjecting the wastewater to various treatment processes. Most often, treatment processes are carried out on continuously flowing wastewaters (continuous flow or "open" systems) rather than as "batch" or a series of periodic treatment processes since large volumes of wastewater are involved. While most wastewater treatment processes are continuous by nature, certain operations, such as vacuum filtration, storage of sludge, addition of chemicals, filtration and removal or disposal of the treated sludge, are routinely handled as periodic batch operations. Wastewater treatment, however, can also be organized or categorized by the nature of the treatment process operation being used, for example, *physical*, *chemical* or *biological*. Physical treatment involves screening, sedimentation, aeration, filtration, floatation etc. Chemical treatment consists of chlorination, ozonation, neutralization, coagulation, adsorption and ion exchange.

Biological treatment can be divided into two types, aerobic and anaerobic. The aerobic treatment, which involves oxygen for the treatment process, comprises of methods based on activated sludge, trickling filtration, oxidation ponds, and lagoons and on aerobic digestion. Anaerobic method, a treatment process carried out without any contact with oxygen, consists of anaerobic digestion, use of septic tanks and lagoons. Wastewater treatment is further classified into primary, secondary and tertiary based on the degree of treatment needed.

The main three stages of waste water handling, collection, treatments and disposal are all potentially odorous, although careful plant design and operation can lessen the effect of odour and help control the general odour problem (**Gostelow et al., 2001**). Sewage can be treated close to where it is created, using a decentralised system (in septic tanks, biofilters or aerobic treatment systems), or be collected and transported via a network of pipes and pump stations to a municipal treatment plant, a centralised system. Sewage collection and treatment is typically subject to local, state and federal regulations and standards. Industrial sources of wastewater often require specialized treatment processes. Sewage treatment generally involves three stages, called primary, secondary and tertiary treatment.

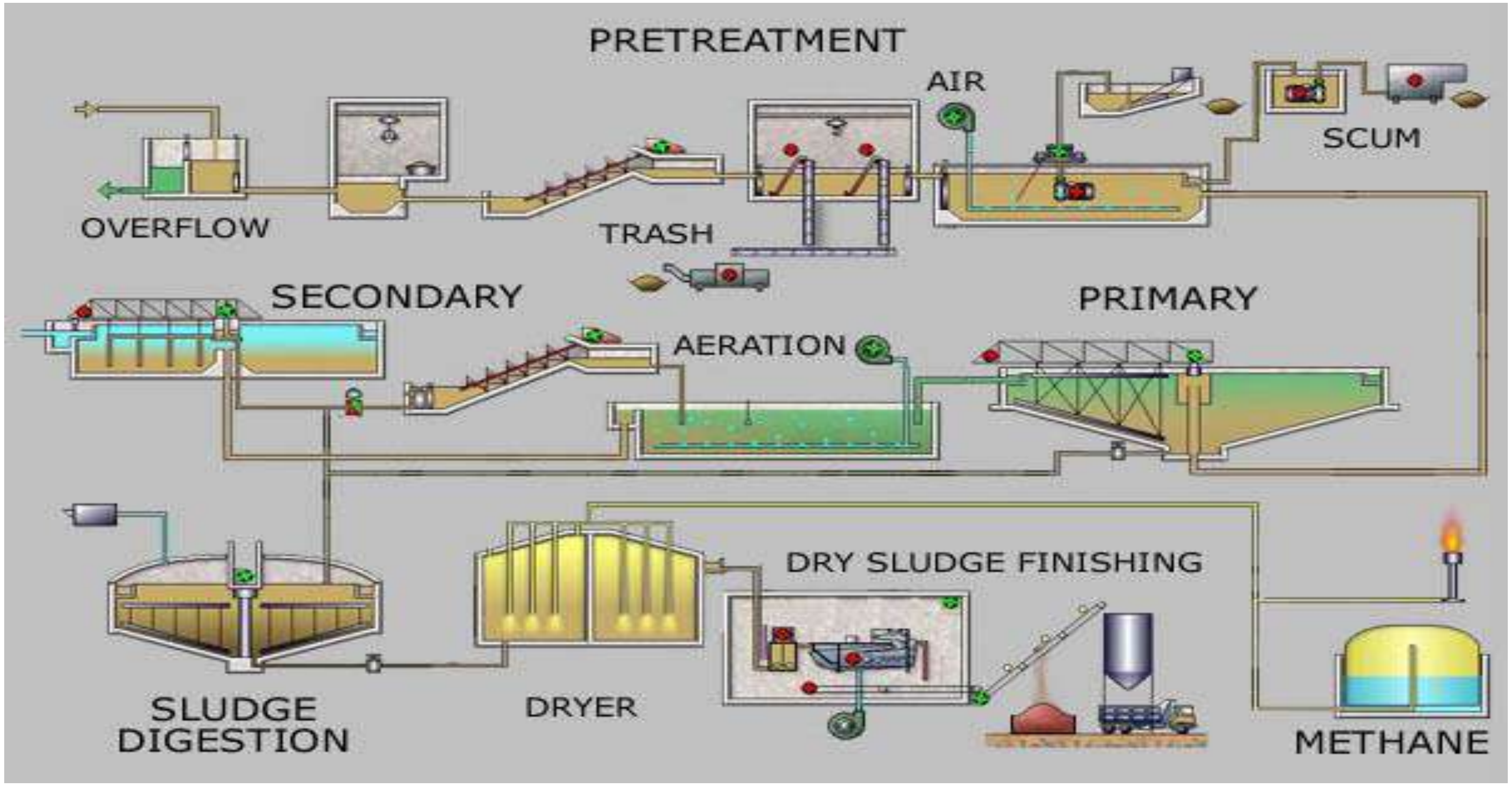


Figure 1.1 Flow diagram of various treatment units of a Sewage Treatment Plant (STP)

1.4.1 *Preliminary Treatment*

Preliminary treatment removes materials that can be easily collected from the raw sewage before they damage or clog the pumps and sewage lines of primary treatment clarifiers. The following devices are commonly used for preliminary treatment:

1. Screens
2. Comminuting devices: grinders, cutters, shredders.
3. Grit chambers
4. Pre-aeration tanks

In addition to the above, chlorination is also considered as a part of the preliminary treatment by which disinfection of the wastewater is carried out.

1.4.2 *Primary Treatment*

During this treatment, most of the solids, that can be settled, are separated or removed from the wastewater by the physical process of sedimentation. When certain chemicals are used with primary sedimentation tanks, some of the colloidal solids are also removed. Biological activity of the wastewater in primary treatment is of negligible importance. The purpose of primary treatment is to reduce the velocity of wastewater sufficiently in order to enhance the residence or contact time within the treatment unit, thereby allowing the solids to settle and the lighter materials to float. Primary devices may consist of the following:

i Septic tanks

ii Chemical feed units

iii Mixing devices

iv Flocculators

In this step, the sewage is collected in a quiescent basin where heavy solids settle to the bottom while oil, grease and lighter solids float to the surface. The settled and floating materials are removed and the remaining liquid may be discharged or subjected to secondary treatment.

Figure 1.2 Primary settling tank of Barahnagar Kamarhati (KMDA) Waste water treatment plant,

1.4.3 *Secondary Treatment*

Secondary treatment depends primarily upon aerobic organisms, which biochemically decompose the organic solids to inorganic or stable organic solids. It is comparable to the zone of recovery in the self-purification of a stream.

The devices used in secondary treatment may be categorised into four groups:

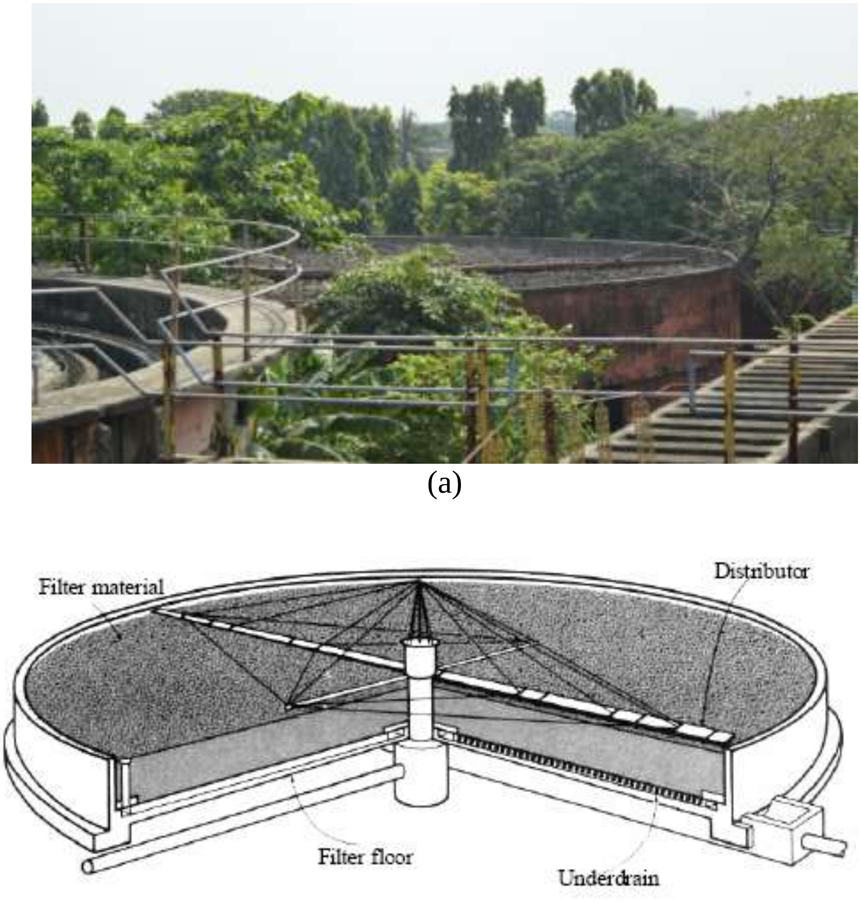
i Trickling filters with secondary settling tanks

ii Activated sludge and modifications within final settling tanks

iii Intermittent sand filters

iv Stabilization ponds

Secondary treatment removes dissolved and suspended biological matter. Secondary treatment is typically performed by indigenous, water-borne micro-organisms in a managed habitat. Secondary treatment may require a separation process in order to remove the micro-organisms from the treated water prior to discharge or tertiary treatment. A secondary treatment system consists of an aeration basin followed by flocculation and sedimentation tanks or an activated sludge system and secondary clarifiers. The aeration basin/ activated sludge system removes organic materials by growing bacteria (activated sludge). The secondary clarifier removes the activated sludge from the water.



(a)

(b)

Figure 1.3 Trickling filter of Barahnagar Kamarhati (KMDA) Waste water treatment plant. (a) top view (b) cutaway view.

1.4.3 Tertiary and Advanced Wastewater Treatment

The terms "primary" and "secondary" treatment have been used to generally describe a degree of treatment, for example, settling and biological treatment of wastewater. Since early 1970's, "tertiary" treatment has come into use to describe additional treatment following secondary treatment. Quite often, this merely indicates the use of intermittent sand filters for the enhanced removal of suspended solids from wastewater. In other cases, tertiary treatment has been used to describe processes which remove plant nutrients, primarily nitrogen and phosphorous, from wastewater. Improvement and upgrading of wastewater treatment units as well as the need to minimize environmental effects has led to the increased use of tertiary treatment. A term, that is rarely used to indicate treatment of a wastewater by methods other than primary or secondary (biological) treatment, is *advanced treatment*. This degree of treatment is usually achieved by chemical (for example coagulation) methods as well as physical methods (flocculation, settling and adsorption using activated carbon) to produce high quality effluent water.

The tertiary system, although not always included due to costs, is becoming more prevalent to remove nitrogen and phosphorous and to disinfect the water before discharge. Treated water is sometimes disinfected chemically or physically (by lagoons or micro-filtration) prior to discharge into a stream, river, bay, lagoon or wetland, or it can be used for the irrigation of a golf course, greenway or park. If it is sufficiently clean, it can also be used for groundwater recharge or agricultural purposes.

1.5 Standard methods for removal of Odour

Conventional methods of odour removal, consisting of biological treatment, chemical treatment, condensation, thermal oxidation, catalytic oxidation, adsorption, absorption etc. have been widely investigated during the last few years. In case of point sources such as that of industries, the odour-causing gas stream can be collected through piping and ventilation system and made available for treatment. The choice of technology is often influenced by the following factors:

- Volume of gas (or vapour) being produced and its flow rate
- Chemical composition of the mixture causing the odour
- Temperature
- Water content of the stream

1.5.1 *Biological Treatment*

Biotechnology based processes are very much recognized as the most competitive methods for treatment of waste gases characterized by high flow rates and low concentrations of contaminant now a days. Thus, bio-filtration is a technology for the biological treatment of waste gases which shows several advantages as compared to the physic-chemical abatements available (Xie et al., 2009; Gaudin et al., 2008). This technique shows more importance as a viable alternative because of its eco-friendliness, energy-savings and low-operating costs (Sakuma et al., 2006; Dennis and John, 2000).

Figure 1.4. Bio-filters for odour control

1.5.2 *Chemical treatment*

The effects of various chemicals in waste water were investigated to establish an effective odour control system for Kuwait Sewage Networks by several researchers (Tomar and Abdullah, 1994; Gallego *et al.*, 2008). The specific chemical method addressed above has got the advantages of low cost, easy treatment and non-toxicity when applied in the malodorous area (Zhang *et al.,* 2008).

1.5.3 *Condensation*

Condensation is a physical process of treatment of waste water for the removal of condensing VOCs from the waste water. The driving force for condensation is over-saturation, which is attained by chilling or pressurisation for both of the waste gas streams. This process will be most efficient for the VOCs with boiling points above 40°C at comparatively high concentration, more than 5000 ppm (Verma *et al.*, 2002).

1.5.4 *Thermal oxidation/ Incineration*

The most secure method available for dealing with dilute organic pollutants is thermal oxidation (with or without catalysts). Thermal oxidisers are basically large heatexchangers with a small combustion chamber in between the heating and cooling stages of the heat-exchanger. Contaminated air is passed through a heat exchanger (either a recuperator or regenerator) to heat up the waste air. This air reaches the combustion chamber, where a flame generated by support fuel (if necessary) effects near-complete oxidation of the pollutant species (Marks and Rhoads, 1991; Ruddy and Carroll, 1993).

1.5.5 *Catalytic oxidation*

Catalytic oxidation reaction can be forced to proceed at much lower temperatures (e.g.200ºC) in presence of a catalyst. Thus, the advantage of this process over thermal oxidation is the reduction in required energy input. Catalytic systems are therefore more favourable where auto-thermal operation is not practical and heat cannot be economically used elsewhere. A number of transition and precious metal catalysts can be used in catalytic oxidizers to destroy various VOCs over a wide range of process conditions.

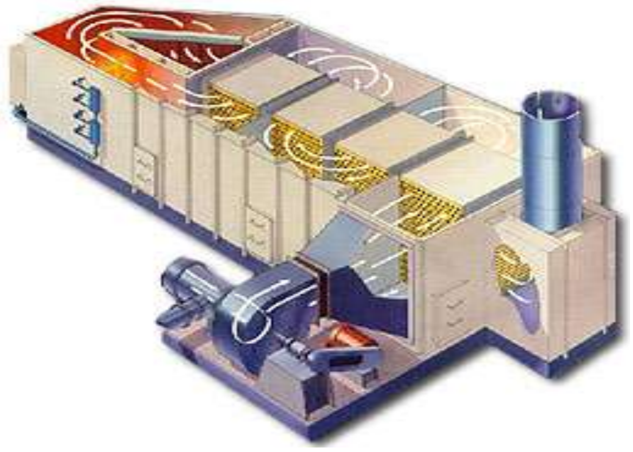


Figure 1.5 A catalytic oxidizer system.

1.5.6 *Absorption of VOCs*

VOCs may also be removed from the gas streams by absorption process. In this process a suitable liquid solvent is contacted with the contaminated air and the soluble VOCs get transferred to the liquid phase. Packed bed and mist scrubbing absorption processes are being used for the removal of VOCs from gas streams.

1.5.7 *Adsorption*

This is an odour abatement technology for gaseous streams containing low concentrations of VOCs (Schlegelmilch *et al.,* 2005). In this process, the adsorbent particles concentrate odorous gases and vapours from air streams and retain them, thus facilitating their subsequent disposal or their conversion to odourless products. Adsorption based VOCs removal efficiencies are usually in the range in between 90 to 99.9%. Volatile Organo Sulphur Compounds (VOSCs) generated in waste water treatment plants are often removed by adsorption (M. Tomar and T.H. Abdullah, 1994; Turk et al. 1989. Waste water contains so many surfactant molecules (*usually cationic surfactants*) coming from household cleaner, shampoo, shaving cream etc.. These surfactants have some effect on adsorption of VOCs by activated carbon (Ahn et al 2007; Chen et al 2014**)**. Adsorption using granular activated carbon (GAC) is a cost-effective and versatile technique for removing VOSCs because of GAC’s large surface area and pore volume **(**Chingombe et al. 2005**)**. GACs are modified and impregnated (Chiang *et al.,* 2002 and Li *et al.,* 2011) in order to increase their adsorption capacity selectively towards specific organic compounds (Ania et al. 2007 and Albishri et al. 2016**)**.

1.5.8 Detection and Assessment of Odour

An electronic nose is a simple instrument that may be used for indirect but rapid detection of odorous compounds. Application of electronic nose technology for monitoring odour from waste water is already reported **(**Dewettinck et al. 2001 and Stuetz et al. 1999). The response is non-specific in nature and it is not applicable for onsite measurements. Assessment of odours is usually carried out by panel based olfactometry, with the help of human sensors (*sniffers*). Specific VOSCs that may be responsible for odour nuisance are analysed by GC-MS and these results are further correlated to olfactometry based measurements [Chiriac et al. 2007, B. Rajbansi and U. Sarkar, 2014].

1.6 Statement of the Problem

Volatile organic compounds (VOCs) include reduced sulphur compounds, nitrogenous compounds, aldehydes, monoaromatics, heterocyclic compounds, mercaptans (organo sulphur compounds), halogenated organic compounds, carbon disulphide etc., specifically coming from various process units in sewage treatment plant (**STP**). These compounds are malodorous and usually some type of VOCs like mercaptans, having a very low range of odour threshold (**OT**) values. These are obnoxious in nature and high risks are associated with a long-term exposer to even low concentrations of mercaptans may cause ill health or respiratory symptoms. It is necessary to assess, quantify and control these odour generating sources within the STP. Batch adsorption experiments are conducted using GACs as adsorbent for the removal of mercaptans like *methyl mercaptan, ethyl mercaptan, di methyl sulphide, carbon di sulphide*. Activated carbon can remove these compounds effectively, but with some limitations. Due to narrower pore apertures, the adsorption of large organic molecule is restricted in GAC. Therefore, modification of GAC is carried out by alkali (NH_3, NaOH, KOH). These functionalized materials (**FAC-NH_3, FAC-NaOH, FAC-KOH**) are roughly super microporous in nature and will be cheaper for the removal of Volatile Organo Sulphur Compounds (**VOSCs)**. A mesoporous alumino-silicate material may also be used for the adsorption process to benchmark the functionalized new materials. But this will be very expensive.

1.7 Overall objective

i. Functionalization of GACs by alkali like NH_3, NaOH, KOH.

ii. Physical and chemical characterization of these new functionalized materials.

iii. Treatment of sewage wastewater containing VOSCs by adsorption using GAC and FACs.

iv. Design of experiments for batch equilibrium analysis of wastewaters containing VOSCs.

v. Assessment of Odour Intensity by standard Sniffer Panel method of Olfactometry.

vi. Application of specific Psychophysical laws, already validated, to evaluate odour concentrations of sewage samples in the semi solid, liquid and gas phases.

vii. Evaluation and validation of the pseudo-kinetics, pore and film diffusions using various models.

Considering the above scenario with regard to sewage odour, an overall odour control procedure was planned to be developed.

1.8 Specific objectives

i. Preparation of FACs using alkali functionalization of pure GAC with NH_3, NaOH and KOH.

ii. Physical and chemical characterization of the adsorbents:

   a. Surface texture of adsorbents by Field Emission Scanning Electron Microscopy (FE-SEM).

   b. Surface area and pore volume by Brunner-Emmett-Taylor (BET) N_2 adsorption/desorption isotherm.

   c. Pore size distribution by Non-Local Density Functional Theory (NLDFT).

   d. Identification of functional groups by Fourier Transforms Infrared Spectroscopy (FT-IR) analysis.

   e. Elemental analysis of the adsorbents by CHNSO analyser for Carbon (C), Hydrogen (H), Nitrogen (N), Sulphur (S) and Oxygen (O).

   f. Quantification of functional groups (carboxylic, phenolic and lactonic) by Boehm titration.

   g. Determination of inherent surface charge by zeta potential analysis at various pHs.

iii. Panel olfactometry (*overall odour*) and GCMS (*specific VOSCs*) based methods of odour assessment.

iv. Analysing the perception of odour using a panel of trained sniffers.

v. Applying a psychophysical model, already parameterized, tested for ‘goodness of fit’ and validated for specific sewage odour, to the odour intensity records of the sniffers in order to arrive at the odour concentration values.

vi. Applying methods of physical adsorption towards control of odour using the following adsorbents.

   a. Granular Activated Carbon (GAC),

   b. Functionalised GACs, namely **FAC-NH_3**, **FAC-NaOH**, **FAC-KOH**.

vii. Correlating the mitigation of odour to the % removal of each of the very sensitive VOSCs contributing towards overall malodour.

1.9 Case Study: *STP site*

❖ □ **Baranagar-Kamarhati** Trickling filter based STP (*under the purview of Kolkata Municipal Development uthority, KMDA*)

1.10 Structure of the thesis

Chapter 2: *Review of Literature*

Various literatures relating the specific objective of the research would be reviewed.

Chapter 3: Methodology I-Alkali Functionalized Granular Activated Carbon: *Synthesis, Physical and Chemical* Characterization.In order to enhance the adsorption capacity, functionalization of standard adsorbents with alkalis is carried out. Physical as well as chemical characterization of functionalized adsorbents is discussed here .

.Chapter 4: Methodology II-Batch adsorption analysis: *Olfactometry and GC-MS based* Analysis.

The development of processes includes:

- Measurement of odour concentration and intensity before and after equilibrium adsorption in batch.
- Comparison of the optimum adsorption capacity of different adsorbents.
- Correlating the percentage mitigation of odour to the percentage removal of each of the very sensitive VOSCs contributing towards the malodour.
- Chapter 5: Methodology III-Kinetic Study: *Pseudo Kinetics, Pore and Film Diffusion*

Adsorption mechanism, involving the following steps would be discussed in this Chapter:

I. solute transport in the bulk-adsorbate movement by the stagnant liquid film surrounding the adsorbent,

II. film diffusion-adsorbate transport through the film,

III. pore-diffusion-adsorbate diffusion through the porous structure to the active sites (molecular diffusion in the pore and/or in the adsorbent surface),

So kinetics and diffusion mechanism includes-

- Determination of first-order and second-order rate constants from Lagergren’s pseudo first-order and Ho’s second-order models.
- Determination of adsorption mechanism by intra-particle diffusion model.
- Evaluation of effect of film resistances by Boyd’s film diffusion model.

Chapter 6: Summary of *Results and Discussion*

A brief summary of the complete work will be given, highlighting the main and the specific conclusions and some useful recommendation for future work. Performance of the adsorbents would be discussed on the basis of statistical outputs obtained using Response Surface Methodology (RSM). There are five appendices attached herewith, in order to supplement the chapters.

Annex I:	Volatile Organic Compounds In and Around a Sewage Treatment Plant
Annex II:	Terms and definitions in odour assessment
Annex III:	Olfactometry
Annex IV:	Henry’s Law Constants for Sulphur base Organic Compounds
Annex V:	Role of Surfactants

Chapter II

Review of literature

This chapter presents a critical review of various works done on the adsorption of VOCs, together with different kinetic models developed to understand the mechanism of the removal process. Various adsorbents are used for the adsorption of VOCs having different characteristics such as surface morphology, surface area, pore size, surface functionality, point of zero charge etc. The following topics related to removal of VOCs using GAC and FACs are reviewed in this chapter: (1) Sources of odours and its treatment processes, (2) Standard and functionalized adsorbents: physical and chemical characterization (3) Olfactometry and GCMS based batch equilibrium analysis: Design of experiment, (4) Control of odour using GAC and FACs for VOSC adsorption and to find out their performance and adsorption capacities with the help of various pseudo-kinetics and diffusion model.

2.1 Sources of odour and its treatment

Waste-water is the combination of liquid or water-carried wastes that originates from usage of water by residences, commercial and industrial establishments, together with groundwater, surface water and storm water all come into the sewer system. Most of the sewerage contains VOCs which are very malodorous. Several well-known research groups (Koe and Shen, 1997; Gostelow *et al.,* 2001; Micone and Guy, 2007; Zarra *et al.,* 2008; Ben-Zen Wu *et al.,* 2006; Krach *et al.,* 2008; Canela and Jardim, 2008; Dincer and Muezzinoglu, 2008) found various common odorants released into the atmosphere from sewerage, disperse and sometimes react in the atmosphere and produce odours in the ambient air that are perceived by people in communities.

Another group of researchers identified some specific odorous compounds which generally represented various types of odour generating mixture (Blonda *et al.*, 2006; Luo and Agnew, 2001; Canela and Jardim, 2008; Dincer and Muezzinoglu, 2008; Zarra *et al.*, 2008; Lehtinen and Veijanen, 2011; Muñoz *et al.*, 2010; Godayol *et al.*, 2011; Saral *et al.*, 2009). In this chapter, we will review the present state of the art of various treatment processes of odor control. The conventional standard methods of odour treatment consists of mist filtration, thermal oxidation, catalytic oxidation, bio-filtration, chemical treatment, adsorption, absorption, etc.. These have been widely investigated in the last few years (Estrada, 2011); several of these studies are presented in the subsequent paragraphs.

2.1.1 *Biological Treatment*

Biotechnological processes are recognized as the most competitive ones for treatment of waste gases characterized by high flow rates and low concentrations of contaminant nowadays. Bio-filtration is a technology for the biological treatment of waste gases which shows several advantages as compared to the physicochemical abatements available (Xie et al., 2009; Gaudin et al., 2008). This technique shows more importance as a viable alternative because of its eco-friendliness, energy-savings and low-operating costs (Sakuma et al., 2006; Dennis and John, 2000).

The first report on biological air treatment units considered treatment of odorous gases from sewage using soil beds (Leson and Winer, 1991). Bio-trickling filters show a high abatement performance while treating H_2S, a highly soluble odorant usually present in sewage treatment plants (STPs), with removal efficiencies higher than 99% with Empty-Bed Residence Time (EBRT) ranging from 2 to 10s (Gokhale et al., 2017; Cox and Deshusses, 2002). According to Zarra et al., 2008, there is a lack of studies on the treatment of off-gases containing mixtures of hydrophobic VOCs and reduced sulfur compounds concentrations typically found in WWTPs, which range from µgm^{-3} to mgm^{-3}. In the membrane bioreactors, the odorous gas is transferred through a membrane to the biofilm, attached to its other side where nutrients and oxygen are provided. These reactors have been used for other waste treatment applications where condition of the stream is such that it has got no possibility of direct contact with the biomass (Van Groenestijn and Hesselink 1993; Ergas, 2001). Chen et al., 2018 has shown that volatile organic sulphide compounds (VOSCs) are usually resistant to biodegradation, thereby limiting the performance of traditional biotechnology dealing with waste gas containing such pollutants especially in a mixture. In this study, a Solid Composite Microbial Inoculant (SCMI) was prepared to remove dimethyl sulphide (DMS) and propanethiol (PT). As compared to the microbial suspension, the prepared SCMI exhibited better storage stability at 4 and 25°C. Inoculation of the SCMI in bio-trickling filters (BTFs) could effectively shorten the start-up period and enhance the removal performance.

2.1.2 *Chemical treatment*

The effects of various chemicals in waste water were investigated to establish an effective odour control system for Kuwait Sewage Networks by several researchers (Tomar and Abdullah, 1994; Gallego *et al.*, 2008). The chemical method addressed above has got advantages of low cost, easy treatment and non-toxicity when applied in the odorous area (Zhang *et al.*, 2008).

Table 2.1 Summary of literature related to chemical and biological technologies for control of hydrogen sulphide emissions in sewer systems (Zhang *et al.*, 2008).

Chemicals	Ratio of chemicals to S (w/w)[a]	Scale and volume of reactor	Sulphide concentration in upstream (mg SL^{-1})	Average elimination (%) of sulfide	Cost[b] (€ $kg^{-1}S$)	References
$FeCl_2.4H_2O$	6.0–7.0:1	Plant scale, 59,000m^{3c}	More than 4.0	90	22.4–26.1	USEPA (1992)
$FeSO_4.7H_2O$	1.7:1	Plant scale, 25,000m^3 d^{-1}	18.0–25.0	95–97	4.8	Tomar and Abdullah (1994)
$FeClSO_4$	1.2:1	Plant scale, 25,000m^3 d^{-1}	18.0–25.0	88–98	4.5	Tomar and Abdullah (1994)
$FeCl_2$ and $FeCl_3^d$	2.5:1	Plant scale, 75,000m^3 d^{-1}	6.4	97	7.2	Padival *et al.*, (1995)
$FeCl_3$	1.5:1	Lab scale, 3.00 L	3.8	100	3.7	Nielsen *et al*,. (2005c)
H_2O_2	4.0:1	Plant scale, 76,000m^3 d^{-1}	15.0	85–90	10.6	Waltrip and Snyder(1985)
H_2O_2	1.5–1.6:1	Plant scale, 2000m^{3c}	8.5	90–95	4.0–4.2	USEPA (1991)
H_2O_2	1.3:1	Plant scale, 25,000m^3 d^{-1}	20.0	87–100	3.5	Tomar and Abdullah (1994)
Cl_2	9.0:1	Plant scale, 90,000m^3 d^{-1}	18.0	100	2.7	Waltrip and Snyder (1985)
Cl_2	10.0–15.0:1	-	-	-	2.8–4.2	USEPA (1991)
NaClO	2.0:1	Plant scale, 25,000m^3 d^{-1}	20.0	96–100	2.6	Tomar and Abdullah (1994)

$Ca(ClO)_2$	1.8:1	Plant scale, 25,000m^3 d^{-1}	20.0	93–100	1.9	Tomar and Abdullah (1994)
NaClO and NaOH[d]	1.0:1	Plant scale, 25,000m^3 d^{-1}	18.2	100	1.9	Tomar and Abdullah (1994)
$KMnO_4$	6.0–7.0:1	–	–	–	18.9–22.0	USEPA (1991)
$NaNO_3$	6.7:1	Lab scale, 0.05 L	54.0	100	12.2	Jenneman *et al.*,(1986)
$NaNO_3$	0.18:1	Lab scale, 1.37 L	35.0	65	0.4	Okabe *et al.*, (2003a)
$NaNO_3$	1.37:1	Lab scale, 1.00 L	10.2	100	2.5	Okabe *et al.*, (2003b)
$NaNO_3$	1.4–4.6:1	Lab scale, 3.00 L	2.5–3.5	90–95	2.5–8.3	Yang *et al.*, (2005)
Nutriox^{TMe}	0.88:1	Plant scale, 3700m^3 d^{-1}	5.1	63–95	2.1	Bentzen *et al.*, (1995)
Nutriox^{TMe}	0.60:1	Pilot scale, 200 L	9.6	95	1.5	Hobson and Yang, (2000)
Nutriox^{TMe}	2.50:1	Plant scale, 15,000m^3 d^{-1}	70.0	95–100	6.0	Einarsen *et al.*,(2000)
Nutriox^{TMe}	0.36:1	Plant scale, 50,000m^3 d^{-1}	70.0	68–95	0.9	Garcia De Lomas *et al.*, (2005)
$Ca(NO_3)_2$	1.92:1	Plant scale, 2000m^3 d^{-1}	2.6	100	4.4	Rodrıguez-Gomez *et al.*, (2005)

$FeCl_2$. $4H_2O$: €105 (100 kg)$^{-1}$; $FeSO_4.7H_2O$: €80 (100 kg)$^{-1}$; $FeClSO_4$: €111 (100 kg)$^{-1}$; $FeCl_3$: €85 (100 kg)$^{-1}$; H_2O_2 (27.5%): €73 (100 kg)$^{-1}$; Cl_2 (99.6%):€28 (100 kg)$^{-1}$; NaClO: €127 (100 kg)$^{-1}$; $Ca(ClO)_2$: €101 (100 kg)$^{-1}$; NaOH: €205 (100 kg)$^{-1}$; $KMnO_4$: €315 (100 kg)$^{-1}$; $NaNO_3$: €35 (100 kg)$^{-1}$; Uutriox^{TM}:€21 (100 kg)$^{-1}$; $Ca(NO_3)_2.4H_2O$: €34 (100 kg)$^{-1}$.

[a] For the iron salts, it is the ratio of Fe to S (w/w); for the nitrate salts, it is the ratio of NO_3^--N to S (w/w); for other chemicals, it is the ratio ofchemical to S (w/w).

[b] The prices of chemicals are provided by Brenntag NV Co. Ltd., VWR Inc., Belgium, Wuhan industrial Co. Ltd., China and Yara IndustrialLimited, Ireland.

[c] The total volume of sewer pipes.

[d] The ratio of $FeCl_3$ to $FeCl_2$ is 1.9:1. The ratio of NaClO to NaOH is 3.5:1.

[e] Nutriox^{TM} is the concentrated calcium nitrate, a commercially available solution of 8.8% NO_3^-, 0.6% NH_4^+ and a density of 1.5 kg L^{-1}.

2.1.3 *Advanced oxidation process*

Advanced oxidation process is a process of oxidation in which oxidation can be accelerated by the generation of hydroxyl radicals. This process usually operates at or near ambient temperature and pressure (Glaze *et al.*, 1987). In order to control different odorous VOCs coming from sewage treatment plant by the process of advanced oxidation technology (Andreozzi *et al.*,1999). Different types of advanced oxidation processes are:

I *Ozonation*- Ozonation can be applied both for the treatment of gases and liquids but is most frequently used to treat aquous solutions. In scrubbers, chemical oxidation of the VOSCs can be obtained by dosing hypochlorite (Van Durme *et al.*,1992). Sulphur containing compounds present in the water phase are effectively oxidised with ozone (Hwang *et al.*, 1994). Sulphides can be effectively removed by ozonation, according to:

$H_2S + O_3 \rightarrow SO_2 + H_2O \rightarrow S + H_2O + O_2$

$CH_3SH + O_3 \rightarrow CH_3\text{-}S\text{-}S\text{-}CH_3 \rightarrow CH_3SO_3H + O_2$

Direct gas phase ozonation is usually too slow to be of interest, except for H_2S. Laplanche et *al.*, 1984 achieved a complete H_2S and methanethiol removal from emissions of a WWTP at significant lower reagent cost in comparison to hypochlorite oxidation.

II *Fenton reagent (H_2O_2/Fe^{2+})*- Tokumura et al. 2012 has shown that in photo–Fenton process VOCs are oxidized in the gas phase. So there are a chance of incompletely oxidized intermediates that are likely to contaminate air and which may adversely affect health. However, in liquid phase oxidation, any incompletely oxidized intermediate produced remains in the liquid phase, so harmful intermediates can be prevented from going into the air.

Table 2.2 Relative oxidation power of some oxidizing species (*Carey, 1992; Techcommentary, 2009*)

Oxidizing species	Relative oxidation power
Hydrogen peroxide	1.31
Ozone	1.52
Atomic oxygen	1.78
Hydroxyl radical	2.05
Positively charged hole on titanium dioxide, TiO2	2.35

III *Photocatalytic processes*- Photocatalysis is a combination of using a semiconductor, a photocatalyst and UV/visible light for the conversion of organic or inorganic compounds. Duczmal and Sobczynski, 1999, Szabo-Bardos *et al.,* 2006 have shown that titanium dioxide (anatase) has an energy band gap of 3.2 eV and can be activated by UV illumination with a wavelength of up to 387.5nm. It is one of the most widely used photocatalysts in industry. Shayegan et al., 2018 reported that TiO_2 is best suited for removing volatile organic compounds in gas phase.

2.1.4 *Non Thermal Plasma (NTP) process*

For the abatement of VOCs, NTP technology has become more important to the scientists for the last two decays (Nunez *et al.,* 1993).

Non-thermal plasmas are generated by applying a sufficiently strong electric field to ensure the discharge of a neutral gas. This creates a quasi-neutral environment containing neutrals, ions, radicals, electrons and UV photons. Due to their light mass, electrons are selectively accelerated by the field and gain high temperatures and the system temperature may be around 10000- 25000K (Kim, 2004) while the background gas remains at room temperature.

The bulk gas molecules like N_2, O_2, and H_2O, are bombarded by the electrons, typically having temperatures ranging from 10,000 K to 250,000 K (1–20 eV). This produces excited gas molecules (N_2^*, O_2^*) which in turn produce secondary electrons, photons, ions and radicals. These electrons, photons, ions and radicals are responsible for the oxidation of VOC molecules. As a result, unstable reactive species like ions and free radicals are formed. Free radicals, such as OH• and O• are highly reactive for the oxidation of VOCs into CO_2, H_2O etc. This has led to great scientific advances, mainly on a laboratory scale. However, large-scale demonstrations of NTP technology for waste gas cleaning are also currently operative (Kim, 2004; Mizuno, 2007).

Although NTP has been frequently proposed in the literature for the removal of VOCs, NO_x and SO_2 (Park *et al.,* 2003, Yamomoto *et al.,* 2003) but they have got some disadvantages like formation of unwanted by products, poor energy efficiency, mineralization etc.

In order to overcome these problems, NTP processes were performed in presence of a catalyst and the technique is known as plasma-catalysis technique. In this process retention time can be increased through adsorption of target molecules (placing the catalysts inside or in close vicinity of the discharge zone), favouring complete oxidation to CO_2 and H_2O (Song *et al.,* 2002).

2.1.5 *Membrane based separation process*

Membrane based separation processes have been widely used for the removal of VOCs over a long period. Different types of membrane technology are described in **Table 2.3**.

Table 2.3 Different types of membrane technology used in industrial application.

Process	*Driving Force*	*Transport Mechanism*
Gas permeation	Concentration gradient	Diffusion transport
Reverse osmosis	Pressure differential	Diffusive solvent transport
Dialysis	Concentration gradient	Diffusive solute transport
Electro- dialysis	Electrochemical potential	Selective ion transport
Gel permeation	Concentration gradient	Diffusive solute transport
Pre-evaporation	Concentration	Selective physicochemical transport of solvent/solute

A very short description of this analysis is represented below.

Behling, (1986); Behling *et al.,* (1988) have chosen poly (ether imide) as the supporting material because it is much more stable to organic vapours than polysulfone. Baker *et al.,* (1987) conducted air and vapour permeation experiments for various polymeric films. Most of the experimental work reported so far (Pinnau *et al.,* 1988, Kimmerle *et al.,*1988 and Paul *et al.,* 1988) is concentrated on composite silicon rubber membranes coated on porous polysulfone substrates. A membrane system for the treatment of low-volume, high vapour concentration gas streams was tested by Wijmans and Helm, (1989), but information on the membrane materials was not disclosed. Buys *et al.,* (1990) used a polyhydantoine and polyimide as the porous support to the silicon rubber-coating layer. Deng *et al.,* (1996) to prepare membranes from their study. **Deng *et al.,* (1996**) have conducted a thorough experimental study on the recovery of organic solvent from air with the help of an aromatic poly membrane. The study promises encouraging results. The resistance of silicon rubber to some organic vapours, for example gasoline, is very high. However, this is a single polymeric material of high organic resistance. In their previous studies, asymmetric aromatic polyimide membranes were investigated for the purpose. It was shown that membranes of both high selectivity and reasonably high permeability could be produced if the conditions of membrane preparation could be properly controlled.

Kujawa J. Et al. 2013 has shown that ceramic membranes have several advantages over polymeric membranes in terms of mechanical resistance, chemical inactivity, non-swelling behaviour, thermal stability and uncomplicated cleaning. Commercial ceramic membranes are usually made from metal oxides like alumina, zirconia, titania etc. These ceramic membrane materials have a hydrophilic character due to the presence of surface hydroxyl groups (-OH). For pervaporative elimination of some volatile organic compounds like methyl tertiary butyl ether, ethyl acetate etc. from water, ceramic membranes should be hydrophobic in nature. The hydrophobization process can be done by using different perfluoro alkylsilanes molecules with ethoxy reactive groups (**Kujawa J. Et al. 2014**).

There are some limitations of this technology, discussed below:

1. As VOCs are comprised of various organics, the membrane has to be designed to allow a range of organics. To some extent progress been made, but it is not yet cost-effective.

2. Membranes are very susceptible to the operating conditions, fouling, and bacterial growth.

3. Membrane-based recovery is generally considered as a slow process. The increase in the process rate is directly proportional to the operating cost.

2.1.6 *Incineration process*

Incineration is the thermal oxidation of VOCs at high temperature. The modern incinerators are designed to accomplish from 95% to 99% decomposition of all types of VOCs. In this process the VOCs concentration should be in the range of 100 to 2000 ppm, nominal residence time ranges from 0.5 to 1 second. In incinerator, combustion of the VOCs takes place at temperatures in between 700-1000 ^{o}F. This operating temperature is a function of the type, concentration and the desired removal efficiencies of VOCs. But the compounds that are difficult to combust or that are present at low inlet concentrations will require greater heat input and retention time in the combustion zone to ensure that the desired removal efficiency is accomplished. Higher removal efficiencies will also require higher temperatures and longer retention times. Thus, incineration is a costly disposal method for treating low concentrations of VOCs. The removal efficiency of more than 99% can be achieved for most organics at temperatures ranging from 750 ^{o}C to 1100 ^{o}C with residence times of 0.5 s to 2.0 s (Marks and Rhoads, 1991; Ruddy and Carroll, 1993).

2.1.7 *Catalytic incineration process*

In order to reduce the operation costs, that is basically the energy cost of combustion, the VOCs are combusted in presence of a catalyst comparatively at lower temperature and the process is known as *catalytic incineration* process. The incoming gas stream is heated, most often in a recuperative heat exchanger followed by additional input from a burner if needed and passed through a honeycomb or monolithic support structure coated with catalyst. The catalytic system is well suited for low concentration operations or those that operate in a cyclic manner, VOC concentration ranges from 100 to 2,000 ppm and the operating temperature in the range 400°C to 500°C. Removal efficiencies in excess of 90% are common with a maximum removal efficiency of 95% (Patkar and Laznow, 1992; Ruddy and Carroll, 1993). Large catalytic systems have been installed, but are not as popular as direct thermal oxidation systems, mainly due to the high costs of catalyst replacement. Catalysts can be sensitive to poisoning by non-VOC chemicals such as sulphur, chlorides and silicon. Many catalyst manufacturers have overcome sensitivity to some of these substances, but every catalyst has susceptibilities that must be considered at the process selection stage.

2.1.8 *Absorption of VOCs*

VOCs may also be removed from the gas streams by absorption process. In this process the liquid solvent is contacted with the contaminated air and the soluble VOCs will transfer to the liquid phase. Packed bed and mist scrubbing absorption processes are being used for the removal of VOCs from the gas streams. In order to improve the vapour liquid contact, packing materials are either randomly dumped or stacked in the tower. In the mist scrubber spray nozzles are used to atomise the liquid streams into tiny droplets. These droplets provide the surface area for liquid vapour contact. This requires a very low pressure drop and must not be fouled by particulate in the incoming gas stream (Ruhl, 1993; Ruddy and Carroll, 1993). Residence times of vapour-liquid contact are low (1–10 s). So the mist scrubbing should only be applied to highly soluble systems and the process is not suitable for cyclic operations as there is a problem of start-up time constraints. It is, however, good for a highly humid air stream (50% RH).

2.1.9 *Condensation of VOC*

Condensation is a physical process of treatment of waste water for the removal of condensing VOCs from waste water. The driving force for condensation is oversaturation, which is attained by chilling or pressurisation or both of the waste gas streams. This process will be most efficient for the VOCs with boiling points above 40°C at comparatively high concentration (> 5000 ppm).

Condensation followed by adsorption is a very good technique (Verma et al, 2002) for removing volatile organic compounds when gaseous effluents contain high level of volatile organic compounds (>1%). When gaseous effluent contains low levels of volatile organic compounds (≤ppm level) then adsorption will be preferred for that.

Polymerisation materials should be avoided in the condensation system due to the potential for fouling the heat exchanger surface. Water-cooled and air-cooled surface condensers are used with a success to remove 95% of the exhaust volume (Walsh, 1967). Condensate is less voluminous and richer in odorous materials. As would be expected, the remaining uncondensed gases are considerably more odorous than those from contact condensers. Condensation is found to be suitable if emission levels of the VOCs are high (>1%) [Gupta and Verma, 2002; Dwivedi *et al.*, 2004].

Dunn and El-Halwagi, (1994) address the problem of optimally selecting and designing condensation systems for the recovery of volatile organic compounds (VOCs) from gaseous emissions. A typical VOC condensation system would require, numerous refrigerants for achieving the desired VOC recovery.

Condensation produces a liquid product that must be treated to remove condensed water and possibly to separate various chemical species.

2.1.10 *Adsorption*

Adsorption is a process in which a solid surface accumulates a concentration of molecules from a gaseous or liquid environment in contact with it. This is an odour abatement technology for gaseous streams containing low concentrations of VOCs (Schlegelmilch *et al.,* 2005). In this process, the adsorbents concentrate odorous gases and vapours from air streams and retain them, thus facilitating their subsequent disposal or their conversion to odourless products (range of removal efficiencies: 90 to 99.9%). Adsorbed odorants such as reduced sulphur compounds (including hydrogen sulphide), are more or less rapidly oxidized to products that are frequently less odorous and sometimes not odorous at all. Different adsorbed odorants, being concentrated and in close proximity to each other on the surface or in the pores of the adsorbent, may interact. Most of these actions favour effective deodorization. Activated carbon is the most commonly used adsorbing material for the removal of VOCs (Schlegelmilch *et al.*, 2005; Yang, 2003).

Waste water is contaminated with various kinds of surfactants coming from household cleaner, shampoo, saving cream etc. These surfactants have some effect on adsorption of VOCs by activated carbon. Chen et al 2014 studied the adsorption behaviour of three polycyclic aromatic hydrocarbons (PAH) in a surfactant solution by activated carbon. The adsorption capacity decreased in the mixed PAH system in comparison to the single PAH system in surfactant solutions as a result of the interactions between components in the mixed system.

Ahn et al 2007 observed that adsorption of TX100 surfactant by activated carbon occurred faster than adsorption of phenanthrene. This indicates that TX100 may cover the surfaces of activated carbon prior to phenanthrene adsorption. Rapid adsorption of surfactant blocks the available pores (< the surfactant) and thus reduce the available surface for phenanthrene.

2.2 Standard and functionalized adsorbents: Physical and chemical characterization

Removal of VOCs by activated carbons (AC) has been studied by many researchers (Lee *et al.,* 2003; Lu *et al.,* 2007; Kim *et al.,* 2006; Li *et al.,* 2011). According to Chelu and Nomine, 1984, AC provides a high sorption capacity towards hydrogen sulphide and VOCs, while adsorption of volatile nitrogenous compounds is poor. Hinokiyama *et al.,* (1991) reported that the presence of H_2S in the waste gas strongly affect the breakthrough time of MeSH on AC. However, comparatively narrow pore aperture of the activated carbon leads to less amount of diffusion and restricted adsorption of heavy organic molecules (Trouvé*et al.* 2012). Functionalization of activated carbon is required to increase the adsorption capacity and improve the selectivity of specific trapped organic compounds.

Turk *et al.,* (1989) observed that an un-impregnated AC, used in conjunction with a small side stream of ammonia gas (7-50 ppmv) as a catalyst, was much more efficient than with NaOH or KOH impregnated AC. Functionalization of activated carbon with NaOH or KOH may react with CO_2 in the air and can form carbonates. This decreases the removal efficiency. Ammonia impregnated activated carbon can remove MeSH 800% more efficiently than un-impregnated AC. NaOH or KOH treated activated carbon will be 300-600% more efficient than un-impregnated AC.

Ozonation can modify the surface property of an activated carbon [Turk *et al.,* 1989 and Chiang *et al.* (2002b)] such as specific surface area, pore volume, and functional groups. Results indicated that specific surface area of precursor activated carbon increased from 783 to 851 m^2/g due to increase in number of micropores (<15 A°). Effect of ozone treatment on the adsorption of volatile organic compounds was explained by methyl-ethyl-ketone (MEK) and benzene. The adsorption capacity of ozone treated activated carbon towards MEK and benzene was much greater than the same by untreated activated carbon.

Various functional groups are introduced on the carbon surfaces by oxidation with suitable oxidizing agents, either in the gas phase or in solution (Moreno-Castilla *et al.* 1995; Malik *et al.* 2002 and Afkhami *et al.* 2007). The same brings changes in the physico-chemical properties of the precursor carbon. Functional groups like –COOH, -OH, -C=O are increased on the carbon surface after the treatment. These oxygen-containing functional groups are mostly hydrophilic in nature and these can easily adsorb the polar species from the solution.

Functionalized activated carbon was synthesized from coffee residue after impregnation with $ZnCl_2$ and CO_2. The experimental parameters were: weight ratio of $ZnCl_2$ to coffee residue (2.5, 3.0 and 3.5), CO_2 soaking times (2, 3 and 4 h) and activation temperatures (600°C, 700°C and 800°C). The activated carbon, thus activated, was characterized for mesopore volume by nitrogen adsorption isotherm at 77 K. It was that the ratio of $ZnCl_2$ to coffee of 3.0:1, CO_2 soaking time of 4 hours and activation temperature of 600° C were the most suitable conditions. At these conditions, the modified AC was characterized by: BET surface area: 900 m^2/g; total pore volume: 1.01 cc/g and mesopore content (ratio of mesopore volume to total pore volume): 92%. The effect of pore diameter was tested by the adsorption of various adsorbates (phenol, methylene blue and erythrosine red). Toluene, with a concentration range in between 100 to 740 ppm was adsorbed on coffee activated carbon. The adsorption capacity of toluene on the coffee derived activated carbon was superior to that of commercial activated carbon.

Nitrogenation can increase the basicity of activated carbon (Rivera-Utrilla*et al.*, 2011). Introduction of nitrogen into carbon can significantly increase the polarity of the carbon surface and hence its specific interaction with polar adsorptive nature becomes prominent. The me group also stated that nitrogenation can also affect the porous structure along with the surface chemical nature of the activated carbon in a form and to an extent that depends on the precursor carbon, chemical agent and the experimental method used. Rare reports have been found where the porous structure remain unchanged [Jansen and Bekkum 1994; Abe *et al.* 2000]. There are reports available where reduction in surface area and microporosity of activated carbon [Palma *et al.* 1995; Xie*et al.* 2000; Przepiórski 2006] after nitrogenation has been reported. Various nitrogen functional groups are introduced as a consequence of the nitrogenation of activated carbon [Rivera-Utrilla*et al.* 2011].

Li et al. (2011) treated coconut shell based carbons chemically by ammonia, sodium hydroxide, nitric acid, sulphuric acid and phosphoric acid in order to determine any improvement in the adsorption ability of hydrophobic VOCs on Granular Activated Carbons (GAC). The saturated adsorption capacities of these functionalized materials were tested on adsorption of o-xylene, a hydrophobic volatile organic compound. Results showed that alkali modified GAC had better o-xylene adsorption capacity. The surface area and pore volume increased and total oxygen containing functional groups were diminished when treated with alkalis. The opposite was observed for acid treatment on GAC.

Alkali functionalized activated carbon had higher adsorption capacity than acid functionalized activated carbon (Liu *et al.*, 2011). This is because alkali treated activated carbons have larger surface area and pore volume and there is a reduction of oxygen containing functional groups. The same group reported that 6.6M solution of ammonia could activate the precursor carbon to the extent that the adsorption capacity went up to the order of 305.70 mg o-xylene/g.

Adsorption capacities of carbon could be improved with different thermal and oxidative treatments (nitric acid and ammonium persulfate) as the same increases basic character of the AC surface. Lemus et al., 2012 discusses the removal of chlorinated volatile organic compounds (Cl-VOCs) from gas streams using these materials.

Singha *et al.*(2013**)** functionalized granular activated carbon (GAC) with HNO_3, HCl and HF acids and found that the surface areas of precursor GAC and the functionalized GACs (FACs) are comparable to each other. However, an enhanced adsorption capacity is seen for the functionalized GACs for chromates and di-chromates. This is explained by the effect of the surface functional groups that are introduced after the modification of GAC with acids.

Hsu et al. 2014 used Jatropha curcas seeds (JS) as the raw material for producing activated carbon by simple thermo-chemical activation with NaOH as a chemical activating agent. Various chlorinated volatile organic compounds (carbon tetrachloride, chloroform, dichloromethane, tetrachloroethylene, trichloroethylene and chlorobenzene) were tested for the single-component adsorption study using the gravimetric adsorption method. Alkaline hydroxides can be used to prepare activated carbon, giving a high specific surface area in the range of 1700–3167 m^2 g^{-1}.

Peng et al. 2016 demonstrates that R850 AC is a promising material for VOC removal and the established Linear Solvation Energy Relationship (LSER) equations are useful to estimate VOC adsorption. R850 AC had the largest surface area and was characterized. LSER was employed in order to understand the interactions between R850 AC and VOCs. The major functional groups on the surface of R850 AC were: C@C, SiAOASi, OAH and CAO (H). IGC indicated that the gas/solid adsorption coefficients ($\log K_d$) for the 16 VOCs lied in the range 4.0–6.1 ($g\ g^{-1}$)/($g\ mL^{-1}$).

Innovative reactivation of AC by CO_2/microwave could expand the pores (Qiu *et al.*, 2017). The mesopore volume increased from 0.122 $cm^3 \cdot g^{-1}$ to 0.270 $cm^3 \cdot g^{-1}$ and a hierarchical pore structure was formed. A gradual decrease in the phenolic hydroxyl and carboxyl groups on the surface of activated carbon enhanced the surface inertia of GAC. The toluene desorption rate of the modified sample increased by 8.81% as compared to that of the original GAC.

Pore size of nitrogen doped carbons distributed in a wide range from micropore (<2 nm) to mesopore (2-20 nm) [Wang et al., (2017)]. This hierarchical porous structure could minimize the diffusion resistance for mass transfer, favouring the efficient transport of reactants to the catalysts. In order to increase the adsorption capacity of activated carbon, it is often treated with alkali and the activated carbon produced by such methodologies is known as functionalized activated carbons (FACs).

2.3 Batch equilibrium analysis

Adsorption is an efficient and cost effective process (Dural *et al.* 2011) for wastewater treatment. Removal efficiency by adsorption depends on the properties of the adsorbents (e.g. specific surface area, porosity, surface polarity of the material) and the characteristics of the adsorbate (e.g. shape, size, charge and hydrophobicity (Michael *et al.*, 2013).

Multicomponent adsorption signifies the competitive adsorption of more than one component and this is specifically important since the industrial effluents contain usually more than one component. Many researchers carried out treatment of wastewater containing more than one organic contaminant by adsorption with activated carbon [Suresh *et al.* 2011; Gun'ko *et al.* 2008; Erto *et al.* 2011; Kumar *et al.* 2011; Lu and Sorial 2004; Lu and Sorial 2009; Erto *et al.* 2012; Al-Degs *et al.* 2007; Matsui *et al.* 2003; Kim andAhn 2010; Tang *et al.* (2012) Quinlivan and Knappe, 2005; Schideman *et al.,* 2007].

Dewettinck *et al.,* 2001 and Pillai *et al.,* 2010 studied the batch equilibrium analysis for odour control in the sewage treatment plants.

2.3.1 Olfactometry based analysis

Odour can be defined as the "perception of smell" or in scientific terms as "a sensation resulting from the reception of stimulus by the olfactory sensory system". A two-step process takes place, leading to an odour sensation. Firstly, human sense of smell is caused by an interaction between molecules in the air and receptor cells located in the nose. This process is a physiological one, yet to be understood completely. The second step comprises of interpretation of the signal as cells are connected with olfactory lobe, which lies at the top of the nose and at the base of the brain.

The *analytical methods* for identifying and quantifying the specific odorants contained in an odorous air sample may give component-specific values, but cannot predict any human sensation in terms of intensity or concentration. In odour intensity terms it can be measured by 'sniffer panel method' (Bliss *et al.,* 1996; Cain *et al.,* 1995; Cain, 1980; Patterson *et al.,* 1993). This method recognises the potentiality of the odorous VOCs emitting in and around a waste water treatment plant.

Here, samples of waste water are taken in two same size Teflon containers (odour free) of sufficient volume in order to ensure that the quantity of odorous sample is adequate for the four trained sniffers and intensity could be correctly recognized. The sniffers use a portable hood, tightly fitted on the Teflon containers to avoid any dilution with the ambient air. The sniffing port (nose shaped) of the hood is placed on the sniffers nose. In this way, waste water samples (before and after adsorption using GAC and FACs) are presented to the sniffer panellists and sniffers make their decisions. Decreasing order of odour intensity indicates the adsorption capacity of activated carbons.

It is difficult to identifying the key volatile organic compounds (VOCs) responsible for a particular odour sensation in STP (Lehtinen and Veijanen, 2011; Kim and Park, 2008). The other option is sensoric measurement. The annoyance assessment (Torres *et al.,* 2010; Henshaw *et al.,* 2006; Sucker *et al.,* 2010; Aatamila *et al.,* 2011) may be related to a combined effect of all the properties (refer Annex-II) like intensity, detectability, character and hedonic tone (pleasantness and unpleasantness). When a sample of odorous gas is progressively diluted, the concentration of odorants decreases, and the intensity of the gaseous sample becomes so low with any further dilution that detection or recognition of the odour is very difficult. This is known as the *'detection threshold'*. The pleasantness or unpleasantness of an odorous sample is given by its *'hedonic tone'*. A pleasant odour may be considered objectionable sometimes by the population exposed to it when the emission is industrial. The objective method of measuring odour, as perceived by human beings, is by panel method. Panel, as discussed by many researchers (Gallego *et al.,* 2008; Nicolas *et al.,* 2006; Canela *and* Jardim, 2008; Blanes-Vidal *et al.,* 2009; Whittington *et al.,* 2011; Bliss *et al.,* 1996) recognises the potentiality of the odorous gases that get emitted in and around a STP. European standard for odour measurement using dynamic olfactometry (European Norm EN 13725, 2003) is used worldwide in the quantification of odour (Hansen *et al.,* 2010; Laor *et al.,* 2010; Sironi *et al.,* 2010; Sarkar and Hobbs, 2002) and it is a very popular one.

A rapid, simple and reliable technique to detect odorous compounds is the electronic nose. To detect or quantify an odour, the odorous molecules are not the only ones detected in this case. All the molecules having a reactivity potential with the sensors will also be detected. Application of electronic nose technology to monitor wastewater is reported (Dewettinck *et al.,* 2001; Stuetz *et al.,* 1998). Sewage odour concentrations are measured from samples taken at different sampling locations in different sewage works. The electronic nose mimics the human olfaction system which consists of three essential elements: an array of olfactory receptor cells (situated in the roof of the nasal cavity), the olfactory bulb (situated just above the nasal cavity) and the brain. An electronic nose has got roughly three equivalent elements: an odour sensor array, a data pre-processor and a pattern recognition engine (Lozano *et al.,* 2010; Schwarzbock *et al.,* 2010; Capelli *et al.,* 2008; Littarru, 2007; Wang *et al.,* 2010; Nake, *et al.*,2005).

2.3.2 GCMS based analysis

GC/MS is used by so many researchers (Ras *et al.,* 2008; Godayol *et al.,* 2011; Pandey and Kim, 2009) for identifying and quantifying component specific odorants contained in an odorous air sample. Sometimes researchers (Zhanga *et al.,* 2010; Ochiai and Sasamoto, 2011; Koziel *et al.,* 2010; Kleeberg *et al.*,2005) used GC/MS to directly find out odorous compounds quantitatively as well as qualitatively. Many researchers analytically measured VOCs or/odorous compounds using GC/MS or GC followed by some specific detectors (Micone and Guy, 2007; Wu *et al.*, 2006; Hwang *et al.,* 1995; Leach *et al.,* 1999). Sampling of various odorous volatile organic compounds (for analysis later) can be done by various processes. Generally SPME (Solid Phase Micro Extraction) (Kleeberg *et al.*, 2005; Lee *et al.*, 2002) needles and various types of sorbent tubes have been (Woolfenden, 2010; Gallegoa *et al.*, 2011; Król *et al.*, 2010; Boeker *et al.*, 2010; Statheropoulos *et al.*, 2005) used for sampling VOCs. Capillary Gas Chromatography (GC) equipped with Pulsed Flame Photometer Detector (PFPD) is the most popular detector, commercially available, for the selective measurement of odorous sulphur, phosphorus, carbon and nitrogen compounds (Cheskis *et al*., 1993). Process conditions and retention times were developed (A. Amirav and H. Jing, 1995) for the analysis of organo sulphur compounds by gas chromatography, equipped with PFPD.

2.4 Kinetics and diffusion studies of adsorption process

Adsorption with GAC can remove many hydrophobic and also some charged odorous compounds from waste water (Le-Minh *et al.*, 2010). Adsorption mechanism involves the following steps:

I. solute transport in the bulk-adsorbate movement by the stagnant liquid film surrounding the adsorbent,

II. film diffusion-adsorbate transport through the film,

III. pore-diffusion-adsorbate diffusion through the porous structure to the active sites (molecular diffusion in the pore and/or in the adsorbent surface),

IV. adsorption-interaction between adsorbate and porous structure (Homem nd Santos, 2011).

The dominant mechanism for the removal of organic compounds is the non-specific dispersive interactions (e.g. van der Waals interactions) in activated carbon adsorption systems. *Multicomponent adsorption* signifies the competitive adsorption of more than one component and this is specifically important since the effluent water contains usually more than one component (Erto*et al.*, 2012, Tang *et al.*, 2012).

Adsorption kinetics of single and binary system follow the pseudo-first order and pseudo-second order kinetic models (Mahmouda *et al.,* 2012; Durala*et al.,* 2011; Ahmaruzzaman and Gayatri, 2010).

Mechanism of adsorption was studied by intra-particle diffusion and film diffusion models by various scientific groups (Tang *et al.*, 2012; Hameed and El-Khaiary, 2008].

Xiang et al. 2008 investigated the adsorption of dibenzofuran (DBF) on three commercial granular activated carbons (GAC) in order to correlate the adsorption equilibrium and kinetics with the morphological characteristics of these activated carbons. The effects of adsorbent morphological properties on the kinetics of the adsorption process were studied. The equilibrium data satisfactorily fitted to the Langmuir isotherm. An intraparticle diffusion model based on the Langmuir isotherm was developed. The surface diffusion coefficients of dibenzofuran on the activated carbon were calculated and a relationship with microporosity was found. As it was expected, the dibenzofuran molecule was found to have more resistances while diffusing through those carbons with narrower pore diameter.

Chen et al 2014 studied the adsorption behaviour of three Polycyclic Aromatic Hydrocarbons (PAH) in surfactant solution by activated carbon. For PAH, experimental adsorption data from single and ternary PAHs in TX100 solution were successfully fitted with the Langmuir isotherm model. This result indicates that an adsorbate monolayer was established during saturation. The adsorption of PAHs in surfactant solutions by AC was well described by the pseudo-second-order kinetics model.

Chapter 3

Methodology I

Alkali Functionalized Granular Activated Carbon: *Synthesis, Physical and Chemical Characterization*

3.0 Foreword

Granular activated carbon (GAC) is one of most important adsorbing agentsthat are suitable for adsorption of gas and vapours. Different types of adsorbing materials such as alumina, silica, zeolites or various inorganic oxides can be used forremoving odorous compounds. However, it is observed that their capacity is about one tenth that of activated carbons (Steijns and Mars, 1977). Adsorption capacity of an adsorbent depends on factors like specific surface area, pore-size distribution, porevolume, inherent surface charge and presence of surface functional groups.But due to low pore aperture, adsorption by activated carbon is limited toadsorbate molecules that are low in molecular sizes. This drawback of the micro porous granular activated carbon (GAC) is mitigated by development of mesoporous materials. Due to larger surface area and pore volume, adsorption capacities of these mesoporous materials are found to be much more, as compared to micro porous activated carbon.Different types of mesoporous materials like mesoporous silica, carbon aerogel, mesoporous alumina, mesoporous carbon etc. are widely used for the adsorption of large size organic components. However, these materials are expensive as compared to the cost of GAC [Price of GAC is INR 0.60/g]for the removal of Volatile Organic Compounds (VOCs). So they cannot be used for a large scale removal of VOCs coming from sources like sewage waste water treatment plants.For adsorbing large size organic components, porosity must be improved in the mesoporous range (pore diameter 2nm to 50nm). Activated carbons are characterized by reasonably high surface area up to about 700-1500m^2/g, high pore volume and a high degree of surface structural and chemical heterogeneity.

Chemical heterogeneity is the result of the presence of atoms other than carbon in the activated carbon matrix (Bohem, 2002; Puri, 1970; Leon *et al.*, 1992).The most common hetero-atom is oxygen, which is present on the carbon surface in the form of acidic, basic, or neutral organic groups such as carboxylic acids, lactones, phenols etc. Adsorption is maximized by using AC with a high specific surface (750-1500 $m^2.g^{-1}$) and a significant portion of its total pore volume in the micro-pore range (less than 2.5 nm diameter) (Turk *et al.*, 1989).

However, microporous activated carbon has got some inherent disadvantages. As a result, it leads to less amount of diffusion and thereby restricted adsorption of heavy and larger components.

Adsorption capacity of GAC can be improved by treating it with various acids or alkaline solution. Functionalization takes place duringtreatment of activated carbon with an acid or alkali solution. As treated waste water is used mainly in agricultural purpose so it should not be acidic in nature. So alkali treated functionalized activated carbon is more effective for the removal of large size volatile organic compounds coming from the waste water treatment plants. Functionalization of activated carbon with alkaline solution is one of the cheapest processes to improve the texture and surface chemistry of GAC. The same induces some kind of supra-porosity (in between micro and mesoporous structure) in the precursor GAC.

Alkaline functionalization is performed by different alkaline solutions like sodium hydroxide (NaOH), potassium hydroxide (KOH), ammonia (NH_3) etc. During functionalization surface chemistry is improved by so many acidic, basicor neutral organic groups like carboxylic acids, lactones, phenols etc. are produced on the GAC surface. Nitrogenation takes place due to the treatment of ammonia solution (NH_3) with GAC and it could increase the basicity of GAC. Introduction of nitrogen to GAC can significantly increase the polarity of carbon surface and hence its specific interaction with polar adsorptive compounds becomes prominent. Nitrogenation can also affect the porous structure along with the surface chemical nature of the activated carbon in a specific form and to an extent that depends on the precursor carbon, chemical reagent and the experimental method used.

3.1Alkaline Functionalization of Activated Carbon

3.1.1 Chemicals

Granular activated carbon (GAC) from SD Fine Chemicals Limited, India (SDFCL) is a commercially available less expensive material, used for the removal of VOCs generated in and around sewage waste water treatment plants. However, the adsorption capacity of GACis not satisfactory for comparatively large size, volatile organic components which have got comparatively low odor threshold numbers. Functionalization by alkali treatment helps to improve the surface chemistry of GAC materials by the introduction of so many acidic, basic or neutral organic groups like carboxylic acids, lactones, phenols etc. on the GAC surface. These surface modified functionalized activated carbons (FACs), particularly ammonium hydroxide treated ones, are expected to have a great potential to be effective on adsorption of comparatively large size, volatile organic components which having low odor threshold values (Li et al. 2011; Z. Merzougui and F. Addoun 2008).

3.1.2 Experimental Procedure

The precursor GAC used for alkaline functionalization is of LR grade (IMDG Code: 4.2/III; UN: 1362; IATA: 4.2) from SD Fine Chemicals Limited, India (SDFCL). At first GAC is sieved through a BS 8 mesh screen and the larger fraction is retained on the screen. The retained fraction is purified by boiling it with distilled water in a water bath for 2 hour under slow stirring condition. Afterwards the same has been washed repeatedly with distilled water in order to remove the fine particles and then dried it in an oven at 105°C for 4 hour before functionalization. This is done to remove the moisture and any volatile materials present on the surface and within pores of the grains. After cooling down to room temperature, this purified GAC is ready for functionalization with alkali treatments (Liu et al.2011; Sun et al. 2008;Ryu et al.2001; Kim et al. 2006; Nowicki et al. 2010).The purified GAC is functionalized with three different alkalis: NH_4OH, KOH and NaOH to improve the adsorption capacity with respect to the precursor GAC.Liquor ammonia (GR grade), KOH (AR grade) and NaOH (AR grade) were purchased from Merck India Limited. For NH_4OH treatment the purified GAC was soaked into an alkaline solution of 6M NH_4OH solution in the ratio 1g/8ml. Then it was heated at 70°C for 2 hour under constant stirring and then placed at 35°C for 24 hours (Li et al. 2011). For KOH treatment, purified GAC was soaked into an alkaline solution of 8M KOH in the ratio 1g/8ml. Then it was heated at 100°C for 2 hour under constant stirring and then placed it at 35°C for 24 hours (Sun et al. 2008).For NaOH treatment, purified GAC was soaked into an alkaline solution of 10M NaOH solution in the ratio 1g/8ml. Then it was heated to 70°Cfor 2 hour under constant stirring and then placed at 35°C for 24 hours (Li et al. 2011).These functionalized activated carbons were then separated and further washed with distilled water until the same becomeneutral. Then they were dried in an oven at 105^{o}C for 4 hour and transferred to desiccators. Now this GAC is ready to act as Functionalized Activated Carbon and is denoted in the text as FAC-NH_3, FAC-NaOH and FAC-KOH.

3.2 Specific Characterization Methods Applied forGAC and FACs

3.2.1BET surface area and porous structure characterization

The BET technique has been used to analyzethe specific surface area, total pore volume and pore size distribution of the experimental sample. The nitrogen adsorption is carried out at77^{o}C using surface area analyzer (Make: Beckman Coulter; Model:SA3100). A sample of 0.30g was degassed under 120^{o}C at 1 bar pressure for 12h. The specific surface area and pore volume were calculated by the t-method of de Boer (Boer et al. 1965). HK method [Horvath and Kawazoe, 1983] was used to determine the pore size distribution of the micro-pores and meso-pores and then this was analyzed using non local density function theory (NLDFT) for all the samples.

3.2.2Surface morphology

The surface morphology of precursor and functionalized activated carbons was characterized using a Scanning Electron Micrograph (SEM) at x3,000 magnification using a field emission scanning electron microscope (FE-SEM). The images of surface morphology were developed and produced using a field emission scanning electron microscope (Make: JEOL; Model: JEM6700F) and this analysis was done with pure and functionalized activated carbons to study the changes of surface morphology and actual loading capacity of these adsorbents.

3.2.3Elemental Analysis

The carbon (C), Hydrogen (H) andNitrogen (N) percentages were analyzedby CHNS analyzer (Make: Perkin Elmer, USA; Model**:** 2400 Series II CHN analyzer). Working conditions of the instrument were set as: the combustion tube temperature=924 ^{o}C; reduction tube temperature=640 ^{o}C. Helium was used as the carrier gas and its pressure was set at 1100-1200millibar.

3.2.4 Analysis of Functional groups using FT-IR

The surface functional groups of pure GAC and FAC samples were characterized by a FT-IR spectrophotometer (Make: Shimadzu, Model**:** IR affinity-1). The spectra were measured using KBr, set as a reference sample in the spectrophotometer. The sample was ground with a mortar and a pestle in order to get a particle size less than 100µm. It is important to control the particle size for getting useful spectra as big particle cause a large slope in the spectral baseline due to scattering of light. The finely ground powder is then mixed with KBr in the ratio of 1:100 and it was then further ground for proper mixing as well as controlling of the mixed sample. Thin pellets of KBr-sample were prepared by KBr pelletizer. The pelletizing action was performed under a pressure of 7600kg/cm^2. The pellets were dried at 383K for 3 hour and this was ready for IR spectral analysis. The FTIR resolution was 4cm^{-1} in the range 500-4000cm^{-1}.

3.2.5Quantitative Measurement of Functional groups by Boehm titration

The titration method suggested by Boehm (O.A.Ekpete and M.JNR Horsfall, 2011) was applied to calculate the acidity of each sample. Activated carbon samples, 0.2g each, were placed into 50ml aqueous solution of the following solutions, 0.05M each: sodium hydroxide, sodium carbonate, sodium bicarbonate and hydrochloric acid. The conical flasks were then sealed with rubber caps and shaken for 24h at 298K, after which the resulting solutions were filtered and 10ml of accurately withdrawn aliquot of filters were titrated by 0.05M HCl in order to estimate the unreacted base or by 0.05M NaOH for the residual acid. The titre values were measured three times for each sample and the acidic or basic functional groups were calculated using the average of three titration data.

3.2.6pH Values at the Point of Zero Charge

Point of zero charge is defined by the pH, above which the total surface of the carbon particle will be negatively charge (Leon et al. 1992, Li et al. 2011). Zeta potential measurement of GAC and FACs were carried out with a zeta potential analyzer (Make:Malvern Co,United Kingdom; Model**:** Zeta- Sizer 2000,) For this analysis approximately 50mg of GAC and FAC samples were powdered with a mortar and pestle, then the samples were dispersed into 500ml of distilled water and allowed them to settle for several minutes. The suspension with colloidal sized particle was collected to determine the zeta potential after addition of 0.01M NaCl solution. In order to get CO_2 free solution, N_2 was bubbled through the solution. The pH of each of the solutions was adjusted in the range 2 to12 by using HCl or NaOH solution under constant stirring condition at 200 rpm for 24 hr at 25^{o}C in order toreach an equilibrium condition.

3.3 Results and Discussion

3.3.1Nitrogen adsorption/desorption analysis for surface characterization:

The N_2 adsorption/desorption isotherm of the untreated GAC and various functionalized materials are shown in Figure3.1. The BET surface area (S_{BET}) and the pore volume of all the samples are obtained after analyzing these N_2 adsorption data with the standard BET isotherm.

The N_2 adsorption/desorption isotherm of the untreated GAC sample gives type I isotherm (Characterized by an almost horizontal line to the P/P_0axis)and the material is micrporous in nature (Shim et al. 2001).The N_2 adsorption/desorption isotherm of alkali (ammonia, KOH, NaOH) treated granular activated carbon can be classified as type II isotherm which are very unusual. High nitrogen adsorption at low P/P_0 relative pressure is the characteristic of the microporous materials (G.D. Waltrip and E.G. Snyder, 1985; Dewettinck et al. 2001).The sharp increase in N_2 uptake at low P/P_0 is suggesting the presence of micropores in the said sample (A.G. Boon, 1995). However, at high P/P_0 the N_2 uptake gradually increases, indicating the existence of antiparticles porosity in this functionalized granular activated carbon. From this isotherm it is seen that functionalized activated carbon shows sharp rise at relatively low pressure followed by slow increase in N_2 uptake at higher P/P_0. This result suggested two types of porous structure, where the super-microporosityof ca. 1.6 nm pore size are generated from the network inside the material and inter particle mesopores result from the self-aggregation of these particles.

The values of BET surface area and pore volume of GAC and alkali treated FACs are compiled in Table 3.1. From this table it is evident that the specific surface area and pore volume are slightly increasing with different alkali treatments. The BET surface area marginally increases in the order of S_{BET} (GAC) < S_{BET} (FAC-NH_3) < S_{BET} (FAC-NaOH) < S_{BET} (FAC-KOH). The surface area and pore volume of GAC and FAC-NH_3 were comparable to each other. This indicates that ammonia treatment of GAC did not change the meso and macropore volume a lot as compared to the original GAC material. The BET surface area (S_{BET}) of FAC-KOH (814 m^2/g) and FAC-

NaOH(792 m^2/g) were slightly higher than that of both GAC (777 m^2/g) andFAC-NH_3 (778 m^2/g).

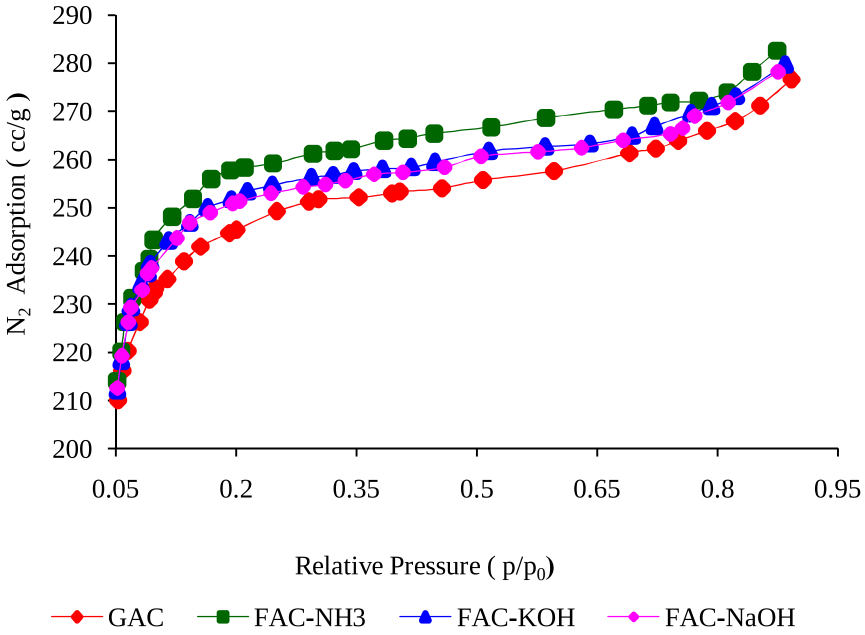


Figure 3.1 N_2 Adsorption isotherm of GAC and alkali treated FACs.

From Table 3.1 it is seen that the pore volume of FAC-KOH and FAC-NaOH were a bit smaller than that of GAC and FAC-NH_3 but did not affect the pore size. All the alkali treated FACs had a total micropore volume little higher than that of the untreated GAC. Significant amount of N_2 adsorption at a relative pressure (P/P_0) below 0.1 indicates that, all the tested materials have microporous structure. However, the isotherm of GAC sample also shows some significant adsorption at a relative pressure (P/P_0) above 0.9, which we attribute to the presence of larger mesopores and macropores into the surface (Mokaya et al. 2013).From Figure 3.1 it is evident that the activation with alkali treatment of GAC leads to marginal increase of N_2 adsorption at lower relative pressure (P/P_0) below 0.1. This again indicates that the microporosity of the GAC is retained and enhanced after activation. The slight widening of the isotherm'knee' to cover the P/P_0 range in between 0.05 and 0.25 is an indication of the creation of the large micropores and mesopores in alkali treated GAC materials.

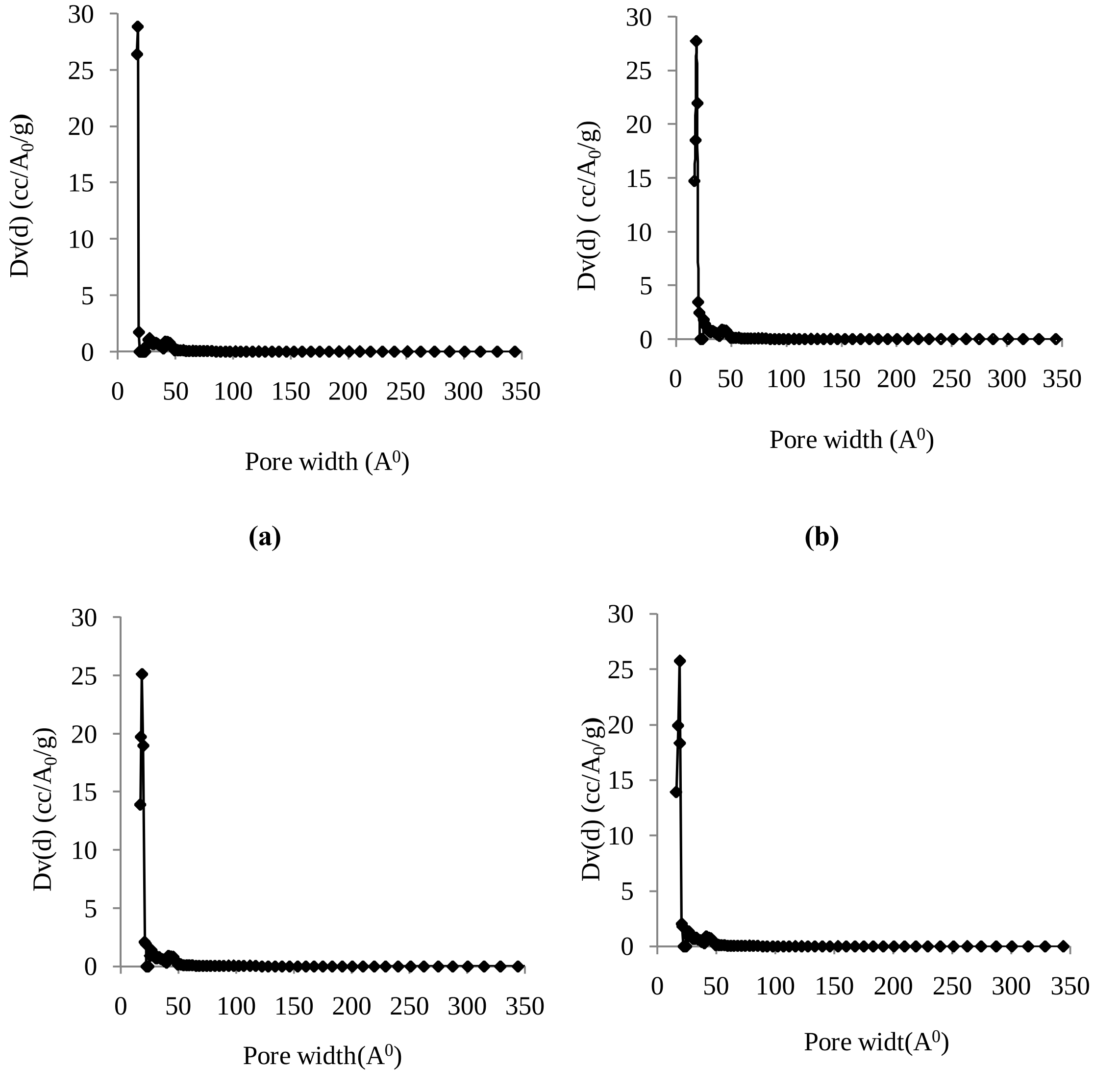
Table 3.1 Result of N_2 Adsorption isotherm for surface area and pore size of GAC and different FACs.

Sample	Surface Area (m^2/g)	Pore Volume (ml/g)	Pore Size (A^0)
GAC	777	0.3853	23.46
FAC-NH3	778	0.3813	23.91
FAC-KOH	814	0.3915	23.76
FAC-NaOH	792	0.3802	23.72

Similar results of BET surface area, pore size and pore volume were obtained by many researchers with the alkali treatment of GAC. Li et al. 2011 has shown that the BET surface area and pore volume of coconut shell based GAC increased from 731 to $868m^2/g$ and 0.168 to 0.176cc/g respectively after treatment with ammonia solution. On treatment with NaOH solution the BET surface area increases from 731 to $846m^2/g$ and pore volume increases from 0.168 to 0.178cc/g.

3.3.2Pore Size Distribution:

Surface texture of GAC and FACs are examined by analyzing the pore size distribution. The characteristics of pore size and pore distribution of tested GAC and FACs are given in Table3.1. All the FAC materials (FAC-NH_3, FAC-KOH and FAC-NaOH) increased their total pore volumes without affecting the mean pore diameters. For GAC [refer to Fig. 3.2(a)], there are mainly two peaks, one at the micro-porous and other at the mesoporous region(above 2.5nm). So it indicates that maximum cumulative pore volume is observed in the micro-porous region with pore diameter ranging from 1.1 to 1.3 nm. The second peak is in the order of meso-porous region with pore width varying from 5 to 5.5nm. The pore size distribution of FAC-NH_3, shown in Fig. 3.2(b) indicates the presence of super micro porosity with a pore diameter of 1.7nm (Dutta et al. 2012).



(a) **(b)**

(c) **(d)**

Figure3.2 Pore size distribution by NLDFT method of a) GAC, b) FAC-NH_3, c) FAC-KOH, d) FAC-NaOH.

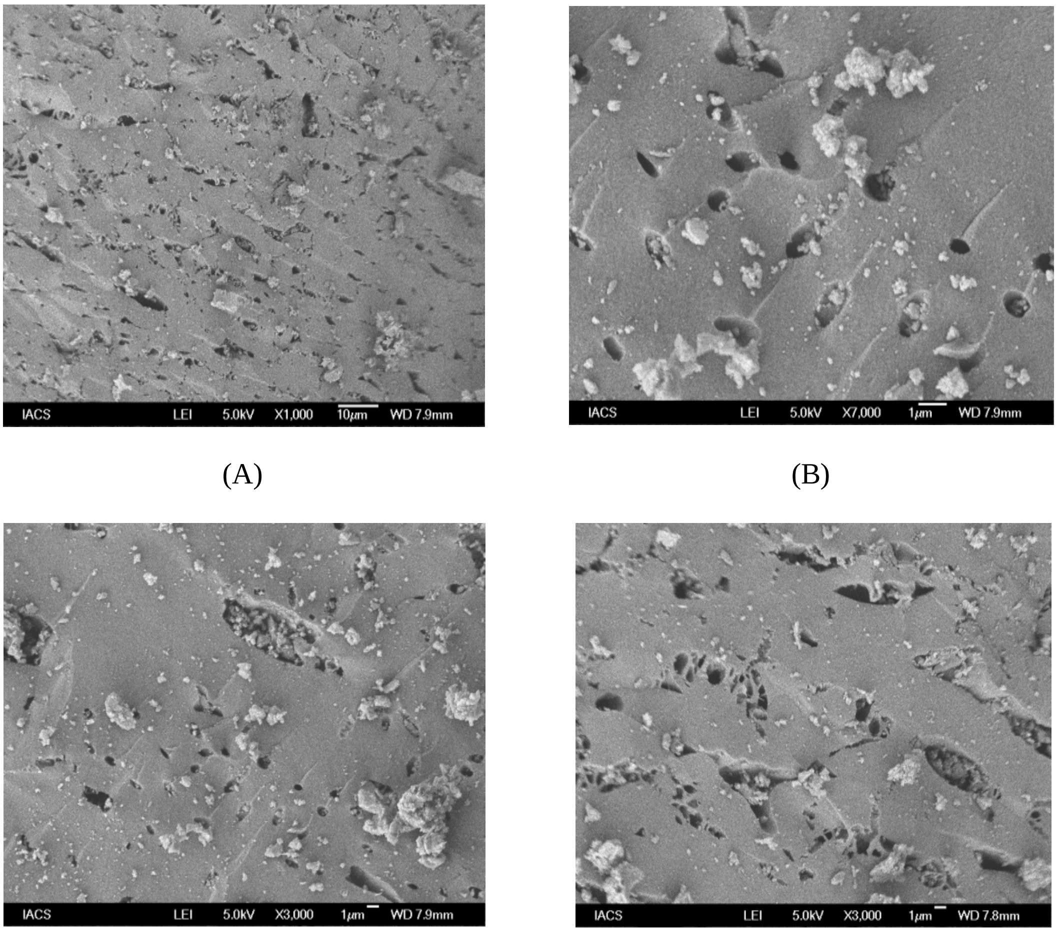
Figure 3.2(b) depicts that maximum cumulative numbers of pores are located in the meso-porous region (pore diameter >2nm). A sharp peak was observed at 1.7nm, in the microporous region and two more sharp peaks were observed at 2.7nm and at 4.1nm, which were in the meso-porous region. In all the cases, KOH activation of GAC samples results in a significant increase in pore volume arising due to the number of micro-pores and meso-pores of sizes 17A^{o} and 26A^{o}, particularly the 26A^{o} pores. Thus the enhance of micropores of size 17A^{o} present in GAC samples converted into mesopores of size 26A^{o} pores with KOH activation.

Thus it could be concluded from the pore size distribution analysis that modification of GAC applying specific alkali treatment, converted the maximum number of micro-pores of GAC into supra-pores and meso-pores.

3.3.3Field Emission- Scanning Electron Microscopic (FE-SEM) Analysis

The FE-SEM images of GAC and FACs are shown in Figure 3.3.GAC,on modification with ammonia solution (FAC-NH_3) exhibited a rough and purified surface. Various pore sizes were observed on the surface and inside the particle. The surface of FAC-KOH and FAC-NaOH were similar, although some pores were blocked. This similarity of surface texture between FAC-KOH and FAC-NaOH is also supported from BET analysis (Table-3.1) and respective pore size distribution curves. Treatment of GAC with NH_4OH seems to bring quite a lot of changes in the surface texture of GAC. From Fig. 3.1(d) it can be observed that the pores on the surface of GAC become larger in size, due to the introduction of functional groups on the poresurfaces.

Similar type of SEM images arealso observed by Li et al. 2011, where coconut shell based activated carbon was functionalized with different acids and bases.



(A) (B)

(C) (D)

Figure3.3 The FE-SEM Pictorial view at ×3000 magnification of GAC and all FACs- (A) GAC, (B) FAC-NH_3, (C) FAC-KOH and (D) FAC-NaOH.

3.3.4Elemental Analysis using a CHNS Analyzer:

The elemental analysis of GAC and FAC materials is carried out using a CHNS analyzer (Make:Elementar, Germany; Model**:**VARIO MICRO CUBE)and the results are given in **Table3.2.** The combustion tube temperature and the reduction tube temperature are kept at 1150°C and 850°C respectively. The pressure of the carrier helium gas is maintained at 1100-1200 millibars. The oxygen content, obtained from the O_2 analyzer (Make:Leco,USA; Model**:** TC 600) is 6.95 (wt. %)for GAC, while the sulfur content is 0.27wt%. The nitrogen content of FAC-NH_3 is 3.4wt%. However, the same is present in lesser amount inGAC and other FACs. The nitrogen content of pure GAC is 0.26wt%, FAC-KOH is 0.21wt% and FAC-NaOH is 0.25wt%. Oxygen content of FAC-$NH_3$is 3.68wt%, FAC-KOH is 5.93wt% and FAC-NaOH is 5.98wt%, which are comparably smaller than the same present in precursor GAC (6.95wt%).Functionalization of GAC has some effect on the oxygen content but little or no effect on the hydrogen content of all the FACs.

Table3.2 Elemental Analysis of GAC and FACs using a CHNS Analyzer.

Adsorbents	Carbon (%W)	Hydrogen(%W)	Nitrogen(%W)	Sulphur (%W)	Oxygen(%W)
GAC	91.68	0.84	0.26	0.27	6.95
FAC-NH_3	90.92	1.85	3.40	0.15	3.68
FAC-KOH	91.36	2.21	0.21	0.29	5.93
FAC-NaOH	91.25	2.16	0.25	0.36	5.98

3.3.5Characterization of various Functional Groups by FT-IR:

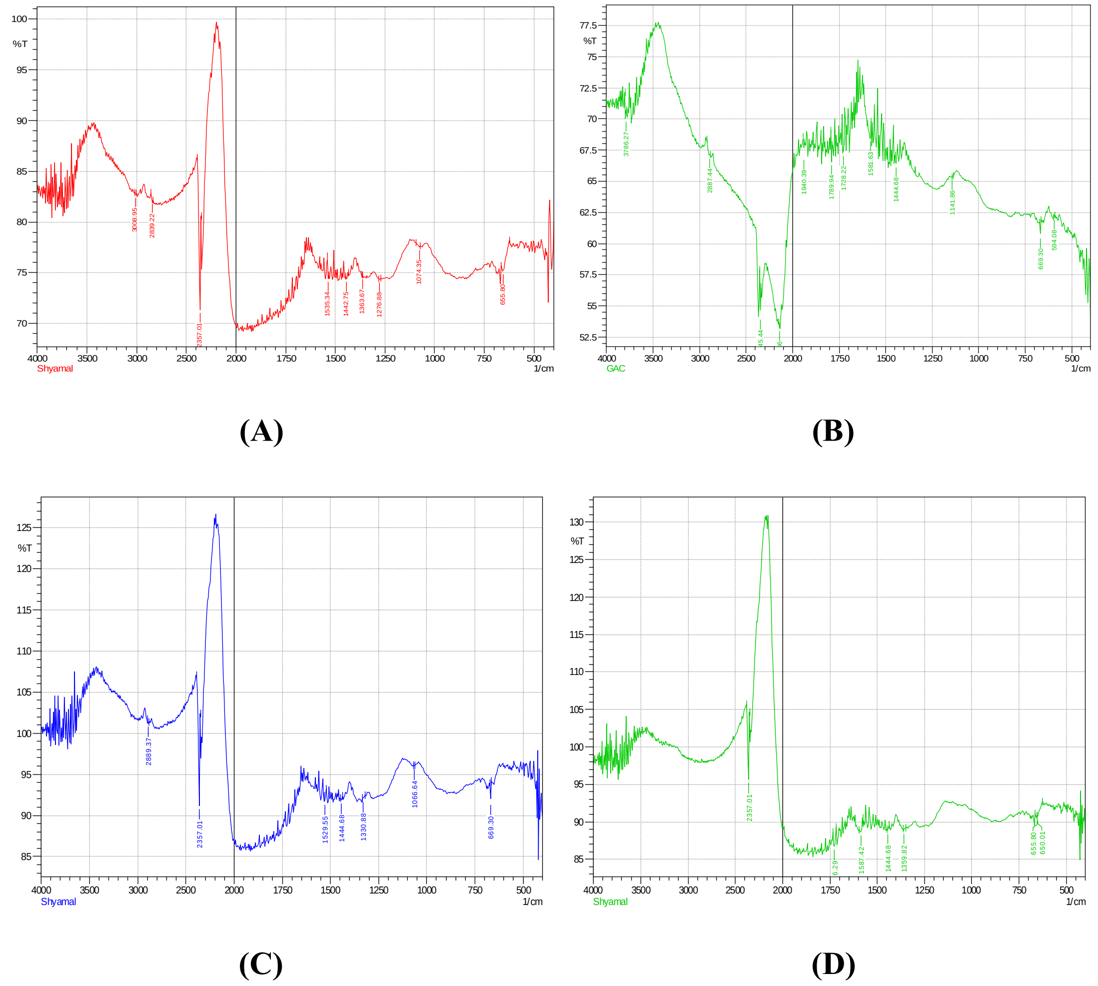
FT-IR analysis of GAC and all FACs is carried out in order to obtain better insight of the functional groups available on various carbon surfaces.This technique is mainly used for qualitative evaluation of the chemical structure of precursor GAC and changed incurred after alkali modification of the same to produce different FACs. It is not easy to get good spectra because carbon adsorbs almost all of the radiation in the visible spectrum. The peaks obtained were usually as a result of some interaction of different types of groups present in the surface (Shen et al. 2008). The recorded spectra of these materials are shown in Table3.3.All the materials exhibited bands in between 2880cm^{-1} to 2845cm^{-1}, which were primarily due to the asymmetric stretching of CH_2 group. The absorption bands of the carbonyl group (2350cm^{-1}) in ketone and phenolic group (1070cm^{-1}) were observed in GAC, FAC-NaOHand FAC-KOH. Cyclic amides are present at band 669cm^{-1} in FAC-NH_3, FAC-NaOH and FAC-KOH and these specific spectra is observed as a result of chemical modification by respective alkali solution. Only FAC- NaOH shows the spectra of carboxylic acid group at 1726cm^{-1}.Figure 3.4 shows the band at 1442cm^{-1}. The same can be assigned to the lactone structure present in all the tested materials (Song et al. 2010). Peak area of the absorption band at 1442cm^{-1} increased much more due to the formation of lactone structure (Shim et al. 2001) specifically for ammonia treated GAC. From the spectra of GAC (refer to Figure 3.4A) and FAC-NH_3 (refer to Figure 3.4B), it is certain that the absorption band in between 1750cm^{-1}-1500cm^{-1} are changed after chemical modification of GAC with ammonia solution.

The absorption band near 1728cm^{-1}, an indication of the presence of carboxylic group, is observed for GACmodified by alkali treatments with NH_3, KOH and NaOH. This indicates that there are still carboxyl structures in the micro-pores which are either inaccessible base or C=O group, that have not been neutralized with alkaline solution.

The bands shown in all the tested materials near 2300cm^{-1} are assigned to carbon-oxygen groups due to the presence of ketone (Bhabendra and Sandle, 1999). But the bands are very weak specifically for FAC-NH_3. In Figure 3.4 FAC-NH_3 shows an increase of the 1600cm^{-1} peak area. The same is attributed to a quinine structure (Chingombeet al. 2005).

Table 3.3 FT-IRanalysis of GAC and various alkali treated FACs.

GAC		FAC-NH_3		FAC-KOH		FAC-NaOH	
Wavelength (cm^{-1})	Functional group	Wavelength (cm^{-1})	Functional group	Wavelength (cm^{-1})	Functional group	Wavelength (cm^{-1})	Functional group
1074.35	-C-OH (stretching)	669.3	Cyclic amides	669	Cyclic amides	655.8	Cyclic amides
1276.88	Alcohols	1444.68	Lactone structure	1066	-C-OH (stretching)	1067.35	-C-OH (stretching)
1363.67	C-N aromatic ring	1581.63	-C-C aromatic stretching	1330	C-N aromatic ring	1359.82	C-N aromatic ring
1535.34	-C-C aromatic stretching	1600	Quinone	1444.68	Lactone structure	1444.68	Lactone structure
2839.22	-C-H stretching (asymmetric)	1729.94	Carboxilic acids	1529.55	-C-C aromatic stretching	1587.42	-C-C aromatic stretching
3008.95	-C-H stretching (symmetric)	2139.06	C=C=N	1600	Quinone	1600	Quinone
		2345.44	C=O in ketone	1726.4	Carboxilic acids	1726.29	Carboxilic acids
		2887.44	C-H stretching (asymmetric)	2357.01	C=O in ketone	2357.01	C=O in ketone
		3786.27	O-H stretching vibration	2887.37	-C-H stretching (asymmetric)	2845.53	-C-H stretching (asymmetric)



(A) **(B)**

(C) **(D)**

Figure 3.4FTIR spectra of (A) GAC, (B) FAC-NH_3, (C) FAC-KOH and (D)FAC-NaOH.

3.3.6 Analysis of various Functional Groups by Boehm Titration:

The acidic functional groups such as phenolic (-OH), lactonic (C=O), carboxylic(-COOH) and basicity were determined by Boehm titration. The result of surface acidic groups of GAC and different FACs are shown in Figure 3.5. The concentration of different surface acidic groups (phenolic group, lactonic group, carboxylic group etc) is higher in case of GAC as compared to FAC- NH_3, FAC-KOHand FAC-NaOH. This is because of the surface acidic groups getneutralized on activation with alkali solution.

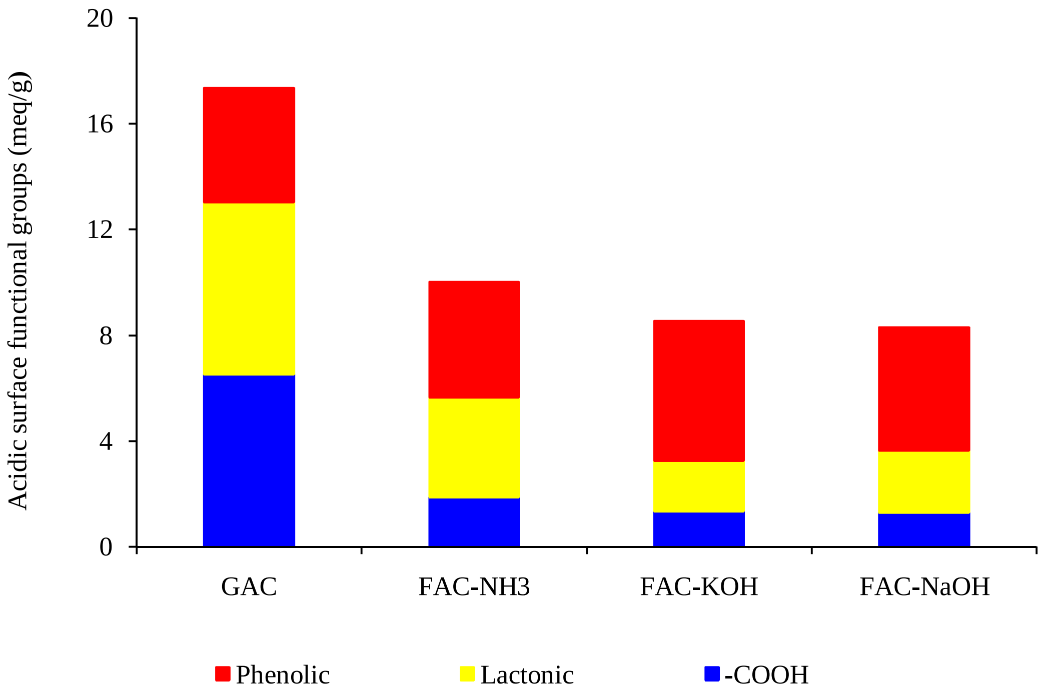


Figure 3.5 Surface Acidic Functional groups of GAC and the FACs.

From**Table 3.4** it is seen that the quantity of surface basic groups of GAC increases on modification with different alkali solutions.Modification of GACwith various alkali solutions introduced different basic groups like C=N, amino, cyclic amides, nitrile group and pyrrole like structure (Li et al. 2011).

Table 3.4 Boehmtitrated concentration of acidic group and basic groups along with pH_{pzc} of GAC and alkaline FACs.

Sample	Acidic Group (meq/g)			Total Acidic Group (meq/g)	Basic Group (meq/g)	pH_{pzc}
	-COOH	Lactonic	Phenolic			
GAC	6.525	6.496	4.33	17.351	1.37	4.56
FAC-NH3	1.873	3.773	4.384	10.03	4.33	7.3
FAC-KOH	1.326	1.911	5.312	8.549	4.56	7.5
FAC-NaOH	1.294	2.345	4.675	8.314	4.47	7.48

3.3.7 Estimation of Point of Zero Charge (pH_{pzc}):

At the point of zero charge,surface charges are effectively neutralized so that the effective (net) surface charge becomes zero and the correspondingpH is known as pH_{pzc}. Thus, the zeta potential of all the materials is a function of pH.

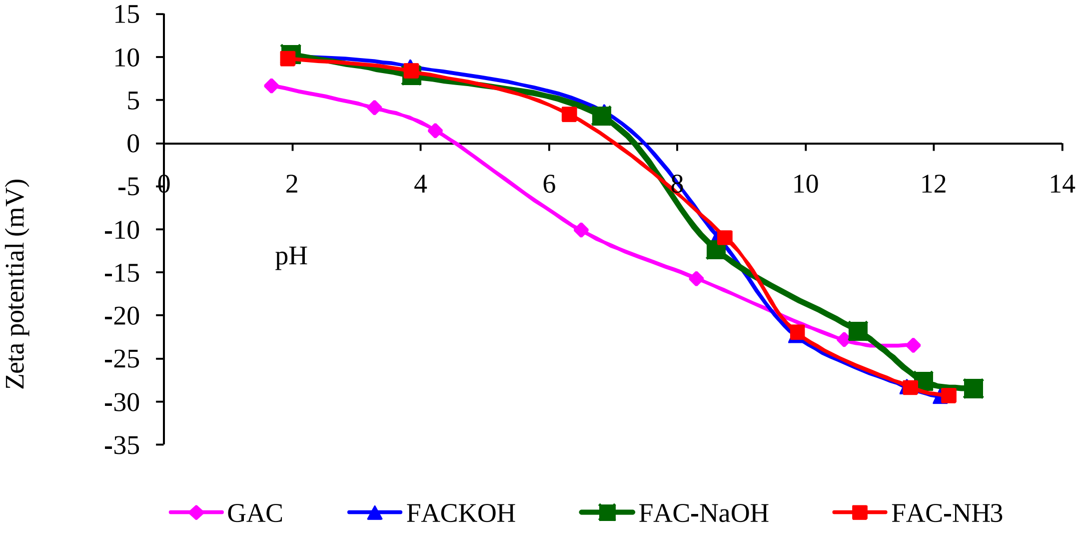


Figure 3.6 Plot of zeta potential (mV) vs pH of GAC, FAC-NH_3, FAC-KOH and FAC-NaOH.

The point of zero charge (pH_{pzc}) of a carbonaceous surface depends on the chemical and electronic properties of the functional groups present on the carbon surface. At the point of zero charge, the surface charges of activated carbons are neutralized so that the net surface charge is zero. High pH_{pzc} values of the FACs, as compared to precursor GAC, are due to the presence of the basic groups (refer Table 3.5). This is primarily due to smaller quantities ofcarboxylic (6.525 meq/g), lactonic (6.496 meq/g) and phenolic (4.333 meq/g) groups present on the surface of FACs, as compared to that of GAC.Figure 3.6 shows the plot of zeta potential (mV) versus pH values of GAC and all the FAC materials. From this figure it is seen that, GAC has got a pH_{pzc} value of 4.5, corresponding to a zeta potential of 0mV. However, the pH_{pzc} value of alkali-functionalized GAC (FACs) shifted to over 7.5. The surface acidic functional groups actually get partially neutralized because of the alkaline treatment of GAC and some basic groups like C=N, amino,cyclic amides, nitrile, pyrrole like structure etc. are introduced onto the GAC surface, thereby providing the basic properties in FACs (Li et al. 2011).

Chapter 4

Batch adsorption analysis:

Olfactometry and GC-MS based Analysis

4.0 Foreword

Odours in sewer systems is produced by anaerobic microbial decomposition of sewage waste water containing high levels of organic matter, nutrients, toxic compounds and chemicals. Most of the odours generated within the sewer system are sulphur based compounds, the predominant compound often being hydrogen sulphide. Organo-sulphur based volatile compounds like carbon disulphide, methyl mercaptan, dimethyl sulphide, ethyl mercaptan, dimethyl disulphide etc., though found in lower concentration, are the key compounds behind most of the odour complaints. These are detectable at very low levels of concentrations and tend to disperse relatively slowly till a concentration level is reached which is far below a concentration that corresponds to an odour nuisance level. These VOSCs are primarily produced due to anaerobic microbial decomposition of proteins. In addition to odour, VOSCs, while present in the gas phase, may affect human health and create corrosion problem.

Majority of malodorous gases, Volatile Organo Sulfur Compounds (VOSCs) produced from various municipal sources associated with sewage treatment works, can cause unpleasant feeling even at low concentrations of these compounds. It has been estimated by Vincent, A. J., 2001that each person discharges *1–1.5 gram sulphur per day* to the sewerage network, of which about 70% is sulphate derived from urine. Boon, A. G., 1995 showed that domestic sewage typically contains 3–6 mg/l organic sulphur (mainly derived from proteinaceous materials) and can contain further organic sulphur from sulphonate in household detergents (*about 4 mg/l*). Inorganic sulphur, in the form of sulphate can also be present, in quantities depending on the hardness of the water, typically in the concentration ranges of 30–60 mg/l.

Odor Control by Adsorption:

Various knowledge gaps associated with odour assessment and control in the environment are addressed by researchers worldwide in different ways. Conventional methods of odour removal, consisting of mist filtration, thermal oxidation, catalytic oxidation, bio-filtration, chemical treatment, adsorption, absorption etc. have been widely investigated during the last few years. Adsorption process is one of the most important odour abatement and controlling process for gaseous streams containing low concentrations of VOCs (Schlegelmilch *et al.,* 2005).It is known that in adsorption the surface of a solid always accumulates a concentration of molecules from its gaseous or liquid environment. The "surface" includes all accessible areas and can therefore be extensive for solids known as adsorbents, that incorporate an inner network of pores, including those with diameters down to molecular dimensions. Adsorbed odorous compounds may simply remain on the adsorbent surface indefinitely if they are stable and relatively unreactive in air. Others, such as reduced sulphur compounds, including hydrogen sulphide, are more or less rapidly oxidised to other products that are mostly less odorous and sometimes not odorous at all. In many instances, the oxidant products are higher in molecular weight and more strongly adsorbed and retained.

Adsorption of VOSCs with Granular Activated Carbon:

Adsorption using granular activated carbon (GAC) is a cost effective and versatile technique for removing VOSCs because of GAC's large surface area and pore volume

(Chingombe et al. 2005). GACs are modified and impregnated (Chiang et al. 2002 and Li et al. 2011)in order to increase their adsorption capacity selectively towards specific organic compounds (Albishri and Marwani, 2016; Ania et al. 2007 and Derylo-Marczewska et al. 2011).

Commercially available adsorbents like GAC and its functionalized materials like FAC-NH_3, FAC-KOH and FAC-NaOH were tested to find out their better adsorption capacity for the removal of malodor in waste water treatment plants. Batch equilibrium analysis is the best tool to know the adsorption capacity of all the adsorbents. In this study, several experiments are conducted to study the batch equilibrium analysis for removing volatile organic components, having very low odor threshold values and contribute towards generation of malodor. Batch analysis was carried out in two steps. In the first step, equilibrium time of adsorption was estimated for different adsorbents for adsorption of each of the odour contributing VOSCs.

In the second step different amounts of adsorbents were used with various concentrations of raw sewage wastewater in order to find out the maximum removal efficiency of each of the adsorbents for a specific VOSC. The adsorption capacity of GAC and FACs were carried out by measuring the concentrations of VOSCs emitted from the sewage waste water taken from a sewage treatment plant before and after adding adsorbents i.e. GAC or FACs.

Assessment of VOSCs:

Three techniques are conventionally used to analyze the concentration of odorous VOSCs at different time intervals with or without using adsorbents during the batch experiment. The techniques used are 1) Olfactometry based technique, 2) Electronic Nose based technique and 3) Analytical technique. The first two techniques are based on sensory analysis and the third one is a GC-MS (Gas Chromatography Mass-Spectrometry) based analysis technique. In the sensory based analysis, use of an electronic nose (E-Nose) is basically an indirect method. The response is non- specific in nature. The system is not applicable for on-site measurement to sense the odor (Micone and Guy, 2007). So assessment of odor can be done by olfactometric technique. In Olfactometry based technique odour intensity can be measured by sniffer panel method. In this technique, a panel consisting a group of trained sniffers is formed by trained persons (Bliss *et al.*, 1996; Cain *et al.*, 1995; Cain, 1980; Patterson *et al.*, 1993) This method is recognized as one of the standard methods to estimate the potentiality of odorous VOCs emitting in and around the waste water treatment plant. On the other hand, specific VOSCs that may be responsible for the malodor, were measured by GC-MS. Removal of odor (estimated by Olfactometry, using a group of trained sniffers) was correlated to the removal of a specific chemical compound with very small odor threshold and larger generation of odor.

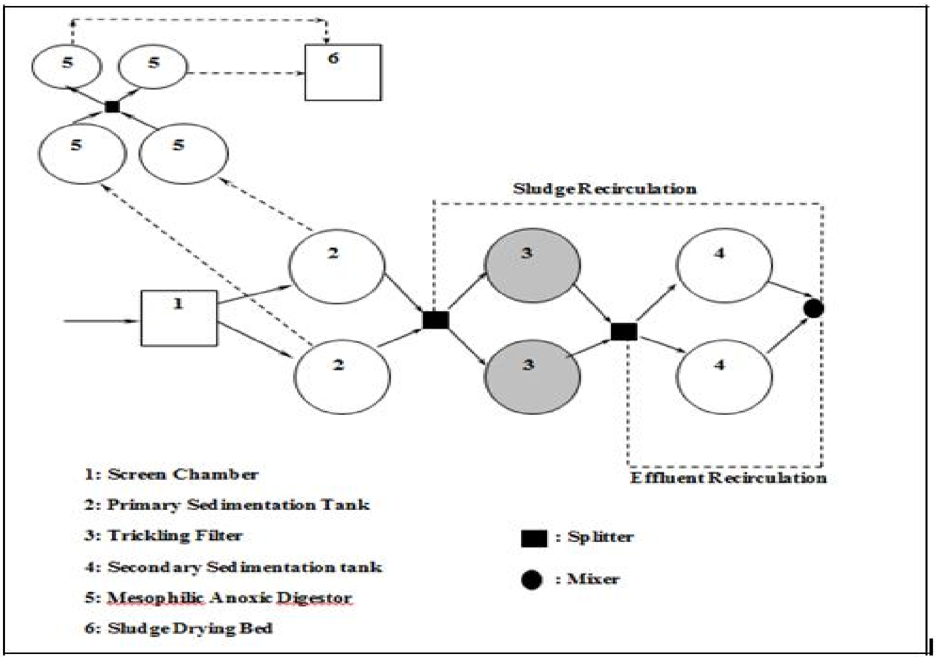


Figure 4.1 Schematic Diagram of Baranagar–Kamarhati Sewage Treatment Plant.

4.1 Experimental

4.1.1 Materials

Adsorption of volatile organosulphur compounds (VOSCs) is a multicomponent adsorption process. For multicomponent batch adsorption study a raw sewage, a source of highest level of malodorous compounds, is collected in a big drum during the period July-September, 2015. Granular Activated Carbon, GAC, (Make:S.D.fine-Chemicals Ltd, India, IMDG Code: 4.2/III; UN: 1362;IATA: 4.2) and Functionalized activated carbons (FAC-NaOH, FAC-KOH and FAC-NH_3) are used as adsorbents.

4.1.2 Experimental procedure:

A case study of olfactometry based batch equilibrium analysis was carried out at the Baranagar-Kamarhati sewage treatment plant (Figure 4.1), which is operated and managed by the Kolkata Municipal Development Authority, Kolkata, India (KMDA). The plant is situated in Mathkol, near Noapara Metro Carshed under Baranagar-Kamarhati Municipality, Baranagar, West Bengal, India (Latitude: 22.6438N;Longitude: 88.3658E).The domestic sewage waste-water is collected from all the house-holds of this particular municipal area and brought into the Dunlop pumping station, which is situated at the middle of this municipal area through sewer-pipes layed underground. The domestic sewage water is taken from this Dunlop pumping station to the waste water treatment plant. The capacity of this plant is 40 MLD (Million Litre per day). The emission level of malodorous compounds is highest in case of raw sewage. Therefore, the sewage water samples were taken from the raw sewage into a big drum during the period of July-September, 2015. The drum was filled with raw sewage, leaving a headspace of around 4000ml and then the lid was tightly locked in-situ using Teflon Tape to prevent any loss of volatile compounds, specifically the VOSCs, by handling during transport and in the laboratory before start of the adsorption and olfactometry based experiments. The ambient air temperature during sampling was 36°C. Samples were collected between 9:30 a.m. and 10:00 a.m. Upon arrival in the laboratory, the jar was weighed. Immediately after that the jar was perforated and then the lid of the sewage water drum was tightly locked and sealed with Teflon seal and tape in order to prevent any leakage of volatile compounds during transportation to the laboratory for completing the experiment of adsorption and olfactometry simultaneously. Weight of the sewage water was taken by differentiation of the weight of the drum filled with sewage water and weight of the empty drum. Experimental time and temperature were noted down. After weighing of the sample drum, the drum was perforated at centre of the lid. Samples of VOSCs were collected from the headspace of the sample drum using a gas sampling pump (Make: Supelco, USA; Model: Escort Elf) shown in Figure 4.2 to pump air samples through small pre-conditioned adsorbent tubes (Make: Supelco, USA; Model: *ORBO 32*; Specification: 6 mm OD, 75 mm in length) as shown in Figure 4.3. Sampling was done at a flow rate of 2 Lmin^{-1}, for 10 minutes thereby pumping in an air volume of 4000 ml. Sorbent tubes were conditioned in the laboratory according to the ambient air sampling methods recommended by the USEPA (Method TO-17), experimented by Leach *et al.,* 1999.Simultaneously, olfactometry was also carried out using panel method, as shown in Figure 4.4. All the tests were carried out inside anodor-free, clean laboratory with selected and trained panelists for psychophysical analysis of odour. The trained sniffers were tested with n-butanol for representativeness, repetitiveness and consistency as per VDI Guidelines for Panel Olfactometry (VDI 3882 Part 1). Immediately after taking the first sample for olfactometry and GCMS analysis, relevant adsorbent was immediately added in the sample for batch adsorption and properly mixed.

Figure 4.2 Escort Elf Air Sampling Pump and Accessories.

After 1.5hr sampling was done at a flow rate of 2 liter per minute, for 10 minutes, olfactometry was carried out simultaneously using a group of trained sniffers using panel method (shown in Figure4.6) and these were repeatedly carried out until equilibrium was attained.

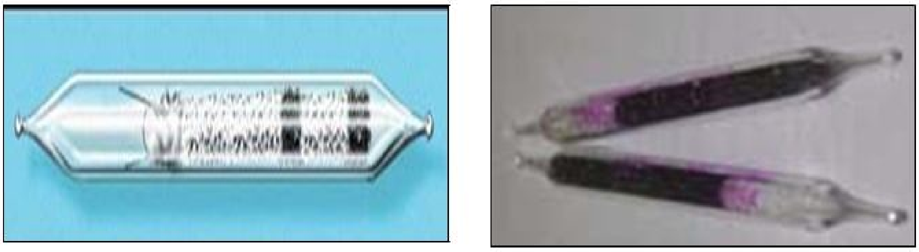


Figure 4.3ORBO 32 sorbent tubes for adsorption of VOSCs and Solvent Desorption Tubes.

Figure4.4 Sampling of VOSCs from headspace of the jar using an Escort Elf airsampling pump using sorbenttubes.

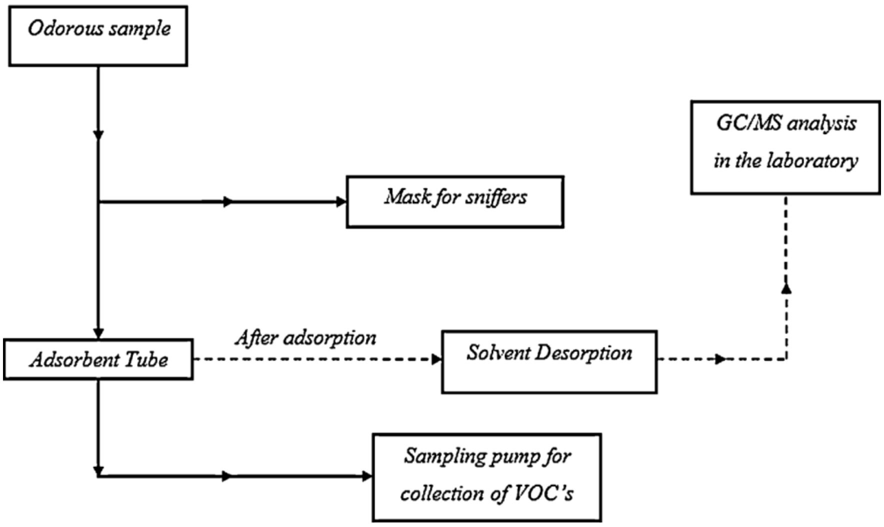


Figure 4.5 Schematic diagram of simultaneous olfactometry and sampling of the odorousVOSCs from headspace of a sampling drum.

4.2 Designing of Experiment

4.2.1 Assessment of odor using Olfactometry in absence of Cationic Surfactant:

All the experiments were performed in an odor-free, clean laboratory with selected group of trained sniffers in order to ensure adequate odour intensity for quantified psychophysical analysis of odor. The sniffers used a portable hood tightly fitted on the Teflon containers to avoid any dilution with ambient air. The sniffing port (nose shaped) of the hood was placed on the sniffer’s nose. The trained sniffers were first smelled with n-butanol for representativeness, repetitiveness and consistency as per VDI guidelines for panel olfactometry. The precursor gas mixture containing VOSCs was collected with Y connector, simultaneously for olfactometric analysis and GC-MS analysis.

In this way, samples were presented to the sniffer panelists (Table 4.1) and sniffers made their decisions before and after adsorption of waste water using GAC and FACs. Decreasing order of odour intensity gives an indication towards the adsorption capacity of activated carbons. After olfactometric analysis of VOSCs from untreated raw sewage, specific amount of adsorbent was added into the sewage sample drum and properly mixed. Samples were then collected at different time intervals using the same method of sampling until an equilibrium condition was reached particularly with respect to the olfactometry outcomes. This experiment was done by batch equilibrium analysis and this analysis was done for several times with GAC and the FACs using varying amount of adsorbents for utilizing the maximum capacity of the same.

Table 4.1 Detail of panel members selected by n-butanol test.

Serial No	Panel Members ID	Age	Sex
1	Sniffer 1	34	Male
2	Sniffer 2	61	Male
3	Sniffer 3	52	Female
4	Sniffer 4	31	Female

4.2.2 Assessment of odor using Olfactometry in presence of a Cationic Surfactant:

Various concentrations (C_1 to C_5) of cationic surfactant, having a very pleasant smell were used for this purpose. Cationic surfactant, of various concentrations, is applied to the sewage samples and mixed well. All the measurements were carried out at six different timings to check the kinetics of adsorption in presence of a surfactant: before mixing surfactant (i.e. 0hr), 1.5hr, 3.0hr, 4.5hr, and 18hr after application of cationic surfactant.

Figure 4.6 Olfactometric Analysis of overall odor.

Odour intensity is the strength of the perceived odour sensation. It is a relative strength of odour above the recognition threshold. It is related to the odorant concentration [Annex IV].

Raw sewage odour concentration and corresponding intensity are correlated by the Beidler's equation,

$I = (k_1 k_2 C)/(1+k_2 C)$. (4.1)

Where values of $k_1$and k_2 are 7.567 and 0.027 respectively (Rajbansi and Sarkar, 2009).

Table4.2 Intensity and nature of odoras per category estimation method.

Intensity	**Nature of Odor**
1	No Odor
2	Very Faint
3	Faint
4	Mild
5	Odorous
6	Strong
7	Very Strong
8	Obnoxious

4.2.3 Control of Odor: Assessment by GC-MS:

Solid Phase Extraction-Solvent Desorption

One of the most common sampling techniques is the adsorption of VOCs on solid sorbents. Once the analytes are trapped into sorbents, they must be released for analysis. The most common extraction techniques are solvent extraction and thermal desorption (TD). Solvent extraction allows higher flow rates, longer sorbent beds and larger total- sample volumes in comparison to TD [Ras*et al.*, 2009;Król*et al.*, 2010;Chiriac*et al.*, 2007]. It is often used for processing passive samples and is said to be the best technique for thermally-labile compounds. However, if the sample is diluted, there is chance of contamination by solvent. Typically, HPLC grade acetonitrile (CH_3CN) is best suited for monitoring a polar compound that is easily transferred efficiently from the charcoal during desorption/solid phase extraction

(Elbir*et al.*, 2007; Woolfenden, 2010). Before analysis, adsorbent tubes were placed inside a refrigerator for some time and 1.0 ml HPLC grade acetonitrile was added as the extraction solvent (ASTM, 1988a; 1988b). Samples were extracted in a 2 ml vial for 15 min. Then extracted samples were stored in a refrigerator until they were analyzed.

Analysis in GC-MS

Extracted samples are analysed using a gas chromatograph (GC) [Make:Thermofisher; Model: Trace 1110, Trace GC] equipped with a Pulse Flame Photometric Detector (PFPD) (Make: Agilent; Model: 5380 PFPD), as it is very selective for determination of low concentration of sulphur compounds in light hydrocarbon matrices like natural gas. The chromatographic column used is GS-GasPro (Length: 60m, Diameter: 0.32mm, 1.80µm) (Make:Agilent; Model: CP8575) and a constant flow rate of the carrier gas (helium) is maintained at 2ml/min. The split ratio is kept at 1:17. Temperature program for the oven is: initial temperature $40^{o}C$, hold for 6min; $40\text{-}120^{o}C$ at $6^{o}C\ min^{-1}$, hold for 5min at $180^{o}C$. Ionization mode of the MS used is electron impact (EI). Detector temperature is kept at $200^{o}C$ with an air flow rate being maintained at 12 ml/min for *air 1* and 13 ml/min for *air 2* with a run time set at 40 min. Compounds are identified by PFPD (mode: *acquiring*) using Chrom-Card software based on their retention times (within ±0.05min of the RT of calibration standard), target and qualifier compounds.

4.3 Result and Discussion

4.3.1 *Olfactomatricbased Result*:

The GAC and FACs are tested for their adsorption capacities for removing the malodor from the waste water treatment plant. Olfactometric analysis of the wastewater sample was observed before and after adsorption using GAC and FACs. Analysis of perception of odour from these sewage samples is given in Table 4.3. From this table it is seen that odor intensity decreases with time for all the adsorbents. However, in case of FAC-NH_3, odor intensity decreases much more with time as compared to other adsorbents. In presence of a cationic surfactant odor intensity decreases more rapidly with time. From Figures 4.7-4.9,it is seen that with increase in surfactant concentration odor intensity decreases very much with time. Generally, the surfactants sustained the intensity of odor until 18hr after spraying if compared to initial level (before spraying). Cationic surfactant kept the level of odor intensity below those of initial level until 18 hr after spraying and particularly showed significant reduction in the odour levels when compared to the initial level at various sampling times after spray (1.5 hr., 3 hrs and 4.5 hrs). Substantial reduction ability of the cationic surfactants with respect to their varying concentrations can be explained on the basis that these elicit detrimental effects on microbial activity responsible for releasing malodor from sewer as well as function as masking agents. This is also a matter of trade-off. However, no further decrease in odor intensity is observed after a certain concentration level of surfactant. In Figures 4.7-4.9 it is seen that the odor intensity decreases with time with more or less similar trend within a surfactant concentration range of 3.5g/l and 4.5g/l. The pleasant odour of cationic surfactant could not mask the malodorous VOSCs beyond the Critical Micellar Concentration (CMC) as there were no further micellar action in between cetrimonium ions and the VOSCs. Immediately after that, the effect of addition of cationic surfactant, in turn, is not effective anymore for decreasing the odor intensity. Surface tension versus concentration ofa cationic surfactant (cetrimide)and an anionic surfactant (SDS[1]) are

---

[1] Sodium dodecyl sulfate, synonymously sodium lauryl sulfate is a synthetic organic compound with the formula $CH_3(CH_2)_{11}SO_4$ Na. It is an **anionic surfactant** used in many cleaning and hygiene products.

shown in Figure 4.10.From this figure it is seen that the surface tension decreases with surfactant concentration upto 550μg/l and afterwards remains constant. This is therefore considered as the Critical Micellar Concentration(CMC)[Annex-V].

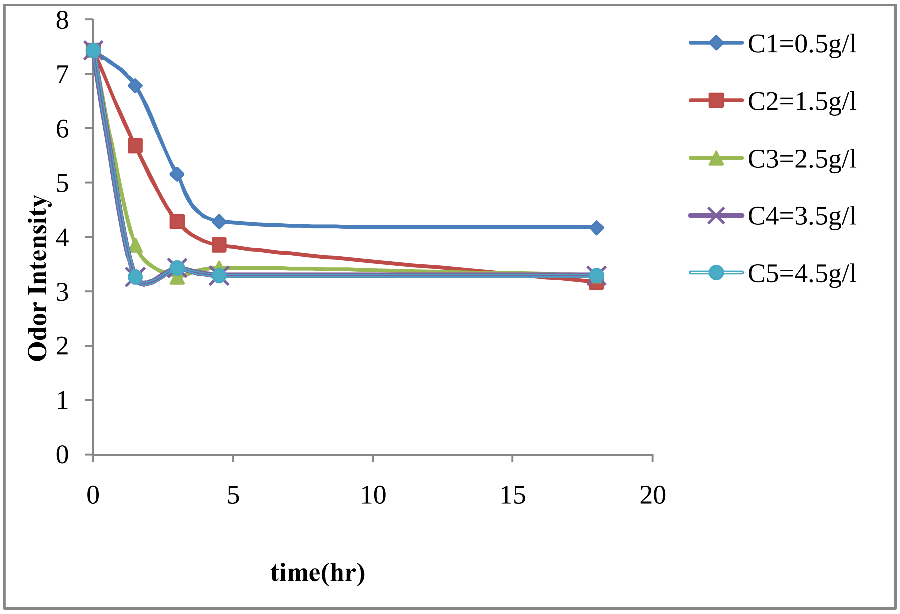


Figure4.7 Odor intensity versus time without adsorbent for various concentrations of raw sewage samples.

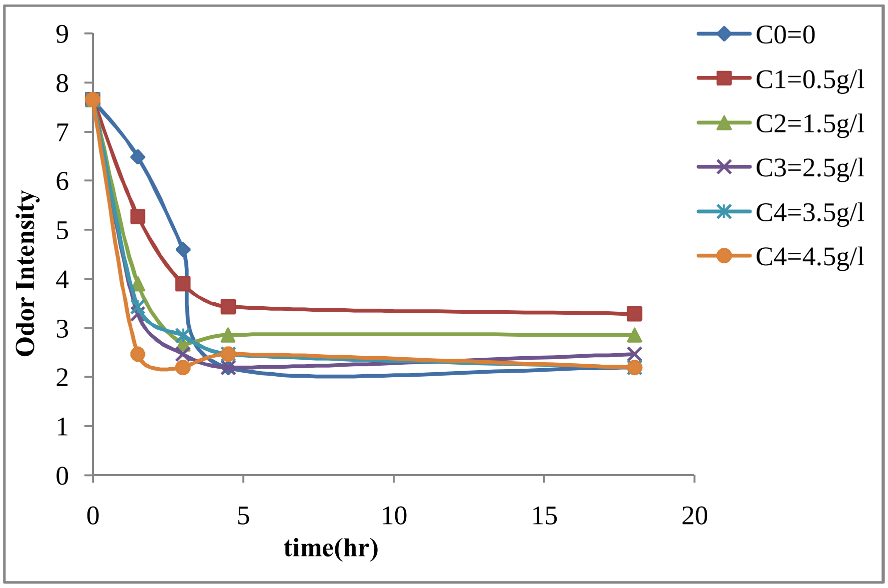


Figure 4.8 Odor intensity versus time in presence of GAC for various concentrations of raw sewage samples.

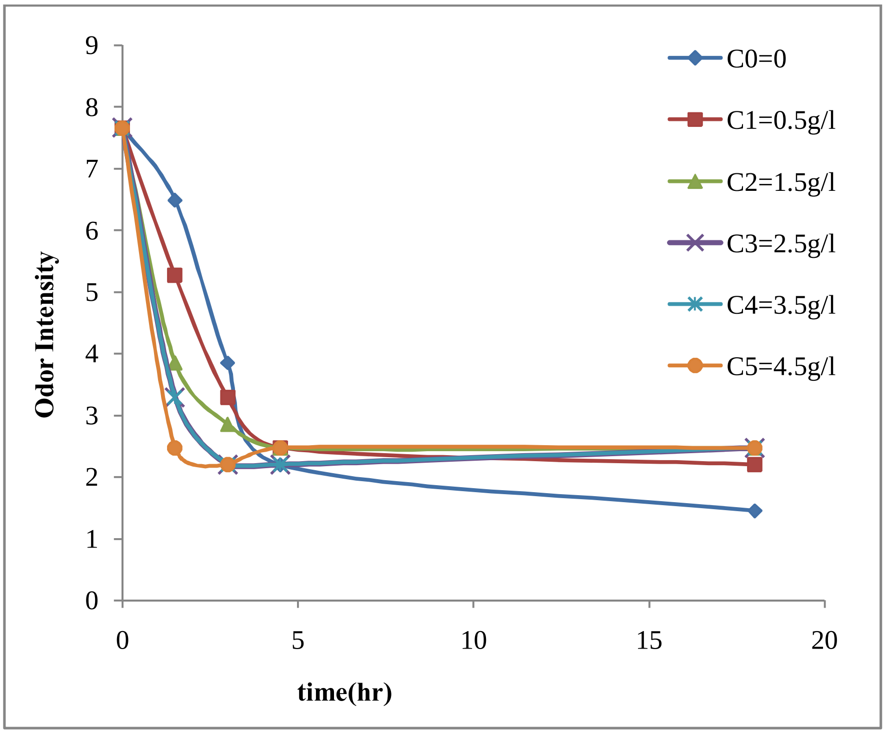


Figure4.9 Odor intensity vuserss time in presence of FAC-NH_3 for various concentrations of raw sewage samples.

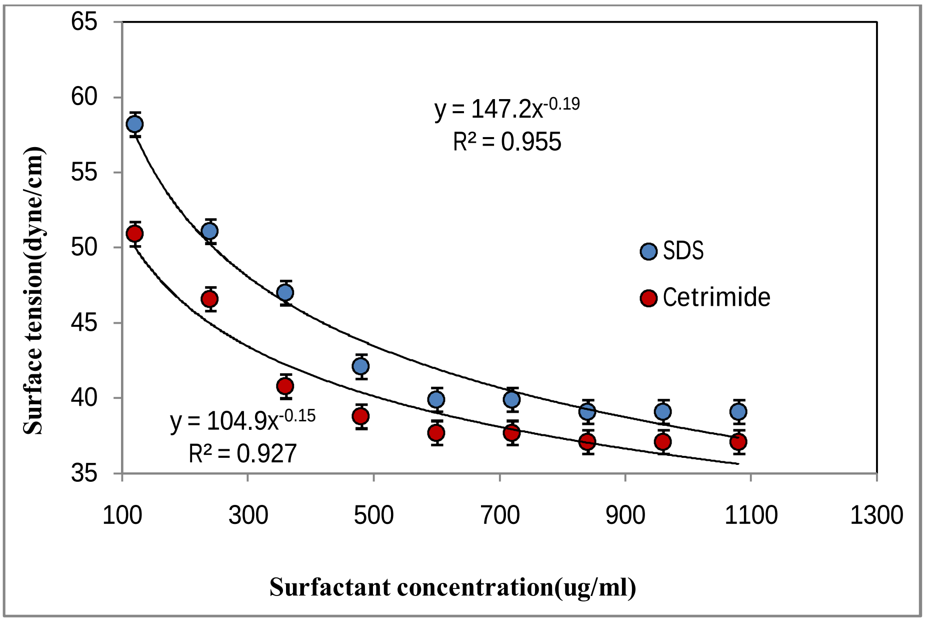


Figure 4.10 Surface tension versus surfactant concentration for a cationic surfactant (Cetrimide) and an anionic surfactant (SDS).

Table4.3 Monitoringodourintensityby psycho-physical outputs for raw sewage samples from Baranagar-Kamarhati STP in absence of a surfactant.

Adsrorbent	Sample No	Time (hr)	Sniffer I			Sniffer II			Sniffer III			Sniffer IV			MeanIntensity
			Tr I	TrII	Avg	Tr I	TrII	Avg	Tr I	TrII	Avg	Tr I	TrII	Avg	
GAC	RS	0	8	7	7.5	8	8	8	7	8	7.5	8	7	7.5	7.661
	RS1	1.5	6	7	6.5	7	7	7	6	6	6	6	7	6.5	6.490
	RS2	3.0	4	5	4.5	5	5	5	4	4	4	5	5	5	4.606
	RS3	4.5	2	3	2.5	3	2	2.5	2	1	1.5	2	3	2.5	2.200
	RS4	18.0	2	3	2.5	3	2	2.5	2	1	1.5	2	3	2.5	2.200
FAC-NH_3	RS	0	8	7	7.5	8	8	8	7	8	7.5	8	7	7.5	7.661
	RS1	1.5	4	5	4.5	5	5	5	4	4	4	5	5	5	4.606
	RS2	3.0	2	3	2.5	3	2	2.5	2	1	1.5	2	3	2.5	2.200
	RS3	4.5	2	1	1.5	2	2	2	1	1	1	2	1	1.5	1.456
	RS4	18.0	2	1	1.5	2	2	2	1	1	1	2	1	1.5	1.456

Cont..

Adsrorbent	Sample No	Time (hr)	Sniffer I			Sniffer II			Sniffer III			Sniffer IV			Mean Intensity
			Tr I	TrII	Avg	Tr I	TrII	Avg	Tr I	TrII	Avg	Tr I	TrII	Avg	
FAC-NaOH	RS	0	8	7	7.5	8	8	8	7	8	7.5	8	7	7.5	7.661
	RS1	1.5	6	7	6.5	7	7	7	6	6	6	6	7	6.5	6.490
	RS2	3.0	3	4	3.5	4	5	4.5	3	4	3.5	4	4	4	3.853
	RS3	4.5	2	3	2.5	3	2	2.5	2	1	1.5	2	3	2.5	2.200
	RS4	18.0	2	1	1.5	2	2	2	1	1	1	2	1	1.5	1.456
FAC-KOH	RS	0	8	7	7.5	8	8	8	7	8	7.5	8	7	7.5	7.661
	RS1	1.5	4	5	4.5	5	5	5	4	4	4	5	5	5	4.606
	RS2	3.0	3	4	3.5	4	5	4.5	3	4	3.5	4	4	4	3.853
	RS3	4.5	2	1	1.5	2	2	2	1	1	1	2	1	1.5	1.456
	RS4	18.0	2	1	1.5	2	2	2	1	1	1	2	1	1.5	1.456

Time variant analysis of perceived odour of a sewage sample before and after adsorption using panel olfactometry and corresponding percentage removal values are given in Table 4.4. It shows that the transient behavior of perceived odouris dependent on the changes in overall concentration of various odorous compounds before and after adsorption and corresponding percentage removal of odour with respect to the same for a particular feed sample.

Table 4.4 Timevariant analysis of perceived odour of a sewage sample before and after adsorption using panel olfactometry and corresponding percentage removal values. *Date of Experiment: 16.09.2015. Weight of sewage water: 10kg. Adsorbent: FAC-NH_3. Weight of adsorbent: 12g.*

Sample No	Sample ID	Time (hr)	Before adsorption Odor concentration O_1(OU/m^3)	After adsorption O_2(OU/m^3)	Odor removal $[(O_1-O_2)/O_1]\times100\%$
1	RS	0	316.2277	316.2277	0
2	RS1	1.5	316.2277	199.5262	36.87
3	RS2	3.0	316.2277	50.1187	84.13
4	RS3	4.5	316.2277	14.125	95.53
5	RS4	18	316.2277	12.5892	96.01

In this batch analysis it is observed that the samples become odourless around 4.5hr after the application of 12g of FAC-NH_3, showing a very good adsorption capacity of the same (Figure 4.11)

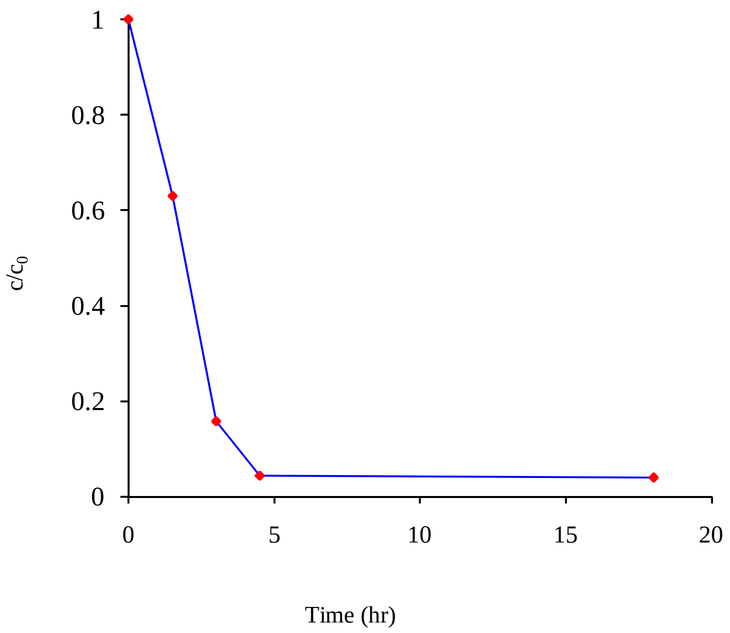


Figure 4.11 Relative odor concentration (*olfactometry*) versus time in batch equilibrium adsorption experiment.

4.3.2 GC-MS based outputs:

Sewage odour concentration, contributed by a combination of specific VOSCs, was also individually estimated by a GC equipped with Pulse Flame Photometric (PFPD) Detector for the volatile organo-sulphur compounds, specifically responsible for odour formation, before and after adsorption. The peak areas of specific compounds for samples collected before and after adsorption using FAC-NH_3 as the adsorbent at different time intervals are shown in Table 4.5(a,b,cand d) for the three principal compounds detected with low odour threshold values. The relative odor concentration versus time (GC-MS based output) are shown in Figure 4.12(a,b,c and d).

Table 4.5 Time-variant concentration of (a) methyl mercaptan (CH_3SH), (b)ethyl mercaptan (C_2H_5SH), (c) dimethyl sulphide (CH_3SCH_3) (d) carbon disulfide (CS_2), before and after adsorption along with percentage removal. *Date of Experiment: 16.09.2015. Weight of sewage water: 10kg. Adsorbent: FAC-NH_3. Weight of adsorbent: 12g.*

(a)

Component	Sample No	Sample ID	Time (hr)	CH_3SH (GC-MS analysis)		CH_3SH Removal $[(A_1-A_2)/A_1]\times100$ %
				Peak area (feed) A_1	*Peak area (after adsorption)* A_2	
Methyl mercaptan (CH_3SH)	1	RS	0	118322.31	118322.31	0
	2	RS1	1.5	118322.31	98030.03	17.154
	3	RS2	3.0	118322.31	24847.69	79.07
	4	RS3	4.5	118322.31	5206.168	95.61
	5	RS4	18	118322.31	3525.996	97.02

(b)

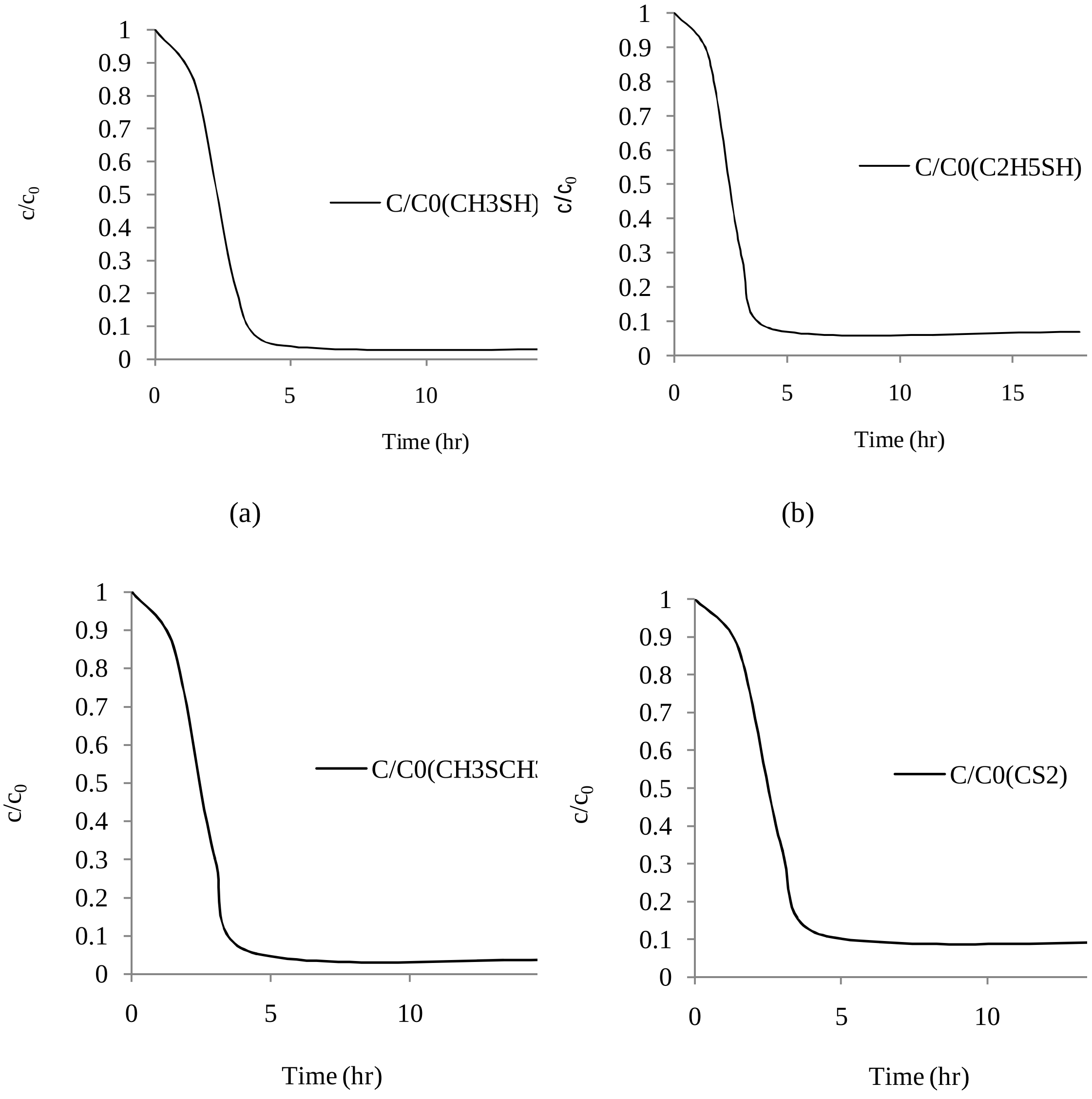
Ethyl mercaptan (C_2H_5SH)	1	RS	0	221942.74	221942.74	0
	2	RS1	1.5	221942.74	193667.23	12.74
	3	RS2	3.0	221942.74	62277.133	71.94
	4	RS3	4.5	221942.74	16934.231	92.37
	5	RS4	18	221942.74	15624.76	92.96

(c)

Dimethyl sulphide (CH_3SCH_3)	1	RS	0	128086.67	128086.67	0
	2	RS1	1.5	128086.67	109770.28	14.31
	3	RS2	3.0	128086.67	38912.73	69.62
	4	RS3	4.5	128086.67	7224.08	94.36
	5	RS4	18	128086.67	5174.7	95.96

(d)

Carbon disulfide (CS_2)	1	RS	0	224366.35	224366.35	0
	2	RS1	1.5	224366.35	194503.19	13.31
	3	RS2	3.0	224366.35	74893.73	66.62
	4	RS3	4.5	224366.35	24366.43	89.14
	5	RS4	18	224366.35	21068.11	90.61



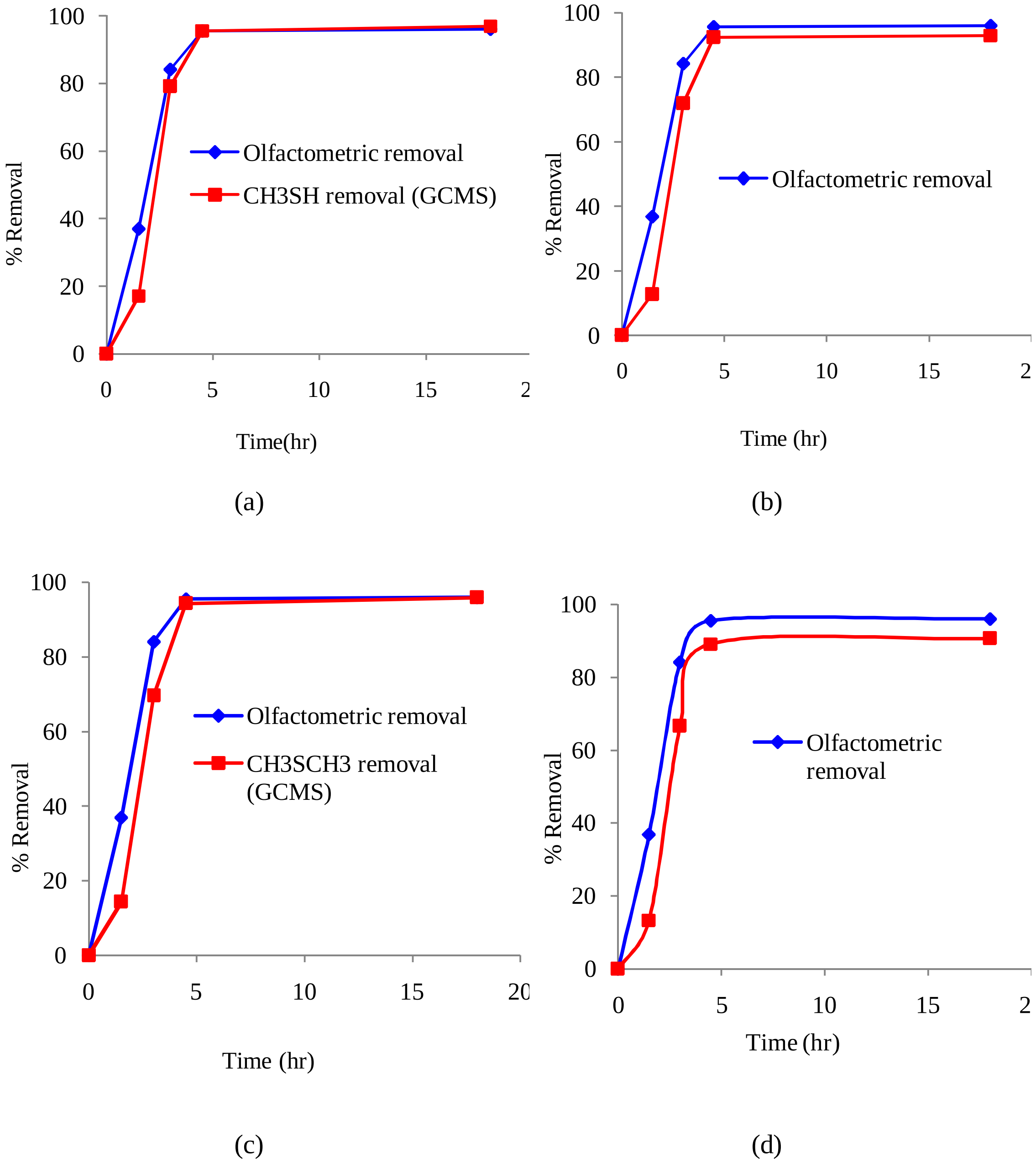
(a) (b)

(c) (d)

Figure 4.12 Time-variant relative concentration of four VOSCs a) CH_3SH, b) C_2H_5SH, c) CH_3SCH_3, d) CS_2 (Detector GC-PFPD) vs time.

Outputs from olfactometry and the same using GC-MS show avery similar trend and these are shown in Figure 4.13. It is observed that, after addition of FAC-NH_3upto 2hr, olfactometry based outputs for % removal of odour did not tally much with the same from GC-MS based outputs for the four different compounds, namely a) CH_3SH, b) C_2H_5SH, c) CH_3SCH_3 and d) CS_2.The rate of adsorptionof methyl mercaptan (CH_3SH) is faster than that of the other three compounds during this period of time. Overall odor did reduce to the same extent as component specific adsorption after approximately 2.5hr. This is because methyl mercaptan has got predominantly low threshold concentration.

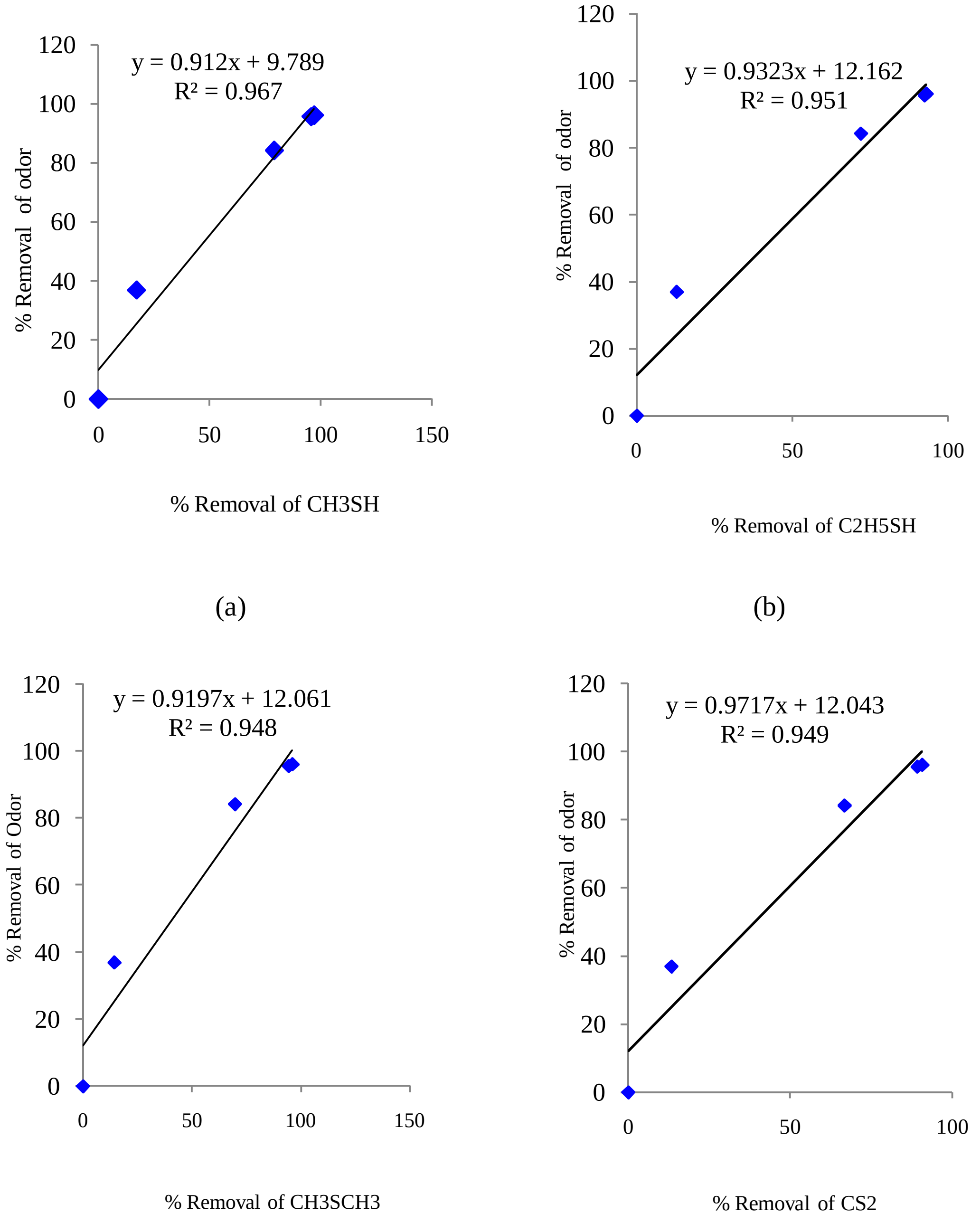
However, equilibrium is achieved more or less in the same time for all VOSCs, approximately 4.5 hr after FAC-NH_3 is added. Odor contributing capacity of these four organo sulphur compounds is measured by linearization of the percentage removal of overall odor (*Olfactometry output*) versus percentage removal of relative concentrations of four compounds (see Figure 4.14).Figure 4.14 revealed that the linear correlation of methyl mercaptan (R^2=0.967) is very high as compared to ethyl mercaptan (R^2=0.951), dimethyl sulphide (R^2=0.948) and that of carbon disulphide (R^2=0.949). So it can be concluded that methyl mercaptan has a large odor contributing potential of the tested sewage waste water sample with respect to the other compounds. For other VOSCs too, removal of overall odour (olfactometry based) is nearly at par with the removal of the specific VOSC.



(a) (b)

(c) (d)

Figure4.13 Percentage removal of overall odor (*olfactometry based output*) and percentage removal of four VOSCs by adsorption (component specific analysis; detector: GC-PFPD) versus time.a) CH_3SH, b) C_2H_5SH, c) CH_3SCH_3 and d) CS_2.



(a) (b)

(c) (d)

Figure 4.14 Percentage removal of odor (*Olfactometry output*) versus percentage removal of each of the four VOSCs.a) CH_3SH, b) C_2H_5SH, c) CH_3SCH_3, d) CS_2.

From the GC-MS output it is seen that the percent removal of specific component with time is lower in presence of cationic surfactant than in absence of the surfactant.Figure 4.15 and 4.16 reveal the adsorption capacity in terms of the percent removal of specific component (VOSC) with time,in presence and in absence of a cationic surfactant (cetrimide).

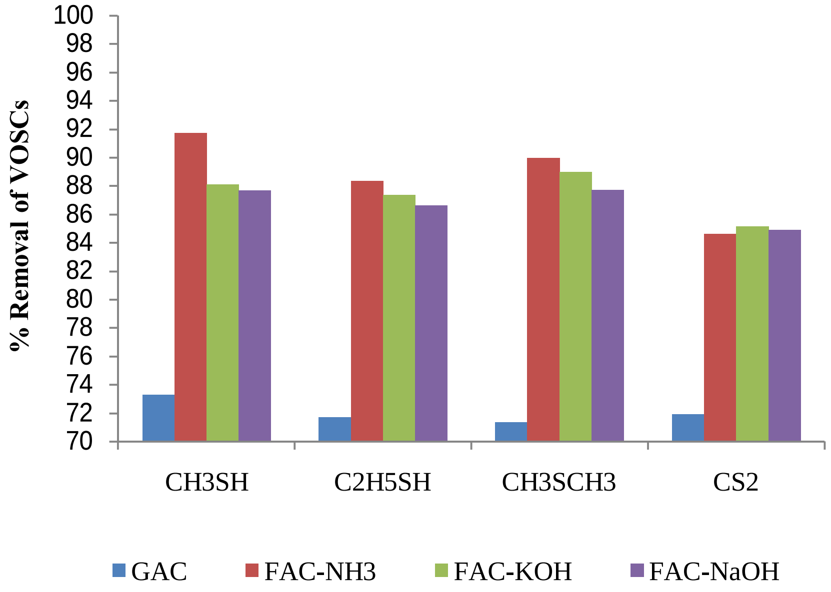


Figure4.15 Percent removal of differentVOSCs [Detector: GC-PFPD] using various adsorbents: GAC, FAC-NH_3, FAC-KOH and FAC-NaOH in presence of a cationic surfactant (cetrimide).

It may be the reason that in absence of a surfactant, the VOSC molecules undergo pure adsorption by pore diffusion (GAC) as well as film diffusion (FACs). So percentage removal becomes high for each of the VOSCs. However, in presence of surfactants, maximum number of pores are blocked primarily by the surfactant molecules. So percent removal occurs maximum through surface diffusion and then pore diffusion. In a working pH of 6.5, the surface of both GAC and the FACs remain negative. In this situation, the cationic surfactant gets attracted towards the carbon surface and fast fills in the pores by pore diffusion. Thus in presence of a cationic surfactant, whose concentration is less than its CMC, much less amount of VOSCs get physi-sorbed through pore diffusion. In this case the functional groups help forming coordination compounds by surface complexation with the VOSCs. Thus FACs becomes very useful for removal of odour in presence of a surfactant.

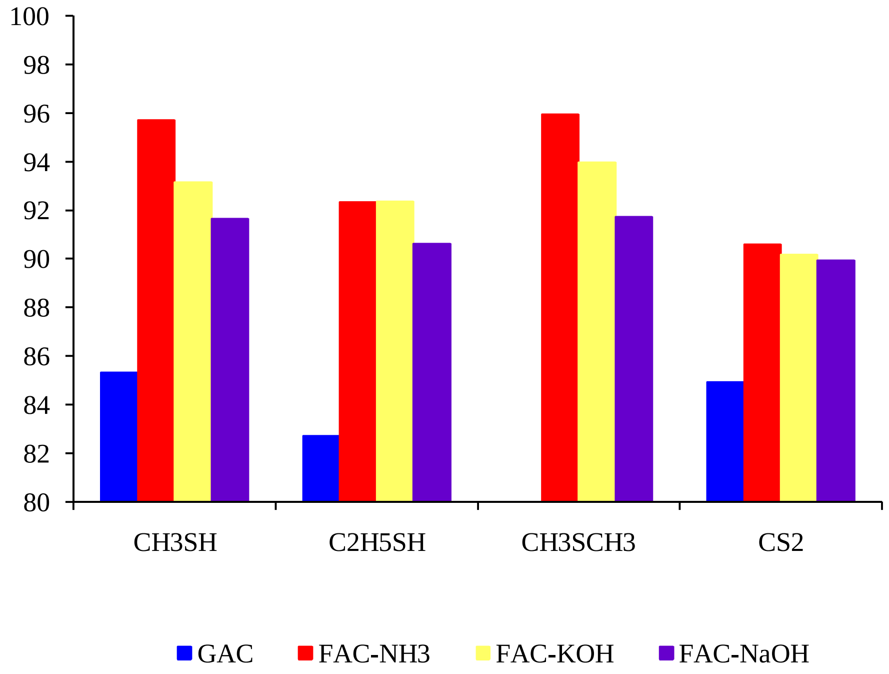


Figure 4.16 Percent removal of differentVOSCs [Detector: GC-PFPD] using various adsorbents: GAC, FAC-NH_3, FAC-KOH and FAC-NaOH in absence of a surfactant.

4.4 Mechanism of adsorption on FACs

Adsorption of mercaptans using activated carbon is pH dependent and enhances in presence of water. Most probably, oxidation takes place because active oxygen radicals are being produced by adsorption of oxygen upon functionalised activated carbon surfaces (Teresa et al. 2002).Oxidation proceeds due to the surface reaction between adsorbed mercaptan and active oxygen radicals. Changes in surface chemistry likely affect the adsorption of methyl mercaptan. As demonstrated elsewhere, MM, after getting adsorbed on activated carbons, is oxidized to Dimethyl Disulphide (DMDS) (Song et al. 2010).

$$CH_3SH \xrightarrow{K_a} CH_3SH_{ads} \tag{4.1}$$

$$CH_3SH_{ads} \xrightarrow{K_s} CH_3SH_{ads-L} \tag{4.2}$$

$$2CH_3SH_{ads-L} + O^*_{ads} \xrightarrow{K_{R1}} CH_3SSCH_{3ads-L} \tag{4.3}$$

Proposed reaction pathways (arrows represent chemical equilibrium) should depend on the apparent pH of the system because MM is able to dissociate (pK_a = 10.3). Moreover, the oxidation of methyl mercaptan to dimethyl di-sulfide can be enhanced by alkali functionalization of activated carbon using various bases like sodium hydroxide, potassium hydroxide, ammonium hydroxide etc. Water is present in the system and the carbon surface is able to produce excess oxygen radicals and hydroxyl radicals. This automatically enhances the oxidation of mercaptans.

There is an apparent improvement of adsorption-catalytic properties of nitrogen containing carbons in desulfurization. The same can be explained from the point of view of the electronic theory of catalysis. The extra *п*- electrons of pyrollic and quaternary nitrogen occupies the high energy states in the conduction band. It is likely that from there, they can be transferred to the adsorbed oxygen and super oxide ions (O_2^{2-}) can be formed (Andrey etal. 2002).Those super oxide ions (O_2^{2-}) can easily trigger the formation of HO* and HO_2* radicals while reacting with water. All the species are much more reactive than molecular oxygen and may oxidize sulphurcompounds, when these are adsorbed on carbon surface.

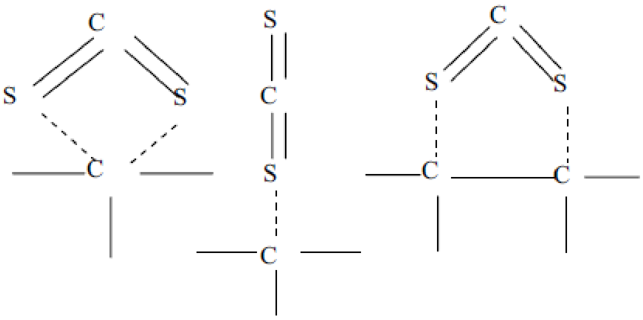
$$CH_3SCH_{ads-L} \xrightarrow{K_H} CH_3S^-_{ads} + H^+ \qquad (4.4)$$

$$2CH_3S^-_{ads} + O^*_{ads} \xrightarrow{K_{R2}} CH_3SSCH_{3ads-L} + O^{2-} \qquad (4.5)$$

$$2H^+ + O^{2-} \rightarrow 2H_2O \qquad (4.6)$$

Where K_a, K_S, K_H, K_R are the equilibrium constants for the processes of adsorption, gas solubility, dissociation and surface reaction.

The adsorption of CS_2 vapors by carbon appears to involve hydrophobic interactions between the CS_2 and C-C layer planes of carbon (Goyal and Dhawan 2009) which may be represented as:



The formation of such C-S complexes has been suggested by Yang et al, 2006.

Chapter 5

Methodology III

Kinetic Study: *Pseudo Kinetics, Pore and Film Diffusion*

5.0 Foreword

Adsorption refers to the physico-chemical process in which the molecules adhere on the surface of the adsorbents. The physical process is due to London Dispersion forces[1] and the chemisorption is due to ionic, covalent or metallic bond that can appear at the active sites on the surface of the adsorbents (Christmann, 2012).The liquid phase adsorption capacity depends on several factors like: pH of the solution used, pore size distribution of the active surface, temperature of the process, molecular size of the substances that adhere to the active surface.

The liquid phase concentration of VOSCs was estimated using Henry's law constant. As the liquid phase concentration of VOSCs is very low in waste water, the Henry's law constant is applicable to interchange the gas phase concentration into liquid phase concentration [See Annex-IV] The values of Henry's law constant for methyl mercaptan is 0.39M/atm, ethyl mercaptan is 0.28M/atm, di-methyl sulfide is 0.16 M/atm and that of CS_2 is 0.055M/atm. The dominating sulphur compounds that occur in the sewer atmosphere are hydrogen sulfide (H_2S), methyl mercaptan (MeSH), ethyl mercaptan (EtSH) and dimethyl sulfide (DMS). (Eric C. Sivret, 2016). Two of the dominating odour contributing compounds found in sewage waste water, namely methyl mercaptan (*odor threshold = 0.0005 ppm*) and ethyl mercaptan (EtSH) [*odor threshold = 0.0003 ppm*]were selected for this part of the study for further investigation. For this study, these two compounds were selected because of their

---

[1] The**London dispersion force** is the weakest intermolecular **force**. The **London dispersion force**is a temporary attractive **force** that results when the electrons in two adjacent atoms occupy positions that make the atoms form temporary dipoles. This **force** is sometimes called an induced dipole-induced dipole attraction.

natural abundance in sewage systems. Since there was limited information about the kinetics of adsorption in relation to these compounds, it was a good opportunity to establish the pseudo-kinetic models of these odour contributing mercaptans.

Kinetic study helps to understand the adsorption mechanism of solute onto an adsorbent. Adsorbates can adsorb either physically or chemically to an adsorbents surface. Physi-sorption is based on the Van der Waals interaction between the adsorbate and the substrate and also between the adsorbed molecules. Whereas, chemisorption occurs when there is formation of a chemical linkage between adsorbate and substrate. So, kinetic study is carried out here in order to determine the adsorption mechanism of methyl mercaptan and ethyl mercaptan by various adsorbents. In this study, the well-known first-order kinetic model of Lagergren (1898) and the second-order kinetic model of Ho and McKay 1999are used in order to examine whether chemical reaction is the rate-controlling step for the mechanism of adsorption of model sewage water containing methyl mercaptan and ethyl mercaptan. The applicability of Lagergren based pseudo-kinetic models is discussed several times by various researchers (Ahmad *et al.* 2007; Ho 2006; Tang *et al.* 2012).

Describing adsorption on adsorbents requires an understanding not only of equilibrium behaviour but also of mass transfer (transport) phenomena. In principle, adsorption kinetics can be determined by several processes:

- Transfer of molecules from the bulk phase to the outer surface of the particle through a fluid boundary layer (film) surrounding the particle (external mass transfer).
- Diffusion of molecules through the liquid in the pores (pore diffusion)
- Diffusion of already adsorbed molecules along the surface of the pores (surface diffusion).

- Elementary processes of adsorption and desorption.

Investigation of diffusion mechanism is done with the help of intra-particle diffusion model and film diffusion model.

5.1Experimental

5.1.1Chemicals

For the kinetic study, a raw sewage solution containing 1.357mg/l of methyl mercaptan and 0.975mg/l of ethyl mercaptan is used. Mechanism for adsorption kinetics is studied using adsorbents like granular activated carbon, GAC (Make:S.D.fine-CHEM Ltd, India, IMDG Code: 4.2/III; UN: 1362;IATA: 4.2) and different functionalized activated carbons (FAC-NH_3, FAC-NaOH and FAC-KOH). Functionalization of GAC is described in details in Chapter III.

5.1.2 Experimental procedure:

12kg of raw sewage was taken into a big drum, leaving a headspace of around 4000ml during the period of July-September, 2015. Then the lid of the drum was tightly locked in-situ using Teflon Tape to prevent loss of volatile compounds by handling during transport and in the laboratory before the start of adsorption.12g each of the adsorbents (GAC, FAC-NH_3, FAC-NaOH and FAC-KOH) was added into the solution separately. Samples are collected initially and every1hr interval invapour phase using sorbent tubes connected to a gas sampling pump until equilibrium is reached. Once the analytes are trapped into sorbents, they must be released for analysis. Before analysis, adsorbent tubes were placed inside a refrigerator for some time and 1.0 ml HPLC grade acetonitrile was added as the extraction solvent (ASTM, 1988a; 1988b). Samples were extracted in a 2 ml vial for 15 mins. Then extracted samples were analyzed by a gas chromatograph (GC) (Make:Thermofisher; Model: Trace 1110, Trace GC) equipped with a Pulse Flame Photometric Detector (PFPD)

(Make: Agilent; Model**:** 5380 PFPD).

5.2Kinetic models

5.2.1*Pseudo First and Second Order Kinetics*

Two widely used kinetic models, proposed by Lagergren, Ho and McKay were used for studying the kinetics of multicomponent adsorption of volatile organosulphur compounds.

The pseudo first order kinetic model is expressed by the following equation:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \qquad (5.1)$$

Where, q_e is the amount of VOSCs adsorbed at equilibrium (g adsorbate/L/g of adsorbent), q_t is the amount of VOSCs adsorbed at time *t* (g adsorbate/L/g of adsorbent) and k_1 (min^{-1}) is the pseudo first-order rate constant. Integrating Eq. (5.1) for the initial conditions q_t = 0 at *t* = 0, we get the linearized form of the model as given below:

$$\log(q_e - q_t) = \log q_e - \frac{k_1.t}{2.3} \qquad (5.2)$$

Plotting $\log(q_e - q_t)$ versus *t*, the values of k_1 and q_e are determined from the slope and intercept respectively.

The second-order kinetic model by Ho and McKay (1999**)** is expressed as follows:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \qquad (5.3)$$

where k_2 (g adsorbate/L/g adsorbent. min) is the pseudo second-order rate constant. Integrating Eq. (5.3) for the initial conditions: at *t* = 0; q_t = 0 gives the linear form, as expressed below:

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2 {q_e}^2} \qquad (5.4)$$

Following equation (5.4), the values of q_e and $k_2$are determined from the intercept and slope of the plot of (t/q_t) versus t, respectively.

5.2.2*Adsorption mechanism by the intra-particle diffusion model*

The intra-particle diffusion model, introduced by Weber and Morris (1963)is one of the most commonly used techniques for identifying the diffusion mechanism (Tang *et al.* 2012). The model can be expressed as follows:

$$q_t = k_i t^{1/2} + I \qquad (5.5)$$

Where$k_i$is the intra-particle diffusion rate constant (g adsorbate/L/g adsorbent.min$^{1/2}$) and I(g adsorbate/L/g adsorbent) is a constant, which approximates the boundary-layer thickness. Larger values of I indicatemore effective boundary layer for masstransfer. When the adsorption mechanism follows an intra-particle diffusion processand this becomes a rate-controlling step, the plot of $q_t$versus $t^{1/2}$ produces a straight line that passes through the origin.

5.2.3*Boyd's film diffusion model*

In order to investigate the contribution of film resistancesduring adsorption of methyl mercaptan and ethyl mercaptan, Boyd's film diffusion model is used (Boyd *et al.* 1947). Te underlying assumption is that the primary resistance to diffusion is due to the boundary layer present around the adsorbent particle. The film diffusion model is given below:

$$F(t) = 1 - \left(\frac{6}{\Pi^2}\right) \sum_{n=1}^{\infty} \left(\frac{1}{n^2}\right) \exp\left(-n^2 Bt\right) \qquad (5.6)$$

Where *F(t)* is the fractional attainment of equilibrium, at different times, *t* (min) and *Bt* is a function of *F(t)*. *F(t)* can be expressed as $F(t) = \frac{q_t}{q_e}$,where q_t and q_e are the amounts of VOSCs adsorbed at time *t* and at equilibrium respectively. Reichenberg (1953) evaluated the approximations given below, by applying Fourier transform and then integrated equation (5.6).

When the value of *F(t)* is greater than 0.85 then,

$$Bt = 0.4977 - \ln(1 - F(t)) \qquad (5.7)$$

With *F(t)* lower than 0.85, *Bt* is given by the following equation:

$$Bt = \left(\sqrt{\Pi} - \sqrt{\Pi - \left(\frac{\Pi^2 F}{3} \right)} \right)^2 \qquad (5.8)$$

If the plot of *Bt* against time produces a straight line that passes through the origin, then it can be concluded that the adsorption process is governed by intra-particle diffusion. If the plot, either linear or nonlinear, does not pass through the origin, it can be concluded that film-diffusion or chemisorption is the major rate-controlling factor during the adsorption process.

5.3Results and Discussion

5.3.1*Kinetic Study*

Two widely used kinetic models, proposed by Lagergren and Ho are used for the study of kinetics of the multi-component adsorption of methyl mercaptan and ethyl mercaptan. From the pseudo-first order and pseudo-second order kinetic plots for the adsorption of methyl mercaptan and ethyl mercaptan, itis observed that equilibrium adsorption is attained after approximately 18 hours for both methyl mercaptan and ethyl mercaptan after adsorption with GAC and FACs. Two kinetic models, namely pseudo-first order[Eq. (5.1)] and pseudo-second order [Eq. (5.3)] are parameterized. The rate constants k_1, k_2 and estimated values of q_e are obtained from the slopes and intercept of the linear plots (see Table5.1) of $\log(q_e - q_t)$ versus *t* [refer Eq. (5.2)] and(t/q_t) versus *t* [refer Eq. (5.4)]. It is observed that pseudo-second order kinetic model gives the best fit in case of these four adsorbents, namely GAC, FAC-NH_3, FAC-NaOH and FAC-KOH. From the correlation coefficient given in Table 5.1and the pseudo first order and pseudo second order plots given in Fig. 5.1-Fig. 5.4, it is seen that for the adsorption of methyl mercaptan and ethyl mercaptan on GAC, the pseudo-second order model gives a better fit in comparison to the pseudo first order model. Many researchers observe similar result for the adsorption of VOSCs by activated carbon (Dural *et al.* 2011).From the correlation coefficients of the pseudo first order and pseudo second order plots for both methyl mercaptan and ethyl mercaptan with FAC-NH_3, FAC-NaOH and FAC-KOH as the adsorbents, it can be concluded that the pseudo second order model fits much better than the pseudo first order model. This may be due to additional chemisorption that takes place on top of pore diffusion and physical adsorption for the functionalized adsorbents like FAC-NH_3, FAC-NaOH and FAC-KOH (Low,1960;DinMohd*et al.,*2009). This shows that methyl mercaptan and ethyl mercaptan adsorb more by chemisorption than pure physical adsorption with all these adsorbents.

Table 5.1 Estimated parameters of pseudo-first order and pseudo-second order kinetic models for adsorption of methyl mercaptan and ethyl mercaptan using GAC, FAC-NH_3, FAC-NaOH and FAC-KOH as the adsorbents in absence of a cationic surfactant.

Adsorbent	Component	C_0 (mg/L)	$q_{e,exp}$ (mg/L/g adsorbent)	Pseudo-first order			Pseudo-second order		
				$q_{e,cal}$ (mg/L/g adsorbent)	k_1 (1/min)	R^2	$q_{e,cal}$ (mg/L/g adsorbent)	k_2 (mg/L min)	R^2
GAC	methyl mercaptan	1.357	1.315	0.6383	0.0115	0.927	1.422	0.1139	0.987
	ethyl mercaptan	1.95	1.373	0.8193	0.0012	0.959	1.3259	0.0723	0.987
FAC-NH_3	methyl mercaptan	1.357	1.361	1.0342	0.0002	0.968	2.0271	0.0638	0.986
	ethyl mercaptan	1.95	1.401	1.0475	0.0009	0.969	1.296	0.066	0.983
FAC-NaOH	methyl mercaptan	1.357	1.3241	0.9529	0.0005	0.975	2.0755	0.0051	0.985
	ethyl mercaptan	1.95	1.359	1.0923	0.0007	0.926	1.1238	0.0042	0.98
FAC-KOH	methyl mercaptan	1.357	1.331	0.8447	0.0014	0.916	1.6475	0.0735	0.984
	ethyl mercaptan	1.95	1.35	2.0491	0.0008	0.9099	1.1016	0.0981	0.981

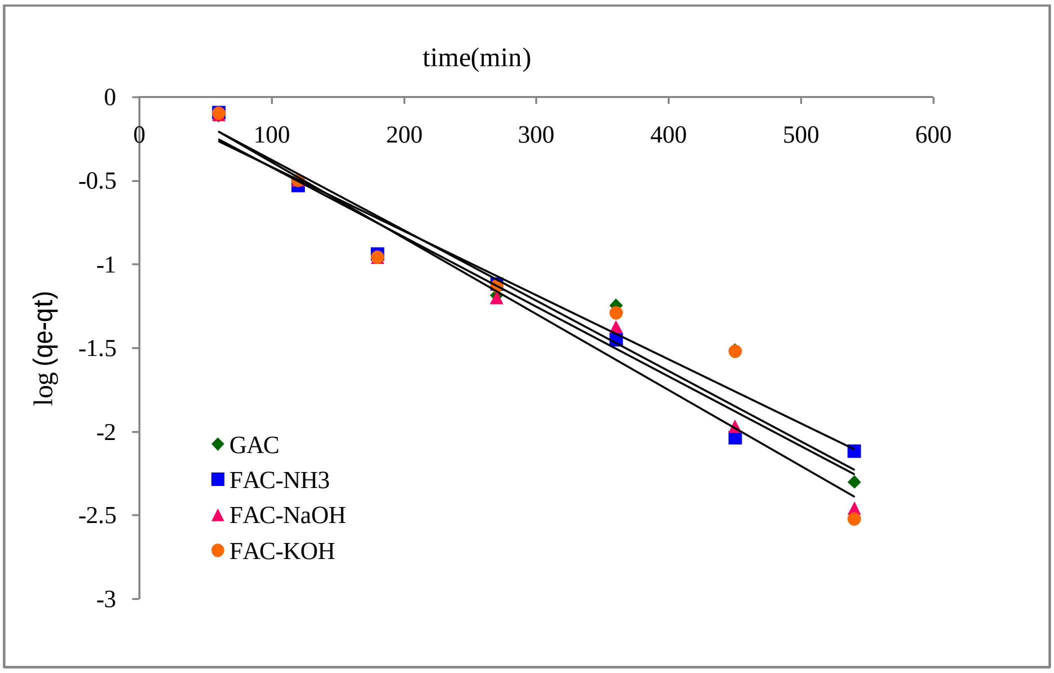


Figure 5.1 Pseudo-first order kinetics for *methyl mercaptan* in absence of a surfactant.

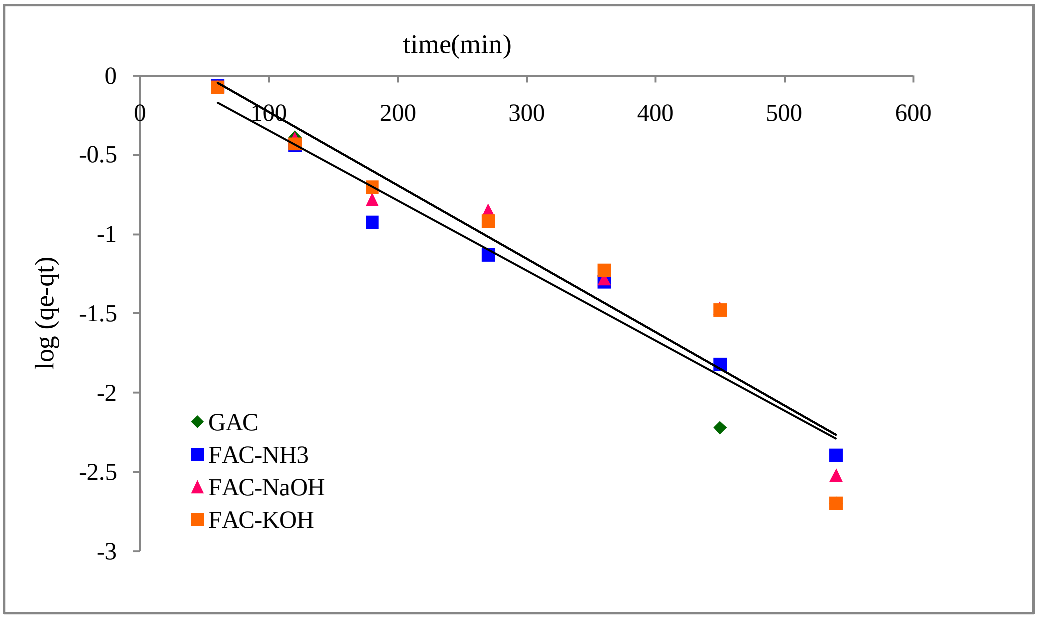


Figure 5.2 Pseudo-first order kinetics for *ethyl mercaptan* in absence of surfactant.

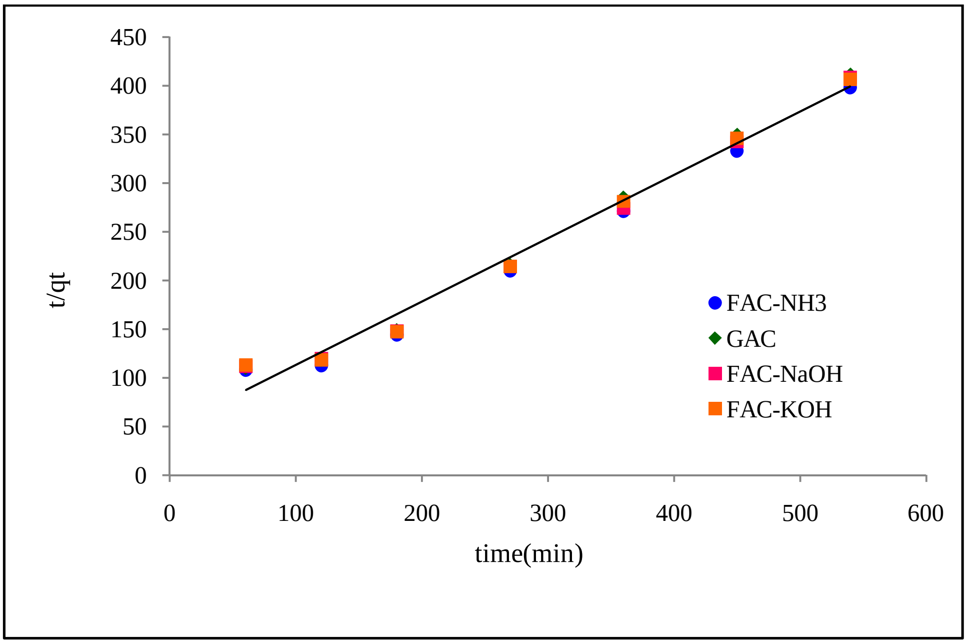


Figure 5.3 Pseudo-second order kinetics for *methyl mercaptan* in absence of surfactant.

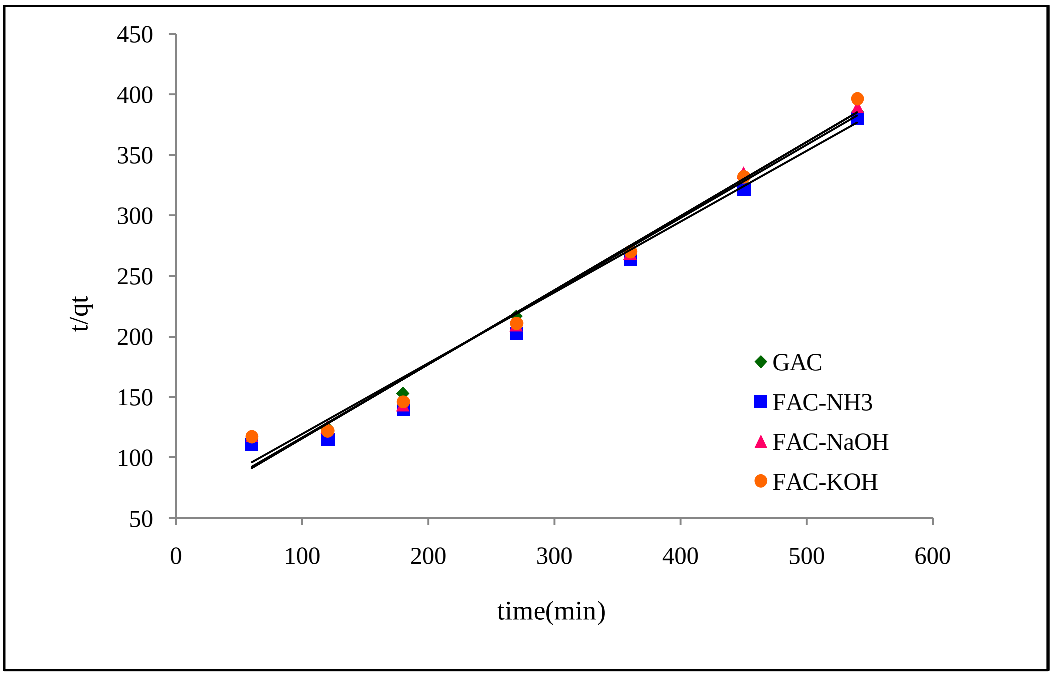


Figure 5.4 Pseudo-second order kinetics for *ethyl mercaptan* in absence of surfactant.

Table 5.2 Estimated parameters of pseudo-first order and pseudo-second order kinetic models for adsorption of methyl mercaptan and ethyl mercaptan by GAC, FAC-NH_3, FAC-NaOH and FAC-KOH in presence of a cationic surfactant (Cetrimide).

Adsorbent	Component	C_0 (mg/L)	$q_{e,exp}$ (mg/L/g adsorbent)	Pseudo-first order			Pseudo-second order		
				$q_{e,cal}$ (mg/L/g adsorbent)	k_1 (1/min)	R^2	$q_{e,cal}$ (mg/L/g adsorbent)	k_2 (mg/L min)	R^2
GAC	methyl mercaptan	1.357	0.8135	0.9315	0.0012	0.933	0.847	0.01023	0.997
	ethyl mercaptan	1.95	0.6135	0.9209	0.0005	0.938	0.722	0.01139	0.996
FAC-NH_3	methyl mercaptan	1.357	1.102	2.0475	0.0009	0.907	0.996	0.016	0.979
	ethyl mercaptan	1.95	0.8091	1.0342	0.0002	0.865	0.8271	0.0138	0.979
FAC-NaOH	methyl mercaptan	1.357	0.8015	2.0923	0.0007	0.886	1.1238	0.012	0.994
	ethyl mercaptan	1.95	0.791	1.0529	0.0005	0.894	0.755	0.011	0.959
FAC-KOH	methyl mercaptan	1.357	0.8003	2.0447	0.0014	0.936	1.0475	0.0135	0.994
	ethyl mercaptan	1.95	0.7891	1.0491	0.0008	0.909	0.8016	0.0181	0.953

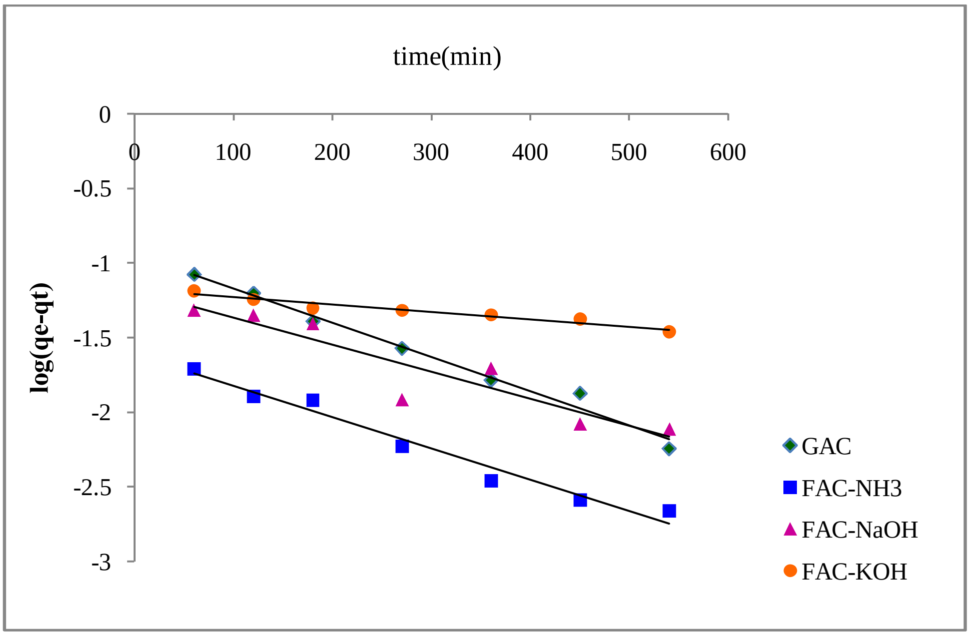


Figure 5.5 Pseudo-first order kinetics for *methyl mercaptan* in presence of a surfactant.

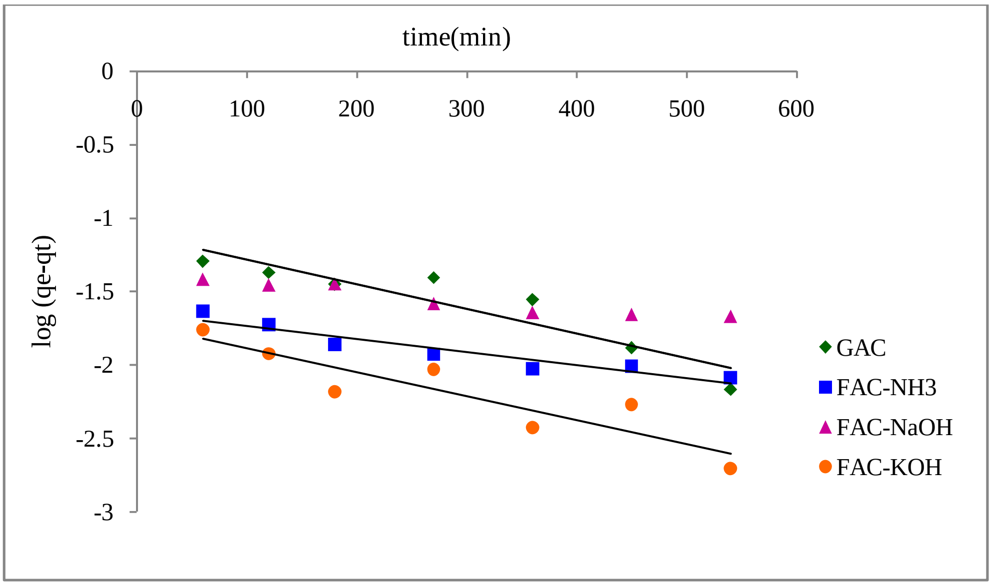


Figure 5.6 Pseudo-first order kinetics for *ethyl mercaptan* in presence of a surfactant.

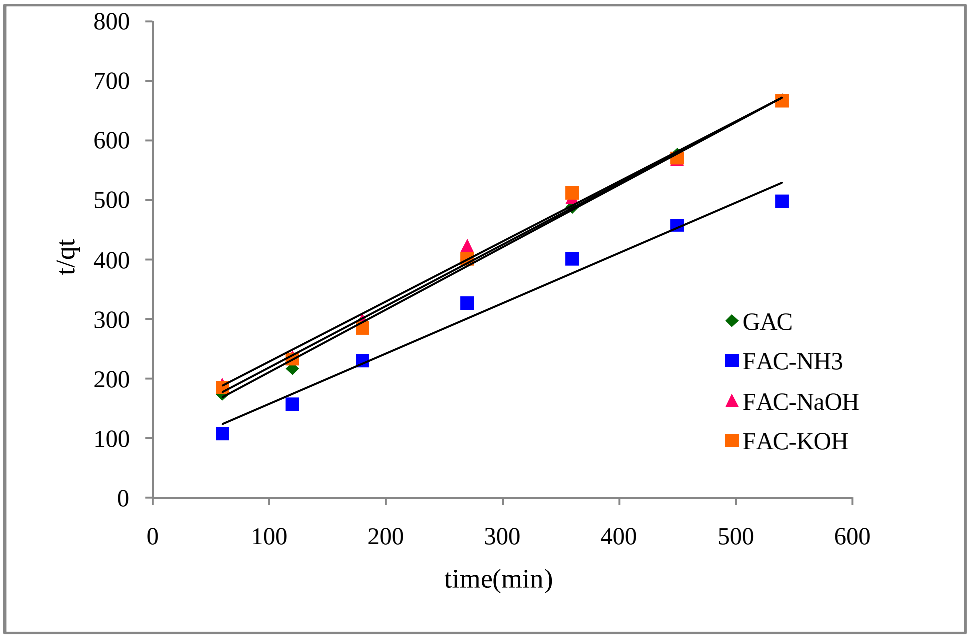


Figure 5.7 Pseudo-second order kinetics for *methyl mercaptan* in presence of a surfactant.

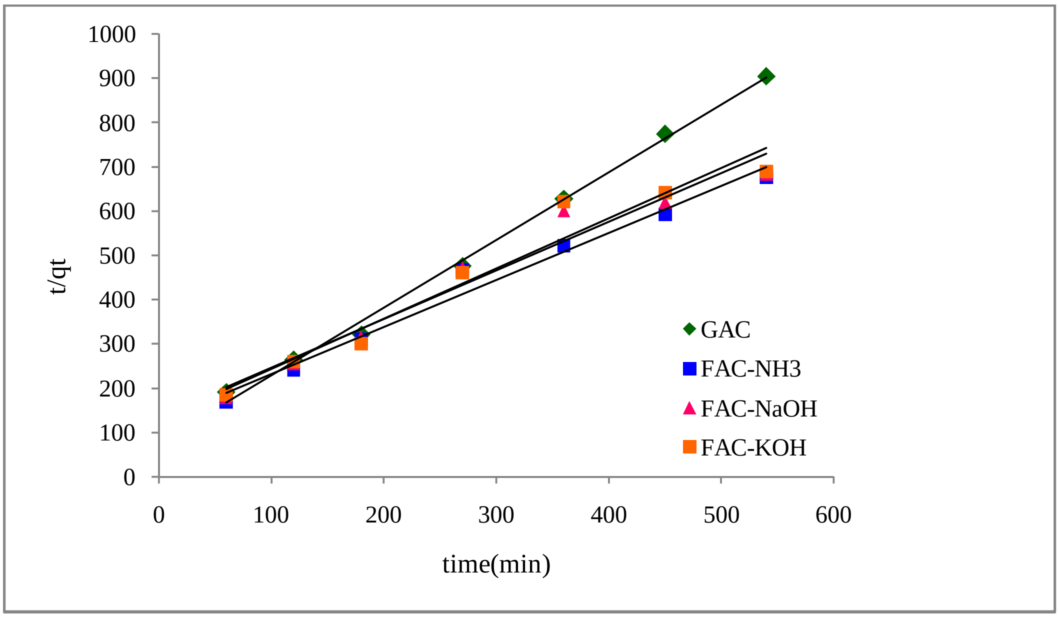


Figure 5.8 Pseudo-second order kinetics for *ethyl mercaptan* in presence of a surfactant.

5.3.2Intra-particle diffusion for GAC and FACs

Weber and Morris (1963) developed the intra-particle diffusion model to detect the mechanism of the adsorption process. The equation of intra-particle diffusion model is given by equation 5.5. According to this model, a plot of $q_t$vs$t^{1/2}$ produces a straight line that passes through the origin if intra-particle diffusion controls the adsorption mechanism. Larger values of the intercept (*I*) indicates stronger influence of the boundary layer (film) during the adsorption process. The intra-particle diffusion rate constant (k_i) and constant parameter (*I*) are obtained from the slope and intercepts of the linear plots respectively (refer Figure 5.9 and 5.10 and Table5.3).After blockage of pores by methyl mercaptan and ethyl mercaptan, intra-particle diffusion no longer influences the adsorption process. For GAC, the intercept values for methyl mercaptan and ethyl mercaptan are both close to zero. If we compare the values of the constant *I* for GAC and FACs, it can be seen that it is closer to zero in case of GAC than in case of FACs. In presence of a cationic surfactant, most of the pores of the adsorbents get blocked by surfactant molecules. So, intra-particle pore diffusion of methyl mercaptan and ethyl mercaptan into the adsorbent molecules occur by much less extent (refer Figure 5.13 and 5.14 and Table 5.4).

5.3.2Film diffusion model

The effect of film resistance in the adsorption of methyl mercaptan and ethyl mercaptan is investigated here using Boyd's film diffusion model. The plot of *Bt* against time produces a straight line, which passes through the origin if intra-particle diffusion is the controlling step in the adsorption process. The intercepts of the film diffusion plot for methyl mercaptan and ethyl mercaptan are given in Table 5.3. If the intercepts are compared for these adsorbents, it is closer to zero for GAC and significantly different from zero in case of FACs. Film diffusion, thus has much less effect on adsorption using GAC. On the other hand, surface complexes are formed at the functional surface sites of FAC materials with these mercaptans on top of pure physical adsorption and the same is endorsed by the pseudo-second order outputs as well as by the pronounced non-zero values of the intercepts obtained in film-diffusion based plots. In presence of a cationic surfactant (*Cetrimide being present as cationic cetrimonium ions*), most of the pores of the adsorbent are quickly blocked by these surfactant molecules. So intra-particle pore diffusion of methyl mercaptan and ethyl mercaptan into the adsorbent molecules plays insignificant role, whereas most of the adsorption occurs by the formation of surface complexes at the functional surface sites of FACs (refer Figure 5.15 and 5.16 and Table 5.4).

Table 5.3 Parameter of intra-particle diffusion model and Boyd's plot for adsorption of methyl mercaptan and ethyl mercaptan by GAC, FAC-NH_3, FAC-NaOH and FAC-KOH in absence of a cationic surfactant.

			Intra-particle diffusion model			Boyd's plot	
Adsorbent	Component	C_0 (mg/L)	k_{ID} (mg/g adsorbent $min^{0.5}$)	I (mg/g adsorbent)	R^2	Intercept	R^2
GAC	methyl mercaptan	1.357	0.041	0.467	0.711	0.355	0.9922
	ethyl mercaptan	1.95	0.047	0.43	0.73	0.363	0.959
FAC-NH_3	methyl mercaptan	1.357	0.043	0.473	0.713	0.158	0.9955
	ethyl mercaptan	1.95	0.049	0.345	0.815	0.182	0.972
FAC-NaOH	methyl mercaptan	1.357	0.043	0.441	0.727	0.215	0.9952
	ethyl mercaptan	1.95	0.048	0.356	0.79	0.385	0.956
FAC-KOH	methyl mercaptan	1.357	0.043	0.445	0.715	0.325	0.999
	ethyl mercaptan	1.95	0.047	0.366	0.796	0.230	0.974

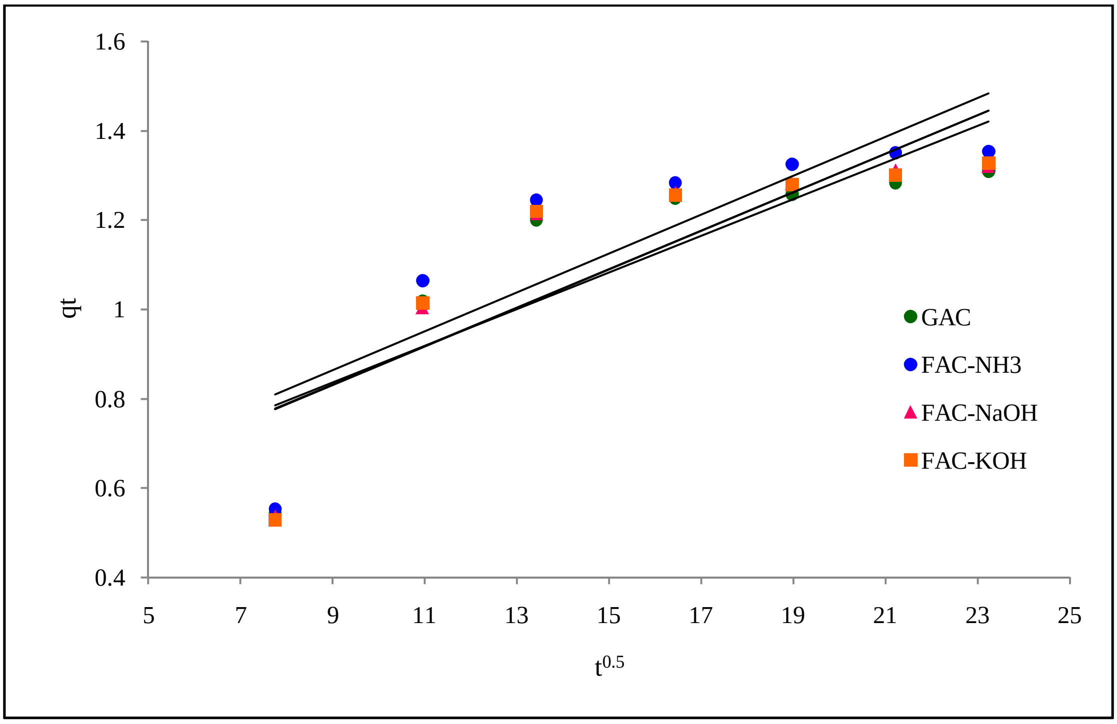


Figure 5.9 Intra-particle diffusion plot for adsorption of *methyl mercaptan* in absence of a surfactant.

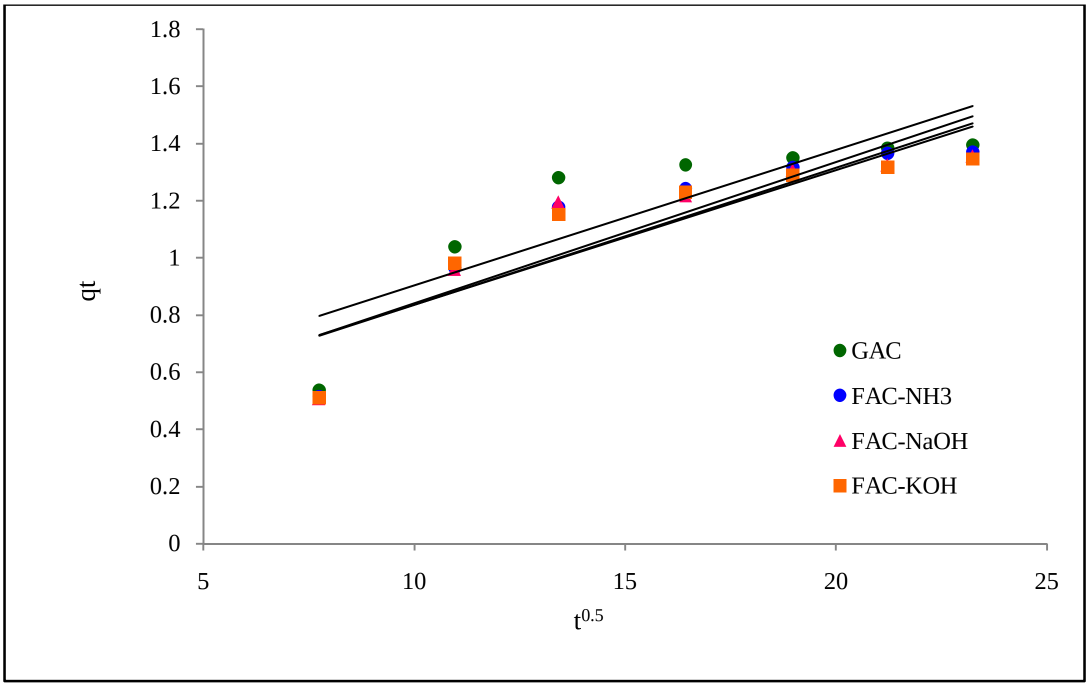


Figure 5.10 Intra-particle diffusion plot for adsorption of *ethyl mercaptan* in absence of a surfactant.

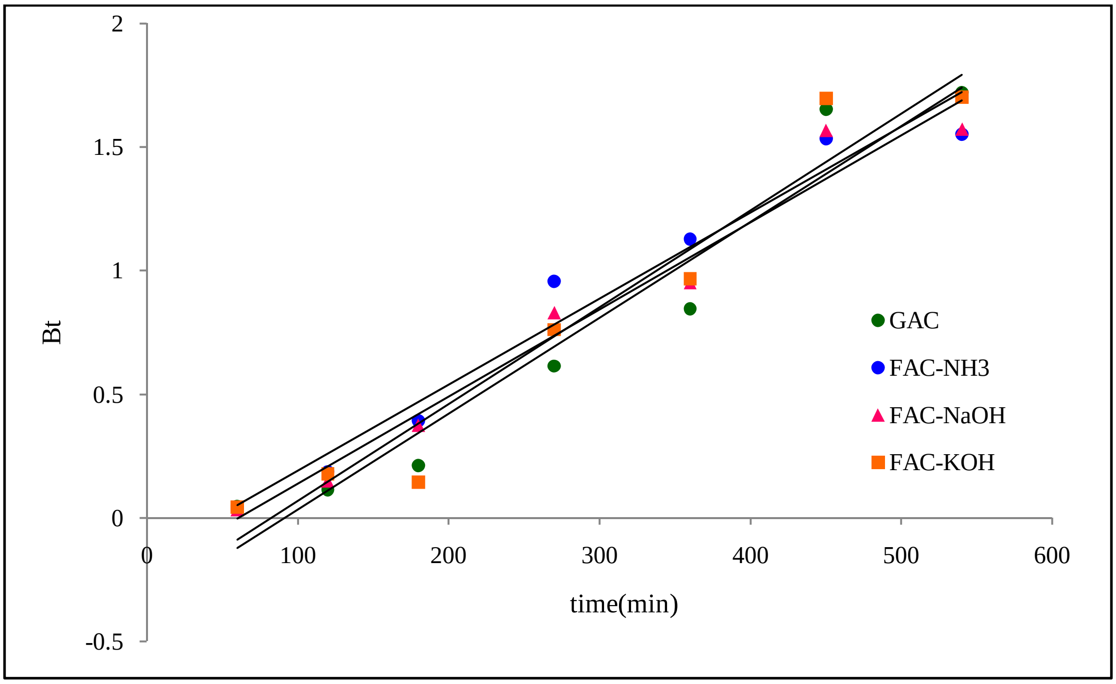


Fig. 5.11 Boyd's film diffusion plot for adsorption of *methyl mercaptan* in absence of a surfactant.

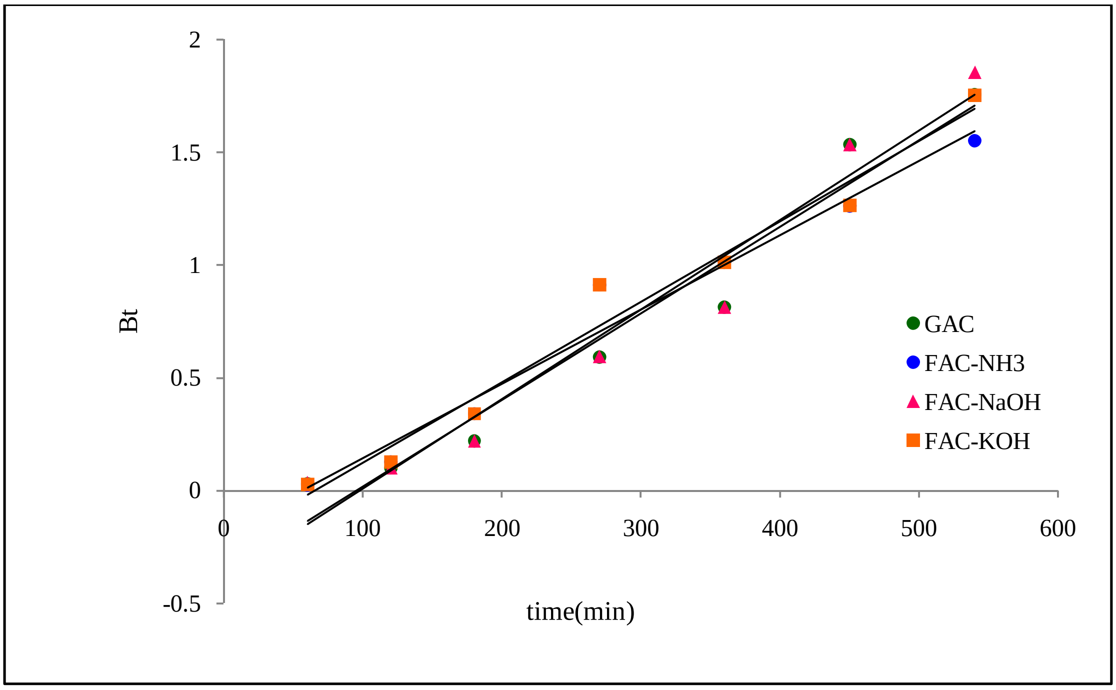


Figure 5.12 Boyd's film diffusion plot for the adsorption of *ethyl mercaptan* in absence of a surfactant.

Table 5.4 Estimated Parameters of intra-particle diffusion model and Boyd's plot for the adsorption of methyl mercaptan and ethyl mercaptan by GAC, FAC-NH_3, FAC-NaOH and FAC-KOH in presence of a cationic surfactant.

			Intra-particle diffusion model			Boyd's plot	
Adsorbent	Component	C_0 (mg/L)	k_{ID} (mg/g adsorbent $min^{0.5}$)	I (mg/g adsorbent)	R^2	Intercept	R^2
GAC	methyl mercaptan	1.357	0.027	0.202	0.931	0.36	0.947
	ethyl mercaptan	1.95	0.015	0.269	0.744	0.313	0.96
FAC-NH_3	methyl mercaptan	1.357	0.029	0.367	0.944	0.157	0.963
	ethyl mercaptan	1.95	0.023	0.204	0.844	0.115	0.937
FAC-NaOH	methyl mercaptan	1.357	0.03	0.142	0.95	0.183	0.955
	ethyl mercaptan	1.95	0.031	0.119	0.909	0.226	0.97
FAC-KOH	methyl mercaptan	1.357	0.029	0.172	0.924	0.304	0.958
	ethyl mercaptan	1.95	0.029	0.137	0.923	0.212	0.974

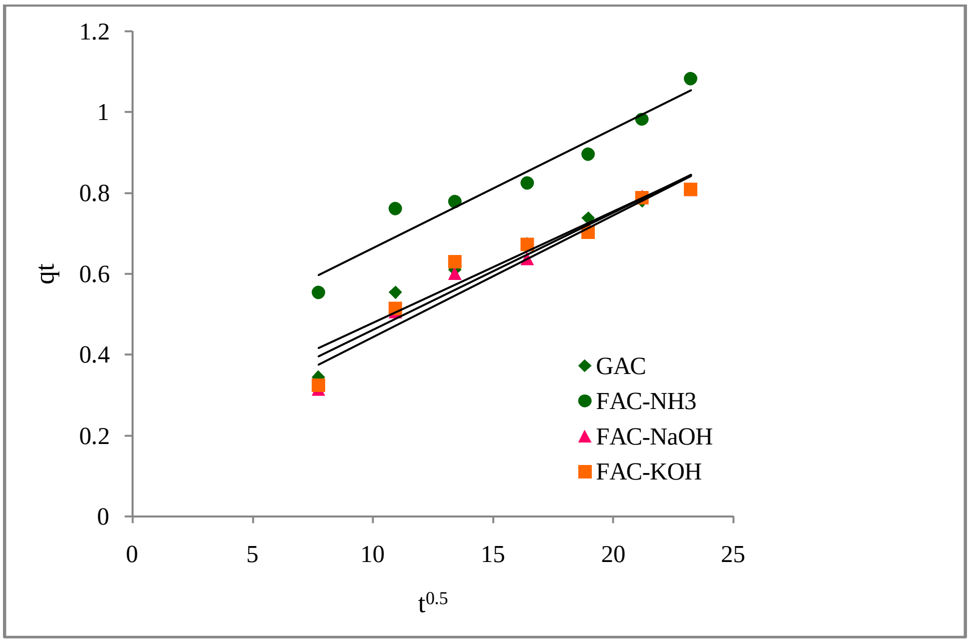


Figure 5.13 Intra-particle diffusion plot for the adsorption of *methyl mercaptan* in presence of a surfactant.

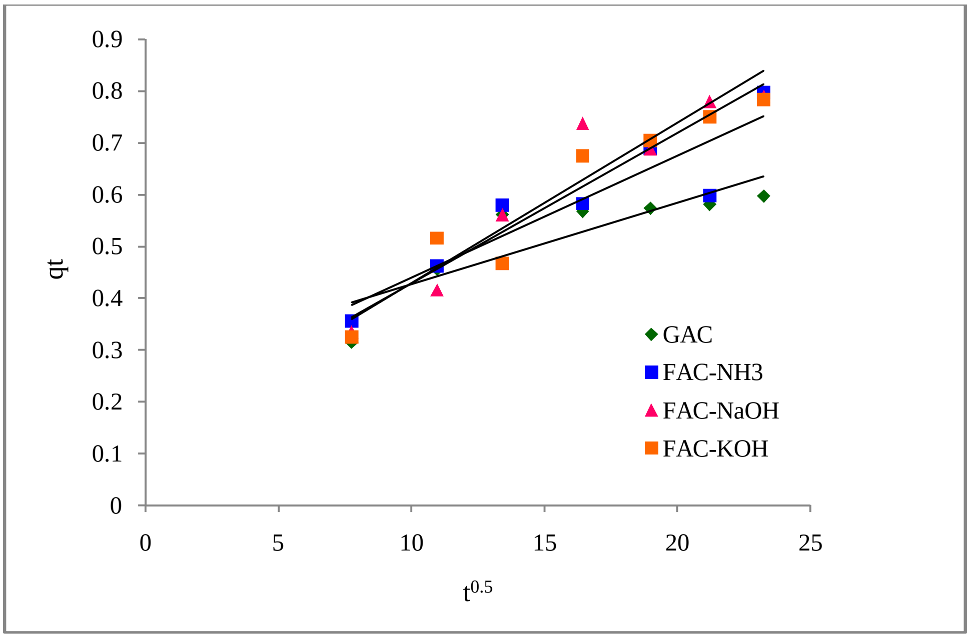


Figure 5.14 Intra-particle diffusion plot for the adsorption of *ethyl mercaptan* in presence of a surfactant.

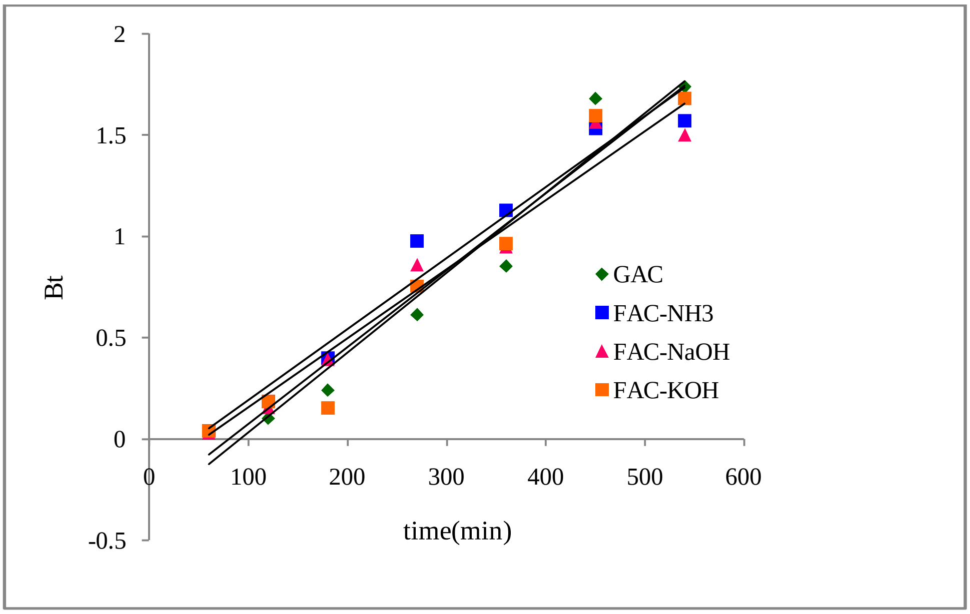


Figure 5.15 Boyd’s film diffusion plot for the adsorption of *methyl mercaptan* in presence of a surfactant.

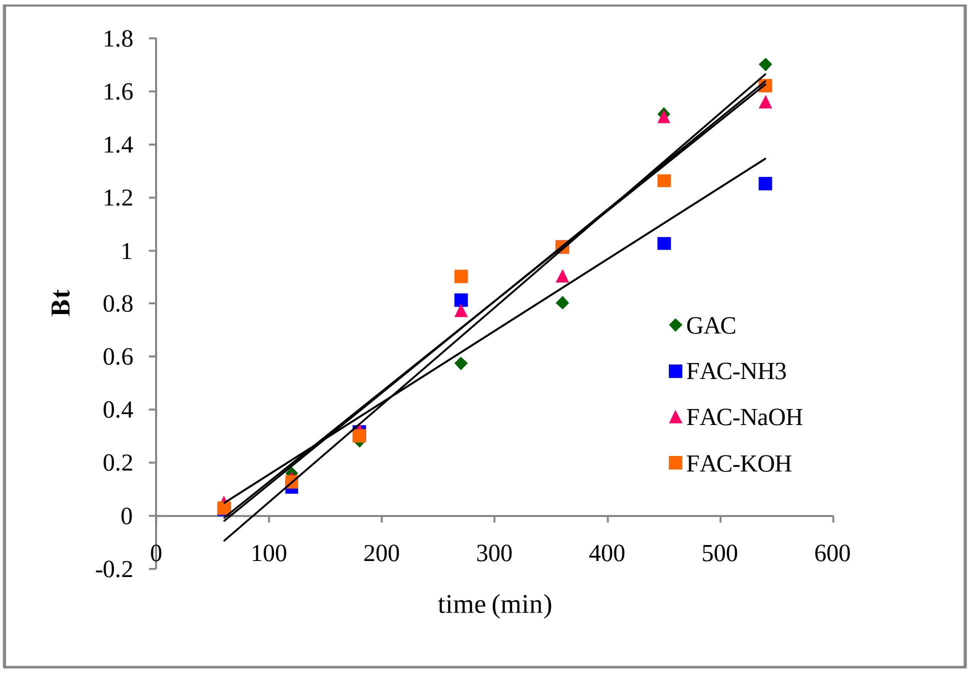


Figure 5.16 Boyd’s film diffusion plot for the adsorption of *ethyl mercaptan* in

presence of a surfactant.

5.4Probable mechanism of surface coordination of Methyl mercaptan and Ethyl mercaptan on GAC and FACs

Hydroxyl/phenolic groups can be adhered to the surface of the solid adsorbent in aqueous system, called hydrous solid (Mahmudov and Huang, 2010, Vaughan and Reed, 2005) and this hydrous solid can act as a multi-protic acid. Activated carbon behaves in a similar way in aqueous systems. Hydrous form of this activated carbon can act as a diprotic acid, which illustrates two definite values of acidity constants in aqueous solution (Boehm, 1994). If C represents the activated carbon surface, then the reactions can be represented by:

$$\underline{C}OH_2^+ \leftrightarrow \underline{C}OH + H^+ \tag{5.9}$$

$$\underline{C}OH \leftrightarrow \underline{C}O^- + H^+ \tag{5.10}$$

These COH_2^+, COH and CO^- represent protonated, neutral andionized surface phenolic/hydroxyl groups. The ionized form of the surface attracts mercaptan compound. Neutral surface sites of the carbon can also bind mercaptans by coordination. Possible surface complex reactions for the adsorption of methyl and ethyl mercaptans on precursor GAC and FACs are expressed as follows:

$$\underline{C}OH + RSH = \underline{C}\,SHR + OH^- \tag{5.11}$$

The oxygenated functional groups can behave like an acid and can make the carbon surface more acidic, which then can be protonated easily by forming coordinate complexes with mercaptans. Relevant reactions are:

$$\underline{C}\text{-}COOH_{(s)} + RSH + H^+_{(aq)} \rightarrow \underline{C}\text{-}COOH_2^+ \ldots SHR \tag{5.12}$$

$$\underline{C}\text{-}C{=}O + RSH + H^+_{(aq)} \rightarrow \underline{C}\text{-}C{=}OH^+ \ldots\ldots SHR \tag{5.13}$$

$$\underline{C}\text{-}OH_{(s)} + RSH + H^+_{(aq)} \rightarrow \underline{C}\text{-}OH_2^+ \ldots\ldots SHR \tag{5.14}$$

Chapter 6

Summary of Outcomes, Concluding Remarks and Recommendations for Future Work

6.0 Foreword

This chapter gives a brief summary of the complete research work, highlights the main and the specific conclusions with the important outcomes of each part of the research and provides recommendations for the future direction of research that should continue after this piece of research.

6.1 Summary

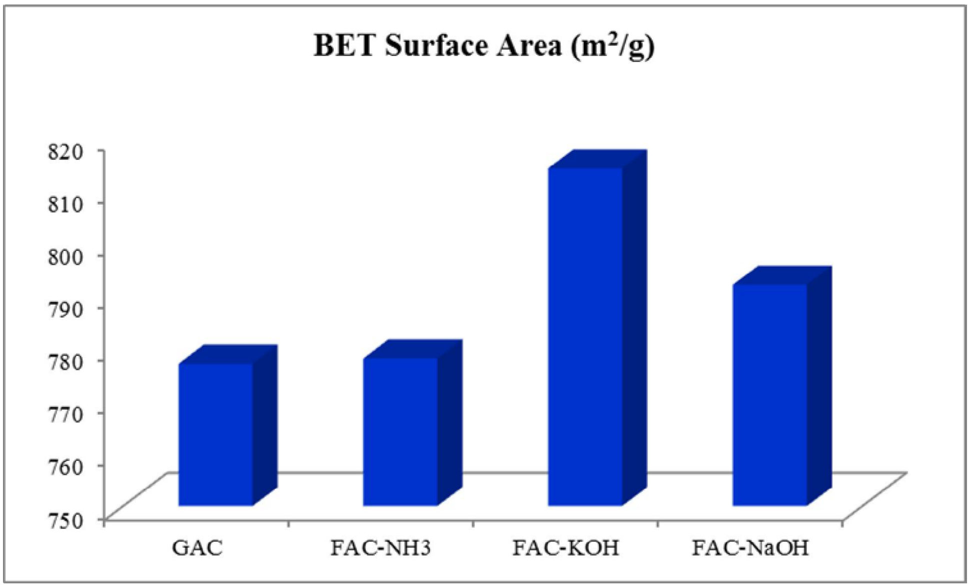
- Volatile Organo Sulphur Compounds (VOSCs) like methyl mercaptan (CH_3SH: OTV= 0.0021ppmV), ethyl mercaptan (C_2H_5SH: OTV= 0.001ppmV), dimethyl sulphide (CH_3SCH_3: OTV= 0.001ppmV), carbon disulphide (CS_2: OTV= 0.21ppmV) are malodorous in nature, causing odour nuisance in and around sewage treatment plants.

- Adsorption, using Granular Activated Carbon (GAC), is an effective technique for the removal of malodorous Volatile Organo Sulphur Compounds (VOSCs) originating from sewage waste water collected from various Sewage Treatment Plants (STPs).

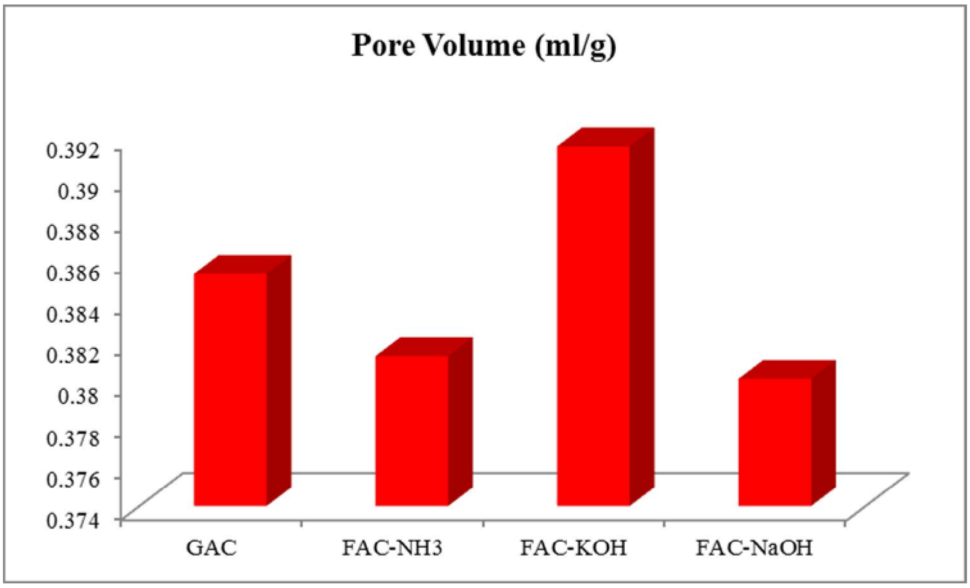
- Adsorption capacity of GAC is enhanced by functionalization with various alkaline solutions.

- Alkali functionalized activated carbons (FACs), having higher surface area and pore volume and reduction of oxygen containing functional groups (refer **Figure 6.1**), perform much better in removing VOSCs in comparison to precursor GAC.

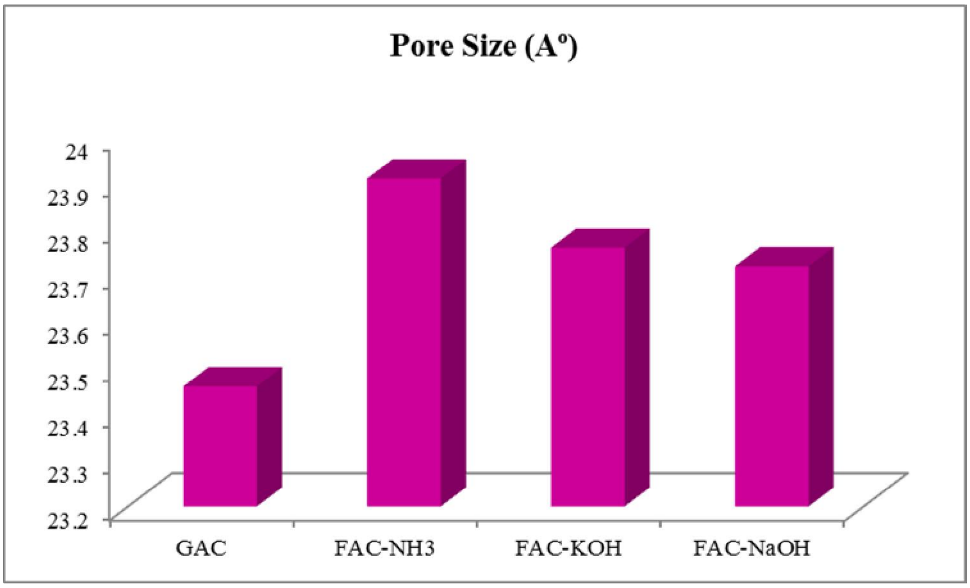
- Different adsorbed odorants (VOSCs), being concentrated and in close proximity to each other on the surface or in the pores of the adsorbent, may interact.



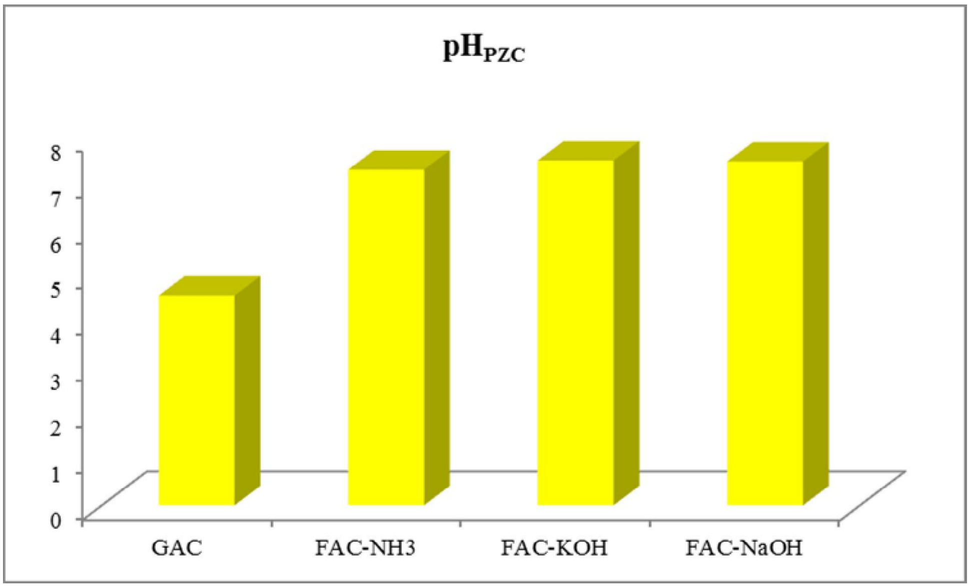
(a)



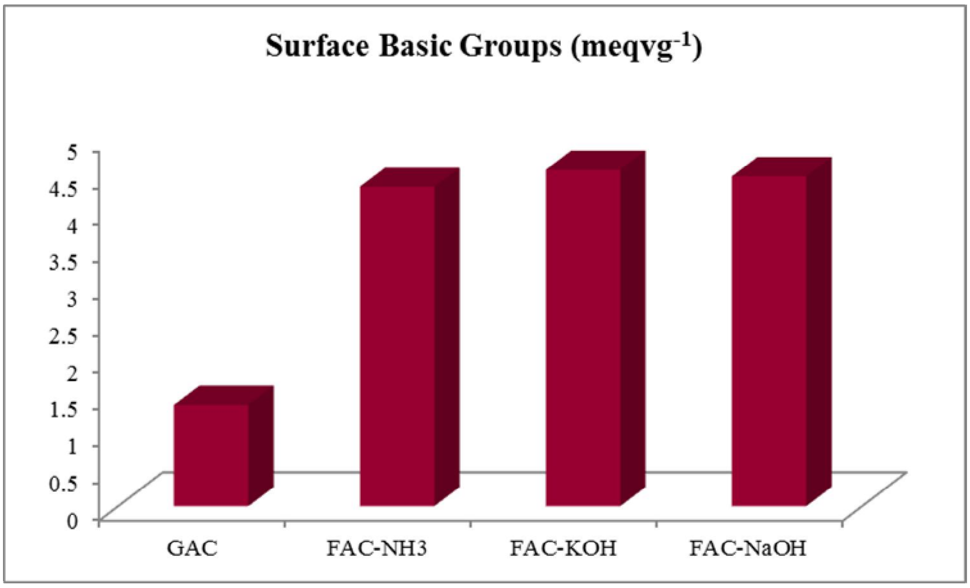
(b)


Pore Size (A°)
24
23.9
23.8
23.7
23.6
23.5
23.4
23.3
23.2
GAC
FAC-NH3
FAC-KOH
FAC-NaOH

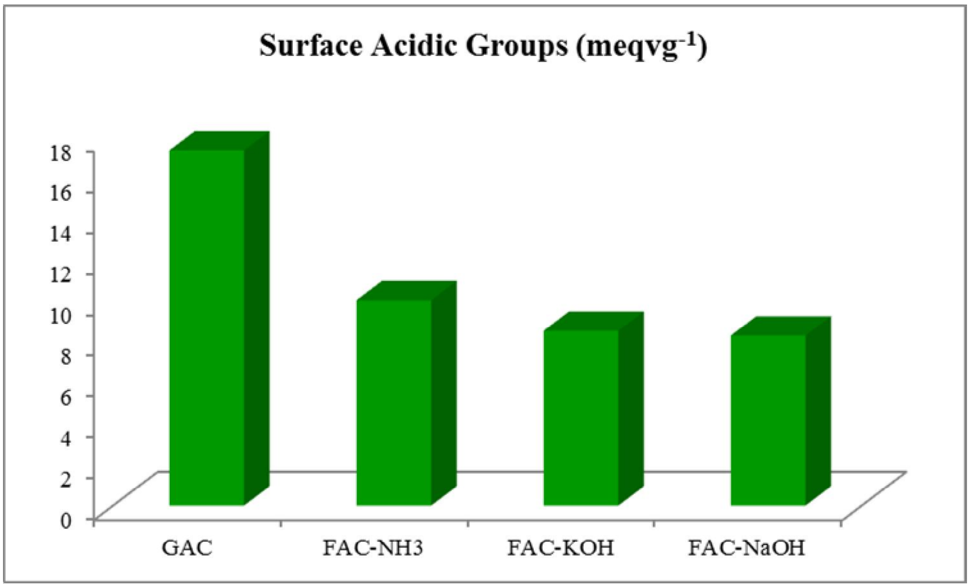
(c)


pH_PZC
8
7
6
5
4
3
2
1
0
GAC
FAC-NH3
FAC-KOH
FAC-NaOH

(d)



(d)



(f)

Figure 6.1 Plots of (a) BET surface area, (b) Cumulative pore volume, (c) Pore size (d) Point of zero charge (pH_{PZC}) , (d) Total surface basic groups (e) Total surface acidic groups.

The adsorption capacity of GAC and FACs increases in the order FAC-NH_3>FAC-KOH > FAC-NaOH > GAC. *This is mainly due to the additional chemisorption primarily due to surface complexation at the functionalized surface sites of the modified GACs.*

- FAC-NaOH or FAC-KOH may react with ambient CO_2 there by forming carbonates. This effectively decreases the removal efficiency.

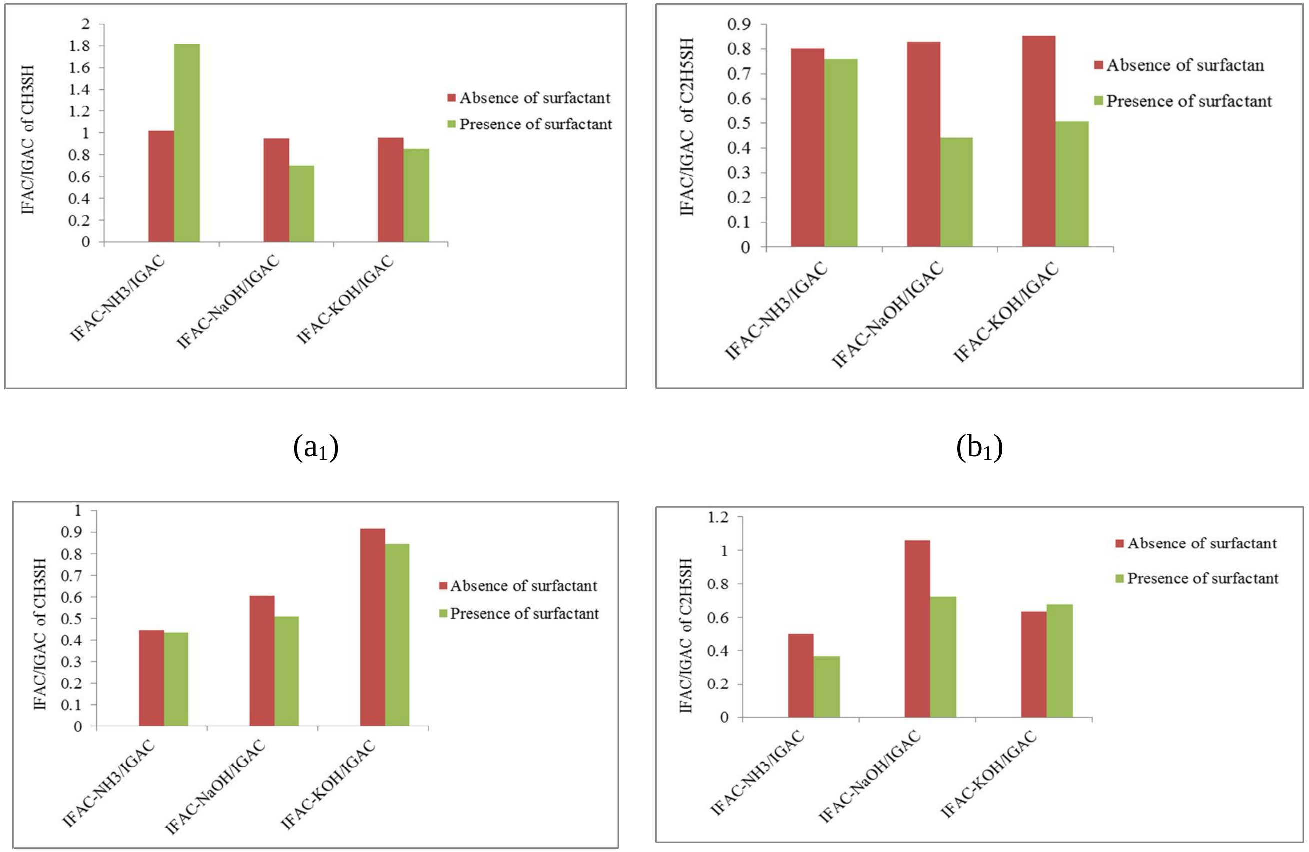
- Odour concentration is measured simultaneously by two techniques: panel olfactometry (sensory measurement based) and component specific analytical measurement (GC-MS based).

- Time variant olfactometry based odor concentration data correlated well with the time variant concentration of VOSCs (GC-MS based) for all four malodorous compounds like methyl mercaptan, ethyl mercaptan, dimethyl sulphide and carbon disulphide.

- Linearization of the percentage removal of overall odour (olfactometry based) versus percentage removal of relative concentrations of the four VOSCs reveals that methyl mercaptan has a very large odor contributing potential ($R^2=0.967$) representing the most obnoxious component of the tested sewage waste water as compared to other three compounds (refer **Figure 4.12** and **Figure 4.13**).

- Simultaneous conversion of methyl mercaptan to dimethyl disulphide leads to its faster removal by FAC-NH_3.

- Intra-particle diffusion is not the only rate-controlling factor. An agreement to pseudo-second-order kinetic model and Boyd's film diffusion model supports that chemisorption is the rate-controlling stage during adsorption (refer **Figure 6.2**).



(a_1) (b_1)

(a_2) (b_2)

Figure 6.2 Plots of I(FAC)/I(GAC) for *pore diffusion model* for (a_1) CH_3SH and (b_1) C_2H_5SH and for *Boyd's Film diffusion model* for (a_2) CH_3SH and (b_2) C_2H_5SH.

- A series of 17 individual experiments were conducted for Response Surface Methodology (RSM) coupled with a Box–Behnken design (BBD). The same was applied in order to optimize the combined effect of three important adsorption conditions, i.e. *type of adsorbent, amount of adsorbent and adsorption time*.
- The results showed that the RSM based on BBD is very much applicable for adsorptive removal of VOSCs from sewage treatment plants (STP).

6.2 Concluding Remarks

- Precursor GAC is compared with alkali treated functionalized GACs (FACs) with respect to each of their capacities towards removal of specific odorous VOSCs and towards abatement of odour as a whole.
- High adsorption capacity is observed for FAC-NH_3.
- The texture and surface chemistry of GAC and various FACs are studied thoroughly and it is observed that alkali treated FACs could dramatically increase the adsorption of each of the key odorous VOSCs.
- On alkali functionalization, surface area and pore volume of GAC increase while the acidic functional groups decrease in number.
- Variation in surface area and porosity of the adsorbents play a key role on adsorption of VOSCs.
- Functionalization by ammonia solution enlarged the surface area and increased the concentration of basic groups, thereby enhancing the uptake of VOSCs into FAC-NH_3 surface.

- The same is found to vary linearly with R^2=0.967 (methyl mercaptan), R^2=0.951 (ethyl mercaptan), R^2=0.948 (dimethyl sulphide) and R^2=0.949 (carbon disulphide).

- The results of this study show that FAC-NH_3 can be successfully used as remarkably better adsorbents, in comparison to GAC and FAC-NaOH.
- The equilibrium adsorption value of methyl mercaptan is 1.32 and ethyl mercaptan is 0.943 for FAC-NH_3 and the same for precursor GAC is 1.255 for methyl mercaptan and 0.922 for ethyl mercaptan.
- Even minor reduction in mass concentration of methyl and ethyl mercaptans could reduce perceived odour intensity by a large amount.
- We find that the functionalized GACs have the micro-pores to adsorb organic molecules as well as the hydrophilic external surface with functional surface sites being able to make complexes with the weakly polar compounds present in the sewage wastewater.
- Functionalization by ammonia solution enlarged the surface area and increased the concentration of basic groups, which enhances the uptake of VOSCs into the FAC-NH_3 surface.
- Three techniques are taken into consideration for controlling the overall odor are: a) time variant olfactometry based odor concentration data correlated with the time variant VOSCs concentration (GC-MS outputs) for all the four malodorous compounds like methyl mercaptan, ethyl mercaptan, dimethyl sulphide and carbon disulphide; b) the correlation of percentage decrease in the olfactometry based odor concentration with the percentage removal of each of the above four major odor contributing compounds.

- Process optimization of the experimental conditions (type of adsorbent, amount of adsorbent and adsorption time) was carried out by means of Box-Behnken design (BBD) of Response surface methodology (RSM).
- Five parameters [olfactometry based removal (%), CH_3SH removal (%), C_2H_5SH removal (%), CH_3SCH_3 removal (%) and CS_2 removal (%)] were chosen to be the responses for the first set of ANOVA analysis. Five quadratic models, which expressed the functional relationship between the five responses and three independent variables, were obtained by ANOVA. The correlation coefficients (R^2) of 0.9972, 0.9984, 0.9983, 0.999 and 0.9972 for olfactometry based removal (%), CH_3SH removal (%), C_2H_5SH removal (%), CH_3SCH_3 removal (%) and CS_2 removal (%) showed good fit of the experimental data to the model.
- Simultaneous optimization was performed on the basis of the desirability function in order to determine the optimal conditions for the olfactometry based removal (%), CH_3SH removal (%), C_2H_5SH removal (%), CH_3SCH_3 removal (%) and CS_2 removal (%). In **Figure 6.4**, maximum olfactometry based removal (77.3954%), CH_3SH removal (80.338%), C_2H_5SH removal (59.1585%), CH_3SCH_3 removal (63.2134%) and CS_2 removal (71.9483%) were obtained at optimum process conditions: type of adsorbent = 1.55689 i.e. *2*, amount of adsorbent = *10.29g*, adsorption time = *2.92hrs.*
- This result indicates that methyl mercaptan (CH_3SH) is the most significant chemical compound that can create odour nuisance out of the following VOSCs: C_2H_5SH, CH_3SCH_3 and CS_2. It also matches with the second set of ANOVA analysis (refer **Tables 6.3** and **6.4**).

6.3 Statistical Analysis: *Regression model representation and ANOVA analysis*

In the present study, Response Surface Methodology is applied with a 3 factor Box-Behnken design (BBD) in order to investigate the correlation between the combined effects of individual processes to all responses over two levels (see **Table 6.1**). Total number of experimental runs (N) = 17 of which 12 factorial points with 5 centre points are included as required for the development of BBD. This is defined as:

$$N = 2k(k-1) + C_0 \qquad (1)$$

(*where k is the no. of factors and* C_0 *is the no. of central points*).

The experimental data were analysed to express the predicted response (Y) as a function of independent variables and a second-order quadratic polynomial fit [refer to Eq. (2)] was obtained.

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} {x_i}^2 + \sum_{i=1}^{k-1} \sum_{j=2}^{k} \beta_{ij} x_i x_j \qquad (2)$$

Where Y is the response, x_i, x_j are the coded variables, β_0 is the intercept, β_i is the linear, β_{ii} is the quadratic and β_{ij} is the interaction coefficients. N is the number of factors studied in the experiment. The complete design matrix based on the range of process variables is presented in **Table 6.1** and **Table 6.2**.

Table 6.1 Experimental design matrix and results of the Box–Behnken design.

Run	Independent variables			Experimental value					Predicted value				
	A	B	C	Y_1	Y_2	Y_3	Y_4	Y_5	Y_1	Y_2	Y_3	Y_4	Y_5
1	1	12	3	74.31	74.34	58.88	61.29	72.57	74.09	76.93	59.75	62.86	71.22
2	1	4	3	72.57	71.39	57.29	59.97	72.001	73.27	71.53	55.70	59.14	69.24
3	3	8	1.5	50.11	7.001	5.11	10.28	12.68	51.46	7.24	3.67	10.38	10.19
4	3	8	4.5	95.73	89.1	90.72	89.15	91.87	94.87	91.19	91.44	89.80	90.25
5	2	8	3	79.48	83.27	60.61	65.7	74.31	79.49	83.27	60.61	65.70	74.31
6	2	4	4.5	95.73	88.85	91.46	86.91	91.73	96.38	88.95	91.61	87.84	92.00
7	2	8	3	79.49	83.27	60.61	65.7	74.31	79.49	83.27	60.61	65.70	74.31
8	1	8	1.5	46.57	13.97	8.87	8.001	8.27	47.43	11.88	8.16	7.36	9.90
9	1	8	4.5	95.73	81.14	77.06	83.94	82.32	94.39	80.90	78.50	83.85	84.81
10	2	12	1.5	55.39	17.16	16.72	14.62	17.39	54.75	17.06	16.57	13.70	17.12
11	2	8	3	79.49	83.27	60.61	65.701	74.31	79.49	83.27	60.61	65.70	74.31
12	2	8	3	79.49	83.27	60.61	65.701	74.31	79.49	83.27	60.61	65.70	74.31
13	3	12	3	79.78	79.07	62.34	66.62	71.94	79.08	78.94	63.94	67.45	74.71
14	2	8	3	79.49	83.27	60.61	65.701	74.31	79.49	83.27	60.61	65.70	74.31
15	2	12	4.5	95.73	92.38	95.96	90.62	95.09	97.29	90.43	93.66	89.14	93.95
16	3	4	3	72.58	77.35	60.83	65.105	70.11	72.79	75.16	59.97	63.53	71.47
17	2	4	1.5	50.11	7.39	8.29	5.89	12.72	48.55	9.35	10.59	7.37	13.86

A = Type of adsorbent [GAC=1; FAC- NH_3=2; FAC -NaOH=3], B = Amount of adsorbent (g), C = Time (h), Y_1 = Relative removal of overall odour by Olfactometry [$(O_0-O_t)/O_0$], Y_2 = $(C_0-C_t)/C_0$ [Methyl mercaptan(CH_3SH)], Y_3 =$(C_0-C_t)/C_0$ [Ethyl mercaptan (C_2H_5SH)], Y_4 = $(C_0-C_t)/C_0$ [dimethyl disulphide (CH_3SCH_3)], Y_5= $(C_0-C_t)/C_0$ [Carbon di sulphide (CS_2)].

Table 6.2_Experimental design matrix and results of the Box–Behnken design.

Run	**A**:Type of adsorbent	**B**:Amount of adsorbent	**D**:Specific component	Experimental value Olfactometry **$(O_0\text{-}O_t)/O_0$**	Predicted value
1	3	8	1	48.75	49.61
2	2	12	1	55.39	56.78
3	2	12	3	55.39	56.78
4	2	8	2	52.37	52.37
5	2	4	1	50.11	48.72
6	3	12	2	51.81	49.56
7	1	12	2	49.002	48.48
8	1	4	2	35.78	38.04
9	3	4	2	43.35	43.88
10	2	8	2	52.37	52.37
11	2	8	2	52.37	52.37
12	1	8	1	47.02	46.16
13	2	4	3	50.11	48.72
14	1	8	3	47.02	46.16
15	2	8	2	52.37	52.37
16	2	8	2	52.37	52.37
17	3	8	3	48.75	49.62

Specific component = [Methyl mercaptan(CH_3SH): 1; Ethyl mercaptan(C_2H_5SH): 2; Dimethyl - sulphide (CH_3SCH_3):3]

Regression and graphical analysis of the experimental data were done using the software Design Expert version 11.0.3.1. (Stat- Ease Inc., USA). The design of experiment builds up a quadratic polynomial equation for adsorption and olfactometry based analysis with the coded variables.

$$Y_1 = 79.49+1.13A+1.78B+22.59C+1.37AB-0.8848AC-1.32BC-3.44A^2-1.24B^2-4.01C^2 \quad (3)$$

$$Y_2 = 83.27+1.41A+2.29B+38.24C-0.4059AB+3.73AC-1.56BC-5.64A^2-2B^2-29.83C^2 \quad (4)$$

$$Y_3 = 60.61+2.11A+2B+39.53C-0.0189AB+4.35AC-0.9826BC-4.22A^2+3.44B^2-10.95C^2 \quad (5)$$

$$Y_4 = 65.7+2.24A+1.91B+38.98C+0.0489AB+0.733AC-1.26BC-2.06A^2-0.3922B^2-15.8C^2 \quad (6)$$

$$Y_5= 74.31+1.43A+1.3B+38.74C+0.3141AB+1.29AC-0.3262BC-4.05A^2+1.4B^2-21.47C^2 \quad (7)$$

$$Y_6 = 52.37+1.73A+4.03B-1.19AB-6.13A^2-1.26B^2+1.64D^2 \quad (8)$$

where A, B,C and D are the coded terms for the four variables that have been selected, i.e. *type of adsorbent, amount of adsorbent, time and specific component,* respectively. A positive sign of the coefficients in these equations indicates synergistic effect, whereas negative sign indicates antagonistic effect on the response (**Ray et al. 2009**). It has been shown that for all equations, the constant was independent of any factor and the linear terms A, B, C, the second-order term D^2 and interaction terms AB (except Eqs. 4, 5 & 8) and AC (except Eq. 3) had a positive influence on the response. The second-order terms A^2, B^2 (except Eqs. 5&7), and C^2, the interaction term BC had a negative effect on the response indicating that with a decrease of the magnitude of these parameters adsorption capacity increases. On the other hand, the linear term D, the interaction terms AD and BD had no effect on the olfactometric analysis. The coefficients of determination (R^2) and analysis of variance (ANOVA) are used to estimate the statistical significance of the main effects and interactions along with justification of the quality of fit.

According to the ANOVA analysis from **Table 6.3 and Table 6.4**, it is shown that the quadratic model is significant having a p value lower than 0.0001 for adsorption as well as for olfactometry based yield.

High R^2 values of 0.9972, 0.9984, 0.9983, 0.999 and 0.9972, respectively and coefficients of variance (CV) for adsorption and olfactometry dependent yield ensured the suitability of the quadratic models to the experimental data.

Table 6.3 ANOVA for response surface quadratic model of adsorption yield.

Source	Y1		Y2		Y3		Y4		Y5	
	F-value	p-value	F-value	p-value	F-value	p-value	F-value	p-value	F-value	p-value
Model	280.14	< 0.0001	471.51	< 0.0001	460.94	< 0.0001	784.52	< 0.0001	277.97	< 0.0001
A-Type of adsorbent	5.99	0.0443	4.26	0.0779	11.17	0.0124	21.34	0.0024	2.91	0.1320
B-Amount of adsorbent	14.91	0.0062	11.28	0.0121	10.04	0.0157	15.45	0.0057	2.41	0.1642
C-Time	2410.01	< 0.0001	3131.24	< 0.0001	3905.27	< 0.0001	6439.68	< 0.0001	2130.53	< 0.0001
AB	4.41	0.0740	0.1764	0.6871	0.0004	0.9838	0.0051	0.9452	0.0700	0.7989
AC	1.85	0.2162	14.92	0.0062	23.70	0.0018	1.14	0.3214	1.18	0.3142
BC	4.11	0.0823	2.60	0.1510	1.21	0.3084	3.34	0.1102	0.0755	0.7914
A^2	29.42	0.0010	35.83	0.0005	23.44	0.0019	9.47	0.0179	12.24	0.0100
B^2	3.80	0.0921	4.49	0.0719	15.61	0.0055	0.3431	0.5764	1.46	0.2668
C^2	39.93	0.0004	1002.59	< 0.0001	157.74	< 0.0001	556.68	< 0.0001	344.51	< 0.0001
R^2	=0.9972		= 0.9984		= 0.9983		= 0.999		=0.9972	
Adjusted R^2	= 0.9937		= 0.9962		= 0.9961		= 0.9977		= 0.9936	
C.V.%	= 1.73		= 2.94		= 3.25		= 2.41		= 3.77	

Similarly, considering the values of coefficients of determination from **Table 6.4**, (R^2 = 0.9397) with a value of the adjusted determination coefficient (adjusted R^2 = 0.8622) and a value of the coefficient of variation (CV = 3.52 %), the model suggests a highly significant goodness of fit.

Table 6.4 ANOVA for response surface quadratic model of olfactometry yield.

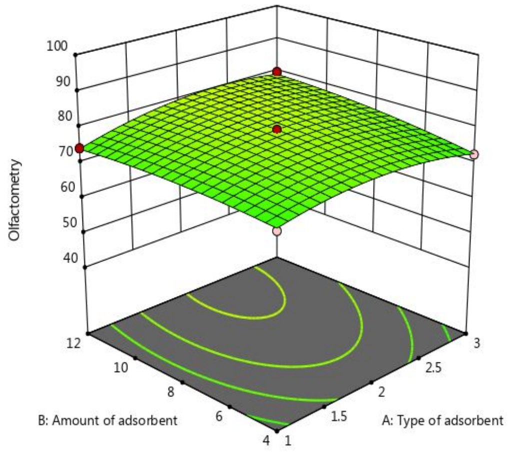
Source	Sum of Squares	df	Mean Square	F-value	p-value	Remark
Model	334.39	9	37.15	12.12	0.0017	significant
A-Type of adsorbent	23.93	1	23.93	7.81	0.0267	
B-Amount of adsorbent	129.86	1	129.86	42.37	0.0003	
C-Specific component	1.250E-09	1	1.250E-09	4.079E-10	1.0000	
AB	5.67	1	5.67	1.85	0.2160	
AC	2.500E-09	1	2.500E-09	8.158E-10	1.0000	
BC	5.684E-14	1	5.684E-14	1.855E-14	1.0000	
A^2	157.98	1	157.98	51.55	0.0002	
B^2	6.69	1	6.69	2.18	0.1832	
C^2	11.30	1	11.30	3.69	0.0963	
Residual	21.45	7	3.06			
Lack of Fit	21.45	3	7.15			

R^2= 0.9397; Adjusted R^2= 0.8622; C.V. %= 3.52.

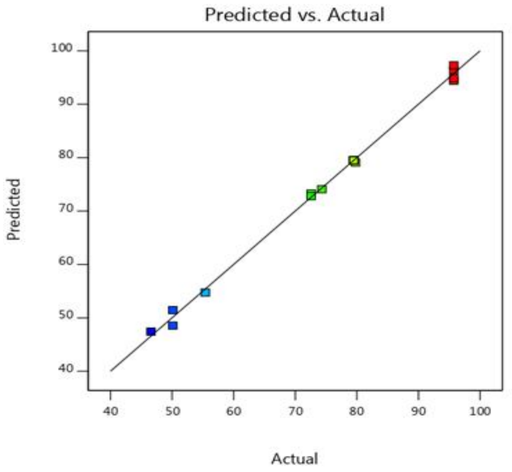
Statistical Analysis (contd.)

The predicted versus observed plots for all responses Y_1 –Y_6 are shown in **Figure 6.3** [(a_2) – (f_2)]. The experimentally obtained data for each run is the actual value whereas the predicted value is evaluated from the model using the prediction equations by the software. It has been observed that most of the data points were well distributed near the fitted straight line, implying that an excellent relationship between the experimental and predicted values of the responses exists for all possible scenarios of the design of experiments. Outcome of all these statistical tests showed that the quadratic models which were developed, have been proved to be successful in capturing the correlation between the process variables and responses quite satisfactorily.

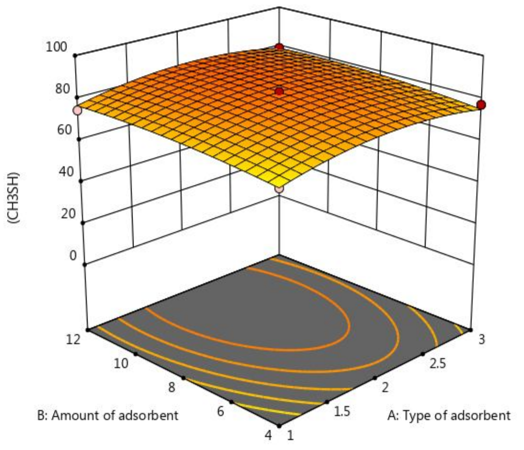
The three-dimensional response surface curves were then plotted as generated by RSM [shown in **Figure 6.3** (a_1) – (f_1)] in order to observe the effect of interaction among various physico-chemical factors used. These curves were also used to determine the optimum operating conditions of the system. It is clearly observed (refer **Table 6.1**) that the percentage removal of overall odour (*olfactometry based output*) increases with increasing adsorption time. The adsorption capacities of all the adsorbents have been found extremely satisfactory for all the specific VOSCs. FAC NH_3 has exhibited the highest adsorption capacity amongst the others.



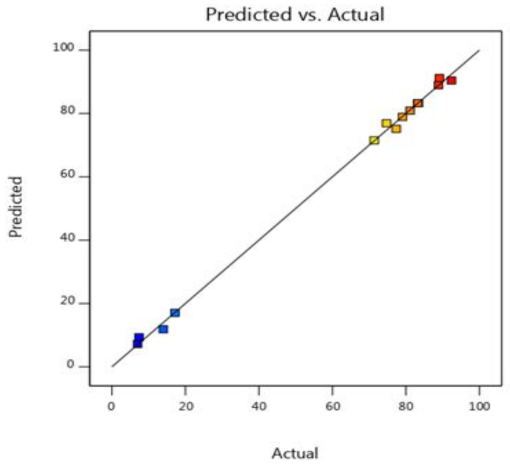
(a₁)



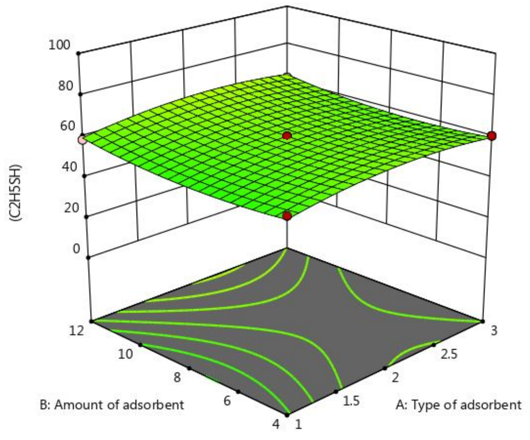
(a₂)



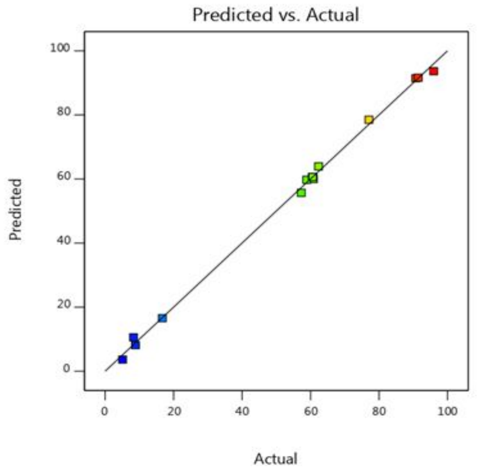
(b₁)



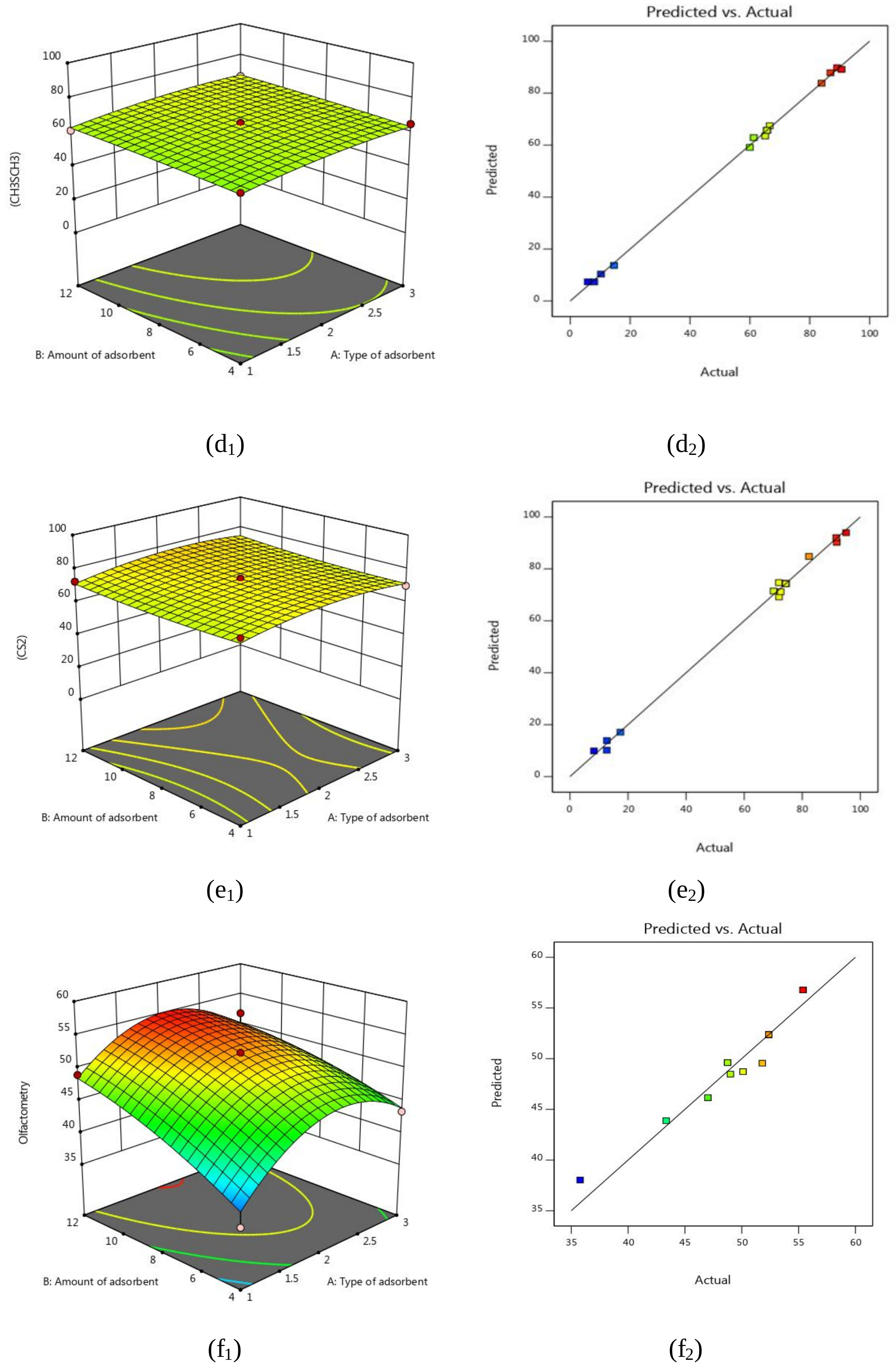
(b₂)



(c₁)



(c₂)



(d$_1$) (d$_2$)

(e$_1$) (e$_2$)

(f$_1$) (f$_2$)

Figure 6.3 [(a$_1$)-(f$_1$)]:Three-dimensional (3D) response surface plots for Adsorption and olfactometry based yield; [(a$_2$)-(f$_2$)]: Correlation of observed and predicted values of response for adsorption and olfactometry based yield.

This model was optimized to give the maximum adsorption capacity. **Figure 6.4** gives the optimal values, as generated by the system. The design methodology should be economical and based on an efficient statistical method. The same should be useful for modelling and analysis of the problem by reducing experimental time.

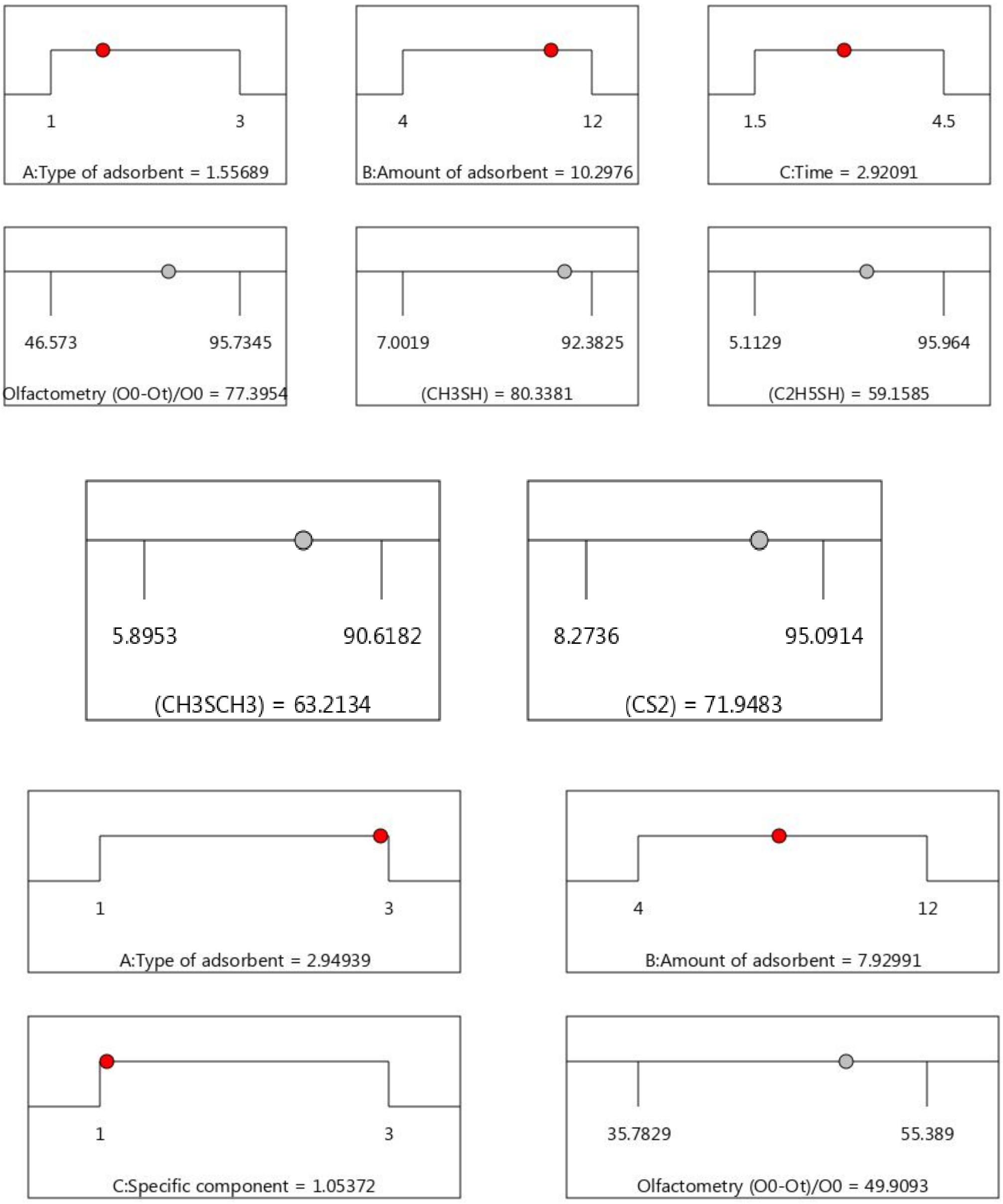


Figure 6.4 Optimized process conditions for the olfactometry based removal (%), CH_3SH removal (%), C_2H_5SH removal (%), CH_3SCH_3 removal (%) and CS_2 removal(%).

6.4 Recommendations for Future Work

- ✓ Sniffer-Panel based olfactometry, in practice is cumbersome, slow, and subject to improvisations. Further, there is no satisfactory provision to check reliability of positive-negative responses of panel. An approach is desired where the diluted odor sample is presented to the panel for discrimination from samples of non-odorous air and results can be related to statistically significant confidence levels. An olfactometer based upon *forced-choice triangle statistical design* could be used in this kind of a study. One diluted odor sample and two non-odorous air blanks are presented dynamically at each dilution level. Each panelist is required to judge which of the three ports is odorous and to signal a choice. Three ports are arranged in a circular symmetrical pattern in order to achieve a double-blind sample presentation. Dynamically diluted stimuli are presented at constant flow rate in ascending concentration order, increasing by a factor of 3 per step. Three odour dilution steps are available on a continuous basis during the evaluation. Evaluation of one sample is routinely completed by a panel of 9 within less than 15 minutes. Statistical data compilation could be achieved by ranking procedures to obtain the average panel odour threshold for each sample.

- ✓ Molecular modeling encompasses all theoretical methods and computational techniques used to model or mimic the behaviour of molecules. The techniques are used in the fields of computational chemistry, drug design, computational biology and material science for studying molecular systems ranging from small chemical systems to large biological molecules and material assemblies. The common feature of molecular modeling techniques is the atomistic level description of the molecular systems. This may include treating atoms as the smallest individual unit (the Molecular mechanics approach), or explicitly modeling electrons of each atom (the quantum chemistry approach). *Molecular modeling of each of CH_3SH, C_2H_5SH, CH_3SCH_3 and CS_2 and in presence of one another would be a challenging work.*

- ✓ Adsorption of CH_3SH, C_2H_5SH, CH_3SCH_3 and CS_2 in presence of *an anionic* and *neutral surfactant* would be another innovative method.
- ✓ Multicomponent adsorption isotherms could be studied, parameterized and new ones developed.
- ✓ A continuous study could be designed based on a packed column (filled with adsorbents) considering effects of variations in bed diameter, bed height, effluent rate and concentrations of specific VOSCs present in the raw sewage. This could be another challenging objective.
- ✓ Scale-up of the present design of the batch analysis could be carried out along with applications of dimensional analysis to arrive at new set of dimensionless groups.

Annex-I

Volatile Organic Compounds In and Around a Sewage Treatment Plant

I. Introduction

Municipal waste-water is the combination of liquid or water-carried wastes basically originating in the sanitaryconveniences of dwellings, commercial or industrial facilities and institutions, inaddition to any groundwater, surface water and storm water that may be present.

Untreated waste-water generally contains high levels of organic material, numerous pathogenic microorganisms, as well as nutrients and toxic compounds. So, anaerobic decomposition of the biodegradable organic waste component by microorganisms in STP produces principal odorous gases. It thus entails environmental and health hazards and consequently, must immediately be conveyed away from its generation sourcesandtreatedappropriatelybeforefinaldisposal.Theultimategoal of waste-water management is the protection of the environment in a manner commensurate with public health and socio-economic concerns.

Principal Constituents of the Gas within a Sewage TreatmentPlant

Gases found in and around STP areas include volatile organo-sulphides and disulphides, volatile fatty acids, amines, *p*-cresol and a range of heterocyclic compounds. The average percentage composition of gases found in and around a STP is reported inTable **I.1**.

Table I.1 Typical constituents found in and around STP works. (Abbott, 1993; Bonnin et al., 1990; Brennan, 1993; Cheremisinoff, 1988; Koe, 1989; Metcalf and Eddy, 1991; Vincent & Hobson, 1998; Young, 1984)

Compound	**Formula**	**Charecter**
Hydrogen sulphide	H_2S	Rotten eggs
Dimethyl sulphide	$(CH_3)_2S$	Decaying vegetables
Diethyl sulphide	$(C_2H_5)_2S$	Nauseating, ether
Diphenyl sulphide	$(C_6H_5)_2S$	burnt rubber
Diallyl sulphide	$(CH_2CHCH_2)_2S$	Garlic
Carbon disulphide	CS_2	Decayed vegetables
Dimethyl disulphide	$(CH_3)_2S_2$	Decayed vegetables
Methyl mercaptan	CH_3S	Decaying cabbage
Ethyl mercaptan	C_2H_5S	Decayed cabbage
Propyl mercaptan	C_3H_7SH	Unpleasant
Butyl mercaptan	C_4H_9SH	Unpleasant
tButyl mercaptan	$(CH_3)_3CSH$	Unpleasant
Allyl mercaptan	CH_2CHCH_2SH	Garlic
Crotyl mercaptan	$CH_3CHCHCH_2S$	Skunk-like
Benzyl mercaptan	$C_6H_5CH_2SH$	Unpleasant
Thiocresol	C_7H_7OS	Skunk, rancid
Thiophenol	C_6H_5SH	Putrid, nauseating, decay
Sulphur dioxide	SO_2	Sharp, pungent, irritating
Ammonia	NH_3	Sharp, pungent
Methylamine	CH_3NH_2	Fishy ,rotten
Ethylamine	$C_2H_5NH_2$	Ammonical
Dimethylamine	C_2H_7N	Putrid, fishy
Pyridines	C_6H_5N	Disagreeable, irritating
Scatole	C_9H_9N	Fecal, nauseating
Indole	C_8H_7N	Fecal, nauseating
Acetic acid	CH_3COOH	Vinegar
Butyic	C_3H_7COOH	Rancid
Valeric	C_4H_9COOH	Sweat
Formaldehyde	HCHO	Acrid, suffocating
Acetaldehyde	CH_3CHO	Fruit ,apple

Compound	Formula	Charecter
Butyraldehyde	C_3H_7CHO	Rancid, sweaty
Isobutyaldehyde	$(CH_3)_2CHCHO$	Fruit
Isovaleraldehyde	$(CH_3)_2CHCH_2CHO$	Fruit ,apple
Acetone	CH_3COCH_3	Fruit ,sweet
Butanone	$C_2H_5COCH_3$	Green apple

Volatile OrganicConstituents

Amongst the VOCs which are generally found in a Municipal STP are the volatile organo-sulphides. Emission potential of these VOC's during various biological degradation phases in the municipal sewage treatment plant was investigated by Bianchi & Varney, 1997. Table I.2 gives concentrations of some of most odorous VOCs concentrations generally found in Sewage Treatment Plant. Table I. shows list of typical concentrations of the substances detected of the LFKW plant located at Stuttgart University Campus and their maximum concentration. The results show the presence of a wide variety of organic sulphides and organic nitrogen-based compounds along with some oxygenated organic compounds and organic acids, mercaptans (R-SH) and amines.

TableI.2 Most odorous pollutant concentrations in and around a Sewage Treatment Plant.

Compound	Odor threshold, (ppm)
Amyl Mercaptan (1-Butanethiol)	0.0003
Crotylmercaptan	0.000029
Dimethylamine	0.047
Dimethyl sulfide	0.001
Dimethyl disulfide	0.0001
Hydrogen sulfide	0.00047
Methyl mercaptan	0.0011
Ethyl mercaptan	0.0003
Skatole (3-methyl indole)	0.0012

Indole	0.14
Thiocresol	0.0001
p-cresol (4-methyl phenol)	0.001
Carbon Disulfide	0.21
Ammonia	0.037
Isovaleric acid	0.41
n-butyric acid	0.01
phenol	0.04

I.3 Odour Marker

Only a few VOCs detected by Gas chromatography/Mass spectrometry (GC/MS) can be considered as markers of the malodour.

Mercaptans contribute to the municipal waste olfactory sensation largely and can be thus used as **odour markers** in order to monitor bad odours. These compounds have been monitored by means of a GC/MS. Usually these compounds are released by the anaerobic decomposition of the biodegradable organic waste component by microorganisms. A strong correlation has been observed between the quantitative monitoring of the VOC's concentration and the general olfactory perception in the environment.

I.4 Sources of Trace Gases

The major source of the VOC's of a Sewage Treatment Plant is the anaerobic condition of the system. The most common causes of odour problems in sewage treatment are the result of microbial respiration or metabolism, in particular under anaerobic conditions. **Table I.3** gives average levels of volatile organic sulfur compounds in μgm^{-3} found at the sampled sections of a sewage management plant. Error! Reference source not found. gives data sets of the olfactometric odor concentrations and chemical concentrations of the samples taken from main treatment units of the Izmir WWTP.

Table I.3 Average levels of volatile organic sulfur compounds in µgm−3 found at the sampled sections of a sewage management plant.

Serial No.	Compound	Gravitational thickening of sludge	Biological settlement tank	Thickening of sludge by flotation	Primary digestion tank
1	Ethyl Mercaptan	n.d	n.d.	21.7	20.0
2	Dimethyl sulfide	5.9	23.9	380.1	1.7
3	Carbon disulfide	2.5	2.5	8.2	9.8
4	Propyl Mercaptan	3.4	4.0	50.3	66.3
5	Butyl Mercaptan	3.9	4.1	33.2	7.9
6	Dimethyl disulfide	n.d	n.d.	31.6	0.5
7	1-Pentanethiol	3.0	n.d	3.8	22.1

n.d.: compound not detected

Table I.4 Data sets of the olfactometric odor concentrations and chemical concentrations of the samples.[DincerandMuezzinoglu,2008]

Sampling point	Odor (OU m^{-3})	TVOC (µgm^{-3})	Aldehydes	Halogenated C.	Mono-aromatics	RSCs
Screens	3730	292	55	31	20	18
Primary settling	4160	533	102	47	43	341
Aeration basin	6430	329	43	236	26	24
Sludge basin	37290	4406	66	172	3971	196
Sludge area	14460	324	109	108	21	86

Table I.5. Odorous pollutant concentrations at WWTP ($\mu g/m^3$) and odor threshold concentrations (OTC) and odor contribution levels of pollutants[DincerandMuezzinoglu,2008]

Pollutants	Screens	Primary settling	Aeration basin	Sludge basin	Sludge area	OTC (µg m^{-3})	Screens	Primary settling	Aeration basin	Sludge basin	Sludge area
Hydrogen sulfide	180	328	23	48	63	12.30	**14.63**	**26.67**	1.87	3.50	5.12
Methyl Mercaptan	n.d	n.d	n.d	9.18	n.d	3.44	n.d	n.d	n.d	2.67	n.d

Ethyl Mercaptan	0.22	n.d	n.d	n.d	n.d	2.11	0.11	n.d	n.d	n.d	n.d
Dimethyl sulfide	0.59	1.24	0.66	21.04	10.04	5.80	0.10	0.21	0.11	3.63	1.73
Carbon disulfide	3.06	9.82	n.d	2.86	1.77	48.30	0.01	0.03	n.d	0.01	0.01
Dimethyl disulfide	1.43	2.05	0.62	119.60	11.41	303.00	0.03	0.04	0.01	2.48	0.24
Acrolein	n.d	5.44	n.d	n.d	4.99	400	n.d	0.01	n.d	n.d	0.01
Butanal	n.d	1.83	0.23	1.63	2.88	12.55	n.d	0.15	0.02	0.13	0.23
Crotanaldehyde	0.14	0.29	0.10	0.21	0.12	344	0.00	0.00	0.00	0.00	0.00
Decanal	3.69	7.68	3.17	4.79	2.59	5.81	0.63	1.32	0.55	0.82	0.45
Heptanal	1.86	3.02	1.65	n.d	1.68	22.8	0.08	0.13	0.07	n.d	0.07
Hexnal	4.77	10.53	3.98	6.11	5.66	57.5	0.08	0.18	0.07	0.11	0.10
Nonanal	6.38	9.14	2.98	3.72	4.73	13.3	0.48	0.69	0.22	0.28	0.36
Octanal	2.04	6.99	3.35	8.17	1.80	7.21	0.28	0.97	0.47	1.13	0.25
Pentanal	0.68	1.44	0.59	1.03	1.02	21.6	0.03	0.07	0.03	0.05	0.05
Propanal	35.65	55.38	27.28	40.70	83.40	3.6	9.90	15.38	**7.58**	11.31	**23.17**
Benzene	0.62	1.40	1.30	3.10	0.55	11800	0.00	0.00	0.00	0.00	0.00
Ethylbenzene	1.22	3.35	1.90	409.18	1.70	400	0.00	0.01	0.00	1.02	0.00

o, m -Xylene	2.60	6.81	3.80	935.36	4.01	850	0.00	0.01	0.00	1.10	0.00
p-Xylene	2.65	7.25	3.91	1254.74	4.32	570	0.00	0.01	0.01	2.20	0.01
Styrene	0.30	0.70	0.46	12.04	0.33	140	0.00	0.01	0.00	0.09	0.00
Toluene	12.56	23.68	14.47	1356.93	10.00	80	0.16	0.30	0.18	**<u>16.96</u>**	0.12
1,1,1-Trichloroethane	0.34	2.16	82.06	21.27	0.69	88000	0.00	0.00	0.00	0.00	0.00
1,4-Dichlorobenzene	7.13	8.04	11.96	8.52	5.76	730	0.01	0.01	0.02	0.01	0.01
Carbon tetrachloride	1.59	1.60	1.51	1.26	2.59	11500	0.00	0.00	0.00	0.00	0.00
Chloroform	1.19	4.62	32.75	13.74	4.23	3000	0.00	0.00	0.01	0.00	0.0
Methylene chloride	16.09	25.07	32.07	36.43	91.74	4100	0.00	0.01	0.01	0.01	0.02
etrachloroethene	3.27	1.79	40.63	12.91	0.94	12000	0.000	0.00	0.00	0.00	0.00
Trichloroethene	1.86	4.05	34.88	78.21	1.97	115000	0.00	0.00	0.00	0.00	0.00

n.d.: not detected

Table I.6 Typical concentrations of of the substances detected of the LFKW plant located at Stuttgart University Campus and their maximum concentration.[Zarra etal.,2008]

Class	Substances	Maximum Concentration
		(mg/m^3)
Sulphurous	Sulphur dioxide	0.67021
	Dimethyl disulphide	0.21259
	Dimethyl trisulphide	0.04549
Ketones	Acetone	0.46179
	2-Butanone	4.53781
	Acetophenone	0.58772
Aldehydes	Benzaldehyde	0.06699
	Trimethyl-benzaldehyde	0.06432
	Decanal	0.02146
	Nonanal	0.01982
Aromatics	Ethyl-benzene	0.01472
	Dimethyl-benzene	0.01767
	1-Ethyl-2-methylbenzene	0.01309
	1,3,5 Trimethylbenzene	0.00836
	p-Xylene	0.04724
	1,2,4-Trimethylbenzene	0.01055
	Benzene	0.02191
	Toluene	0.50921
Terpenes	Limonene	0.11463

Annex-II

Terms and definitions in odour assessment

I. Terms and definitions in odour assessment

In order to investigate gas samples of unknown composition with regard to their property to induce odour sensations, following terms and definitions have been found quite useful. The sensory properties of odour are both qualitative and quantitative and one does not usually know the rules of interaction of an individual with the resulting odour. The types of human responses sought depend on the particular sensory property that is measured. Odour intensity, detectability, character, and hedonic tone (pleasantness and unpleasantness) are few of the representative sensory properties of odour. The combined effect of these properties may be related to particular annoyance levels that may be caused by one or more odour events.

The following terms and definitions conform to the Guideline **VDI 2449** Part 2 and Standard **DIN 6879**. *The following terms and definitions are restricted to the property "odour".*

Odor [ASTM, 1998]

Perception resulting from simulating the olfactory receptors; in a broader sense, the term is sometimes used to refer to the combination of sensations resulting from stimulation of the entire nasal cavity.

Odour Intensity

The strength of the perceived odour sensation is generally termed as odour intensity. It depends on the odorant concentration in a complex way, which has been discussed in **Chapter 5**. The intensity of an odour is perceived directly, without knowing the concentration of the odorous gas sample or of the degree of dilution of the odorous sample needed to eliminate odour.

Odorant concentration ($c_{od,cs}$)[VDI 2449]

The odorant concentration of the gas sample to be measured (single compound or mixture) is determined by dilution with neutral air down to the odour threshold. The numerical value of the odorant concentration results from the volume flows of the gas sample and the neutral air at the moment when the odour threshold is reached. The unit of the quantity "odorants concentration" is odor unit (OU) divided by volume unit (m^3), thus OU/m^3.

Odor unit (OU)

Based on the definition of the odour threshold, 1 OU is the very quantity (number of molecules) of odorants which just induces an odour sensation when dispersed in 1 m^3 of neutral air. 1 OU/m^3 is also the benchmark of the odorant concentration scale (c_{od}). This is also called D-T (dilution to threshold ratio).

Odour detection threshold

When a sample of odorous gas is progressively diluted, the concentration of odorants decreases, and the intensity of odour weakens simultaneously, but not in direct proportion to the extent of the dilution. The intensity of the gaseous sample becomes so low with any further dilution that detection or recognition of the odour is very difficult. At some statistically defined point of dilution, the *detection threshold* is reached. With little bit less dilution (i.e. higher odorant concentration) odour is recognised and the dilution is called *recognition threshold*.

The concentration of odorous substances at *detection threshold* level leads to an odour impression with 50% of the defined population. The odorant concentration at the threshold is 1 OU/m^3 by definition.

Odour recognition threshold

The lowest physical intensity at which an odour stimulus is correctly identified a specified percent of the time.

Hedonic tone

Odours of equal intensity may differ in character. Hedonic tone is a character of odour that identifies its place on a scale of pleasantness and unpleasantness. However, an

otherwise pleasant odour may be considered objectionable by the exposed population in the context of industrial emission and pollution hazards.

Odour Annoyance [NRC,1979]

Annoyance experienced by a population exposed to an air-pollution odour is a combined result of the intensity, character, and hedonic tone of the odour, as well as of the frequency and duration of the exposure. It is quite difficult to measure annoyance.

Olfactometer

Olfactometers are instruments in which a gas sample (odorous sample) is diluted with neutral air in a defined ratio. This dilution is presented to test subjects (panellists) as a smell sample. The panellists are offered several dilution steps.

Neutral air

Neutral air is air in a defined thermodynamic state (T,p, and particularly humidity). It must not contain interfering components at concentrations which induce odour sensations or influence the sense of smell. Neutral air is used as dilution air and/or reference air.

Smell sample

The panellist is offered a smell sample for assessment. A smell sample may be

- A gas sample at defined dilution,
- neutral air (e.g. as a blank or reference air)
- an undiluted gas sample

Panelist [ASTM,1998]

A general term for any individual responding to stimuli in a sensory test.

Panel [ASTM, 1998]

A group of panellists chosen to participate in a sensory test.

Perception [ASTM,1998]

The awareness of the effect of stimuli.

Receptor

A cellular structure mediating the physiological response to the presence of physical or chemical agents.

Repeatability *(r)*

The repeatability *r* is “the value below which the absolute difference between two single test results obtained using the same method, on identical test material, under the same conditions” may be expected to lie with 95% probability [**VDI 2449**]. This would mean using the same panel, same apparatus, same laboratory and within a short interval of time.

Reproducibility *(R)*

The reproducibility R is "the value below which the absolute difference between two single test results on identical material obtained using the same method, on identical test material but under different conditions" may be expected to lie with 95% probability [**VDI 2449**]. This would mean different panellists, different apparatus, different laboratories and/or different times.

Representativity

The panel selected for the olfactometric measurement has to be a representative sample of the population defined by the task. The frequency distribution of odour impressions from a given measurement object (gas sample) has to correspond to the frequency distribution of the population with a satisfactory approximation. This condition will normally be met with 8 to 15 panellists selected at random, if the statistical population is defined to be the real population.

Sensitivity

The ability to perceive qualitatively or quantitatively, or both, one or more stimuli by means of the sense organs.

Supra-threshold

Pertaining to a stimulus above the specified threshold.

The procedure for odour measurement, sampling, principles of operation of a dynamic dilution olfactometer, presentation of odour concentrations and the triangular forced choice technique will be discussed in APPENDIX-III.

Annex-III

Olfactometry

Olfactometry

Olfactometry is the controlled presentation of odorants and the registration of the resulting sensations in man. It is a complete measuring method as defined by Guideline **VDI 3881**, Part 1 [**VDI 3881,1986**]. The main field of application of this guideline is the determination of odour thresholds and odorant concentrations of gas samples collected for air pollution prevention. The practical application of olfactometry is to investigate gas samples of unknown composition with regard to their property to induce odour sensations.

Possible tools for measurement of odour are:

Field Panels

Use of expert field panels that ‘sniff out’ the situation around a source, but cannot provide a quantitative description that could be used objectively in specific cases.

Population Panels

Panels are chosen usually from residents usually living around the source. They are asked to assess the odour intensity in the ambient air at their residence at a specific time every day. It can indicate a general trend in the annoyance but not suitable to provide a useful regulatory tool.

Chemical-Analytical Method

Gas Chromatography failed together with Mass Spectroscopy in this area as odour is rarely an additive result of the concentrations in the mixtures and are often determined in trace concentrations, even below detective threshold.

Olfactometry

All odour threshold measurements involve the determination of the number of dilutions of an odorous gas sample required to render it nonodorous. The devices designed are called **olfactometers** and are essential in studies of the contributions of odour to air pollution.

Olfactometer: Construction

An olfactometer consists of a dilution air pump, peristaltic odor pump, signal box, air rotameters, deodorizing chamber, six sets of sniffing ports, two manifolds and Teflon sample lines. This instrument provides six dilution stations each equipped with a set of three glass sniffing ports. Two of the ports emit deodorized room-air while the third discharges the odorous gas diluted with deodorized air.

Olfactometer: Response system

There are two forms of dynamic olfactometry response systems:

a) *Yes/No Response*

This is where each panel has only one sniffing port. They must indicate when they can detect an odour in the air stream.

b) *Forced Choice Response*

This is where panellists have 2 or more sniffing ports. At any one time only one port may contain an odour, the other(s) contain odour free air. The panellist must sniff each port and attempt to pick which one contains the odour. They must make a choice even if they cannot detect any odour.

Although more complex to implement, the forced choice technique is more sensitive than the simple yes/no technique. The increased sensitivity is due to the elimination of conservative response bias in panellists [**ASTM**,**1998**].

Olfactometer: Principle of Operation

Ternary Forced-Choice Method

A dilute sample is presented with two odourless samples. The panelist must identify which sample contains the odorant, and signals his choice by depressing a push button placed at the selected port. The testing continues until the subject becomes consistently correct in the identification of the odorous sample. This olfactometer operated with a ternary forced-choice principle with approximately six trained panelists is up until the best possible way of analysing odour in terms of delectability, reproducibility, reliability and repeatability of the results. However it becomes a cost effective affair in totality as the fixed cost itself includes setting up an air-conditioned laboratory, supply of dry filtered compressed air, installation of the olfactometer complete with its accessories, availability of a suitable sampling unit and a panel of minimum 4-6 trained odour sniffers. Over and above there is a running cost of supply of special plastic sampling bags, activated carbon filters etc.

Individual Thresholds Method by Dravnieks[Cheremisinoff and Young,1975]

The simplest form of this method involves estimating the threshold dilution for each individual panellist. The logarithms of these individual thresholds are averaged. The odour threshold is equal to the antilogarithm of this average.

Dynamic olfactometry methodology can differ in the following ways:

- Type of response system;
- Number of panellists;
- Selection and screening of panellists;

Annex-IV

Henry's Law Constants for Sulphur base Organic Compounds

Phase equilibrium governs the distribution of molecular species between two or more phases. For a molecular solute, vapor−liquid phase equilibrium isgiven by equation IV-1(symmetric convention):

$$Py_i\emptyset_i^V = x_i H_i P_{solv}^{sat} exp\left(\int_{P_{solv}^{sat}}^{P} \frac{v_i^{\infty}}{RT} dP\right) \qquad \text{(IV-1)}$$

where y_i and x_i are respectively the vapor and liquid compositions, P is the pressure, $\Phi^V$is the fugacity coefficient (equal to one as we consider that, at atmospheric pressure, when the vapor phase is considered as an ideal gas), $H_i^{P_{solv}^{sat}}$is the Henry's law coefficient at the solvent vapor pressureand the exponential term is the Pointing factor. This last quantity can be considered equal to unity. Consequently, equation IV-1 can be written as

$$Py_i = x_i H_i P_{solv}^{sat} \qquad \text{(IV-2)}$$

Henry's law constants (solubilities) of trace gases of potential importance in environmental chemistry (atmospheric chemistry,waste water treatment, . . .) have been collected and converted into a uniform format. Waste water contains very low concentration (dilute solution) of volatile organo-sulphur compounds. So Henry's law constants are valid for this waste water, as it behaves like an ideal solution.

Data Table

Substances	K_H (M/atm)	References	Type
Methanethiol	0.33	Hine and Weimar [1965]	M
CH_3SH	0.39	Przyjazny et al. [1983]	M
(methyl mercaptan)	0.71	Russel et al. [1995]	E
	0.2	De Brayn et al. [1995]	M
	0.26	USEPA [1982]	X
Ethanethiol	0.36	Hine and Mookerjee [1975]	V
C_2H_5SH	0.28	Przyjazny et al. [1983]	M
(ethyl mercaptan)	0.22	Vintenberg et al. [1975]	M
	0.26	Kerl and Lindinger [1997]	M
	0.34	Yaw and Yang [1992]	?
1 propanethiol	0.25	Przyjazny et al. [1983]	M
C_3H_7SH			
1 butanethiol	0.22	Przyjazny et al. [1983]	M
C_4H_9SH	0.11	Yaw and Yang [1992]	?
Thiophenol	0.3	Hine and Weimar [1965]	V
C_6H_5SH	0.3	Hine and Mookerjee [1975]	V
Thioanisole	0.41	Hine and Weimar [1965]	V
$C_6H_5SCH_3$	0.41	Hine and Mookerjee [1975]	V
	0.55	Hine and Weimar [1965]	V
di-methyl sulphide	0.16	Lovelock et al. [1972]	M
CH_3SCH_3	0.62	Vintenberg et al. [1975]	M
(DMS)	0.56	Przyjazny et al. [1983]	M
	0.44	Cline and Bates [1983]	C
	0.62	Gaffny and Synum [1984]	X
di-ethyl sulphide	0.46	Hine and Mookerjee [1975]	V
$C_2H_5SC_2H_5$	0.56	Przyjazny et al. [1983]	M

Substances	**K_H (M/atm)**	**References**	**Type**
di-propyl sulphide $C_3H_7SC_3H_7$	0.33	Przyjazny et al. [1983]	M
di-methyl di-sulphide CH_3SSCH_3 (DMDS)	0.84 0.96	Vintenberg et al. [1975] Przyjazny et al. [1983]	M M
di-ethyl di-sulphide $C_2H_5SSC_2H_5$	0.47 0.67	Vintenberg et al. [1975] Przyjazny et al. [1983]	M M
Thiophene C_4H_4S	0.44 0.34	Przyjazny et al. [1983] Yaws and Yang [1992]	M ?
di-methyl sulfoxide CH_3SOCH_3 (DMSO)	1400	Gmehling et al. [1981]	X
di-methyl sulfone CH_3SOOCH_3	>50000	De Brayn et al. [1995] Yaws and Yang [1992]	E ?
Carbon di-sulfide CS_2	0.056 0.055 0.052 0.076	Rex [1906] De Brayn et al. [1995] Yaws and Yang [1992] USEPA [1982]	X M ? X
Carbonyl sulphide COS	0.033 0.021 0.022	Hempel [1901] Winkler [1906] De Brayn et al. [1995]	X X M

‘M’	Original publication of a measured value (e.g. head-space or bubble column technique as explained by Betterton [1992]).
‘V’	Vapor pressure of the pure substance is used to determine the Henry's law constant (c=p for a saturated solution).
‘C’	The paper that is cited here refers to another reference which I could not obtain (e.g. personal communication, Ph.D. thesis, internal papers etc.).
‘X’	I haven't seen the paper that I cite here. I found it referenced by another paper or I know about it through others.
‘?’	The cited paper doesn't clearly state how the value was obtained.
‘E’	The value is estimated. Estimates are only listed if no reliable measurements are available for that compound.

Annex-V

Role of Surfactants

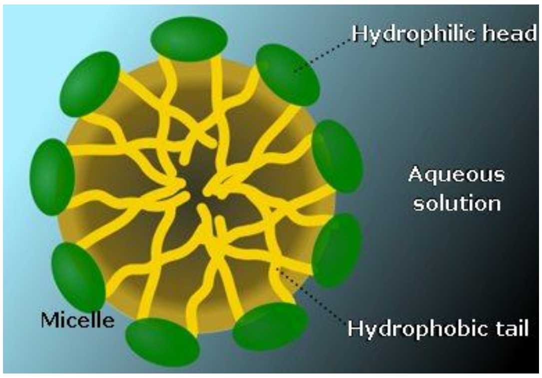


Fig. V.1 Schematic representation of micelle.

The adsorption of surfactant is a process of transfer of surfactant molecules from bulk solution phase to the adsorbent surface/interface. Forces like electrostatic attraction, covalent bonding, hydrogen bonding, hydrophobic bonding and solvation of various species determine the behavior of surfactants at the interface. Kinetics and equilibrium adsorption of surfactants at the solid-liquid interface depend on the nature of surfactants and the nature of the solid surface. Three types of interactions are generally involved in the adsorption of a surfactant at solid/liquid interface.

I. The attractive or repulsive interaction between the hydrophilic group and the surface,

II. The attractive interaction between the hydrophobic group and the surface, and

III. The lateral interactions that occur between adsorbed surfactants.

For surfactants, the most important interactions between the hydrophilic group and the surface are the electrostatic and hydrogen bonding. Electrostatic interactions are most important for ionic surfactants. If the surfactant and the adsorbent are oppositely charged, the rate of adsorption is very fast and the equilibrium time is less. On the other hand, if surfactant and the adsorbent are similarly charged, repulsion forces take place and minor adsorption is resulted.

Generally, at lower CMC[1], the surfactants have the greater tendency to get adsorbed at the solid surface. But above the CMC, the monomer concentration of the surfactants decreases due to the formation of micelle. A schematic representation of a micelle is given in **Fig. V.1**.

The mechanisms by which surface-active molecules adsorb on the solid substrate from aqueous solution are given below:

a. *Ion Exchange:* similarly charged surfactant ions replace the counter ions adsorbed on the substrate from the solution.
b. *Ion pairing:* adsorption of surfactant ions from solution on the opposite charged sites, which are unoccupied by counter ions.
c. *Hydrophobic bonding:* this is the mechanism of adsorption when there is an attraction between a hydrophobic group of adsorbed molecule and a molecule present in the solution.
d. *Adsorption by polarization of π electrons:* when the surfactant contains electron rich aromatic nuclei and the solid adsorbent has strong positive sites, the adsorption occurs due to the attraction between electron rich aromatic nuclei of the adsorbate and the positive sites on the adsorbent.

---

[1] *The critical micelle concentration is defined as the concentration of surfactants above which micelles form and all additional surfactants added to the system go to micelles.*

e. *Adsorption by dispersion forces:*Adsorption by London-van der Waals force between adsorbate and adsorbent increases with the increasing molecular weight of the adsorbate.

Applications of surfactant

i. Mineral or particulate floatation

Ore or mineral floatation is the most important example of particulate floatation used in industries. Particulates, which have been successfully removed from suspension by flotation, include bacterial spores, algae, clays and colloidal precipitates. Like ore flotation, each of these processes requires the addition of a suitably charged surfactant and either adjustment of pH or addition of an ion that promotes the adsorption of surfactant on the surface of the particulate.

ii. Surfactants and carbon regeneration

Activated carbon is widely used to remove organic pollutants from wastewater. When breakthrough occurs the carbon should be regenerated which requires the removal of adsorbed organics from the carbon surface. In this method, a concentrated surfactant solution is passed through the adsorber containing the spent carbon, and the adsorbate desorbs and gets solubilized in the micelles.

iii. Filtration of ultra fine particles

Removal of particulate contaminants is very important in many industries like water reclamation facilities, water treatment, microelectronics and pharmaceutical industries. Particle removal by filtration is very difficult especially for ultra fine particles. Deposition of small particles on the surface of the filter is enhanced by the adsorption of proper surfactant on the filter surface, which can lower the energy barrier between the particles, and the filter surface.

iv. Stability of particulate suspension

Industries such as paint, printing ink, pharmaceutical, etc. require the stability of particle and colloidal slurries. The shielding of surface charges on the particles causes particle settling, which destabilizes the suspension and would result in coagulation and subsequent settling. It is seen that addition of conventional stabilizing agent, like ionic surfactants and polymers, can increase the stability of the particle.

v. Deinking from paper and plastic film

Surfactants are necessary for the removal of ink from fibre during pulping step and to cause the pigment particles to be separated from the paper fibre by floatation. This method is also used for plastic recycling. The cationic surfactants are the most effective whereas the anionic surfactants are the least effective in removing the printing ink from plastic film because the binder is an acidic acrylate with a negative charge.

vi. Detergency

In the process of detergency, the surfactant molecules are adsorbed on both soil and fabric surfaces. The surfactants loose the soil from the fabric and also deflocculate the particles by attaching themselves to the soil and fabric and thereby reducing the attraction between them.

References

Aatamila M., Verkasalo P.K., Korhonen M.J., Suominen A.L., MaijaRiittaHirvonen M-R., Viluksela M.K. and Nevalainen A. (2011) Odour annoyance and physical symptoms among residents living near waste treatment centres. *Environmental Research*, 111,164-170.

Abe M, Kawashima K, Kozawa K, Sakai H and Kaneko K. "Amination of activated carbon and adsorption characteristics of its aminated surface", Langmuir 16(2000) 5059-5063.

Adib F., Bagreev A. and Bandosz T. J. (1999b) Effect of pH and surface chemistry on the mechanism of H_2S removal by activated carbons. J. Coll. *Interface Sci.* 216,360-369.

Afkhami A, Madrakian T, Karimi Z and Amini A. "Effect of treatment of carbon with sodium hydroxide solution on its adsorption capacity for the adsorption of some cations", Colloid Surf.A 304 (2007) 36-40.

Ahamed YA."Adsorption kinetics performance of packed bed adsorber for phenol removal using activated carbon from dates stones", J. Hazard.Mater. 170 (2007) 763-770.

Akhter M, Keifer J, Chughtai A, Smith D (1985): The absorption band at 1590 cm− 1 in the infrared spectrum of carbons. Carbon 23, 589-591.

AlbishriH.M. and MarwaniH.M., Chemically modified activated carbon with tris (hydroxymethyl) aminomethane for selective adsorption and determination of gold in water samples, Arabian Journal of Chemistry 9 (2016) S252-S258.

Al-Degs Y, Khraisheh MAM, Allen SJ, Ahmad MN and Walker GM. "Competitive adsorption of reactive dyes from solution: Equilibrium isotherm studies in single and multisolute systems", Chem. Eng. J. 128 (2007) 163–167.

Ahmaruzzaman M and Gayatri SL. "Batch adsorption of 4-nitrophenol by acid activated jute stick char: Equilibrium, kinetic and thermodynamic studies", Chem. Eng. J. 158 (2010) 173–180.

Ania C., Cabal B, Pevida C, ArenillasA, Parra J, Rubiera F, J. Pis, Removal of naphthalene from aqueous solution on chemically modified activated carbons, Water research 41 (2007) 333-340.

Anfruns, A., Canals-Batlle, C., Ros, A., Lillo-R ´odenas, M.A., Linares-Solano, A., Fuente, E., Montes-Mor´an, M.A., and Martin, M.J.,Removal of odour causingcompounds using carbonaceous adsorbents/catalysts prepared fromsewage sludge. Paper presented at the 3rd IWA International Conference on Odour and VOCs, Barcelona, Spain (2008, October).

Ariano P.F., Davi I., Martini R., Molina P., Morello M. and Romano R., An intrigrated approach to investigation and monitoring of odour emmissions from composting plants: the experience of Provincia di Torino (Italy).*Chemical Engineering Transaction*, 23, (2010) 117-122.

ASTMMethod D 3686-84: Standard practice for sampling atmospheres to collect organic compound vapors (activated charcoal tube adsorption method). *Annual Book of ASTM Standards,*11.03: (1988a)234–240.

ASTM Method D 3687-84: Standard practice for analysis of organic compound vapors collected by the activated charcoal tube adsorption method. *Annual Book of ASTM Standards,*11.03: (1988b) 241–246.

Baker R.W., Yoshioka N., Mohr J.M., Khan A.J., Separation of organic vapours from air. J Membrane Sci.31: (1987) 259-271.

Behling R.D., Separation of hydrocarbon from air. In Proceedings of the 6th Annual Membrane Technology Planning Conference.Session V-4, (1986) Cambridge.

Behling R.D.,Ohlrogge K., Peinemann K.V., Kyburz E., The separation of hydrocarbons from waste vapour streams. AIChESymposium Series.48(1988)(272): 68.

Bentzen G., Smith A.T., Bennet D., Webster N.J., Reinholt F., Sletholt E., Hobson, J., Controlled dosing of nitrate for prevention of H_2S in a sewer network and the effects on the subsequent treatment process. Water Sci. Technol. 31: (1995) 293–302.

Bliss PJ, Schulz TJ, Senger T, Kaye R.B., Odour measurement-factor affecting olfactometry panel measurement. Water Sci Technol. 34: (1996) 549-556.

Blanes-Vidal V., Hansen M.N., Adamsen A.P.S., Feilberg A., Petersen S.O. and Jensen B.B., Characterization of odor released during handling of swine slurry: Part I. Relationship between odorants and perceivedodor concentrations. *Atmospheric Environment* 43, (2009)2997–3005.

Blonda M., Di Pinto A. C., Laera G., Palumbo R. and Pollice A., Activated Sludge Diffusion For Odour Removal - Effects Of H_2S On The Biomass. *Environmental Technology*, Vol. 27. (2006) pp875-883.

Boehm H., Some aspects of the surface chemistry of carbon blacks and other carbons, Carbon 32 (1994) 759-769.

Boeker P., Haas T., Diekmann B. and Lammers P.S., New odour sampling method: adsorption and reconstitution of odours. *Chemical engineering Transactions*, 23, (2010) 49-54.

Boon A.G., Septicity in sewers: causes, consequences and containment, Water Science and Technology 31 (1995) 237-253.

Boyd GE, Adamson AW and Myers Jr. LS.“The exchange adsorption of ions from aqueous solutions by organic zeolites. II. Kinetics”, J. Am. Chem. Soc. 69 (1947) 2836–2848.

Buys H.C.W.M., Martens H.F., Troos L.M., Van Heuven J.W., Tinnemans A.H.A., New intrinsic separation characteristics of poly membranes of organic vapour/nitrogen mixtures. In Proceedings of the International Conference on membraneand membrane processes, Chicago. pp. 83(1990).

Cain W.S., Moskowitz H.R., Psychophysical scaling of odor, Human responses to environmental odors (1980) 1-32.

Cain WS, Stevens JC , Nickou CM, Giles A, Johnston I, Garcia-Medina M.R., Life span development of odour identification, learning and olfactory sensitivity. Perception 24:(1995)1457-1472

Canela M. C. and Jardim W. F**.**, Identification and photocatalytic destruction of malodorous compounds in sewage.*Environmental Technology*, Vol. 29. (2008) pp673-679.

Capelli L., Sironi S., Rosso R.D., Céntola P. and Grande M.II., A comparative and critical evaluation of odour assessment methods on a landfill site. *Atmospheric Environment* 42,(2008) 7050–7058

Carey J.H., An introduction to AOP for destruction of organics in waste water. Water pollution. Res. J. Can. 2: (1992) 1-21.

Central Pollution Control Board(CPCB), Guidelines on odour pollution & its control. Ministry of Environment & Forests, Govt. of India, PariveshBhawan, East Arjun Nagar, Delhi – 1100 32, (2008) pp.6-57.

Chen G., Dussert B. W. and Suffet I. H., Evaluation of granular activated carbons for removal of methylisoborneol to below odor Threshold concentration in drinking water. *Wat.Res.* Vol. 31, No. 5, (2014) pp.1155-1163.

Cheng, X., Peterkin, E.D., and Burlingame, G.A., Study of the effect of DMSO on VOS odour production in a wastewater plant.*Water Science and Technology* 55,(2007). 327–333.

Chiang HL, Huang CP, Chuang P.C., The surface characteristics of activated carbon as affected by ozone and alkaline treatment. Chemosphere 47: (2002) 257-265.

Chingombe P., Saha B., Wakeman R., Surface modification and characterisation of a coal-based activated carbon, Carbon 43 (2005) 3132-3143.

Chiriac R, Carre J., Perrodin Y., Fine L., Letoffe J.-M., Characterisation of VOCs emitted by open cells receiving municipal solid waste, Journal of Hazardous Materials 149 (2007) 249-263.

ChristmanP.N., Industrial Odor Technology Assessment. *Ann Arbor Science Publishers,*Michigan(2012).

Cline, J. D. and T. S. Bates. Dimethyl sulfide in the equatorial Pacific Ocean: A natural source of sulfur to the atmosphere. Geophys. Res. Lett., 10, 949-952, 1983.

Cox HHJ, Deshusses MA (2002) Co-treatment of H_2S and toluene in a biotrickling filter. Chem. Eng. J. 87: 101–110.

Daifullah A.A.M. and Girgis B.S., Impacts of surface characteristics of activated carbon on adsorption of BTEX , colloids., surf., A: Physicochem. Eng. Aspects 214(2003)181-193.

de Boer J.H., Linsen B.G., Plas T, van Zonder G.J., Studies on the pore systems in catalysts. VII. Description of the pore dimensions of carbon blacks by t-method. Journal of catalysis 4(1965)649-53.

De Bruyn, W. J., E. Swartz, J. H. Hu, J. A. Shorter, P. Davidovits, D. R. Worsnop, M. S. Zahniser, and C. E. Kolb. Henry's law solubilities and Setchenow coefficients for biogenic reduced sulphur species obtained from gas-liquid uptake measurements. J.Geophys. Res., 100D, 7245-7251, 1995.

Deng S., Sourirajan A., MatsuuraT., Study of volatile hydrocarbon emission control by an aromatic poly (ether imide) membrane. IndEngChem Res.34(12): (1996) 4494-4500.

Denga H., Li G., Yanga H., Tanga J., Preparation of activated carbon from cotton stalk by microwave assisted KOH and K_2CO_3 activation, Chemical engineering journal 163 (2010) 373-381.

Dennis Mc, John B., Biofiltration as an odour abatement strategy. Biochem. Eng. J. 5: (2000) 231–242.

Derylo-Marczewska A., Buczek B., Swiatkowski A., Effect of oxygen surface groups on adsorption of benzene derivatives from aqueous solutions onto active carbon samples, Applied Surface Science 257 (2011) 9466-9472.

Derylo-Marczewska A., Swiatkowski A., Biniak S., Walczyk M., Effect of properties of chemically modified activated carbon and aromatic adsorbate molecule on adsorption from liquid phase, Colloids and Surfaces A: Physicochemical and Engineering Aspects 327 (2008) 1-8.

Dewettinck, K. Van Hege, W. Verstraete, The electronic nose as a rapid sensor for volatile compounds in treated domestic wastewater, Water Research 35 (2001) 2475-2483.

Din A.T.M., Hameed B., Ahmad A.L., Batch adsorption of phenol onto physiochemical-activated coconut shell, Journal of Hazardous Materials 161 (2009) 1522-1529.

Dincer F, Muezzinoglu A., Odor-causing volatile organic compounds in wastewater treatment plant units and sludge management areas. J. Environ Sci. Heal A. 43: (2008) 1569–1574.

Duczmal L., Sobczynski A., Photocatalytic Water purification: Destruction of resorcinol by irradiated titania. React. Kinet. Catal. Lett. 66(2): (1999) 289-295.

Dunn R.F.,, El-Halwagi M.M., Optimal design of multicomponent VOC condensation systems.J Hazard Mater.:(1994) 187–206.

Dural MU, Cavas L, Papageorgiou SK and Katsaros FK. “Methylene blue adsorption on activated carbon prepared from Posidonia oceanic (L.) dead leaves: Kinetics and equilibrium studies”, Chem. Eng. J. 168 (2011) 77–85.

Dutta A, Patra AK and Bhaumik A. “Porous organic–inorganic hybrid nickel phosphonate: Adsorption and catalytic applications”, MicroporousMesoporous Mater. 155 (2012) 208–214.

Dwivedi P., Gaur V., Sharma A., Verma N., Comparative study of removal of volatile organic compounds by cryogenic condensation and adsorption by activated carbon fiber. Sep Purif Technol.39: (2004) 23–37.

Einarsen AM, Esoy A, Rasmussen A, Bungum S, Sveberg M., Biological prevention and removal of hydrogen sulphide in sludge at Lillehammer wastewater treatment plant. WaterSci. Technol. 41 (6):, (2000) 175–187.

Ekpete O., Horsfall M., Preparation and characterization of activated carbon derived from fluted pumpkin stem waste (Telfairia occidentalis Hook F), Res. J. Chem. Sci 1 (2011) 10-17.

Elbir T., Cetin B., Cetin E., Bayram A. and Odabasi M., Characterization of Volatile Organic Compounds (VOCs) and Their Sources in the Air of Izmir, Turkey. *Environ Monit Assess* 133: (2007) 149–160.

Ergas S., Membrane bioreactors. In: KennesC, VeigaMC(eds) Bioreactors for waste gas treatment. Kluwer, Dordrecht. (2001) pp 163–177.

Erto A, Lancia A and Musmarra D. “A Real Adsorbed Solution Theory model for competitive multicomponent liquid adsorption onto granular activated carbon”, MicroporousMesoporous Mater. 154 (2012) 45–50.

Estrada JM, Bart Kraakman, NJR, Muñoz R, Lebrero R (2011) A comparative analysis of odour treatment technologies in wastewater treatment plants. Environ. Sci. Technol. 45: 1100–1106.

Fairchild E.J. and Stokinger H.E., Toxicological studies on organic sulphur compounds (1986).

Fanning P.E., Vannice M.A., A DRIFTS study of the formation of surface groups on carbon by oxidation, Carbon 31 (1993) 721-730.

Fatima A. and Zoulikha M., Effect of oxidant treatment of date pit activated carbons application to the treatment of waters. Journal of desalination, 222 (2008) 394-403.

FrechenF.B., Odour emissions of wastewater treatment plants-recent German experiences. *Water Science and Technology* 30(4), (1994)35–46.

Gaffney, J. S. and G. I. Senum.In L. Newman, editor, Gas-Liquid Chemistry of Natural Waters, pages 51-57.NTIS TIC-4500, UC-11, BNL 51757, Brookhaven National Laboratory, 1984.

Gallego E., Soriano C, Roca F.X., Perales JF, Alarcón M.,Guardino X Identification of the origin of odour episodes through social participation, chemical control and numerical modeling. Atmos Environ. 42: (2008)8150–8160.

Ganigue, R, Gutierrez O, Rootsey R, Yuan Z., Chemical dosing for sulfide control in Australia: An industry survey. Water Res. 45: (2011) 6564-6574.

Garcia De Lomas, J., Corzo, A., Gonzalez, J.M., Andrades, J.A., Iglesias, E., Montero M.J., Nitrate promotes biological oxidation of sulfide in wastewater: experiment at plant-scale. Biotechnol. Bioeng. 93 (4): (2005) 801–811.

Glaze W.H., Kang J.W., Chapin D.H., The chemistry of water treatment processes involving ozone hydrogen peroxide and ultraviolet radiation. Ozone-Sci Eng. 9: (1987) 335-352.

Gmehling, J., P. Rasmussen, and A. Fredenslund.Vapor-liquid equilibria by UNIFAC group contribution. Revision and extension. 2. Ind. Eng. Chem. Process Des. Dev., 21, 118, 1981.

Godayol A., Alonso M., Besalú E., Sanchez J.M. and Anticó E., Odour causing organic compounds in wastewater treatment plants: Evaluation of headspace solid-phase microextraction as a concentration technique. *Journal of Chromatography A*, 1218, (2011) 4863–4868.

GostelowP., Parsons S.A., and Stuetz R.M., Odour measurement in sewagetreatment: A review. *Water Research* 35(2001) 579–597.

Goyal M., Dhawan R. and Bhagat M., Adsorption of dimethyl sulfide vapors by activated carbons. *Colloids and Surfaces A: Physicochem.* Eng. Aspects 322, (2008) 164–169.

Gregg S.J., Sing K.S.W., Salzberg H., Adsorption surface area and porosity, Journal of The Electrochemical Society 114 (1967) 279C-279C.

Gun'ko VM, Turov VV, Kozynchenko OP, Palijczuk D, Szmigielski R, Kerus SV, Borysenko, MV, Pakhlov EM and Gorbik PP. "Characteristics of adsorption phase with water/organic mixtures at a surface of activated carbons possessing intraparticle and textural porosities", Appl. Surf. Sci. 254 (2008) 3220–3231.

Hameed BH and El-Khaiary MI. "Malachite green adsorption by rattan sawdust: Isotherm, kinetic and mechanism modeling", J. Hazard. Mater.159 (2008) 574–579.

Homem V, Santos L., Degradation and removal methods of antibiotics from aqueous matrices: A review. J. Environ. Manage. 92: (2011) 2304-2347.

Hansen N., Rindel K., Bioscrubbing, an effective and economic solution to odour control at wastewater treatment plants, Water Science and Technology 41 (2000) 155-164.

Hansen M., Feilberg A. and Adamsen A., Stability of Volatile Reduced Sulphur compounds in the dilution system of an Olfactometer. *Chemical Engineering Transactions* 23, (2010)67-72.

Hempel, W. UeberKohlenoxysul_d. Z. Angew.Chem., 14, 865-868, 1901.

Henshaw P., Nicell J. and Sikdar A., Parameters for the assessment of odour impacts on communities, *Atmospheric Environment* 40,(2006) 1016–1029.

Hine, J. and WeimarR. D., Jr. Carbon basicity. J. Am. Chem. Soc., 87, (1965)3387-3396.

Hine, J. and MookerjeeP. K., The intrinsic hydrophilic character of organic compounds.Correlations in terms of structural contributions. J. Org. Chem., 40, (1975)292-298.

Hinokiyama K., Nishida K, OsakoM., MutoN., Adsorbent characteristics of hydrogen sulfide and methyl mercaptan in single and mixed systems, International journal of environmental studies 38 (1991) 25-40.

Ho YS and McKay G. ‘‘Pseudo-second Order Model for Sorption Processes’’, Process Biochem. 34 (1999) 451-465.

Ho YS. “Review of second-order models for adsorption systems”, J. Hazard.Mater. 136 (2006) 681–689.

Hobson J. and Yang G., Odour mapping using H_2S measurements. In R. Stuetz and F.B. Frechen (Eds.), Odours in wastewater treatment: Measurement, modelling and control (Chapter 11) (2001) IWA, London, England.

Hobson J, Yang G (2000) The ability of selected chemicals for suppressing odour development in rinsing mains. Water Sci. Technol. 41 (6): 165–173.

Horvath G., Kawazoe K., Method for the calculation of effective pore size distribution in molecular sieve carbon. J. Chem. Eng. Jpn 16(6)(1983)470-475.

Hwang Y., Matsuo T., Hanaki K., Suzuki N., Removal of odourous compounds in waste water by using activated carbon, ozonation and aerated biofilter. Water Res. 28(11): (1994)2309-2319.

Jansen RJJ and Bekkum H., “Amination and ammoxidation of activated carbons”, Carbon32(8) (1994), 1507-1516.

Jenneman G.E., McInerney M.J., Knapp R.M., Effect of nitrate on biogenic sulfide production. Appl. Environ. Microbiol. 51 (5): (1986)1205–1211.

Karl T. and LindingerW., Henry's law constants (1997),personal communication.

Kim H.H.,Nonthermal plasma processing for air-pollution control: a historical review, current issues, and future prospects, Plasma Processes and Polymers. 1: (2004) 91–110.

Kim KJ and Ahn HG. “The adsorption and desorption characteristics of a binary component system of toluene and methylethylketone on activated carbon modified with phosphoric acid”, Carbon 48 (2010) 2198–2202.

Kim K.J., Kang C.S., You Y.J., Chung M.C., Woo M.W., Jeong W.J., Park N.C., Ahn H.G., Adsorption-desorption characteristics of VOCs over impregnated activated carbons, Catal. Today,111(2006)223-228.

Kimmerle K., Bell C.W, Gudernatch G., Chmiel H., Solvent recovery from air. J Membrane Sci.36: (1988) 477-488.

KleebergK.K.,LiuY.,JansM.,SchlegelmilchM.,StreeseJ.andStegmann**R.,**Development of a simple and sensitive method for the characterization of odorous waste gas emissions by means of solid-phase microextraction (SPME) and GC–MS/olfactometry . *Waste Management* 25, (2005) 872–879.

Kobia M., Removal of Cr(VI) from aqueous solutions by adsorption onto hazelnut shell activated carbon: kinetic and equilibrium studies, Bioresource Technology 91(2004)317-321.

Koe LCC, Tan YG (1987) GC-MS analysis of odourous emissions from the dissolved air floatation units treating surplus activated sludge at a waste water treatment works. Int. J. Environ. Stud. 30: 37-44.

Koziel J., Yang X., van Leeuwen H., Jenks W. and Laor Y., Treatment of odorous vocs with ultraviolet light. *Chemical Engineering Transactions.* 23, (2010) 263-268.

Krach K.R., Burns B.L.B.R., Mangus J., Butler H.G. and Cole C., Bench and full-scale studies for odor control from lime stabilized biosolids: The effect of mixing on odor generation. *Bioresource Technology* 99, (2008) 6446–6455.

Król S., Zabiegała B., Namieśnik J., Monitoring VOCs in atmospheric air II. Sample collection and preparation, TrAC Trends in Analytical Chemistry 29 (2010) 1101-1112.

Kujawa J.,Kujawski W., Koter S., Jarzynka K., Rozicka A, Bajda K., Cerneaux S,Persin M, Larbot A., Membrane distillation properties of TiO2 ceramic membranes modified by perfluoroalkylsilanes. Desalin. Water Treat. 51: (2013) 1352-1361.

Kumar S, Zafar M, Prajapati JK, Kumar S and KannepalliS.“Modeling studies on simultaneous adsorption of phenol and resorcinol onto granular activated carbon from simulated aqueous solution”, J. Hazard. Mater.185 (2011) 287–294.

Kutics K. and Suzuki M., Adsorption of organics on surface modified activated carbon fibers. In: 2nd Korea- Japan Symposium on sep. Tech., Seoul, South korea(1990) p.395.

Lagergren S. “Zurtheorie der sogenannten adsorption gelosterstoffe”, K. Sven. Vetenskapsakad.Handl. 24 (1898) 1–39.

Laor Y., Ozer Y., Ravid U., Hannan A. and Orenstein P.,Methodological aspects of sample collection for dynamic Olfactometry. *Chemical Engineering Transactions* 23,(2010) 55-60.

Laplanche A., Bonnin C., Darmon D., Comparative study of odours removal in a wastewater treatment plant by wet scrubbing and oxidation by chlorine or ozone. In : Characterization and control of odoriferous pollutants in process Industries, Elsevier science B.V., Amsterdam, (1984)pp. 277-294.

Leach J., Blanch A. and Bianchi A.C., Volatile organic compounds in an urban airborne environment adjacent to a municipal incinerator, waste collection centre and sewage treatment plant. *Atmospheric Environment* 33,(1999) 4309-4325.

Le-Minh N, Khan SJ, Drewes JE andStuetz RM. “Fate of antibiotics during municipal water recycling treatment processes”, Water Res. 44(15) (2010) 4295-4323.

Lehtinen J. and Veijanen A., Odour monitoring by combined TD–GC– MS–sniff technique and dynamic Olfactometry at the Wastewater Treatment Plant of low H_2S concentration. *Water Air Soil Pollut* ,218: (2011) 185–196.

Lee Y.W., Kim H.J., Park J.W., Choi B.U., Choi D.K., Adsorption and reaction behaviour for the simultaneous adsorption of NO-NO_2 and SO_2 on activated carbon impregnated with KOH. Carbon 41(2003)1881-1888.

Leon C.A., Lion Y. and Radovic L.R., Interfacial chemistry and electrochemistry of carbon surfaces, In: Chemistry and physics of carbon.(P.A. Thrower, ed), Marcel Dekker, New York, 24(1992)213-310.

Leson, G., Chavira, R., Winer, A., and Hodge, D., Experiences with a full scale biofilter for control of ethanol emissions. Paper presented at the 88th Annual Meeting of the Air and Waste Management Association, San Antonio,Texas, (1995, June). 95-MP9A.04.

Li L., Liu S., Liu J., Surface modification of coconut shell based activated carbon for the improvement of hydrophobic VOC removal, Journal of hazardous materials 192 (2011) 683-690.

Littarru P., Environmental odours assessment from waste treatment plants: Dynamic olfactometry in combination with sensorial analysers "electronic noses", Waste Management 27 (2007) 302-309.

Liu X, QuanX, Bo L, Chen S andZhao Y. "Simultaneous pentachlorophenol decomposition and granular activated carbon regeneration assisted by microwave irradiation", Carbon 42 (2011) 415-422.

Lopez-Ramon M.V., Stoeckli F., Moreno-Castilla C., Carrasco-Marin F., On the characterization of acidic and basic surface sites on carbons by various techniques, Carbon 37 (1999) 1215–1221.

Lovelock J. E., MaggsR. J., and RasmussenR. A., Atmospheric dimethyl sulphide and the natural sulphur cycle. Nature,(1972) 452-453.

Lozano J., Martin de la Vega P., Martinez De Salazar E., Alvarez F.,MoreraJ. and Aguilera T., Odour Discrimination from Wastewater Treatment Plants with a Portable Electronic Nose . *Chemical Engineering Transactions*, 23,(2010),165-170.

Lu C.Y., Wey M.Y., Simultaneous removal of VOC and NO by activated carbon impregnated with transition metal catalysts in combustion flue gas . Fuel processing technology 88(2007)557-567.

Lu C.Y., Wey M.Y., Chen L.I., Application of polyol process to prepared AC-supported nanocatalyst for VOCs oxidation. Applied catalysis A: General325(2007)163-174.

Luo J. and Agnew M.P., Gas characteristics before and after biofiltration treating odorous emissions from animal rendering processes. *Environmental Technology*, 22, (2001) pp.1091–1103.

Lu Q and Sorial GA. “The role of adsorbent pore size distribution in multicomponent adsorption on activated carbon”, Carbon 42 (2004) 3133–3142.

Mahmoud DK, Salleh MAM, Karima WAWA, Idris A and Abidina ZZ. “Batch adsorption of basic dye using acid treatedkenaffibre char: Equilibrium,kinetic and thermodynamic studies”,Chem. Eng. J. 181–182 (2012) 449–457.

Mahmudov R and Huang CP. "Perchlorate removal by activated carbon adsorption, Sep. Puri.Technol 70 (2010) 329-337.

Malik DJ, Strelko V, Streat M and Puziy AM.“Characterisation of novel modified active carbons and marine algal biomass for the selective adsorption of lead”, Water Res. 36 (2002) 1527–1538.

Marks J.R., Rhoads T., Planning saves time and money, when installing VOC controls. Chem Process**.**5: (1991) 42.

Marwani A., Artoni R., Barausse A., Palmeri L., Pittarello A.and Benzo **M.,**Modeling Odour Dispersion from Composting Plants: Comparison with Electronic Nose Measurements. *Chemical Engineering Transaction,* 23, (2016) 2197- 2202.

Matsui Y, Fukuda Y, Inoue T and Matsushita T. “Effect of natural organic matter on powdered activated carbon adsorption of trace contaminants: characteristics and mechanism of competitive adsorption”, Water Res. 37 (2003) 4413–4424.

Merzougui Y. and Addoun Y, Effect of natural organic matter on powdered activated carbon adsorption of trace contaminants: characteristics and mechanism of competitive adsorption”, Water Res. 37 (2008) 4413–4424.

Michael I, Rizzo L, McArdellCS, ManaiaCM, Merlin C, Schwartz T, DagotC and Fatta-KassinosD.“Urban wastewater treatment plants as hotspots for the release of antibiotics in the environment: A review”, Water Res. 47 (2013) 957-995.

Micone P.G. and Guy C. (2007) Odour quantification by a sensor array: An application to landfill gas odours from two different municipal waste treatment works. *Sensors and Actuators B* 120,628–637.

Mizuno A (2007) Industrial applications of atmospheric non-thermal plasma in environmental remediation, Plasma Phys Contr F. 49: A1–A15.

Mokaya O, Fakhri A and Adami S. “Isotherm, thermodynamic, kinetics, and adsorption mechanism studies of Ethidium bromide by single-walled carbon nanotube and carboxylate group functionalized single-walled carbon nanotube”,J. Colloid Interface Sci. 395 (2013) 224–229.

Moreno-Castilla C, Carrasco-Marín F, Maldonado-Hódar FJ and Rivera-UtrillaJ.“Effects of non-oxidant and oxidant acid treatments on the surface properties of an activated carbon with very low ash content”, Carbon 36 (1998) 145-151.

Nake A., Dubreuil B., Raynaud C. and Talou T., Outdoor in situ monitoring of volatile emissions from wastewater treatment plants with two portable technologies of electronic noses *Sensors and Actuators B: Chemical, 106,* (2005) *36-39.*

Nicolas J., Craffe F., Romain A.C., Estimation of odor emission rate from landfill areas using the sniffing team method. Waste Management, 26 (2006) 1259–1269.

Nielsen AH, Vollertsen J, Hvitved-Jacobsen T., Kinetics and stoichiometry of sulfide oxidation by sewer biofilms. Environ. Water Res. 39: (2005) 4119–4125.

Nowicki P., Wachowska H., Pietrzac R., Active carbons prepared by chemical activation of pulm stones and their application in removal of NO_2, Journal of hazardous materials. 181(2010)1088-1094.

Nunez CM, Ramsey G.H., Ponder W.H, Abbott J.H, Hamel LE, Kariher P.H., Corona destruction: an innovative control technology for VOCs and air toxics, Air Waste 43: (1993) 242–247.

Ochiai N. and Sasamoto K. (2011) Selectable one-dimensional or two- dimensional gas chromatography–olfactometry/mass spectrometry with preparative fraction collection for analysis of ultra-trace amounts of odor compounds. *Journal of Chromatography A,* 1218, 3180–3185.

Okabe S, Ito T, Satoh H, Watanabe Y (2003a) Effect of nitrite and nitrate on biogenic sulfide production in sewer biofilms determined by the use of microelectrodes. Water Sci. Technol. 47 (11): 281–288.

Padival NA, Weiss J.S., Arnold R.G., Control of Thiobacillus by means of microbial competition—implications for corrosion of concrete sewers. Water Environ. Res. 67: (1995) 201–205.

Palma MC, Silva IF, Lodewyckx P, Orfao JJM and Lobo LS.“Effect of HNO_3andNH_3 treatment on the catalytic oxidation of carbon catalysed by Cu, Mo, andtheir mixture at eutectic composition”, J.A. Pajares, J.M.D. Tascón (Eds.),Coal Science, vol. 1, Elsevier, Amsterdam(1995) 691–694.

Pandey R.A., MudliarS.N.andBorgaokarv S., Treatment of waste gas containing diethyldisulphide (DEDS) in a bench scale biofilter. *Bioresource Technology* 100,(2009) 131–135.

Park J.Y., Jung J.G., Kim J.S., Rim G.H., Kim K.S., Effect of nonthermal plasma reactor for CF4 decomposition, IEEE T Plasma Sci. 31: (2003) 1349–1354.

Patkar A.N., Laznow J., Hazardous air pollutant control technologies. Hazmat World.*2*: (1992) 78.

Patterson M.Q., Stevens J.C., Cain W.S., Cometto-Muniz J.E., Detection thresholds for an olfactory mixture and its three constituent compounds, Chemical Senses 18 (1993) 723-734.

Paul H., Philip C, Gerner F.J, Strathmann H., Removal of organic vapour from air by selective membrane permeation. J Membrane Sci.36: (1988)363-372.

PillaiS.M,WangG.P.,GallagherE.,DunlopM.andStuetzR.M.,Direct headspace analysis of broiler chicken litter odorants,*Chemical Engineering Transactions,* 23, (2010)207-212.

Pinnau I., Wijmans J.G, Blume I, Kuroda T, Peinemann K.V.,Gas permeation through composite membranes. J Membrane Sci, 37:(1988) 81-88.

PrzepiórskiJ.“Activated carbon surfaces in environmental remediation”, (ed.) TJ Bandosz (New York: Elsevier Academic Press) (2006) 421–474.

PrzyjaznyA., JanickiW., ChrzanowskiW., and StaszewskiR., Headspace gas chromatographic determination of distribution coefficients of selected organosulphur compounds and their dependence on some parameters. J. Chromatography, 280, (1983)249-260.

Puri B.R., Surface complexes on carbon. In: Chemistry and physics of carbon.(P.L Walker, Jr, ed), Marcel Dekker, New York, 6(1970)191-282.

Qu F., Zhu L., Yang K., Adsorption behaviors of volatile organic compounds (VOCs) on porous clay heterostructures (PCH), Journal of hazardous materials 170 (2009) 7-12.

Quinlivan PA, Li L and Knappe DRU.“Effects of activated carbon characteristics on the simultaneous adsorption of aqueous organic micropollutants and natural organic matter”, Water Res. 39 (2005) 1663–1673.

Rajbansi B., Sarkar U., Evaluation of odour intensity from activated sludge based sewage treatment works, Desalination and Water Treatment 12 (2009) 360-368.

RajbansiB., SarkarU., HobbsS.E., Hazardous odor markers from sewage wastewater: a step towards simultaneous assessment, dearomatization and removal, Journal of the Taiwan Institute of Chemical Engineers 45 (2014) 1549-1557.

Ras M.R., Borrull F., Marcé R.M, Sampling and preconcentration techniques for determination of volatile organic compounds in air samples, TrAC Trends in Analytical Chemistry 28 (2009) 347-361.

Ray S., Lalman J.A., Biswas N., Using the Box-Benkhen technique to statistically model phenol photocatalytic degradation by titanium dioxide nanoparticles. Chem Eng J 150:(2009)15–24.

Rex A.,Uber die Loslichkeit der Halogenderivate der Kohlenwasserstoffe inWasser. Z. Phys. Chem., 55, (1906) 355-370.

Rivera-Utrilla J, Sánchez-Polo M, Gómez-Serrano V, Álvarez PM, Alvim-Ferraz MCM and Dias JM.“Activated carbon modifications to enhance its water treatment applications.An overview”, J. Hazard.Mater. 187 (15) (2011) 1-23.

Rodriguez-Gomez LE, Delgado S, Alvarez M, Elmaleh S., Inhibition of sulfide generation in a reclaimed wastewater pipe by nitrate dosage and denitrification kinetics. Water Environ. Res. 77: (2005) 193–198.

Ruddy E. N., CarrollL.A., Select the best VOC control strategy. ChemEngProg.89: (1993) 28-35.Russell C. J., DixonS. L. and JursP. C., Computer-assisted study of the relationship between molecular structure and Henry's law constant. Anal. Chem., 64, (1992)1350-1355.

Ruhl M.J., Recover VOCs via adsorption on activated carbon.ChemEngProg.July,89: (1993) 37–41.

Ryu J., Lopez-Peinado A, Moreno-Castilla C and Lopez-Gonzalez JD. “Reactivity of Spanish coal chars in dry air: Effect of the addition of potassium carbonate and acetate”, Fuel 66 (2001) 237-241.

Saral A., Demir S. and Yıldız S., Assessment of odorous VOCs released from a main MSW landfill site in Istanbul-Turkey via a modelling approach. *Journal of Hazardous Materials* 168, (2009) 338–345.

Sarkar U. and Hobbs S.E., Odour from municipal solid waste (MSW) landfills: A study on the analysis of perception. *Environment International* 27, (2002) 655–662.

Schideman L.C., Snoeyink V.L., Mariñas B.J., Ding L., and Campos C., “Application of a three-component competitive adsorption model to evaluate and optimize granular activated carbon systems”, Water Res. 41 (2007) 3289 – 3298.

Schlegelmilch M, Streese J, Stegmann R., Odour management and treatment technologies: an overview. Waste manage. 25: (2005) 928-939.

Schwarzbock T., Waschnewski J., Frey M., Rouault P. and Gnirss R., Evaluation of Electronic Noses for Online Control of Odour Emissions from Sewer Systems. *Chemical Engineering Transactions,* 23, (2010)183-188.

Shen J.W., Park S.J., Ryu S.K., Effect of modification with HNO_3 and NaOH on metal adsorption by pitch-based activated carbon fibers, Carbon 39 (2008) 1635-1642.

Singha S, Sarkar U and Luharuka, P.“Functionalized granular activated carbon and surface complexation with chromates and bi-chromates in wastewater”, Sci. Total Environ. 447 (2013) 472–487.

Sironi S., Capelli L., Céntola P., Rosso R.D. and Grande M.II., Continuous monitoring of odours from a composting plant using electronic noses. *Waste Management* 27(2007)389–397.

Song Y.H., Kim S.J., Choi KI, Yamamoto T., Effects of adsorption and temperature on a nonthermal plasma process for removing VOCs, J Electrostat. 55: (2010)189-201.

Steijns M. and Mars P., Catalytic oxidation of hydrogen sulphide. Influence of pore structure and chemical composition of various porous substances, Ind. Eng. Chem. Res. Dev.16 (1977) 35-41.

Stone H., Oliver S.M., Beidler’s theory and human taste stimulation, Attention, Perception, & Psychophysics 1 (1966) 358-360.

Statheropoulos M., Agapiou A. and Pallis G., A study of volatile organic compoundsevolvedinurbanwastedisposalbins.*AtmosphericEnvironment*39, (2005) 4639–4645.

Stuetz T. R., Fenner R., Engin G., Assessment of odours from sewage treatment works by an electronic nose, H 2 S analysis and olfactometry, Water Research 33 (1999) 453-461.

Stuetz R.M., Frechen F.B., Odours in wastewater treatment, IWA publishing, 2001.

Sucker K., Both, R., Bischiff, M., Guski, R., and Winneke, G., Odor frequency and odor annoyance. Part I: assessment of frequency, intensity and hedonic tone Downloaded of environmental odors in the field. *International Archives of Occupational and Environmental Health* 81, (2008) 671–682.

Su W., Zhou Y.P., Wei L.F., Sun Y., Zhou L., Effect of microstructure and surface modification on the hydrogen adsorption capacity of active carbon, New carbon mater.22(2007)135-139.

Sun R.Q., Sun L.B., Chun Y., Xu Q.H., Catalytic performance of porous activated carbons obtained by chemical activation,Carbon 46 (2008) 1757-1764.

Suresh S, Srivastava VC and Mishra IM.“Adsorptive removal of phenol from binary aqueous solution with aniline and 4-nitrophenol by granular activated carbon”, Chem. Eng. J. 171 (2011) 997– 1003.

Svetlana B., Andrey B. and Teresa J.B., Effect of Surface Characteristics on Adsorption of Methyl Mercaptan on Activated Carbons, *Ind. Eng. Chem. Res.*, 2002, *41* (17), pp 4346–4352.

Szabo- Bardos E., Petervari E, El-Zein V., Horvath A., Photocatalytic decomposition of aspartic acid over bare and silver deposited TiO2. J. photochem. Photobiol. A184 (1-2): (2006) 221-227.

Terzyk A.P., The influence of activated carbon surface chemical composition on the adsorption of acetaminophen in vitro part II. TG,FTIR and XPS analysis of carbons and the temperature dependence of adsorption kinetics at the pH, colloids., surf., A: Physicochem. Eng. Aspects 177(2001)23-45.

Tokumura M., Wada Y., Usami Y., Yamaki T., Mizukoshi A., Noguchi M., Yanagisawa Y., Method of removal of volatile organic compounds by using wet Scrubber coupled with photo-Fenton reaction- Preventing emission of by-products, Chemosphere 89: (2012) 1238-1242.

Tomar M., Abdullah T.H.A.,, Evaluation of chemicals to control the generation of malodorous hydrogen-sulfide in wastewater. Water Res. 28: (1994) 2545–2552.

Torres A., Vaz F., Neves M.I.B., Hangartner M. and Sucker K., Approach to characterize a sub-group susceptible to odour annoyance, *Chemical Engineering Transactions,* 23, (2010) 129-134.

Trouvé A, Batonneau-Gener I.,Valange S., Bonne M. and MignardS.,“Tuning the hydrophobicity of mesoporous silica materials for the adsorption of organic pollutant in aqueous solution”, J. Hazard. Mater. 201-202 (2012) 107–114.

Tsai J.H., Chiang H.M., Huang G.Y., Chiang H.L.. Adsorption characteristics of acetone, chloroform and acetonitrile on sludge derived adsorbent, commercial granular activated carbon and activated carbon fibers. Journal of hazardous materials 154(2008)1183-1191.

Turk A, Sakalis E, Lessuck J, Karamitsos H, Rago O., Ammonia injection enhances capacity of activated carbon for hydrogen sulphide and methyl mercaptan. Environ. sci. technol. 23: (1989) 1242-1245.

US-EPA, Reference Guide to Odor Thresholds for Hazardous Air Pollutants Listed in the Clean Air Act Amendments of 1990, US Environmental Protection Agency Air Risk Information Support Center,(1992)(EPA600/R-92/047).

US-EPA.Air and steam stripping of toxic pollutants. Tech. Rep. EPA-68-03-002, Industrial Environmental Research Laboratory, Cincinnati, (1982)USA.

VanDurme GP, McNamara B.F., McGinley C.M., Bench scale removal of odour and volatile organic compounds at a composing facility. Water Environ Res. 64(1), (1992) 19-27.

Van Groenestijn J.W., Hesselink P.G., Biotechniques for air pollution control. Biodegradation 4: (1993) 283–301.

Vaughan Jr. RL and Reed BE. Modeling As(V) removal by an iron oxide impregnated activated carbon using the surface complexation approach, Water Res. 39 (2005) 1005-1014.

VDI-guideline 3940, Determination of Odorants in Ambient Air by Field Inspection, October 1993, VDI-Handbuch Reinhaltung der Luft, (1993)Vol.1.

VDI 3475 Part 1, *Emission* control - Biological waste treatment facilities- Composting and anaerobic digestion; Plant capacities more than approx. 6000 Mg/a,2003-01.

Verma N., Gupta V.K., Removal of volatile organic compounds by cryogenic condensation followed by adsorption. Chem Eng Sci. 57(14):(2002) 2679–2696.

Vincent A., Sources of odours in wastewater treatment, Odours in wastewater treatment: Measurement, modelling and control (2001) 69-90.

Vitenberg, A. G., B. V. Io_e, Z. S. Dimitrova, and I. L. Butaeva.Determination of gas-liquid partition coefficients by means of gas chromatographic analysis. J. Chromatography, 112, (1975)319-327.

Waltrip G.D., Snyder G.E., Elimination of odor at six major wastewater treatment plants. J. WPCF 57: (1985) 1027–1032.

Whittington F.M., Zammerini D., Nute G.R., Baker A., Hughes S.I.and **Wood J.D.,**Comparison of heating methods and the use of different tissues for sensory assessment of abnormal odours (boar taint) in pig meat. Meat Science 88 , (2011) 249–255.

Winkler L.W.,Gesetzmfassigkeitbei der Absorption der Gase in Flussigkeiten. Z. Phys. Chem., 55, (1906)344-354.

Wijmans JG, Helm V.D., A membrane system for separation and recovery of organic vapours from gas stream, AIChE symposium Series 272. AIChE: New York, 85: (1989) 74.

Woolfenden, E.,Sorbent-based sampling methods for volatile and semi- volatile organic compounds in air Part 1: Sorbent-based air monitoring options. *Journal of Chromatography A*, 1217,(2010) 2674–2684.

Wu B-Z., FengTien-Zhi., Sree U., Chiu Kong-Hwa.and Lo Jiunn-Guang., Sampling and analysis of volatile organics emitted from wastewater treatment plant and drain system of an industrial science park. *AnalyticaChimicaActa*576,(2006) 100–111.

Xie Z., Wang F., Zhao N., Wei W. and Sun Y., Hydrophobisation of activated carbon fiber and the influence on the adsorption selectivity towards carbon disulfide . *Applied Surface Science* 257 ,(2011) 3596–3602.

Yamamoto T., Rajanikanth B.S., Okubo M., Kuroki T., Nishino M., Performance evaluation of nonthermal plasma reactors for NO oxidation in diesel engine exhaust gas treatment, IEEE T Ind Appl. 39: (2003) 1608–1613.

Yang G, Hobson J., Use of chemicals for septicity and odour prevention in sewer networks, Odours in wastewtreat, pp. (2001) 270–292.

Yang R.T., Adsorbents: Fundamentals and applications, John Wiley and Sons, New York, 2003.

Yang J., Juan P., Shen Z., Guo R., Jia J., Fang H. and Wang Y.,“Removal of carbondisulfide from water via adsorption on activated carbon fiber” Carbon , Vol. 44, (2006) pp. 1367-1375.

Yaws C. L. and Yang H.C., Henry's law constant for compound in water. In C. L. Yaws, editor, Thermodynamic and Physical Property Data,Gulf Publishing Company, Houston, TX, (1992) pages 181-206.

Zarra T, Naddeo V Belgiorno V, Reiser M, Kranert M., Odour monitoring of small wastewater treatment plant located in sensitive environment. Water Sci. Technol. 58: (2008) 89–94.

Zhang L., Schryver P.D., Gusseme B.D., Muynck W.D., Boon N., Verstraete W., Chemical and biological technologies for hydrogen sulphide emission control in sewer systems: A review. Water Res. 42: (2008) 1-12.

Zhang S., Cai L., Koziel J.A., Hoff S.J., Schmidt D.R., Clanton C.J., Jacobson L.D., Parker D.B. and Heber A.J., Field air sampling and simultaneous chemical and sensory analysis of livestock odorants with sorbent tubes and GC–MS/olfactometry. *Sensors and Actuators B* 146, (2010)427–432.

1. **List of publication(Journals):**

- Alkaline functionalization of granular activated carbon for the removal of Volatile Organo Sulphur Compounds (VOSCs) generated in Sewage Treatment Plants, *Shyamal Jana* and *Ujjaini Sarkar*, ***Journal of Environmental Chemical Engineering*, 6 (2018) 3510–3519.**

- Application of an Alkali Functionalized Material for Treating Pharmaceutical Wastewater Containing Chlorohexidine Gluconate and Cetrimide, Debasree Banerjee, *Shyamal Jana, Ujjaini Sarkar and Debasri Roy*, ***Clean-Soil, Air, Water*, 2016, 44(2), 169-179**

2. **List of Patents:** None

3. **List of Presentations in National/International:**

- **Jana S.,** and Sarkar U. Synthesis and characterisation of a novel alkali functionalised super-microporous material: Performance with respect to an expensive mesoporous aluminosilicate (MCM-41). *Fourth International Conference on Multifunctional, Hybrid and Nanomaterials (HYMA, 2015)*; 9-13 March, 2015.

- **Shyamal Jana** and U. Sarkar, Poster presentation entitled 'Alkali Functionalization of Granular Activated carbon for adsorption of Volatile Organo Sulphur Compound', National Seminar on *Innovative Process Technology for sustainable Development* dated 23rd - 24th Feb, 2018 at IIChE Auditorium & K.P. Bose Auditorium, Jadavpur University Campus.

Journal of Environmental Chemical Engineering 6 (2018) 3510–3519

Contents lists available at ScienceDirect

Journal of Environmental Chemical Engineering

journal homepage: www.elsevier.com/locate/jece

Alkaline functionalization of granular activated carbon for the removal of Volatile Organo Sulphur Compounds (VOSCs) generated in Sewage Treatment Plants

Shyamal Jana, Ujjaini Sarkar*

Department of Chemical Engineering, Jadavpur University, Kolkata, 700032, India

ARTICLE INFO

Keywords:
VOSCs
Sewage treatment plant
GAC
Odour
Sensory measurement
GC–MS

ABSTRACT

Adsorption, using Granular Activated Carbon (GAC), is an effective technique for the removal of mal-odorous Volatile Organo Sulphur Compounds (VOSCs) originating from sewage waste water collected from various Sewage Treatment Plants (STPs). Adsorption capacity of GAC is enhanced by functionalization with various alkaline solution. Alkali functionalized activated carbons (FACs), having higher surface area and pore volume and reduction of oxygen containing functional groups, perform much better in removing VOSCs in comparison to precursor GAC. Different adsorbed odorants (VOSCs), being concentrated and in close proximity to each other on the surface or in the pores of the adsorbent, may interact. The adsorption capacity of GAC and FACs increases in the order FAC-NH_3 > FAC-KOH > FAC-NaOH > GAC. FAC-NaOH or FAC-KOH may react with ambient CO_2 thereby forming carbonates. This effectively decreases the removal efficiency. Odour concentration is measured simultaneously by two techniques: panel olfactometry (sensory measurement based) and component specific analytical measurement (GC–MS based). Time variant olfactometry based odour concentration data correlated well with the time variant concentration of VOSCs (GC–MS based) for all four malodorous compounds like methyl mercaptan, ethyl mercaptan, dimethyl sulphide and carbon disulphide. Linearization of the percentage removal of overall odour (olfactometry based) versus percentage removal of relative concentrations of the four VOSCs reveals that methyl mercaptan has a very large odour contributing potential ($R^2 = 0.967$) representing the most obnoxious component of the tested sewage waste water as compared to other three compounds. Simultaneous conversion of methyl mercaptan to dimethyl disulphide leads to its faster removal by FAC-NH_3.

1. Introduction

With growing population, industrialization and urbanization, odour problem has become an objectionable issue. Urbanization, without proper sanitation facilities, is a major cause of odour nuisance. Rapid growth of industrialization has aggravated the problem due to generation of obnoxious odour caused by mostly volatile organo-sulphur compounds. These compounds are mostly generated through industrial operations. Nowadays, people in and around the sewage treatment plants (STPs) are quite concerned about the bad effects of malodorous gases on human life. The same is primarily caused by emission of volatile organo-sulphur compounds (VOSCs), which have very low odour threshold[1] values and a high negative hedonic tone[2] [1].

Odours in sewer systems is produced by anaerobic microbial decomposition of sewage waste water containing high levels of organic matter, nutrients, toxic compounds and chemicals. Most of the odours generated within the sewer system are sulphur based compounds, the predominant compound often being hydrogen sulphide[2]. Organo-sulphur based volatile compounds like carbon disulphide, methyl mercaptan, dimethyl sulphide, ethyl mercaptan, dimethyl disulphide etc., though found in lower concentration, are the key compounds behind most of the odour complaints. These are detectable at very low levels of concentrations [3–5] and tend to disperse relatively slowly till a concentration level is reached which is far below a concentration that corresponds to a nuisance level. These VOSCs are primarily produced due to anaerobic microbial decomposition of proteins [6]. In addition to odour, VOSCs, while present in the gas phase, may affect human health and create corrosion problem.

---

* Corresponding author.
E-mail address: ujjaini.sarkar@jadavpuruniversity.in (U. Sarkar).

[1] **Odour Threshold:** The lowest physical intensity at which an odour stimulus is correctly identified for a specified percentage of time.

[2] **Hedonic Tone:** Odours of equal intensity may differ in character. Hedonic tone is a character of odour that identifies its place on a scale of pleasantness and unpleasantness. However, a pleasant odour may be considered objectionable by the exposed population in the context of industrial emission and pollution hazards.

https://doi.org/10.1016/j.jece.2018.05.022
Received 17 January 2018; Received in revised form 8 May 2018; Accepted 9 May 2018
Available online 20 May 2018

An electronic nose is a simple instrument that may be used for indirect but rapid detection of odorous compounds. Application of electronic nose technology for monitoring odour from waste water is already reported [7–9]. The response is also nonspecific in nature and it is not applicable for onsite measurements. Assessment of odours is done by panel based olfactometry, with the help of human sensors [10]. Specific VOSCs that may be responsible for odour are measured by GC–MS and these results are further correlated to olfactometry based measurements [11].

Various knowledge gaps associated with odour assessment and control in the environment are addressed by researchers worldwide in different ways. Conventional methods of odour removal, consisting of mist filtration, thermal oxidation, catalytic oxidation, bio-filtration, chemical treatment, adsorption, absorption etc. have been widely investigated during the last few years [12–14]. VOSCs generated in waste water treatment plants are often removed by adsorption [11,15,16]. Adsorption using granular activated carbon (GAC) is a cost effective and versatile technique for removing VOSCs because of GAC's large surface area and pore volume [17]. GACs are modified and impregnated [18,19] in order to increase their adsorption capacity selectively towards specific organic compounds [20–22].

The main objective of the present research work is to develop functionalized granular activated carbon (FAC) for enhanced adsorption of specific odorous VOSCs generated in STPs. In this study, functionalized activated carbons (FACs) are prepared with various types of alkaline treatment applied on precursor GAC. Physical and chemical properties of different FACs, along with their adsorption capacities for VOSCs, are investigated. Various effects of adsorbate concentration, adsorption time, quantity of impregnated carbon on adsorption performance are studied. Furthermore, batch adsorption equilibrium analysis is carried out using standard physical as well as chemisorption isotherms [23].

2. Materials and methods

2.1. Materials

Many researchers modified the surface properties of activated carbon with alkaline functionalization [24]. Granular activated carbon [Make: SD Fine chemicals Limited, India; Grade: LR grade, IMDG Code 4.2/III; UN:13621ATA:4.2] is used as the main precursor. Liquor ammonia (GR grade), sodium hydroxide (AR grade) and potassium hydroxide (AR grade) are purchased from Merck India Limited. Before chemical treatment of GAC, it is first sieved through a BS8 mesh screen and the larger size-fraction is retained on the screen.

2.2. Functionalization of activated carbon

Screened GAC is then purified after boiling with distilled water in a water bath for 2 h under slow stirring condition and then washed repeatedly with distilled water to remove the fine particles. Afterwards, the same is dried in an oven at 105 °C for 4 h. For the preparation of FAC [25], purified GAC is soaked into an alkaline solution of 6.6 M NH_4OH solution, 10 M NaOH and 9 M KOH solutions separately in the ratio 1 g/8 ml at 70 °C for 2 h with constant stirring and then placed at 35 °C for 24 h. The functionalized GACs are then separated and purified with distilled water until they are neutral. Afterwards, these are dried in an oven at 105 °C for 4 h and transferred to desiccators before use.

2.3. Characterization of FACs and GAC

The surface morphology of activated carbon samples is analysed by a Field Emission Scanning Electron Microscope (FE-SEM) [Make: JEOL; Model: JEM 6700F]. BET technique is used to analyze the specific surface area, total pore volume and pore size distribution of GAC and the FACs. Nitrogen adsorption isotherm is generated at 77 °C using a surface area analyser [Make: Beckman Coulter; Model: SA3100]. Initially H-K method [20] is used to determine the pore size distribution of micro-pores and meso-pores. Ultimately these are analysed by Non-Local Density Function Theory (NLDFT) for all the FACs and GAC. Surface functional groups of GAC and FACs are characterized using a Fourier Transform Infrared (FT-IR) spectrophotometer [Make: Shimadzu, Japan; Model: IR Affinity-1]. The spectra are measured using KBr pellets as reference sample. The FTIR spectra are recorded at 4 cm^{-1} resolution with 45 scans per sample.

Boehm titrations are carried out in order to determine acidic or alkaline surface functional groups like carboxylic, lactonic and phenolic groups present in FACs and GAC [26]. Activated carbon samples (0.2 g each) are added into 50 ml aqueous solution of sodium hydroxide, sodium carbonate, sodium bicarbonate and hydrochloric acid solution (each of 0.05 M concentration) respectively. Then the suspension is filtered and an accurately measured amount of aliquot of the filtrates is back titrated using 0.05 M HCl solution in order to neutralize the excess base. For measuring the basic groups, the filtrate is back titrated using 0.05 M NaOH solution. The amount of base neutralized by the acidic functional groups present in the FACs and GAC is measured in milliequivalent (meq) per gm of adsorbent. As already known, Na_2CO_3 reacts with carboxylic and lactonic groups, $NaHCO_3$ reacts with the carboxylic group, NaOH reacts with all the three acidic groups and HCl reacts with the basic group(s) present in various activated carbon samples.

Surface charge of the samples is measured by a Particle Size Analyzer (Make: Malvern; Model: ZEN 3690 Zeta-sizer Nano ZS 90). Very dilute solution of each of the FACs and GAC is prepared by dispersing approximately 40 mg of ground sample in 500 ml of distilled water. In order to get CO_2 free solution, N_2 is bubbled through the solution. pH of the solution is adjusted in the range of 2 to 12 by using HCl or NaOH under constant stirring at 200 rpm for 24 h at 25 °C to reach an equilibrium condition. Point of zero charge (pH_{pzc})[3] of the total surface of various adsorbents (GAC and FACs) is estimated by plotting the zeta potential as a function of pH [27].

2.4. Adsorption of VOSCs

Raw sewage, a source of highest level of malodorous compounds, is collected in a big drum during the period July-September 2015. The drum is filled with raw sewage, leaving a headspace of approximately 4000 ml, with its lid tightly locked instantaneously using Teflon seals and tape. This is done in order to prevent any loss while analysing the volatile organic compounds (*GCMS based component specific analysis and olfactometry based analysis considering odour as a combination of several VOSCs*) before and after adsorption using FACs and GAC. Average ambient air temperature during sampling is 39 °C. After weighing, the lid of the drum is perforated at the top and volatile organic compounds (VOCs) are collected from the headspace using an air sampling pump (Make: Supelco,USA; Model:Escort Elf). Air samples are collected through charcoal tubes (Make: Supelco, USA; Model: ORBO 32; Specification: 6 mm OD, 75 mm in length) according to the air sampling guidelines recommended by USEPA (Method TO-17) [28]. Flow rate of the sampling pump is maintained at 2 lpm with a sampling flow time of 10 min. Simultaneously, olfactometry is carried out using trained sniffers by panel method as per VDI guidelines.

2.5. Odour analysis

Assessment of odour is carried out in two different ways, one is based on olfactometry and the other one is a volatile organic component specific GCMS based analysis. In order to determine the initial

---

[3] **pH_{pzc}** is the pH value at which a solid submerged in an electrolyte exhibits zero net electrical charge on the surface.

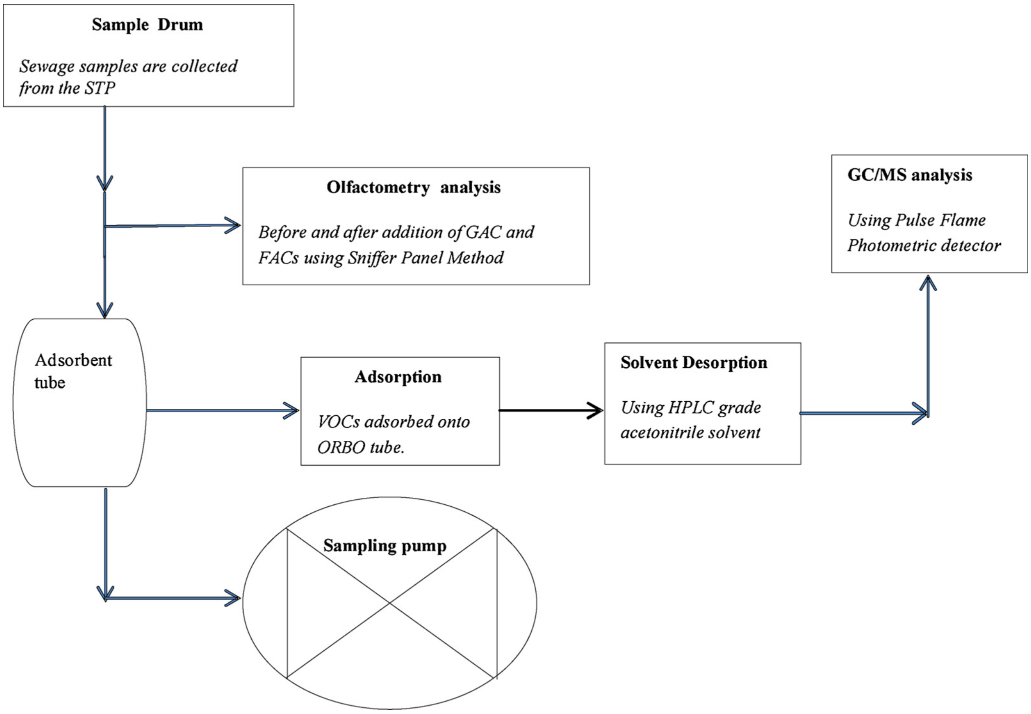


Fig. 1. Schematic diagram of simultaneous olfactometry and sampling of the odorous VOCs from headspace of a sampling drum using an Escort Elf air sampling pump through ORBO tube.

concentration of odorous material, the precursor gas mixture, containing various types of VOCs, is collected simultaneously for olfactometry as well as GCMS analysis. Olfactometry is carried out using trained sniffers by panel method. All the tests are carried out inside an odour free, clean laboratory with selected trained panellists for the psychophysical analysis of perceived odour (*following VDI guidelines for panel olfactometry*). The trained sniffers are first tested and then screened with *n*-butanol for representativeness, repetitiveness and consistency. After completion of olfactometry tests for few hours in the beginning, 12 g each of GAC or FACs is added to the sewage wastewater for each set of experiments and well mixed. This is done for the batch equilibrium analysis. Samples are collected simultaneously (at different time intervals) for component specific GCMS based analysis and olfactometry (see Fig. 1) till equilibrium is attained. Sampling is stopped till the olfactomery outputs did not change any further. For GCMS analysis the gaseous sample is collected into a sorbent tube [29,30]. After sampling, each sorbent tube is placed inside a tightly capped 5.0 ml special air-tight tube holder in order to prevent any ambient contamination from the materials of sorbent tube [31,32]. These are further processed for solid phase extraction and desorption of the VOCs using a solvent (usually HPLC grade acetonitrile).

2.5.1. Solid phase extraction-Solvent desorption

Widely accepted sampling technique for VOCs is by adsorption on sorbent tube with a solid phase [33]. After adsorption of VOCs on sorbent tube, they must be released from the tube by solvent extraction (SE) for further analysis using GCMS. Typically HPLC grade acetonitrile (CH_3CN) is the best suited solvent for dissolving a polar compound that is easily transferred from the solid phase of the sorbent tube into the solvent during desorption/solid phase extraction. Adsorbed samples are extracted in a 2 ml vial using 1 ml acetonitrile (solvent) for 15 min. Extracted samples are then stored in a refrigerator until analysed.

Extracted samples are analysed using a gas chromatograph (GC) (Make:Thermofisher; Model: Trace 1110, Trace GC) equipped with a Pulse Flame Photometric Detector (PFPD) (Make: Agilent; Model: 5380 PFPD), as it is very selective for determination of low concentration of sulphur compounds in light hydrocarbon matrices like natural gas. The chromatographic column used is GS-GasPro (Length: 60m, Diameter: 0.32 mm, 1.80 μm) (Make: Agilent; Model: CP8575) and a constant flow rate of the carrier gas (helium) is maintained at 2 ml/min. The split ratio is kept at 1:17. Temperature program for the oven is: initial temperature 40 °C, hold for 6 min; 40–120 °C at 6 °C min^{-1}, hold for 5 min at 180 °C. Ionization mode of the MS used is electron impact (EI). Detector temperature is kept at 200 °C with an air flow rate being maintained at 12 ml/min for *air 1* and 13 ml/min for *air 2* with a run time set at 40 min. Compounds are identified by PFPD (mode: acquiring) using Chrom-Card software based on their retention times (within ± 0.05 min of the RT of calibration standard), target and qualifier compounds.

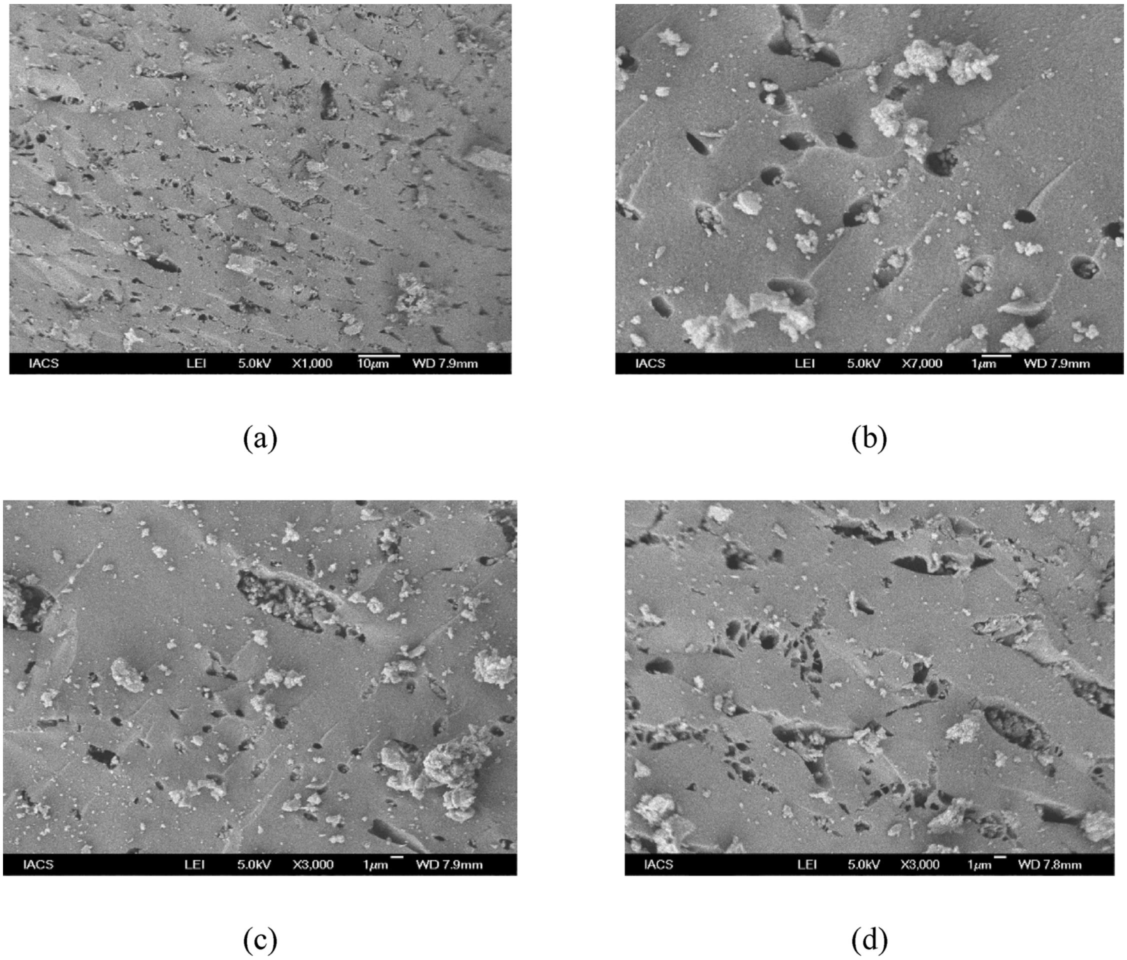
3. Results and discussions

3.1. Characterisation of GAC and FACs: texture

FE-SEM images of GAC and FACs are shown in Fig. 2. GAC, modified by ammonia solution (FAC-NH_3) exhibited a rough and purified surface. Various pore sizes are observed on the surface and inside the particle. Surfaces of FAC-KOH and FAC-NaOH are quite similar, although some pores are blocked.

Similarity of surface texture between FAC-KOH and FAC-NaOH is also supported by BET analysis (refer Fig. 3 and Table 1) and the pore size distribution curve (Fig. 4). The BET surface area (S_{BET}) of FAC-KOH (814 m^2/g) and FAC-NaOH (792 m^2/g) are slightly higher than that of GAC(777 m^2/g) and FAC-NH_3 (778 m^2/g). This indicates that the ammonia treatment of GAC could not change the meso and macropore volume a lot as compared to those of original GAC. From Table 1 it is seen that pore volume of FAC-KOH and FAC-NaOH are slightly smaller than that of GAC and FAC-NH_3. Total micropore volume of all the alkali treated GACs is slightly higher than that of untreated GAC (*precursor*). Significant amount of N_2 adsorption at a relative pressure (p/p_0) below 0.1 indicates that, all the tested materials have microporous structure.

Activation of GAC with alkali treatment leads to a nominal increase of N_2 adsorption at lower relative pressure (p/p_0) below 0.1, as shown in Fig. 3. Pore size distribution (see Fig. 4) indicates that the



(a) (b) (c) (d)

Fig. 2. FE-SEM pictorial view at ×5000 magnification for GAC and all FACs. (a) GAC, (b) FAC-NH_3, (c) FAC-KOH and (d) FAC-NaOH.

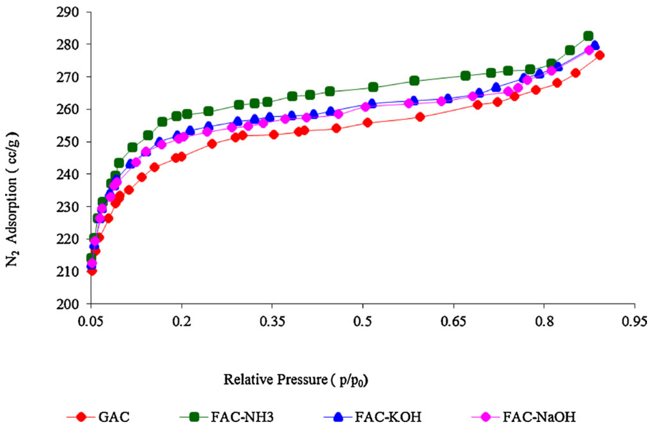


Fig. 3. N_2 Adsorption isotherm of GAC and alkali treated FACs.

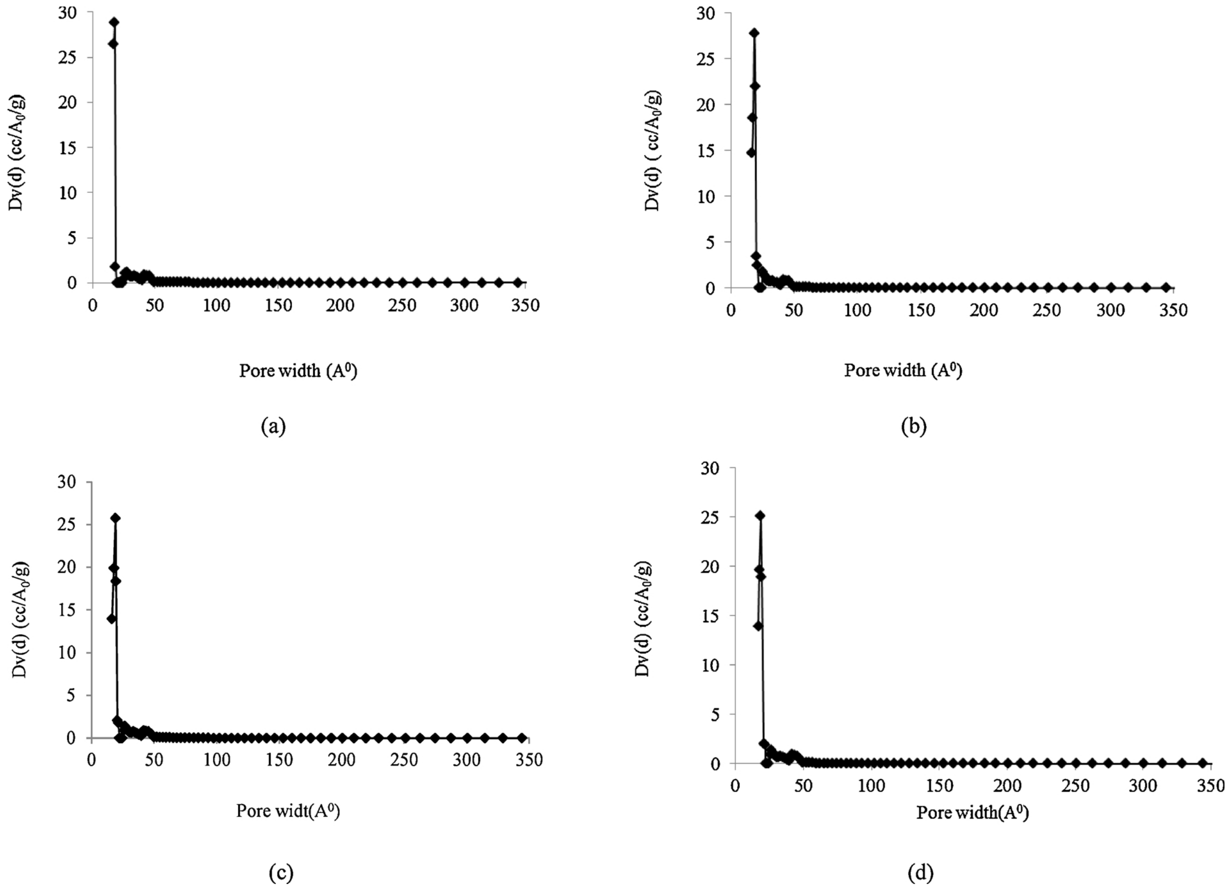
Table 1
Result of N_2 adsorption isotherm for surface area and pore size of GAC and different FACs.

Adsorbent	GAC	FAC-NH_3	FAC-KOH	FAC-NaOH
Surface area (m^2/g)	777	778	814	792
Pore Volume (ml/g)	0.3853	0.3813	0.3915	0.3802
Pore size (Å)	23.46	23.91	23.76	23.72
pH_{PZC}	4.56	7.3	7.5	7.48
Acidic ($meqvg^{-1}$)	17.351	10.03	8.549	8.314
Basic ($meqvg^{-1}$)	1.37	4.33	4.56	4.47

microporosity of GAC is retained and enhanced after activation. Slight widening of the isotherm 'knee' to cover the p/p_0 range in between 0.05 and 0.25 is an indication of the creation of large micropores and mesopores in alkali treated GAC.

3.2. Characterization of GAC and FACs: surface oxygen based functionality

FTIR analysis of the precursor GAC and FACs is carried out in order to obtain a better insight of the functional groups available on the carbon surfaces. It is not easy to get good spectra because carbon adsorbs almost all of the radiation in the visible spectrum. Thus, the peaks obtained are usually due to some kind of interaction in between various groups present in the surface [34]. Recorded spectra of these materials are shown in Table 2. All the materials exhibited bands at 2880 cm^{-1} to 2845 cm^{-1}, which are probably due to the asymmetric stretching of CH_2 group. The absorption bands of the carbonyl group (2350 cm^{-1}) of ketone and phenolic groups (1070 cm^{-1}) are observed in GAC, FAC-NaOH and FAC-KOH. Cyclic amides are present at a band 669 cm^{-1} in FAC-NH_3, FAC-NaOH and FAC-KOH and these spectra are due to some chemical modifications of GAC by alkali solution. Peak area of the absorption band at 1442 cm^{-1} increased due to the formation of lactone [35] after treatment of GAC with ammonia. The absorption band near 1728 cm^{-1}, an indication of the presence of carboxylic group, is observed for GACs modified with alkali treatment with NH_3, KOH, NaOH. This indicates that there are still carboxyl structures in the micropores which are either inaccessible basic or C=O groups, probably not yet neutralized with alkaline solution. The bands shown near 2300 cm^{-1} are assigned to carbon-oxygen groups due to the presence of ketone. But these bands are very weak for FAC-NH_3. Increase in peak



(a) (b) (c) (d)

Fig. 4. Pore size distribution curves. (a) GAC, (b) FAC-NH_3, (c) FAC-KOH and (d) FAC-NaOH.

Table 2
FTIR analysis of GAC and various alkali treated FACs.

GAC		FAC-NH_3		FAC-KOH		FAC−NaOH	
Wavelength (cm^{-1})	Functional group	Wavelength (cm^{-1})	Functional group	Wavelength (cm^{-1})	Functional group	Wavelength (cm^{-1})	Functional group
1074.35	−C−OH (stretching)	669.3	Cyclic amides	669	Cyclic amides	655.8	Cyclic amides
1276.88	Alcohols	1444.68	Lactone structure	1066	−C−OH (stretching)	1067.35	−C−OH (stretching)
1363.67	C−N aromatic ring	1581.63	−C−C aromatic stretching	1330	C−N aromatic ring	1359.82	C−N aromatic ring
1535.34	−C−C aromatic stretching	1600	Quinone	1444.68	Lactone structure	1444.68	Lactone structure
2839.22	−C−H stretching (asymmetric)	1729.94	Carboxilic acids	1529.55	−C−C aromatic stretching	1587.42	−C−C aromatic stretching
3008.95	−C−H stretching (symmetric)	2139.06	C=C=N	1600	Quinone	1600	Quinone
		2345.44	C=O in ketone	1726.4	Carboxilic acids	1726.29	Carboxilic acids
		2887.44	C-H stretching (asymmetric)	2357.01	C=O in ketone	2357.01	C=O in ketone
		3786.27	O−H stretching vibration	2887.37	−C−H stretching (asymmetric)	2845.53	−C−H stretching (asymmetric)

area for the band at 1600 cm^{-1} in FAC-NH_3, attributed to a quinine structure, is also reported.

3.3. Chemical characterisation of GAC and FACs: boehm titration

The surface acidic groups of GAC and different FACs are shown in Fig. 5. Concentration of various surface acidic groups (phenolic group, lactonic group, carboxylic groups etc.) is higher in case of GAC as compared to FAC- NH_3, FAC-KOH and FAC-NaOH. This is because the surface acidic groups get neutralized on activation with different alkali solutions. From Table 1 it is seen that the total quantity of basic groups of FACs increases. Different basic groups like nitrile, amino, cyclic amides and pyrrole like structure are introduced after surface functionalization.

3.4. Characterisation of GAC and FACs: point of zero charge

Fig. 6 shows the plot of zeta potential (mV) versus pH of GAC and the FACs. From this figure it is seen that, GAC has a pH_{pzc} value of 4.5 corresponding to a zeta potential of 0 mV. But the pH_{pzc} value of alkali functionalized GACs shifted to over 7.5. This is because of the partial neutralization of specific surface acidic functional groups and

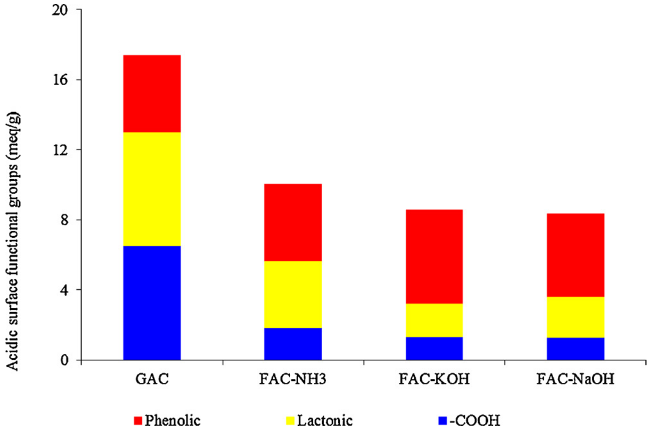


Fig. 5. Oxygen containing acidic surface functional groups of GAC and various FACs.

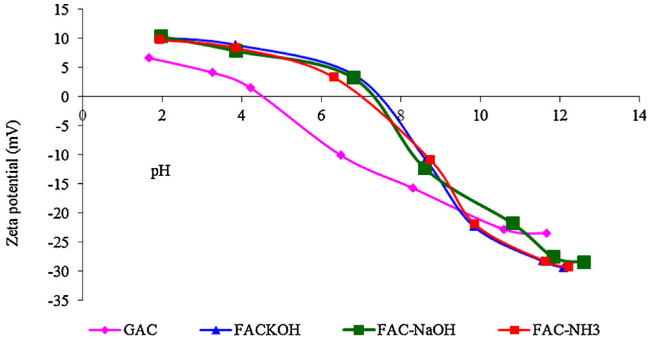


Fig. 6. Plot of zeta potential (mV) vs pH for GAC, $FAC\text{-}NH_3$, FAC-KOH and FAC-NaOH.

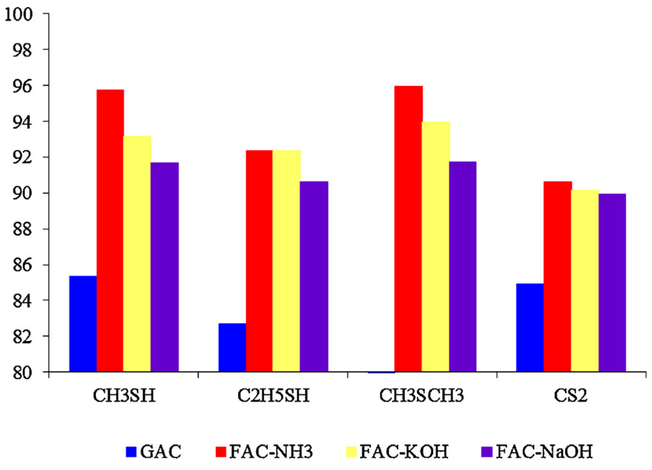


Fig. 7. Percent removal of different VOSCs [Detector: GC-PFPD] using various adsorbents: GAC, $FAC\text{-}NH_3$, FAC-KOH and FAC-NaOH.

introduction of some basic groups like C=N, amino, cyclic amides, nitrile, pyrrole like structure etc. onto GAC surface after functionalization. This generally provides the material with basic properties [27].

3.5. Batch equilibrium adsorption analysis

The GAC and FACs are tested for their adsorption capacities for malodorous VOSCs. A variation in VOSCs concentration from the drum containing waste water sample is observed before and after adsorption by GAC and FACs. The same is monitored by the panel sniffers (olfactometry) at the second port of the Y-connector just before the sorbent tube inlet (see Fig. 1). Tests are carried out continuously till equilibrium is achieved when the GAC and FACS are completely saturated with VOSCs after liquid phase adsorption. The adsorption capacities of GAC and FACs are shown in Fig. 7. From this figure it is seen that the adsorption capacities of $FAC\text{-}NH_3$, FAC-NaOH and FAC-KOH are much higher as compared to untreated GAC. Amount of VOSCs adsorbed per gram of adsorbent is found to be very high for $FAC\text{-}NH_3$ as compared to that of precursor GAC or any of FAC-NaOH and FAC-KOH. These phenomena could be explained with the help of physical characterization of the adsorbents, as described in Section 3.1. The super microporous structure of $FAC\text{-}NH_3$ helps in the adsorption of malodorous VOSCs like methyl mercaptan (CH_3SH), ethyl mercaptan (C_2H_5SH), di-methyl sulphide (CH_3SCH_3) and carbon di-sulphide (CS_2) much more, as evident from the pore size distribution of various adsorbents (refer Fig. 4). FAC-NaOH and FAC-KOH may react with CO_2 present in the ambient air and form carbonates. This decreases the removal efficiency.

Table 3
Time variant analysis of perceived odour of a sewage sample before and after adsorption using panel olfactometry and corresponding percentage removal values. *Date of Experiment: 16.09.2015. Weight of sewage water: 10 kg. Adsorbent: $FAC\text{-}NH_3$. Weight of adsorbent: 12 g.*

Sample No	Sample ID	Time (hr)	Before adsorption Odor concentration $O_1(OU/m^3)$	After adsorption $O_2(OU/m^3)$	Odor removal $(O_1\text{-}O_2)/O_1) \times 100\%$
1	RS	0	316.2277	316.2277	0
2	RS1	1.5	316.2277	199.5262	36.87
3	RS2	3.0	316.2277	50.1187	84.13
4	RS3	4.5	316.2277	14.125	95.53
5	RS4	18	316.2277	12.5892	96.01

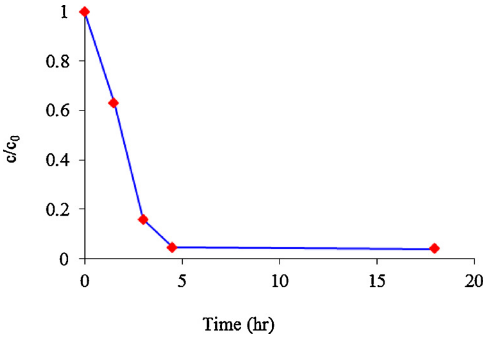


Fig. 8. Relative odour concentration (*olfactometry*) versus time in batch equilibrium adsorption experiment.

In Fig. 7 it is seen that the adsorption capacity of 12 g $FAC\text{-}NH_3$ is higher as compared to that of GAC, FAC-KOH and FAC-NaOH for the removal of malodorous VOSCs. For CH_3SH, adsorption capacities of GAC, $FAC\text{-}NH_3$, FAC-KOH and FAC-NaOH are in the ratio 85.34:95.72:93.15:91.67. Similarly for C_2H_5SH the same is GAC:$FAC\text{-}NH_3$:FAC-KOH: FAC-NaOH: 82.73:92.35:92.37:90.63.

In case of CH_3SCH_3, adsorption capacities of GAC, $FAC\text{-}NH_3$, FAC-KOH and FAC-NaOH are in the ratio 78.37:95.96:93.97:91.75. Similarly for CS_2 the ratio is GAC:$FAC\text{-}NH_3$:FAC-KOH: FAC-NaOH: 84.94:90.61:90.17:89.94.

Sewage samples are collected from the sewage treatment plant located at Baranagar Kamarhati, Kolkata, West Bengal, India. Analysis of perception of odour from these sewage samples is given in Table 3. It shows the transient behaviour of perceived odour which is dependent on the changes in overall concentration of various odorous compounds before and after adsorption and corresponding percentage removal of odour with respect to the same for a particular feed sample.

In this batch analysis it is observed that the samples become odourless around 4.5hr after the application of 12 g of $FAC\text{-}NH_3$,

Table 4

Time-variant concentration of (a) methyl mercaptan (CH_3SH), (b) ethyl mercaptan (C_2H_5SH), (c) dimethyl sulphide (CH_3SCH_3) (d) carbon disulfide (CS_2), before and after adsorption along with percentage removal. *Date of Experiment: 16.09.2015. Weight of sewage water: 10 kg. Adsorbent: FAC-NH$_3$. Weight of adsorbent: 12 g.*

Component	Sample No	Sample ID	Time (hr)	CH_3SH (GC–MS analysis)		CH_3SH Removal $(A_1\text{-}A_2)/A_1) \times 100$ %
				Peak area (feed) A_1	*Peak area (after adsorption) A_2*	
(a)						
Methyl mercaptan (CH_3SH)	1	RS	0	118322.31	118322.31	0
	2	RS1	1.5	118322.31	98030.03	17.154
	3	RS2	3.0	118322.31	24847.69	79.07
	4	RS3	4.5	118322.31	5206.168	95.61
	5	RS4	18	118322.31	3525.996	97.02
(b)						
Ethyl mercaptan (C_2H_5SH)	1	RS	0	221942.74	221942.74	0
	2	RS1	1.5	221942.74	193667.23	12.74
	3	RS2	3.0	221942.74	62277.133	71.94
	4	RS3	4.5	221942.74	16934.231	92.37
	5	RS4	18	221942.74	15624.76	92.96
(c)						
Dimethyl sulphide (CH_3SCH_3)	1	RS	0	128086.67	128086.67	0
	2	RS1	1.5	128086.67	109770.28	14.31
	3	RS2	3.0	128086.67	38912.73	69.62
	4	RS3	4.5	128086.67	7224.08	94.36
	5	RS4	18	128086.67	5174.7	95.96
(d)						
Carbon disulfide (CS_2)	1	RS	0	224366.35	224366.35	0
	2	RS1	1.5	224366.35	194503.19	13.31
	3	RS2	3.0	224366.35	74893.73	66.62
	4	RS3	4.5	224366.35	24366.43	89.14
	5	RS4	18	224366.35	21068.11	90.61

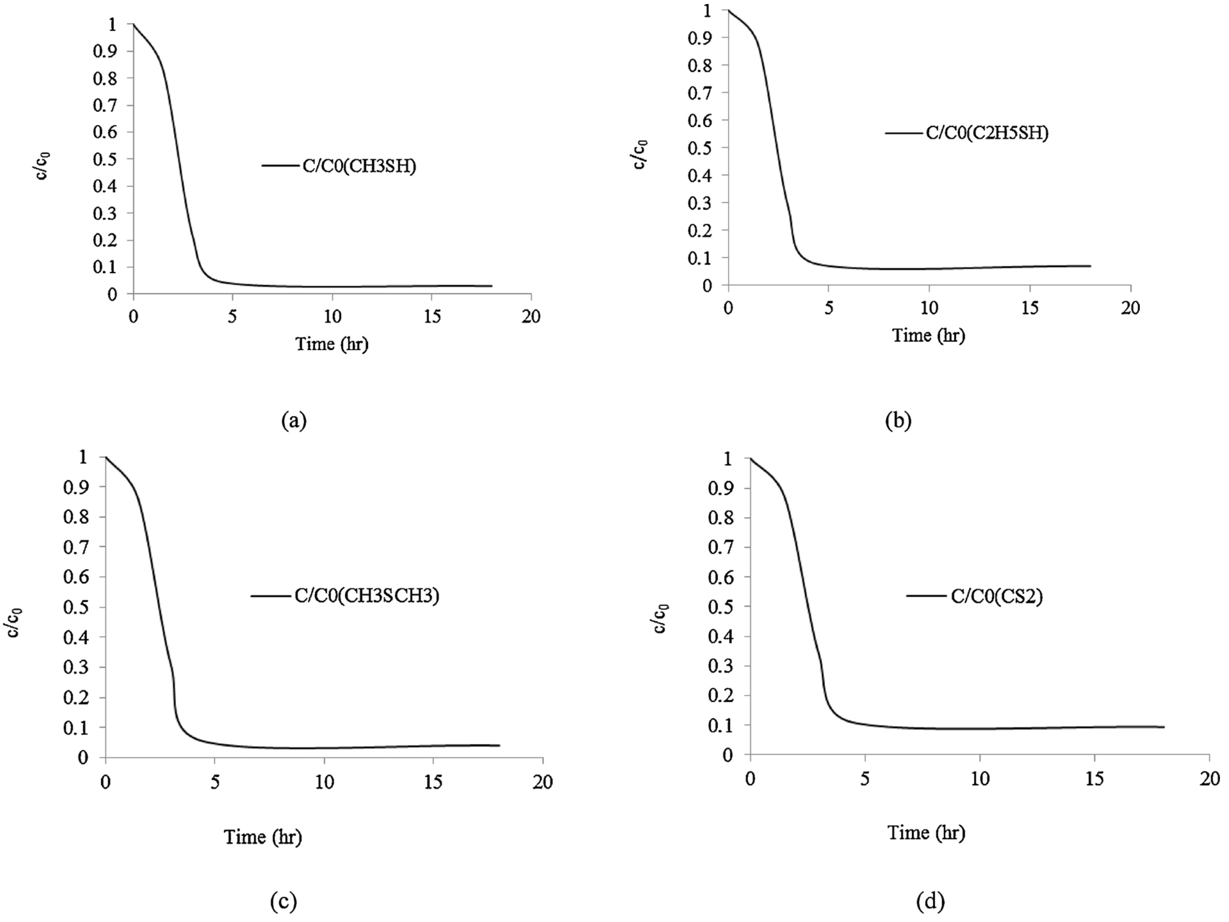


Fig. 9. Time-variant relative concentration of four VOSCs a) CH_3SH, b) C_2H_5SH, c) CH_3SCH_3, d) CS_2 (Detector: GC-PFPD) versus time.

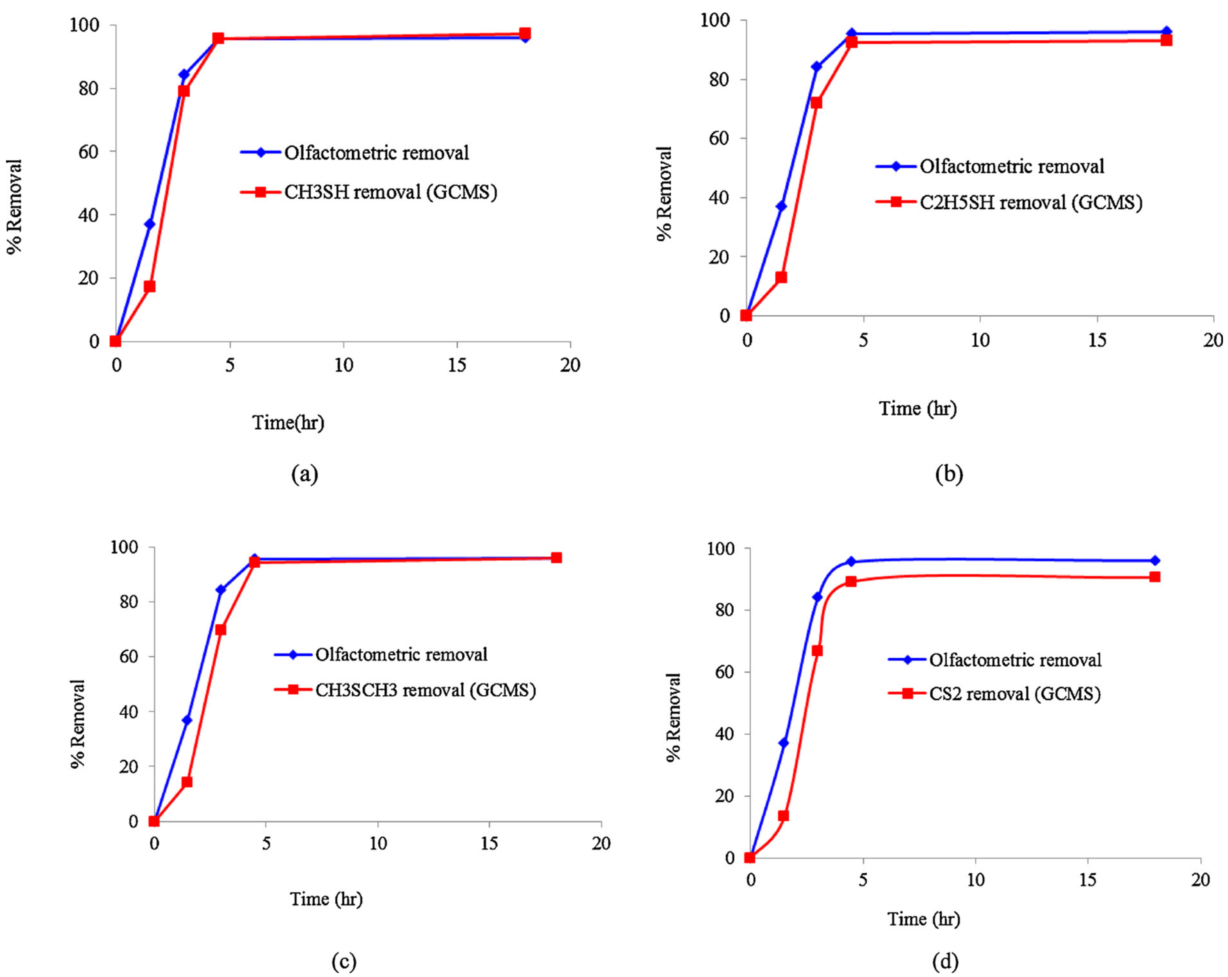


Fig. 10. Percentage removal of overall odour (*olfactometry based output*) and percentage removal of four VOSCs by adsorption (component specific analysis; detector: GC-PFPD) versus time. a) CH_3SH, b) C_2H_5SH, c) CH_3SCH_3, d) CS_2.

showing a very good adsorption capacity of the same (see Fig. 8).

Similar estimation is also carried out for specific malodours VOSCs with detections in GC–MS. The peak areas of specific compounds for samples collected before and after adsorption using $FACNH_3$ as the adsorbent at different time interval are shown in Table 4 for the four malodorous VOSCs detected with low odour threshold values. The odour threshold value for methyl mercaptan is 3.44 $\mu g\, m^{-3}$, ethyl mercaptan is 2.11 $\mu g\, m^{-3}$, dimethyl sulphide is 5.80 $\mu g\, m^{-3}$ and carbon disulfide is 48.30 $\mu g\, m^{-3}$ [36].

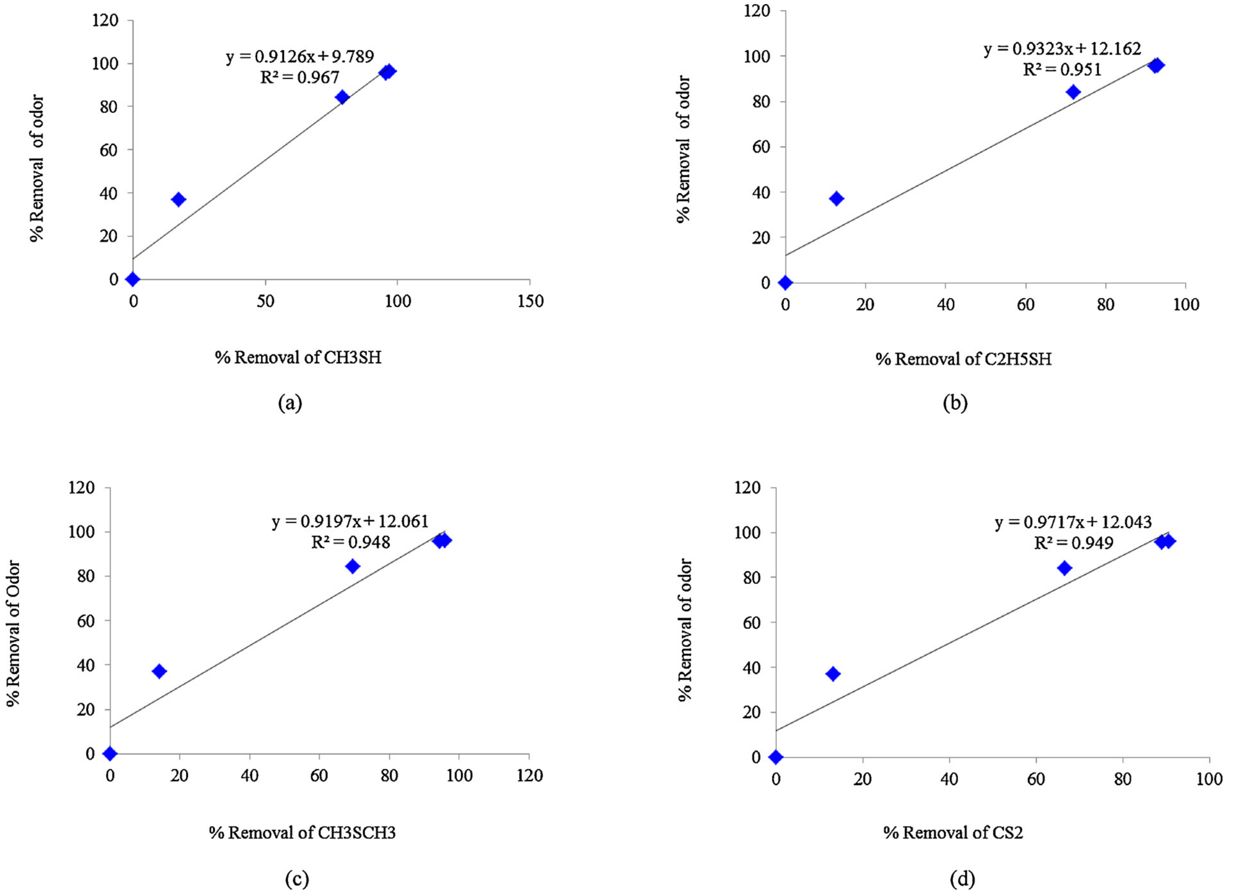
Analysis of perception of the malodour from raw sewage samples of the STP is carried out using well- known psychophysical models [11,37]. Simultaneously specific component analysis (GCMS) is also carried out for the same samples collected using the sorbent tube fitted along the other port of the Y-connector. Beidler's law is applied in order to convert the intensity reports to equivalent odour concentration in relevant units [38,39].

Perceived odour intensity is an indirect measure of the cumulative effect of concentration of a number of VOSCs (with relatively low odour thresholds like methyl mercaptan, ethyl mercaptan, dimethyl sulphide and carbon disulfide) analysed by GC equipped with a Pulse Flame Photometric Detector (GC-PFPD). These compounds are typically representative of sewage odour. Fig. 9 shows the relative odour concentration versus time until equilibrium is attained. The results show a very similar trend for all the four compounds, as observed from Fig. 9, where c_0 and c are the GC–MS based initial and time-variant concentration of various VOSCs respectively. It is observed that the time to reach equilibrium adsorption is approximately 4.5 h for all the four VOSCs. Outputs from olfactometry and the same using GC–MS show a very similar trend and these are shown in Fig. 10. It is observed that, after addition of FAC-NH_3 upto 2hr, olfactometry based outputs for% removal of odour did not tally much with the same from GC–MS based outputs for the four different compounds. The rate of adsorption of methyl mercaptan is faster than that of the other three compounds during this period of time. Overall odour did reduce to the same extent as component specific adsorption after approximately 2.5 h. This is because methyl mercaptan has got predominantly low threshold concentration.

However equilibrium is achieved more or less in the same time for all VOSCs, approximately 4.5 h after FAC-NH_3 is added. Odor contributing capacity of these four organo sulphur compounds is measured by linearization of the percentage removal of overall odour (*Olfactometry output*) versus percentage removal of relative concentrations of four compounds (see Fig. 11). Fig. 11 revealed that the linear correlation of methyl mercaptan (R^2 = 0.967) is very high as compared to ethyl mercaptan (R^2 = 0.951), dimethyl sulphide (R^2 = 0.948) and that of carbon disulphide (R^2 = 0.949). So it can be concluded that methyl mercaptan has a large odour contributing potential of the tested sewage waste water with respect to the other compounds. For the other VOSCs also, removal of overall odour is nearly at par with the removal of the specific VOSC.

4. Mechanism of adsorption on FACs

Adsorption of mercaptans using activated carbon is pH dependent



(a) (b)

(c) (d)

Fig. 11. Percentage removal of odour (*Olfactometry output*) versus percentage removal of relative concentration of four VOSCs. a) CH_3SH, b) C_2H_5SH, c) CH_3SCH_3, d) CS_2.

and enhances in presence of water. Most probably, oxidation takes place because active oxygen radicals are being produced by adsorption of oxygen upon functionalised activated carbon surfaces [40]. Oxidation proceeds due to the surface reaction between adsorbed mercaptan and active oxygen radicals. Changes in surface chemistry likely affect the adsorption of methyl mercaptan. As demonstrated elsewhere, MM, after getting adsorbed on activated carbons, is oxidized to Dimethyl Disulphide (DMDS) [41].

$$CH_3SH \overset{K_a}{\rightarrow} CH_3SH_{ads} \tag{1}$$

$$CH_3SH_{ads} \overset{K_s}{\rightarrow} CH_3SH_{ads-L} \tag{2}$$

$$2CH_3SH_{ads-L} + O^*_{ads} \overset{K_{R1}}{\rightarrow} CH_3SSCH_{3ads-L} \tag{3}$$

Proposed reaction pathways (arrows represent chemical equilibrium) should depend on the apparent pH of the system because MM is able to dissociate ($pK_a = 10.3$). Moreover, the oxidation of methyl mercaptan to dimethyl di-sulphide can be enhanced by alkali functionalization of activated carbon using various bases like sodium hydroxide, potassium hydroxide, ammonium hydroxide etc. Water is present in the system and the carbon surface is able to produce excess oxygen radicals and hydroxyl radicals. This automatically enhances the oxidation of mercaptans.

There is an apparent improvement of adsorption-catalytic properties of nitrogen containing carbons in desulfurization. The same can be explained from the point of view of the electronic theory of catalysis. The extra π- electrons of pyrollic and quaternary nitrogen occupies the high energy states in the conduction band. It is likely that from there, they can be transferred to the adsorbed oxygen and super oxide ions (O_2^{2-}) can be formed [42]. Those super oxide ions (O_2^{2-}) can easily trigger the formation of HO^* and HO_2^* radicals while reacting with water. All the species are much more reactive than molecular oxygen and may oxidize sulphur compounds, when these are adsorbed on carbon surface.

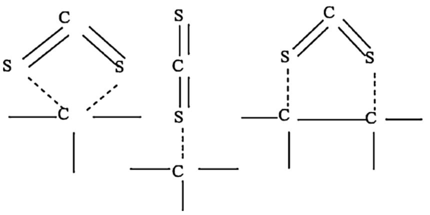
$$CH_3SCH_{ads-L} \overset{K_H}{\rightarrow} CH_3S^-_{ads} + H^+ \tag{4}$$

$$2CH_3S^-_{ads} + O^*_{ads} \overset{K_{R2}}{\rightarrow} CH_3SSCH_{3ads-L} + O^{2-} \tag{5}$$

$$2H^+ + O^{2-} \rightarrow 2H_2O \tag{6}$$

Where K_a, K_S, K_H, K_R are the equilibrium constants for the processes of adsorption, gas solubility, dissociation and surface reaction.

The adsorption of CS_2 vapors by carbon appears to involve hydrophobic interactions between the CS_2 and C-C layer planes of carbon [43] which may be represented as:



The formation of such C-S complexes has been suggested by Yang et al., 2006 [44].

5. Conclusions

Precursor GAC is compared with alkali treated functionalized GACs

(FACs) with respect to each of their capacities towards removal of specific odorous VOSCs and towards abatement of odour as a whole. High adsorption capacity is observed for FAC-NH_3. The texture and surface chemistry of GAC and various FACs are studied thoroughly and it is observed that alkali treated FACs could dramatically increase the adsorption of each of the key odorous VOSCs. On alkali functionalization, surface area and pore volume of GAC increase while the acidic functional groups decrease in number. Variation in surface area and porosity of the adsorbents play a key role on adsorption of VOSCs. Functionalization by ammonia solution enlarged the surface area and increased the concentration of basic groups, thereby enhancing the uptake of VOSCs into FAC-NH_3 surface. The adsorption capacity of GAC and FACs increases in the order FAC-NH_3 > FAC-KOH > FAC-NaOH > GAC. Two results are sincerely considered for the overall control of malodour from STPs: a) correlation of time variant olfactometry based odour concentration data with time variant VOSCs concentration (GC–MS outputs) for all the four malodorous compounds like methyl mercaptan, ethyl mercaptan, dimethyl sulphide and carbon disulphide; b) correlation of percentage decrease in the olfactometry based odour concentration with percentage removal of each of the above four major odour contributing VOSCs. The same is found to vary linearly with $R^2 = 0.967$ (methyl mercaptan), $R^2 = 0.951$ (ethyl mercaptan), $R^2 = 0.948$ (dimethyl sulphide) and $R^2 = 0.949$ (carbon disulphide). Linearization of the percentage removal of overall odour (Olfactometry output) versus percentage removal of relative concentrations of four compounds reveals that methyl mercaptan has a very large odour contributing potential ($R^2 = 0.967$) for the tested sewage waste water as compared to other three compounds. Simultaneous conversion of methyl mercaptan to dimethyl disulphide leads to its faster removal by FAC-NH_3.

Acknowledgments

The authors acknowledge Thermo Fisher India Limited, Nasik Factory, for carrying out GC–MS analysis at their industrial facility using PFPD (Pulse Flame Photometric Detector). The authors would like to thank Mr. Vivek Bharadwaj, Executive Engineer and Mr. Asim Nag (Ganga Action Plan, Phase-I), Kolkata Municipal Development Authority (KMDA), West Bengal, India, for their kind cooperation to allow the first author to carry-out on-site experiments at their Baranagar-Kamarhati Sewage treatment plant. The authors are also grateful to the Indian Association for the Cultivation of Science, Raja S.C. Mullik Road, Kolkata-700032, for carrying out some tests for the characterization of GAC and FACs at their central facility.

References

[1] M.R. Ras, F. Borrull, R.M. Marcé, Sampling and preconcentration techniques for determination of volatile organic compounds in air samples, TrAC Trends Anal. Chem. 28 (2009) 347–361.
[2] A. Vincent, Sources of odours in wastewater treatment, Odours in Wastewater Treatment: Measurement Modelling and Control, (2001), pp. 69–90.
[3] K. Hinokiyama, K. Nishida, M. Osako, N. Muto, Adsorbent characteristics of hydrogen sulfide and methyl mercaptan in single and mixed systems, Int. J. Environ. Stud. 38 (1991) 25–40.
[4] M.Q. Patterson, J.C. Stevens, W.S. Cain, J.E. Cometto-Muniz, Detection thresholds for an olfactory mixture and its three constituent compounds, Chem. Senses 18 (1993) 723–734.
[5] G.D. Waltrip, E.G. Snyder, Elimination of odor at six major wastewater treatment plants, J. (Water Pollut. Control Fed.) (1985) 1027–1032.
[6] A.G. Boon, Septicity in sewers: causes, consequences and containment, Water Sci. Technol. 31 (1995) 237–253.
[7] T. Dewettinck, K. Van Hege, W. Verstraete, The electronic nose as a rapid sensor for volatile compounds in treated domestic wastewater, Water Res. 35 (2001) 2475–2483.
[8] R. Stuetz, R. Fenner, G. Engin, Assessment of odours from sewage treatment works by an electronic nose, H 2 S analysis and olfactometry, Water Res. 33 (1999) 453–461.
[9] R.M. Stuetz, F.-B. Frechen, IWA publishing, Odours in wastewater treatment, 2001.
[10] P.E. Fanning, M.A. Vannice, A DRIFTS study of the formation of surface groups on carbon by oxidation, Carbon 31 (1993) 721–730.
[11] B. Rajbansi, U. Sarkar, S.E. Hobbs, Hazardous odor markers from sewage wastewater: a step towards simultaneous assessment, dearomatization and removal, J. Taiwan Inst. Chem. Eng. 45 (2014) 1549–1557.
[12] V.K. Gupta, N. Verma, Removal of volatile organic compounds by cryogenic condensation followed by adsorption, Chem. Eng. Sci. 57 (2002) 2679–2696.
[13] N. Hansen, K. Rindel, Bioscrubbing, an effective and economic solution to odour control at wastewater treatment plants, Water Sci. Technol. 41 (2000) 155–164.
[14] G. Yang, J. Hobson, Use of chemicals for septicity and odour prevention in sewer networks, Odours in Wastewater Treatment: Measurement Modelling and Control, (2001), pp. 269–292.
[15] M. Tomar, T.H. Abdullah, Evaluation of chemicals to control the generation of malodorous hydrogen sulfide in waste water, Water Res. 28 (1994) 2545–2552.
[16] A. Turk, E. Sakalis, J. Lessuck, H. Karamitsos, O. Rago, Ammonia injection enhances capacity of activated carbon for hydrogen sulfide and methyl mercaptan, Environ. Sci. Technol. 23 (1989) 1242–1245.
[17] P. Chingombe, B. Saha, R. Wakeman, Surface modification and characterisation of a coal-based activated carbon, Carbon 43 (2005) 3132–3143.
[18] H.-L. Chiang, C. Huang, P. Chiang, The surface characteristics of activated carbon as affected by ozone and alkaline treatment, Chemosphere 47 (2002) 257–265.
[19] L. Li, S. Liu, J. Liu, Surface modification of coconut shell based activated carbon for the improvement of hydrophobic VOC removal, J. Hazard. Mater. 192 (2011) 683–690.
[20] H.M. Albishri, H.M. Marwani, Chemically modified activated carbon with tris (hydroxymethyl) aminomethane for selective adsorption and determination of gold in water samples, Arab. J. Chem. 9 (2016) S252–S258.
[21] C. Ania, B. Cabal, C. Pevida, A. Arenillas, J. Parra, F. Rubiera, J. Pis, Removal of naphthalene from aqueous solution on chemically modified activated carbons, Water Res. 41 (2007) 333–340.
[22] A. Derylo-Marczewska, B. Buczek, A. Swiatkowski, Effect of oxygen surface groups on adsorption of benzene derivatives from aqueous solutions onto active carbon samples, Appl. Surf. Sci. 257 (2011) 9466–9472.
[23] A. Derylo-Marczewska, A. Swiatkowski, S. Biniak, M. Walczyk, Effect of properties of chemically modified activated carbon and aromatic adsorbate molecule on adsorption from liquid phase, Coll. Surf. A 327 (2008) 1–8.
[24] O. Ekpete, M. Horsfall, Preparation and characterization of activated carbon derived from fluted pumpkin stem waste (Telfairia occidentalis Hook F), Res. J. Chem. Sci. 1 (2011) 10–17.
[25] J.W. Shim, S.J. Park, S.K. Ryu, Effect of modification with HNO 3 and NaOH on metal adsorption by pitch-based activated carbon fibers, Carbon 39 (2001) 1635–1642.
[26] H. Boehm, Some aspects of the surface chemistry of carbon blacks and other carbons, Carbon 32 (1994) 759–769.
[27] M.V. Lopez-Ramon, F. Stoeckli, C. Moreno-Castilla, F. Carrasco-Marin, On the characterization of acidic and basic surface sites on carbons by various techniques, Carbon 37 (1999) 1215–1221.
[28] P. Littarru, Environmental odours assessment from waste treatment plants: dynamic olfactometry in combination with sensorial analysers electronic noses, Waste Manage. 27 (2007) 302–309.
[29] S.J. Gregg, K.S.W. Sing, H. Salzberg, Adsorption surface area and porosity, J. Electrochem. Soc. 114 (1967) 279C–279C.
[30] F. Qu, L. Zhu, K. Yang, Adsorption behaviors of volatile organic compounds (VOCs) on porous clay heterostructures (PCH), J. Hazard. Mater. 170 (2009) 7–12.
[31] R. Chiriac, J. Carre, Y. Perrodin, L. Fine, J.-M. Letoffe, Characterisation of VOCs emitted by open cells receiving municipal solid waste, J. Hazard. Mater. 149 (2007) 249–263.
[32] S. Król, B. Zabiegała, J. Namieśnik, Monitoring VOCs in atmospheric air II. Sample collection and preparation, TrAC Trends Anal. Chem. 29 (2010) 1101–1112.
[33] A.T.M. Din, B. Hameed, A.L. Ahmad, Batch adsorption of phenol onto physiochemical-activated coconut shell, J. Hazard. Mater. 161 (2009) 1522–1529.
[34] R.Q. Sun, L.B. Sun, Y. Chun, Q.H. Xu, Catalytic performance of porous activated carbons obtained by chemical activation, Carbon 46 (2008) 1757–1764.
[35] H. Denga, G. Li, H. Yanga, J. Tanga, Preparation of activated carbon from cotton stalk by microwave assisted KOH and K_2CO_3 activation, Chem. Eng. J. 163 (2010) 373–381.
[36] F. Dincer, A. Muezzinoglu, Odor-causing volatile organic compounds in wastewater treatment plant units and sludge management areas, J. Environ. Sci. Health Part A 43 (2008) 1569–1574.
[37] B. Rajbansi, U. Sarkar, Evaluation of odour intensity from activated sludge based sewage treatment works, Desalin. Water Treat. 12 (2009) 360–368.
[38] W.S. Cain, H.R. Moskowitz, Psychophysical scaling of odor, Human responses to environmental odors, (1974), pp. 1–32.
[39] H. Stone, S.M. Oliver, Beidler's theory and human taste stimulation, Attention Perception Psychophysics 1 (1966) 358–360.
[40] J.B. Teresa, B. Svetlana, B. Andrey, Effect of surface characteristics on adsorption of methyl mercaptan on activated carbons, Ind. Eng. Chem. Res. 41 (17) (2002) 4346–4352.
[41] W.L. Song, M.A. Wan, D. Wan, M.G. Lee, Adsorption characteristics of methyl mercaptan dimethyl disulfide, andtrimethylamine on coconut-based activated carbons modified with acid and base, J. Ind. Eng. Chem. 16 (2010) 973–977.
[42] B. Andrey, S. Bashkova, T. Bandosz, M. Angel, D. Irina, T. Yuriy, Nitrogen enriched activated carbons as adsorbents and catalysis in desulfurization technologies, Ind. Eng. Chem. Res. 41 (2002) 17.
[43] M. Goyal, R. Dhawan, Adsorptive removal of vapors of toxic sulfur compounds using activated carbons, Int. J. Chem. Mol. Eng. 3 (3) (2009) 157–162.
[44] J. Yang, P. Juan, Z. Shen, R. Guo, J. Jia, H. Fang, Y. Wang, Removal of carbondisulfide from water via adsorption on activated carbon fiber, Carbon 44 (2006) 1367–1375.

CLEAN
Soil Air Water

Debasree Banerjee[1]
Shyamal Jana[1]
Ujjaini Sarkar[1]
Debasri Roy[2]

[1]Department Of Chemical Engineering, Jadavpur University, Kolkata, India
[2]School of Water Resources Engineering, Jadavpur University, Jadavpur, Kolkata, India

Research Article

Application of an Alkali Functionalized Material for Treating Pharmaceutical Wastewater Containing Chlorhexidine Gluconate and Cetrimide

Two different types of mesoporous adsorbents and one microporous adsorbent were used for the adsorption of chlorhexidine gluconate and Cetrimide. Chlorhexidine gluconate and Cetrimide are widely used in antiseptic solutions, mouthwashes, and germicidal hand rinses, etc. Scanning electron microscopy images, N_2 adsorption/desorption isotherms, pore size distribution, Fourier transform infrared spectra and points of zero charge illustrate that significant changes occur on the activated carbon after functionalization with NH_4OH when compared to the precursor granular activated carbon (GAC). The adsorption capacity of the novel alkali functionalized activated carbon (FAC-NH_3) was found to be comparable with the highly expensive mesoporous aluminosilicate MCM-41 for both chlorhexidine gluconate and cetrimide. For a wide concentration range, adsorption with FAC-NH_3 is approximately three times more in comparison to GAC for both compounds. Chlorhexidine gluconate forms surface complexes with the functional groups present in the super microporous FAC-NH_3. This fact is also supported by kinetic studies, where pseudo first-order and second-order models, intra-particle diffusion, and Boyd's plots showed evidences to support chemisorption, on top of pure physical adsorption.

Keywords: Adsorption; Antiseptics; Mesoporous material; Microporous activated carbon; Modeling

Received: May 2, 2014; *revised:* June 26, 2014; *accepted:* July 15, 2014

DOI: 10.1002/clen.201400340

Additional supporting information may be found in the online version of this article at the publisher's web-site.

1 Introduction

Treatment of pharmaceutical wastewater by adsorption with activated carbon is executed by various researchers [1–4]. Activated carbon is known as the most commonly used adsorbent for wastewater treatment. However, comparatively narrow pore aperture of the activated carbon leads to less amount of diffusion and restricted adsorption of heavy and larger organic molecules [5]. This drawback of the microporous activated carbon demands for the development of various types of mesoporous materials. Various kinds of mesoporous materials (*e.g.*, mesoporous silica, carbon aerogel, mesoporous carbon, etc.) are widely used by many researchers during the recent years for the adsorption of large size organic pollutants from wastewater [5–10].

In order to increase the adsorption capacity of activated carbon, it is often treated with acids and alkali and the activated carbon produced by such methodologies are called functionalized or modified carbon. The adsorption capacity is mainly dependent on the texture and surface chemistry of the activated carbon [11–13]. In this study, an attempt was made to develop a mesoporous material by functionalization of activated carbon with NH_4OH. Rivera-Utrilla et al. [14] reported that nitrogenation could increase the basicity of activated carbon. The introduction of nitrogen to carbon can significantly increase the polarity of the carbon surface and hence its specific interaction with polar adsorptive compounds becomes prominent. The review of Rivera-Utrilla et al. [14] also stated that nitrogenation can also affect the porous structure along with the surface chemical nature of the activated carbon in a form and to an extent that depends on the precursor carbon, chemical agent, and the experimental method used. Only few reports have been found where the porous structure remain unchanged [15, 16], or a reduction in surface area and microporosity [17–19] after nitrogenation on activated carbon occurs. Various nitrogen containing functional groups are introduced as a consequence of nitrogenation of the activated carbon [14].

Correspondence: Dr. U. Sarkar, Department Of Chemical Engineering, Jadavpur University, Kolkata 700032, India
E-mail: Usarkar@chemical.jdvu.ac.in

Abbreviations: **BET**, Brunauer-Emmett-Teller; **BOD**, biochemical oxygen demand; **COD**, chemical oxygen demand; **EC**, effective concentration; **FACL**, functionalized activated carbon; **FTIR**, Fourier transform IR spectroscopy; **GAC**, granular activated carbon; **HPLC**, high performance liquid chromatography; **IC**, inhibitory concentration; **LC**, lethal concentration; **MW**, molecular weight; **NLDFT**, non-local density functional theory; **pH_{pzc}**, point of zero charge; **SEM**, scanning electron microscopy; **SSQ**, sum of squares

Chlorhexidine gluconate (molecular weight (MW) = 897.77 g/mol), a cationic bisbiguanide, and cetrimide (MW = 364.45 g/mol), a cationic surfactant, are often present in various combinations within many of the antibacterial pharmaceutical solutions and these, in combination, have been found to be very effective for all categories of microbes including bacteria, yeast, and viruses [20]. Though effective as antibacterial agents for human cells, this combination can also destroy useful bacteria and microbes for plant growth if discharged into inland surface water body without any treatment. Considering the sizes of these two compounds, MCM-41 and the new functionalized activated carbon, FAC-NH_3 were used to remove them from pharmaceutical solutions. The toxicity of chlorhexidine gluconate towards fish (*Brachydanio rerio*) is correlated to the lethal concentration LC_{50} (96 h) = 10.4 mg/L and LC_0 = 10.0 mg/L (OECD Test Guideline 203) [21], towards crustaceans (*Daphnia pulex*) by the half maximal effective concentration EC_{50} (48 h) = >0.05–<0.10 mg/L (DEV, DIN 38412) and towards algae (*Scenedesmus subspicatus*) by the half maximal inhibitory concentration IC_{50} (72 h) = 0.011 mg/L (OECD Test Guideline 201) [22]. Sub-acute toxicity of chlorhexidine gluconate to green algae is prominent, with IC_{50} (10 days) = 4.4 mg/L. Its chemical oxygen demand (COD) value is 2 19 000 mg/L and the biochemical oxygen demand (BOD_5) value is 0 mg/L. Cetrimide is an antiseptic agent with detergent properties. It is very toxic to aquatic organisms. Its toxicity towards fish (*Danio rerio*) is noted with LC_{50} (96 h) = 1.81 mg/L (OECD Test Guideline 203) [21]. The toxicity to crustaceans (*Daphnia magna*) is also noted with EC_{50} (48 h) = 0.022 mg/L (OECD Test Guideline 202) [23]. The toxicity to green algae (*Pseudokirchneriella subcapitata*) is given by IC_{50} (72 h) = 0.0054 mg/L (OECD Test Guideline 201) [22]. Considering the eco-toxicological effects of chlorhexidine gluconate and Cetrimide, it can be stated that extreme exposure to these compounds is harmful for animals also. However, there is no norm or regulation for the permissible limit that should be maintained before discharging the pharmaceutical wastewater containing these compounds into inland surface water body.

Multicomponent adsorption signifies the competitive adsorption of more than one component which is specifically important since the industrial effluents contain usually more than one component [24]. Single component adsorption systems are most studied by far, though they represent simplified model systems. On the other hand, multi-component adsorption portrays a more practical scenario, which includes the competitions among the adsorbates for the same adsorption sites of the solid surface, interactions between adsorbed molecules and consequently a great variation in the adsorption capacity of the involved analytes.

This study mainly focuses on the removal of chlorhexidine gluconate and Cetrimide from pharmaceutical wastewater. Banerjee et al. [25] studied the role of acid functionalized granular activated carbons (GACs) for the removal of pure chlorhexidine gluconate. Banerjee et al. [26] also reported the multi-component adsorption of chlorhexidine gluconate and Cetrimide using commercial GAC.

The main objective of this work was to analyze the multicomponent adsorption of chlorhexidine gluconate and Cetrimide using three different kinds of adsorbents: commercial, alkali functionalized, and mesoporous. Modeling of multicomponent systems is a difficult task, as compared to single component based systems, and not much information has been found on the removal of chlorhexidine gluconate in combination with Cetrimide. This paper gives an insight about the adsorption and modeling of these two particular components using well-known multicomponent adsorption models namely, the modified competitive Langmuir-like model and the LeVan-Vermeulen model.

2 Materials and methods

2.1 Chemicals used

The mesostructured aluminosilicate (SiO_2/Al_2O_3), MCM-41 (hexagonal) (CAS No: 1318-02-1) was purchased from Sigma–Aldrich, India. Granular activated carbon, LR grade, was purchased from S D Fine-CHEM, India.

Ammonia solution (NH_4OH), GR grade, was purchased from Merck, India. An antiseptic solution containing 0.6% (w/v) Cetrimide and 0.3% (v/v) chlorhexidine gluconate was used. The pure components Cetrimide (MW = 364.45 g/mol) (CAS No: 57-09-0) and chlorhexidine gluconate (MW = 897.77 g/mol) (CAS No: 18472-51-0) were purchased from Sigma–Aldrich, Germany, for single component adsorption experiments.

2.2 Synthesis

2.2.1 Preparation of supra-porous activated carbon

GACs were added to an alkaline solution of 6 M NH_4OH, 1 g GAC in 8 mL NH_4OH solution, and kept on a hot plate at 70 °C for 2 h under constant stirring. The treated GACs were then separated from the alkaline solution by decantation and washed with distilled water (conductivity: 0.5 μS/cm, pH: 7.5) thoroughly. Thereafter, they were dried in an oven at 105 °C for 4 h and transferred to a desiccator before using and were called functionalized activated carbon (FAC-NH_3) in this study.

2.3 Physical characterization

2.3.1 Scanning electron microscopy (SEM)

SEM images of GAC, MCM-41, and FAC-NH_3 were carried out using a JEOL JEM 6700F field emission SEM at 7000× magnification [26].

2.3.2 N_2 adsorption/desorption

The Brunauer-Emmett-Teller surface area along with the pore volume of GAC, MCM-41, and FAC-NH_3 samples were determined by nitrogen adsorption/desorption isotherms, carried out in a Beckmann Coulter SA3100 surface area analyzer at 77 K [26]. The material was degassed at 393 K for 12 h before analysis and the maximum pressure was maintained at 1 bar.

2.3.3 Nonlocal density functional theory (NLDFT)

NLDFT was used to examine the distribution of pores in GAC, mesoporous MCM-41 and FAC-NH_3 [24].

2.3.4 Fourier transform infrared spectroscopy (FTIR)

FTIR was applied (IR Affinity-1, Shimadzu, Japan) at a resolution of 4 cm^{-1} with 45 scans per sample in order to determine the functional groups that were prevalent in the adsorbent samples. The adsorbent samples were ground in a mortar pestle and then mixed with KBr in a ratio of 100:1 [26].

2.3.5 Point of zero charge (pH_{pzc})

pH_{pzc} was determined by a Malvern zeta sizer, (Nano-Z, ZEN 2600 Nano Series, Malvern) for GAC, MCM-41 and FAC. 0.1 M nitric acid (HNO_3) and 0.1 M potassium hydroxide (KOH) were added to the sample solution at 25 °C in order to maintain the pH values within a range of 2–12 [27]. Average zeta potentials for the adsorbent samples were measured at each pH condition. The acidity or basicity of the adsorbent surface and pH_{pzc} were determined by measuring the zeta potential.

2.4 Adsorption of chlorhexidine gluconate and Cetrimide

2.4.1 Experiments: batch equilibrium study

For pure component adsorption, solutions of chlorhexidine gluconate of concentrations in the range of 0.01–0.8/100 mL and solutions of Cetrimide in the concentration range of 0.01–0.8 g/100 mL were prepared. 0.1 g of each adsorbent was added to the solutions. The optimum equilibrium adsorption time for both the pure components as well as the multicomponent components was found to be 48 h. An experiment for batch equilibrium analysis for multicomponent adsorption was done using an antiseptic solution containing 0.6% (w/v) Cetrimide and 0.3% (v/v) chlorhexidine gluconate. Solutions of various concentrations (0.5–4/25 mL) were prepared with de-ionized water. The pH of the solution was measured using a pH meter (PB11, Sartorius) [27] and was found to be within the range of 7–8. 25 mL of the solutions were given into 100 mL beakers and after adding 0.1 g adsorbent, it was kept for 48 h (the equilibrium time was optimized beforehand) at ambient temperature until equilibrium was reached. The samples were then filtered using Whatman 1 (125 mm) filter paper. The concentrations of chlorhexidine gluconate and Cetrimide solutions were measured by high performance liquid charmatography (HPLC) before and after adsorption (after the attainment of equilibrium).

2.4.2 HPLC based analytical procedure

The analysis of chlorhexidine gluconate and Cetrimide was done by HPLC equipped with two reciprocating pumps (pump 515, Waters). The temperature of the column oven was set at 35°C. The detection of the compounds was done with a UV detector (UV detector 2489, Waters) at 205 nm. Simultaneous determination of the concentrations of chlorhexidine gluconate and Cetrimide was done by a C18 column (OmniSpher 5, Varian) with a dimension of 250 × 4.6 mm and a particle size of 5 μm by HPLC. The mobile phase used in the column was acetonitrile/water (+ 0.1 M perchloric acid + 2 g sodium octanosulphonate as the ion-pairing agent), 750:250, v/v. The flow rate of the mobile phase was maintained at 0.8 mL/min. All chemicals were HPLC grade and were purchased from Sigma–Aldrich, India.

2.4.3 Statistical analysis

The error analysis of the isotherm and adsorption kinetic models was done by sum of squares (SSQ) method by Eq. (1)

$$SSQ = \sum_{i=1}^{n} \frac{(\text{Predicted} - \text{Observed})^2}{N - k - 1} \qquad (1)$$

where N is the number of samples and k is the number of parameters used in the equations.

3 Results and discussion

3.1 Characterization of the adsorbent materials

The SEM images of GAC, MCM-41, and FAC-NH_3 at 7000× magnification (Supporting Information Fig. S1a–c) show that the sizes of the pores on the surface of GAC were much smaller than that of MCM-41 and FAC-NH_3. Some mesopores can be seen on the GAC, but those are much less in quantity than for MCM-41 and FAC-NH_3.

The surfaces and pore volumes of GAC and FAC-NH_3 were comparable to each other (777 m^2/g and 0.3853 cc/g and 778 m^2/g and 0.3813 cc/g, respectively). The BET surface area of MCM-41 was found to be 735 m^2/g, which is comparable to GAC and FAC-NH_3, but the pore volume of MCM-41 (0.6141 cc/g) was about 1.6× higher than that of GAC and FAC-NH_3.

Two visible peaks could be observed in the pore size distributions of GAC, given in the inset of Fig. 1a, one at the microporous region and the other at the mesoporous region (>2 nm pore width). The isotherm of modified activated carbon (FAC-NH_3), shown in Fig. 1b, depicts a type II isotherm. It can be noticed from the figure that at high p/p_0 the N_2 uptake gradually increased, which denotes the presence of intra-particle porosity [28]. The results from the study suggested the presence of super-micro porosity in the FAC-NH_3 sample with a peak pore diameter of 1.7 nm [28, 29]. The pore size distribution of FAC-NH_3, shown in the inset of Fig. 1b, depicts that maximum cumulative numbers of pores are located in the mesoporous region (*i.e.*, >2 nm). A sharp peak could be observed at 1.7 nm, which was in the microporous region, and two more sharp peaks could be seen at 2.7 and 4.1 nm, which were in the mesoporous region. Thus, it could be concluded from the pore size distribution study that the modification of the activated carbon with alkali converted the maximum number of microspores of GAC into supra-pores and mesopores. The N_2 adsorption/desorption of MCM-41 revealed a type IV isotherm with type H1 hysteresis loop according to IUPAC nomenclature [30]. From Fig. 1c it could be observed that the nitrogen isotherms were completely reversible signifying uniformity in size and tubular unidirectional mesopores. In addition, the steep nitrogen uptake at a relative pressure of 0.5–0.6, related to the capillary condensation of N_2, specified uniformity of the pores. The sharp adsorption and desorption branches of the hysteresis loop indicated narrow mesopore size distribution and high pore volume. The pore size distribution of MCM-41 obtained from the NLDFT method (inset of Fig. 1c), showed a sharp peak at 5.6 nm pore width. So, it was apparent that large numbers of pores were situated in the mesoporous region (*i.e.*, >2 nm) for the MCM-41 material.

The FTIR spectra of GAC showed a band at 3041 cm^{-1} which represents the asymmetric and symmetric stretching of $-C-H$ bond in aliphatic CH, CH_2, and CH_3 [27]. A band at 1492 cm^{-1} can be assigned either to an $O-H$ deformation vibration or $C-H$ bending vibrations [27]. No significant functional groups could be seen in the FTIR spectra of GAC.

The FTIR spectra of FAC-NH_3 represented a peak at 3428 cm^{-1}, which could be assigned to hydroxy group [31]. A sharp peak at 2919 cm^{-1} showed the presence of asymmetric and symmetric stretching of $-C-H$ bond in the aliphatic CH, CH_2, and CH_3 [27]. A peak at 1628 cm^{-1} signified the presence of a quinone group [31, 32].

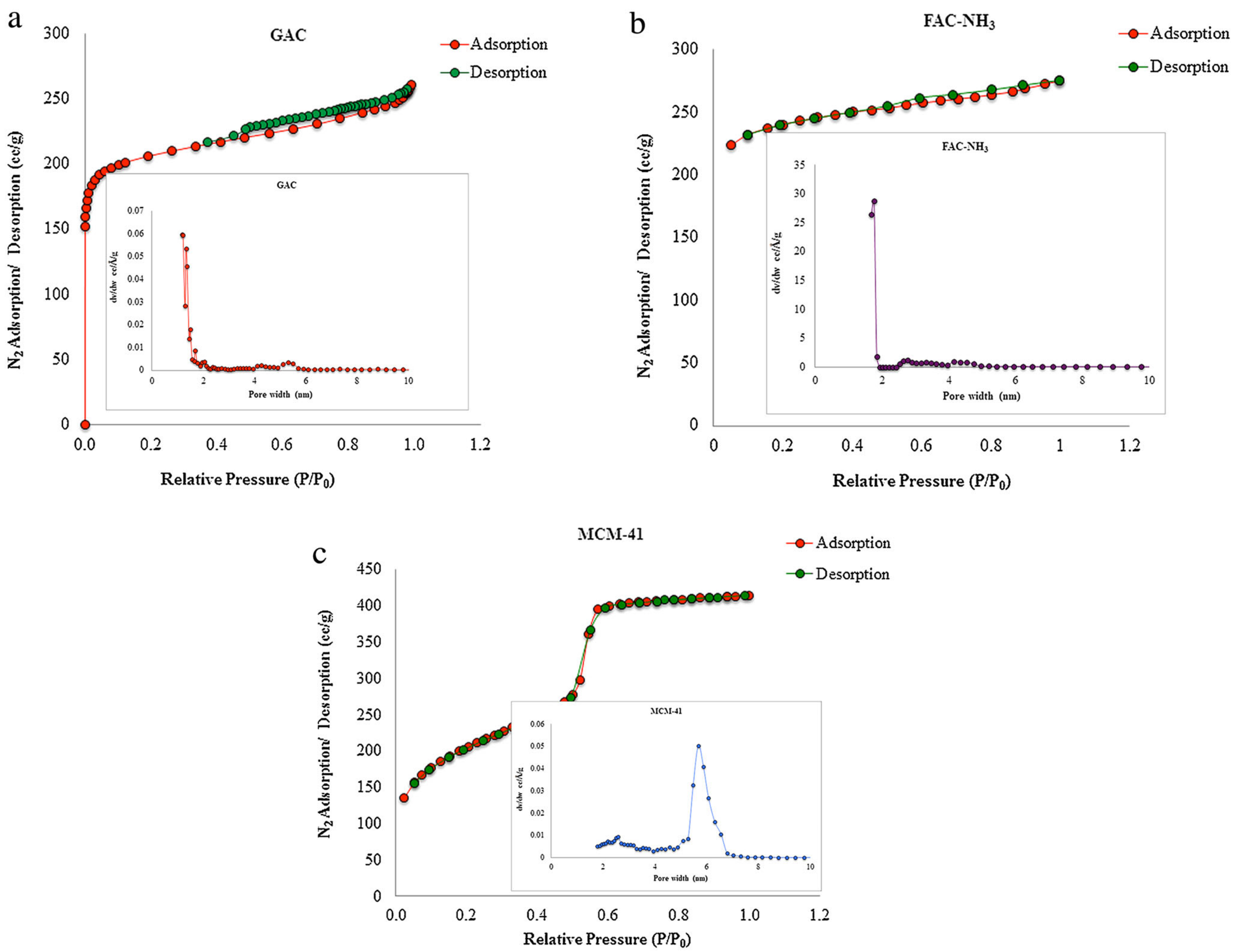


Fig. 1. N_2 adsorption-desorption isotherms and pore size distribution of (a) GAC, (b) FAC-NH_3, and (c) MCM-41.

Carbonate, lactone and –C–OH bond of phenolic group could be seen by three small peaks at 1573 cm^{-1} [33], 1486 cm^{-1} [34], and 1073 cm^{-1} [35], respectively. Comparing the FTIR spectra of unmodified and modified activated carbon it can be noticed that a large number of functional groups have attached on the surface of the precursor GAC after modification with NH_3. These functional groups form surface complexes with chlorhexidine gluconate. The existences of numerous functional groups increased the adsorption capacity of FAC-NH_3 as compared to GAC.

The FTIR spectrum of MCM-41 $(SiO_2)_{0.9875}(Al_2O_3)_{0.0125} \cdot H_2O$ shows a broad band at 3298 cm^{-1}, representing surface silanols and adsorbed water molecules [36]. The band at 1647 cm^{-1} signifies the adsorbed water molecule [37], which indicated that MCM-41 is hydrophilic. The next band at 1084 cm^{-1} is attributed to asymmetric stretching vibration of Si–O–Si [37, 38]. The vibrational modes of SiO_2 could be observed, which are the rocking mode at 457 cm^{-1}, the symmetrical stretching mode at 808 cm^{-1}, and the asymmetric stretching mode at 1084 cm^{-1} [38]. The FTIR spectra of the three adsorbent materials are shown in Supporting Information Fig. S2.

The FTIR spectrum of GAC, after adsorption of chlorhexidine gluconate and Cetrimide, depicts two additional peaks at 2358 and 648 cm^{-1} which are assigned to the nitrile (C≡N) group and C–H deformation vibration, respectively. From the FTIR spectra of FAC-NH_3 before and after adsorption, it could be seen that there is no addition of new peaks after the adsorption of chlorhexidine gluconate and Cetrimide. However, there is an increase in asymmetric and symmetric stretching of –C–H bond at 2919 cm^{-1} from the peak area 0.38–2.71% after the adsorption of chlorhexidine gluconate and Cetrimide. The peak area of the quinone group, present at 1528 cm^{-1}, also increased from 0.67 to 0.75% after adsorption. There is also an increase in the peak area of phenolic group from 5.89 to 7.07% after adsorption. It could be noticed from the FTIR spectrum of MCM-41, before and after adsorption of chlorhexidine gluconate and Cetrimide that the peak area at 1083 cm^{-1} decreased from 62.67 to 38.61%. Adsorption of chlorhexidine gluconate and Cetrimide by MCM-41 also gave a sharp peak in the FTIR spectrum at 2924 cm^{-1}, which is probably due to the CH of the methyl group [36]. Another sharp peak, new after adsorption at 2358 cm^{-1}, represents the hybrid vibration of silanes (Si–H) and the peak at 1473 cm^{-1} denotes the presence of C=C stretching vibrations in the aromatic rings [39]. The peak at 1647 cm^{-1} present before adsorption is missing after adsorption. Moreover, the peak areas at 457, 808, and 1083 cm^{-1} decreased from 3.37, 21.36, and 62.67% to 3.13, 6.96, and 38.61%, respectively. The FTIR spectra of GAC, FAC-NH_3, and MCM-41 are given in Supporting Information Fig. S3.

Table 1. Parameter estimation outputs of the Langmuir adsorption isotherm for the pure components

Adsorbent	Component	Parameter q_{max} (g/100 mL/g)	k (100 mL/g)	RR^{22}	SSQ
GAC	Chlorhexidine gluconate	0.0682	112.36	0.99	0.0005
	Cetrimide	0.2767	9.36	0.99	0.0063
FAC-NH_3	Chlorhexidine gluconate	1.06	277.78	0.99	0.0193
	Cetrimide	0.4069	3.07	0.98	1.08E−05
MCM-41	Chlorhexidine gluconate	1.73	42.55	0.99	0.0056
	Cetrimide	0.3694	113.64	0.99	0.0001

3.2 pH_{pzc}

The pH_{pzc} could be determined from the plot of zeta potential (mV) versus pH (Supporting Information Fig. S4). The pH values corresponding to pH_{pzc}, obtained from the fitted line corresponding to the isoelectric point (zeta potential of the solution = 0 mV), were found to be 4.576, 5.279, and 2.244 for GAC, FAC-NH_3 and MCM-41, respectively. All experiments of the batch equilibrium analysis were conducted at a pH of approximately 7–8, keeping the surface negative. The negative charge of the MCM-41 surface helps enhancing the adsorption of both di-cationic chlorhexidine gluconate and cetrimonium ions in comparison to GAC and FAC-NH_3. The net available zeta potentials for MCM-41 were −21.51 and −23.44 mV for a working pH of 7 and 8, respectively. On the other hand, the net available zeta potentials for adsorptions onto GAC surfaces were −11.31 and −15.29 mV and for FAC-NH_3 −8.22 and −13.53 mV at pH 7 and 8, respectively. For a working pH of 6.5, the ratio of available zeta potentials of FAC-NH_3, GAC, and MCM-41 was 1:1.62:3.59.

3.3 Batch equilibrium adsorption

3.3.1 Single component adsorption

Validation of the two multicomponent models used, namely, the modified competitive Langmuir like model and the LeVan Vermeulen model required the fitment of the single component data to the Langmuir adsorption isotherm equation. Therefore, the batch equilibrium analysis with the pure components chlorhexidine gluconate and Cetrimide were done separately using GAC, FAC-NH_3, and MCM-41 as adsorbents. Banerjee et al. [26] showed the batch equilibrium study of the pure components Cetrimide and chlorhexidine gluconate using GAC as an adsorbent and the fitment of the adsorption data in Langmuir adsorption isotherm. A similar experimental procedure was followed for the batch adsorption analysis using FAC-NH_3 and MCM-41. The values of the parameters q_{max} and k (obtained from the slope and intercept, respectively, of the Langmuir fit), the correlation coefficients (r^2) and the SSQ values for the three adsorbents are given in Table 1. Good fitments for both chlorhexidine gluconate and Cetrimide in the Langmuir equation were observed with high correlation coefficients (>98%) for all three adsorbents. When comparing the SSQ values it can be noticed from Table 1 that for the pure component chorhexidine gluconate the value of SSQ is highest for FAC-NH_3 (0.0193) and is least for GAC (0.0005).

3.3.2 Multicomponent adsorption

Two well-known multicomponent models, namely the modified competitive Langmuir-like model (model 1) and the LeVan-Vermeulen model (model 2), explained by Banerjee et al. [26], were evaluated to predict the multicomponent adsorption of chlorhexidine gluconate and Cetrimide by GAC, FAC-NH_3 and MCM-41. The modified competitive Langmuir-like model and the LeVan-Vermeulen model are described in the Supporting Information.

Table 2. Competitive Langmuir like adsorption isotherm and Levan-Vermeulen model parameters for chlorhexidine gluconate and Cetrimide obtained from E04USA program

Adsorbent	Model	Parameter A (100 mL/g)	B (100 mL/g)	$X_{m,1}$ (g/100 mL/g adsorbent)	$X_{m,2}$ (g/100 mL/g adsorbent)	$SSQ_{Chlorhexidine\ gluconate}$	$SSQ_{Cetrimidde}$
GAC	Model 1	19.85	36.12	0.1249	0.10	1.89E−06	2.46E−05
	Model 2	23.92	28.78	0.1072	0.0972	8.52E−06	4.4E−05
FAC-NH_3	Model 1	351.86	416.79	0.292	0.0816	3.04E−05	0.0012
	Model 2	7.35	4.5	0.4069	0.0669	0.0025	0.018
MCM-41	Model 1	4.66	10685.9	0.0065	0.0646	0.0001	0.0004
	Model 2	4.66	161.33	1.73	0.3694	0.0002	0.0076

The parameters of the two models were determined using the NAG Fortran Builder 5.3 and NAG Fortran Library. The nonlinear SSQ function was minimized by the E04USA function from the library using some constraints. The optimized values of the model parameters (A, B, $X_{m,1}$, $X_{m,2}$) and SSQ values obtained from Eq. (1) are given in Table 2. The observed and predicted amounts of chlorhexidine gluconate and Cetrimide adsorbed (obtained by computing the optimized values of the model parameters for both model 1 and model 2) were plotted against the equilibrium concentration of the two compounds respectively (Fig. 2). From the fitment of the predicted amount adsorbed versus the equilibrium concentration of both components and the residual concentration values are given in Supporting Information Table S1, it could seen that both model 1 and model 2 fit better for Cetrimide in comparison to chlorhexidine gluconate for GAC. Banerjee et al. [26] showed the fitment of the modified competitive Langmuir-like model and the LeVan-Vermeulen model for the adsorption of chlorhexidine gluconate and Cetrimide by GAC. Model 1 performed well for the adsorption of chlorhexidine gluconate and Cetrimide by FAC-NH_3. For MCM-41, both model 1 and model 2 fit

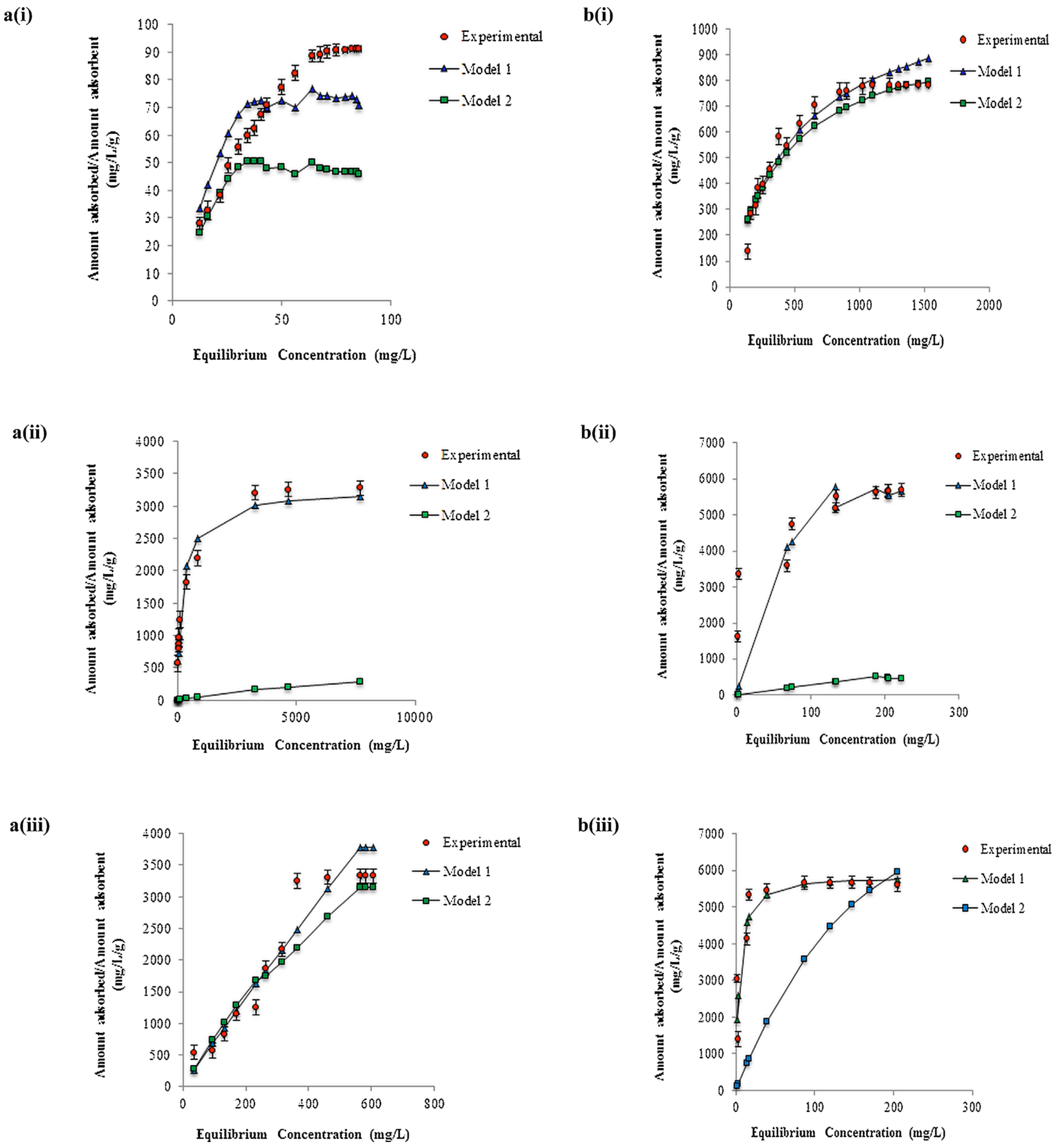


Fig. 2. Experimental and predicted amount adsorbed of (a) chlorhexidine gluconate and (b) Cetrimide from model 1 and model 2 by (i) GAC, (ii) FAC-NH_3. and (iii) MCM-41.

well for the adsorption of chlorhexidine gluconate. On the other hand, model 1 fit much better for Cetrimide than model 2 in case of MCM-41. Model 1 supported the two step adsorption process of Cetrimide by MCM-41, where the first step is ascribed to the role of negative surface charges with respect to the positive cetrimonium ions and the second step is attributed to the hydrophobic interaction of the surfactant tails between themselves at the solid–solution interface.

3.3.2.1 Comparison of the adsorption capacity of GAC, FAC-NH$_3$, and MCM-41

The amount of chlorhexidine gluconate and cetrimide adsorbed by GAC, FAC-NH$_3$, and MCM-41 are shown in Fig. 3a and b. The adsorption capacities of FAC-NH$_3$ and MCM-41 were higher compared to GAC. This phenomenon could be explained by the physical characterization of the adsorbents described before. The mesoporous MCM-41 and super microporous FAC-NH$_3$ easily adsorb the large chlorhexidine gluconate and Cetrimide molecules as compared to the microporous GAC. As the net available zeta potential is maximum in MCM-41 for the working pH of 6.5 and 7, it enhanced the adsorption of positive cetrimonium ions much more than the other two adsorbents. It could be seen from Fig. 3b that the maximum adsorption capacities of FAC-NH$_3$ and MCM-41 for the adsorption of Cetrimide were 5666.76 and 5666.64 mg/g, respectively, as compared to that of GAC with 550.64 mg/g.

For the adsorption of chlorhexidine gluconate (Fig. 3a), the maximum adsorption capacities of FAC-NH$_3$ and MCM-41 were 5666.76 and 5666.64 mg/g, respectively, compared to that of GAC with 148.52 mg/g. The chlorhexidine gluconate molecule forms surface complexes with the functional groups present in FAC-NH$_3$. Adsorption on MCM-41 is mainly due to van der Waals force driven pure physical adsorption for chlorhexidine gluconate. An enhanced zeta potential (−20.27 mV) at a working pH of 6.5 allows cetrimonium ions to come close to the negative surface very fast before they get physically adsorbed.

3.4 Costing

FAC-NH$_3$ was prepared from GAC and liquid ammonia (NH$_4$OH). The price of GAC is INR 0.59/g and the price of GR grade liquid ammonia is INR 200/L. So, the cost of preparing 1 g of FAC-NH$_3$ is INR 2.19, whereas the price of mesoporous ammonium silicate is INR 1666.76/g. The adsorption capacity of FAC-NH$_3$ is comparable to MCM-41, and you can say that it serves the purpose of a highly expensive adsorbent material.

3.5 Kinetic study

Two widely used kinetic models, proposed by Lagergren [40], were used for studying the kinetics of the multicomponent adsorption of chlorhexidine gluconate and Cetrimide. Pseudo-first order and second order kinetic equations were explained by Banerjee et al. [26]. From the correlation coefficient of the pseudo kinetic plot (Supporting Information Fig. S5) and SSQ values (Table 3) it can be seen that the pseudo-second order model gave a better fit as compared to the pseudo-first order model for all three adsorbents. This may be due to the chemisorption on top of pore diffusion and physical adsorption, specifically for FAC-NH$_3$ and MCM-41.

3.5.1 The intra-particle and film diffusion model

Weber and Morris [41] developed the intra-particle diffusion model to detect the mechanism of the adsorption process. The equation of the intra-particle diffusion model is given by Banerjee et al. [25]. According to this model, a plot of q_t versus $t^{1/2}$ (Fig. 4) will generate a straight line passing through the origin if intra-particle diffusion governs the adsorption process [42]. A large value of the intercept (I) indicates more influence of the boundary layer over the adsorption process. The intra-particle diffusion plots of chlorhexidine gluconate and Cetrimide were divided into two segments for understanding the actual adsorption mechanism over time. A similar nature of adsorption for the three adsorbents could be observed from this study. The values of I are summarized in Table 4 which showed that all of them are very close to zero for both chlorhexidine gluconate and Cetrimide in the first segment for all three adsorbents. In the next segment, the values of I increased. After Cetrimide and chlorhexidine gluconate molecules block the pores, intra-particle diffusion no longer influences the adsorption process. Comparing the values for I for GAC, FAC-NH$_3$, and MCM-41 it could be seen that it these were closest to zero in case of GAC, followed by MCM-41 and then FAC-NH$_3$. Thus, adsorption by intra-particle diffusion is maximum for GAC and the same is least for FAC-NH$_3$. The ratio of the intercepts for chlorhexidine gluconate for the first phase of

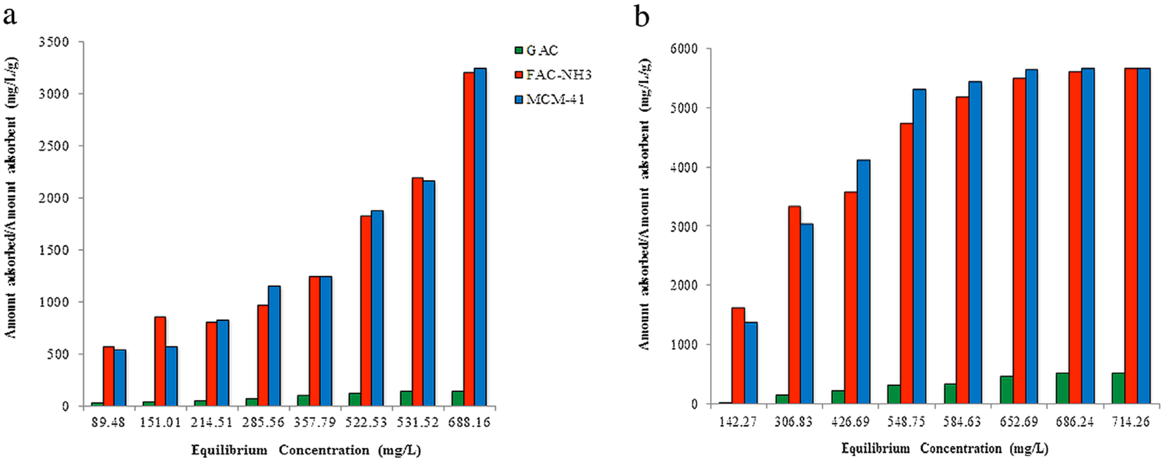


Fig. 3. Comparison of the amount of (a) chlorhexidine gluconate and (b) Cetrimide adsorbed by GAC, FAC-NH$_3$, and MCM-41

Table 3. Parameters of pseudo-first order and pseudo-second order kinetic models for the adsorption of chlorhexidine gluconate and Cetrimide by GAC, FAC-NH$_3$ and MCM-41

				Pseudo-first order				Pseudo-second order			
Adsorbent	Component	C_0(g/L)	$q_{e,exp}$(g/L/g adsorbent)	$q_{e,cal}$(g/L/g adsorbent)	k_1(1/min)	R^2	SSQ	$q_{e,cal}$(g/L/g adsorbent)	k_2(g/L min)	R^2	SSQ
GAC	Chlorhexidine gluconate	0.318	0.0269	0.0209	0.0004	0.939	0.0004	0.022	0.1139	0.9922	9.15E−07
	Cetrimide	0.6	0.0222	0.0193	0.0012	0.9933	1.47E−05	0.0259	0.0723	0.9932	7.96E−07
FAC-NH$_3$	Chlorhexidine gluconate	0.318	0.054	0.0529	0.0005	0.994	3.84E−06	0.0755	195.4	0.9952	8.6E−07
	Cetrimide	0.6	0.0919	0.0923	0.0007	0.9868	0.00053	0.1238	240.91	0.9954	2.59E−06
MCM-41	Chlorhexidine gluconate	0.318	0.0399	0.0447	0.0014	0.9369	0.0007	0.0475	32.71	0.999	5.51E−07
	Cetrimide	0.6	0.1009	0.0491	0.0008	0.9099	0.0053	0.1016	22.39	0.9967	1.6E−05

adsorption is 1(GAC):71(FAC-NH$_3$):43(MCM-41), ensuring formation of surface complexes in the order of FAC-NH$_3$ > MCM-41 > GAC.

The effect of the film diffusion on chlorhexidine gluconate and Cetrimide adsorption was investigated by the film diffusion model, proposed by Boyd. This model predicts that the primary resistance to diffusion is the boundary layer around the adsorbent sample [43]. The plot of *Bt* against *t* [43] produces a straight line (Fig. 4), which passes through the origin when the intra-particle diffusion governs the adsorption process. The film-diffusion or chemical reaction is another governing factor in the adsorption process if the plots, either linear or nonlinear, diverge from the origin [44]. The intercepts of the film diffusion plot for chlorhexidine gluconate and Cetrimide are given in Table 4. When comparing the intercepts (corresponding to Cetrimide) for the three adsorbents, it could be noticed that they were significantly different from zero for all adsorbents (0.1763, 0.0594, and 0.0404 for GAC, FAC-NH$_3$, and MCM-41, respectively). When the concentration of Cetrimide in the solution is 0.6 g/L, which is its critical micelle concentration, the adsorption is dependent on film diffusion. Similarly, the intercept (with respect to chlorhexidine gluconate) was closest to zero in case

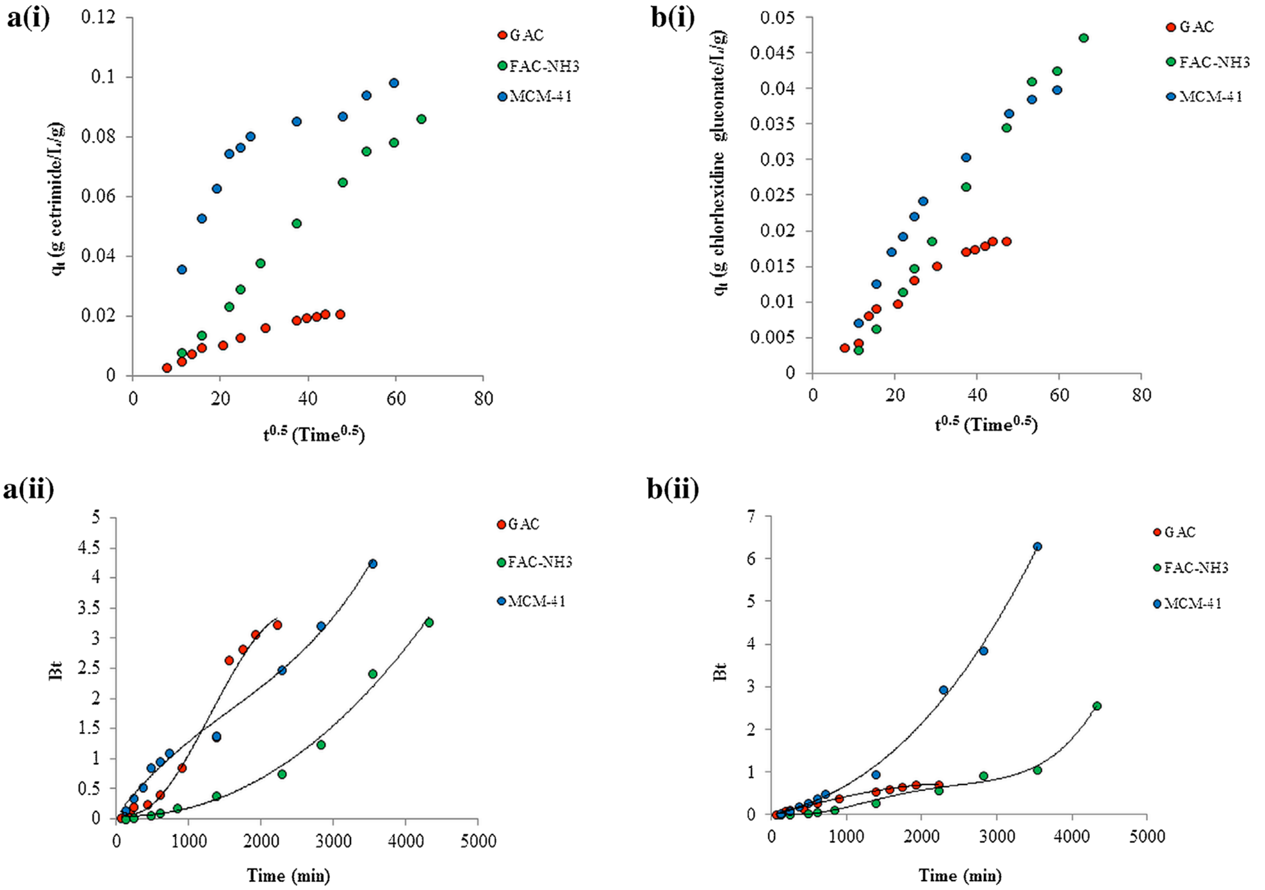


Fig. 4. (i) Intra-particle diffusion and (ii) film diffusion plot for (a) Cetrimide and (b) chlorhexidine gluconate adsorption on GAC, FAC-NH$_3$, and MCM-41

Table 4. Parameters of intra-particle diffusion model and Boyd's plot for the adsorption of chlorhexidine gluconate and Cetrimide by GAC, FAC-NH$_3$ and MCM-41

Adsorbent	Component	C_0 (g/L)	Intra-particle diffusion model						Boyd's plot	
			k_{ID1}(g/L/g adsorbent min$^{0.5}$)	I_1(g/g adsorbent)	R^2	k_{ID2}(g/L/g adsorbent min$^{0.5}$)	I_2(g/g adsorbent)	R^2	Intercept	R^2
GAC	Chlorhexidine gluconate	0.318	0.0005	−0.0001	0.9437	0.0002	0.0107	0.8846	−0.0236	0.9934
	Cetrimide	0.6	0.0006	−0.0001	0.9382	0.0003	0.0085	0.9529	0.1763	0.9735
FAC-NH$_3$	Chlorhexidine gluconate	0.318	0.0009	−0.0071	0.9959	0.0006	0.0057	0.9462	0.0932	0.9917
	Cetrimide	0.6	0.0017	−0.0121	0.9951	0.0011	0.0145	0.9459	0.0594	0.991
MCM-41	Chlorhexidine gluconate	0.318	0.0011	−0.0043	0.9936	0.0004	0.0149	0.9546	0.0229	0.9967
	Cetrimide	0.6	0.0028	0.0076	0.9673	0.0006	0.0617	0.8606	0.0404	0.9924

of adsorption by GAC and MCM-41, as compared to FAC-NH$_3$ (−0.0236, 0.0932, and 0.0229 for GAC, FAC-NH$_3$, and MCM-41, respectively). Film diffusion, thus has the least effect on the adsorption by GAC and MCM-41 among the three adsorbents.

When the pH of the solution is maintained around 7–8 for all batch study experiments, the negative surface of the adsorbents ($pH_{pzc} = 4.576$, 5.279, and 2.244 for GAC, FAC-NH3, and MCM-41, respectively) attracts the cetrimonium ions much faster. The mesopores which remain vacant after the adsorption of Cetrimide, were filled by chlorhexidine gluconate. Chlorhexidine gluconate underwent chemisorption, most probably because of the formation of surface complexation with the functional groups present on FAC-NH$_3$.

4 Conclusion

Adsorption capacities of three types of adsorbents were compared in this study. Large organic molecules like chlorhexidine gluconate and Cetrimide, widely used in antiseptic solutions, were removed using microporous GAC, FAC-NH$_3$ and a mesoporous aluminosilicate material (MCM-41). The results of physical characterization showed that the microspores of GAC were transformed to super micropores after the modification with NH$_4$OH. The pore volume of MCM-41 is about 1.6× higher than that of the other two adsorbents, which shows that it can adsorb heavy organic molecules like Cetrimide and chlorhexidine gluconate primarily by physical adsorption. FTIR analysis depicted that a large number of oxygenated functional groups have been added to the surface sites of activated carbon after its functionalization with NH$_4$OH. Chlorhexidine gluconate is composed of two gluconic acid molecules that are present in aqueous systems as $C_6H_{12}O_7^-$. The NH$_4$OH treatment resulted in a more alkaline carbon surface, which is helpful in the adsorption of acidic agents [34]. The zeta potential study showed that the net available electrostatic driving force for MCM-41 was maximum amongst the three adsorbents, which attracts the positive cetrimonium ion more compared to the other two adsorbents. The adsorption mechanisms for the adsorbents were revealed by kinetic studies. The intra-particle diffusion model depicted that at the beginning of the experiment the adsorption mechanism is governed by intra-particle diffusion for all materials, GAC, FAC-NH$_3$, and MCM-41. Later, when chlorhexidine gluconate and Cetrimide block the pores of the adsorbents, the adsorption mechanism no longer followed intra-particle diffusion. To judge the effect of film diffusion during adsorption, Boyd's film diffusion model was applied. For all adsorbents, it could be seen that film diffusion had a strong influence at the later stage of the adsorption process. This study showed that for the adsorption of large size molecules like chlorhexidine gluconate and Cetrimide, adsorbents with mesopores are much more effective, as compared to microporous adsorbents like GAC. It could be seen from the batch study that the uptake capacity of FAC-NH$_3$ is comparable to MCM-41 for both chlorhexidine gluconate and Cetrimide. The maximum adsorption capacities of FAC-NH$_3$ for the adsorption of chlorhexidine gluconate and Cetrimide were 3207.93 (3248.53 mg/g for MCM-41; 148.52 mg/g for GAC) and 5666.76 mg/g (5666.64 mg/g for MCM-41; 550.64 mg/g for GAC), respectively. Thus, it could be concluded that alkali functionalized activated carbon can effectively remove chlorhexidine gluconate and Cetrimide from pharmaceutical wastewater, with an equivalent efficiency to the expensive MCM-41.

Acknowledgement

The authors recognize the grant provided by Department of Science and Technology (DST-WTI), India for conducting the research. The authors would also like to thank the Indian Association for the Cultivation of Science, Kolkata, India, for carrying out some material testing (FE-SEM and BET) in their laboratory.

The authors have declared no conflict of interest.

References

[1] D. P. Grover, J. L. Zhou, P. E. Frickers, J. W. Readman, Improved Removal of Estrogenic and Pharmaceutical Compounds in Sewage Effluent by Full Scale Granular Activated Carbon: Impact on Receiving River Water, *J. Hazard. Mater.* **2011**, *185*, 1005–1011.

[2] S. Sadhukhan, S. Singha, U. Sarkar, Adsorption of Para Chloro-Meta-Xylenol (PCMX) in Composite Adsorbent Beds: Parameter Estimation Using Nonlinear Least Square Technique, *Chem. Eng. J.* **2009**, *152*, 361–366.

[3] D. E. Wurster, K. A. Alkhamis, L. E. Matheson, Prediction of Adsorption From Multicomponent Solutions by Activated Carbon Using Single-Solute Parameters, *AAPS Pharm. Sci. Tech.* **2002**, *3* (*3*), 53–60.

[4] Z. Yu, S. Peldszus, P. M. Huck, Adsorption of Selected Pharmaceuticals and an Endocrine Disrupting Compound by Granular Activated Carbon, 1. Adsorption Capacity and Kinetics, *Environ. Sci. Technol.* **2009**, *43*, 1467–1473.

[5] A. Trouvé, I. Batonneau-Gener, S. Valange, M. Bonne, S. Mignard, Tuning the Hydrophobicity of Mesoporous Silica Materials for the Adsorption of Organic Pollutant in Aqueous Solution, *J. Hazard. Mater.* **2012**, *201–202*, 107–114.

[6] N. Baccile, F. Babonneau, Organo-Modified Mesoporous Silicas for Organic Pollutant Removal in Water: Solid-State NMR Study of the Organic/Silica Interactions, *Micropor. Mesopor. Mater.* **2008**, *110*, 534–542.

[7] A. W. Marczewski, Kinetics and Equilibrium of Adsorption of Organic Solutes on Mesoporous Carbons, *Appl. Surf. Sci.* **2007**, *253*, 5818–5826.

[8] Z. Wu, Y. Meng, D. Zhao, Nanocasting Fabrication of Ordered Mesoporous Phenol-formaldehyde Resins with Various Structures and Their Adsorption Performances for Basic Organic Compounds, *Micropor. Mesopor. Mater.* **2010**, *128*, 165–179.

[9] Y. H. Kim, B. Lee, K. H. Choo, S. J. Choi, Selective Adsorption of Bisphenol A by Organic-Inorganic Hybrid Mesoporous Silicas, *Micropor. Mesopor. Mater.* **2011**, *138*, 184–190.

[10] V. V. Cotea, C. E. Luchian, N. Bilba, M. Niculaua, Mesoporous Silica SBA-15, a New Adsorbent for Bioactive Polyphenols From Red Wine, *Anal. Chim. Acta* **2012**, *732*, 180–185.

[11] M. A. Lillo-Ródenas, D. Cazorla-Amorós, A. Linares-Solano, Behaviour of Activated Carbons with Different Pore Size Distributions and Oxygen Groups for Benzene and Toluene Adsorption at Low Concentrations, *Carbon* **2005**, *43*, 1758–1767.

[12] A. P. Terzyk, The Influence of Activated Carbon Surface Chemical Composition on the Adsorption of Acetaminophen (Paracetamol) in Vitro, Part II. TG, FTIR, and XPS Analysis of Carbons and the Temperature Dependence of Adsorption Kinetics at the Neutral pH, *Colloid. Surf. A* **2001**, *177*, 23–45.

[13] H. L. Chiang, C. P. Huang, P. C. Chiang, The Surface Characteristics of Activated Carbon as Affected by Ozone and Alkaline Treatment, *Chemosphere* **2002**, *47*, 257–265.

[14] J. Rivera-Utrilla, M. Sánchez-Polo, V. Gómez-Serrano, P. M. Álvarez, M. C. M. Alvim-Ferraz, J. M. Dias, Activated Carbon Modifications to Enhance its Water Treatment Applications, an Overview, *J. Hazard. Mater.* **2011**, *187* (*15*), 1–23.

[15] R. J. J. Jansen, H. Bekkum, Amination and Ammoxidation of Activated Carbons, *Carbon* **1994**, *32* (*8*), 1507–1516.

[16] M. Abe, K. Kawashima, K. Kozawa, H. Sakai, K. Kaneko, Amination of Activated Carbon and Adsorption Characteristics of its Aminated Surface, *Langmuir* **2000**, *16*, 5059–5063.

[17] M. C. Palma, I. F. Silva, P. Lodewyckx, J. J. M. Orfao, L. S. Lobo, Effect of HNO_3 and NH_3 treatment on the catalytic oxidation of carbon catalysed by Cu, Mo, and their mixture at eutectic composition, in coal science, in Proceedings of the Spain International Conference on Coal Science (Eds. J. A. Pajares, J. M. D. Tascón), Elsevier, Amsterdam **1995**, Vol. 1, pp. 691–694.

[18] F. Xie, J. Phillips, I. F. Silva, M. C. Palma, J. A. Menendez, Microcalorimetric Study of Acid Sites on Ammonia- and Acid-Pretreated Activated Carbon, *Carbon* **2000**, *38*, 691–700.

[19] J. Przepiórski, *Activated Carbon Surfaces in Environmental Remediation*, (Ed.: T. J. Bandosz), Elsevier Academic Press, New York **2006**, pp. 421–474.

[20] G. J. Kaplowitz, M. Cortell, Chlorhexidine: A Multi-Functional Antimicrobial Drug, *Acad. Dent. Ther. Stomatol.* **2005**.

[21] OECD Guidelines for the Testing of Chemicals, Section 2: Effects on Biotic Systems 203— Fish, Acute Toxicity Test, OECD, Paris, France **1992**.

[22] OECD Guidelines for the Testing of Chemicals, Section 2: Effects on Biotic Systems 201— Alga, Growth Inhibition Test, OECD, Paris, France **1984**.

[23] OECD Guidelines for the Testing of Chemicals, Section 2: Effects on Biotic Systems 202— Daphnia sp. Acute Immobilisation Test, OECD, Paris, France **1981**.

[24] A. Erto, A. Lancia, D. Musmarra, A Real Adsorbed Solution Theory Model for Competitive Multicomponent Liquid Adsorption onto Granular Activated Carbon, *Micropor. Mesopor. Mater.* **2012**, *154*, 45–50.

[25] D. Banerjee, U. Sarkar, D. Roy, Multicomponent Adsorption of Chlorhexidine Gluconate in Presence of a Cationic Surfactant: Role of Electrostatic Interactions and Surface Complexation, *J. Environ. Chem. Eng.* **2013**, *1*, 241–251.

[26] D. Banerjee, U. Sarkar, S. Chakraborty, D. Roy, Removal of a Cationic Bisbiguanide Using Functionalized Activated Carbons (FACs), *Process Saf. Environ. Prot.* **2014**, *92* (*6*), 957–972.

[27] S. Singha, U. Sarkar, P. Luharuka, Functionalized Granular Activated Carbon and Surface Complexation with Chromates and Bi-chromates in Wastewater, *Sci. Total Environ.* **2013**, *447*, 472–487.

[28] A. Dutta, A. K. Patra, A. Bhaumik, Porous Organic-inorganic Hybrid Nickel Phosphonate: Adsorption and Catalytic Applications, *Micropor. Mesopor. Mater.* **2012**, *155*, 208–214.

[29] M. Armandi, B. Bonelli, F. Geobaldo, E. Garrone, Nanoporous Carbon Materials Obtained by Sucrose Carbonization in the Presence of KOH, *Micropor. Mesopor. Mater.* **2010**, *132*, 414–420.

[30] W. Zhang, Z. Qu, X. Li, Y. Wang, D. Ma, J. Wu, Comparison of Dynamic Adsorption/Desorption Characteristics of Toluene on Different Porous Materials, *J. Environ. Sci.* **2012**, *24* (*3*), 520–528.

[31] J. Coates, Interpretation of Infrared Spectra, A Practical Approach, *Encyclopedia of Analytical Chemistry*. (Ed.: R. A. Meyers), John Wiley & Sons, Chichester **2000**, pp. 10815–10837.

[32] A. N. A. El-Hendawy, Influence of HNO3 Oxidation on the Structure and Adsorptive Properties of Corncob-Based Activated Carbon, *Carbon* **2003**, *41*, 713–722.

[33] W. Sheen, Z. Li, Y. Liu, Surface Chemical Functional Groups Modification of Porous Carbon, *Recent Pat. Chem. Eng.* **2008**, *1*, 27–40.

[34] J. Przepiórski, M. Skrodzewicz, A. W. Morawski, High Temperature Ammonia Treatment of Activated Carbon for Enhancement of CO_2 Adsorption, *Appl. Surf. Sci.* **2004**, *225*, 235–242.

[35] W. Tomaszewski, V. M. Gun'ko, J. Skubiszewska-Zięba, R. Leboda, Structural Characteristics of Modified Activated Carbons and Adsorption of Explosives, *J. Colloid. Interf. Sci.* **2003**, *266*, 388–402.

[36] N. I. Taib, S. Endud, M. N. Katun, Functionalization of Mesoporous Si-MCM-41 by Grafting With Trimethylchlorosilane, *Int. J. Chem.* **2011**, *3* (*3*), 2–10.

[37] L. Bǎjenaru, S. Nǎstase, C. Matei, D. Berger, Studies on the Synthesis of Mesoporous Aluminosilicates as Carries for Drug Delivery Systems, *Univ. Politech. Bucuresti Sci. Bull., Ser. B* **2011**, *73* (4), 45–50.

[38] L. C. Juang, C. C. Wang, C. K. Lee, Adsorption of Basic Dyes onto MCM-41, *Chemosphere* **2006**, *64*, 1920–1928.

[39] G. Socrates, *Infrared and Raman Characteristic Group Frequencies Tables and Charts*. John Wiley & Sons, Chichester, UK **2001**.

[40] S. Lagergren, Zur Theorie der Sogenannten Adsorption Gelöster Stoffe, *Kungliga Svenska Vetenskapsakad. Handlingar* **1898**, *24*, 1–39.

[41] W. J. Weber, J. C. Morris, Kinetics of Adsorption on Carbon From Solution, *J. Sanit. Eng. Div. Proc. Am. Soc. Civil Eng.* **1963**, *89*, 31–59.

[42] B. Tang, Y. Lin, P. Yu, Y. Luo, Study of Aniline/ε-Caprolactam Mixture Adsorption From Aqueous Solution onto Granular Activated Carbon: Kinetics and Equilibrium, *Chem. Eng. J.* **2012**, *187*, 69–78.

[43] D. Reichenberg, Properties of Ion Exchange Resins in Relation to Their Structure, III. Kinetics of Exchange, *J. Am. Chem. Soc.* **1953**, *75*, 589–598.

[44] M. I. El-Khaiary, G. F. Malash, Common Data Analysis Errors in Batch Adsorption Studies, *Hydrometallurgy* **2011**, *105*, 314–320.