

INTRODUCING A NEW TRIO EFFECTS PORTABLE WATER TREATMENT PLANT
FOR RURAL AREAS.

AKINDOYO EDWARD OLUWASOGA
(KKE11009)

A thesis submitted in fulfillment of the
requirements for the award of degree of
Master of Chemical Engineering with Entrepreneurship.

Faculty of Chemical and Natural Resources Engineering
UNIVERSITI MALAYSIA PAHANG

JANUARY 2013.

ABSTRACT

Water is Life, the quantity, usage, consumption and the importance of water in our daily activities, domestic purposes and industrial cannot be overemphasized, thus water remains an important aspect of the Human existence as we cannot do without water. The treatment and removal of MTBE (Methyl Tert-Butyl Ether) in water especially from petrochemical waste water is of immense importance and had been a challenging one because most of the available techniques in its removal can only remove part and not the whole, it is on this note that the treatment measure here shall be adopting a Trio effect to remove this contaminant from a sample of contaminated water. Treatment of Methyl Tert-Butyl Ether (MTBE) from wastewater supplies presents specific challenges due to the physicochemical properties of MTBE which depend strongly on its hydrophilic nature, and translate into a high solubility in water. MTBE has very low Henry's constant and very low affinity for common adsorbents. An investigation was carried out for the treatability of methyl tert-butyl ether (MTBE) in synthetic wastewater. In this research, experimental rig and bench-scale studies using granular activated carbon (GAC) and hydrogen peroxide (H_2O_2) were conducted to observe the treatability of MTBE in synthetic wastewater. An experimental rig was built up that consist of three conjugated system. Subsequently, MTBE was amended to the H_2O_2 and air flow, followed by adsorption treatment with GAC. Generally, the major finding suggests that the longer cycle pulsation time (3 minutes open valve + 5 seconds closed valve) with air flow rate at 6 L/min over the synthetic wastewater caused a greater removal of MTBE. The result of this study can help to provide specific guidance into process parameter selection for treating MTBE in wastewaters. The optimum operating conditions are very important for treating the wastewater effectively in a larger scale. Moreover, this project shall be looking also into the commercialization of this plant to the market, thus markets surveys, researches and other techniques are also be carried out to introduce the plant to the market.

ABSTRAK

Air merupakan aspek penting dalam kehidupan manusia. Oleh itu penggunaan air secara efisien amat ditekankan berikutan kepentingannya dalam semua aktiviti kehidupan harian dan industri. Rawatan dan penyingkiran MTBE (Methyl Tert-Butyl Ether) di dalam kandungan air terutama dari sisa air petrokimia merupakan satu cabaran kerana kebanyakan teknik yang sedia ada tidak dapat menyingkirkan bahan ini secara keseluruhan. Oleh yang demikian, kaedah Trio telah digunakan untuk menyingkirkan bahan tercemar ini dari sampel air yang telah tercemar. Proses rawatan Methyl Tert-Butyl Ether (MTBE) dari bekalan sisa air yang tercemar menghadapi beberapa cabaran khusus kerana sifat-sifat fizikal-kimia MTBE seperti hidrofilik dan mempunyai tahap kelarutan yang tinggi di dalam air. Selain itu, MTBE mempunyai pemalar Henry yang rendah untuk penjerap. Kajian telah dijalankan untuk merawat MTBE di dalam sisa air sintetik. Dalam kajian ini, eksperimen skala pelantar menggunakan granul karbon yang telah diaktifkan (GAC) dan hidrogen peroksida (H_2O_2) telah dijalankan untuk menilai kebolehrawatan MTBE di dalam sisa air sintetik. Eksperimen secara pelantar ini mempunyai tiga sistem berkonjugat. Selepas itu, MTBE telah dipinda dengan aliran angin dan H_2O_2 diikuti oleh penjerapan dengan GAC. Secara umumnya, hasil kajian menunjukkan kitaran masa yang lebih lama iaitu kadar denyutan (3 minit injap terbuka + 5 saat injap tertutup) dengan dara aliran udara adalah 6L/min terhadap sisa air sintetik telah menyebabkan penyingkiran MTBE yang lebih banyak. Hasil kajian ini dapat memeberikan panduan yang spesifik terhadap proses penyingkiran MTBE. Keadaan optimum adalah sangat penting untuk merawat sisa air di dalam skala yang lebih besar. Selain daripada itu, kajian ini amat sesuai untuk dikomersialkan. Justeru, kajian yang lebih mendalam akan dilaksanakan agar kajian ini akan menepati ciri-ciri komersial.

TABLE OF CONTENTS

| CHAPTERS | TITLE | PAGES |
|-----------------|--|--------------|
| | TITTLE PAGE | i |
| | THESIS CONFIDENTIAL STATUS | ii |
| | SUPERVISOR’S DECLARATION | iii |
| | STUDENT’S DECLARATION | iv |
| | ACKNOWLEDGEMENT | v |
| | ABSTRACT | vi |
| | TRANSLATION OF ABSTRACT | vii |
| | TABLE OF CONTENTS | viii |
| | LIST OF TABLES | ix |
| | LIST OF FIGURES | x |
| | LIST OF ABBREVIATIONS | xi |
| | LIST OF APPENDIXES | xii |
| 1 | INTRODUCTION | 1 |
| | 1.1 Background of Study | 1 |
| | 1.1.1 Adsorption Process | 3 |
| | 1.1.2 Factors on which Adsorption depends | 6 |
| | 1.1.3 Types of Adsorption | 7 |
| | 1.1.4 Advanced Oxidation Processes (AOPs) | 11 |
| | 1.1.5 Methyl Tertiary Butyl Ether (MTBE) | 13 |
| | 1.1.6 Properties of Methyl Tertiary Butyl Ether (MTBE) | 15 |
| | 1.1.7 Methyl Tertiary Butyl Ether (MTBE) Treatment Process | 17 |
| | 1.2 Problem Statement | 18 |
| | 1.3 Objectives | 19 |
| | 1.4 Scope of Study | 19 |
| | 1.5 Mission | 20 |
| | 1.6 Keys to Success | 20 |
| | 1.7 Significance of the Research | 20 |

| | | |
|----------|--|----|
| 2 | LITERATURE REVIEW | |
| 2.1 | Introduction | 21 |
| 2.2 | Granular Activated Carbon (GAC) | 23 |
| 2.2.1 | Isotherm Testing | 24 |
| 2.2.2 | Dynamic Column Testing | 25 |
| 2.2.3 | Importance of GAC | 28 |
| 2.3 | Air Stripping | 29 |
| 2.3.1 | Aeration Technologies | 30 |
| 2.4 | Oxidation Process | 33 |
| 2.4.1 | AOP Technologies | 34 |
| 2.5 | Hydrogen Peroxide (H ₂ O ₂) | 34 |
| 2.6 | Ozone (O ₃) | 35 |
| 2.7 | UV System | 38 |
| 2.8 | Hydrogen Peroxide And Fenton's Reagent | 39 |
| 2.9 | Hydrogen Peroxide And UV Light | 42 |
| 2.10 | Hydrogen Peroxide And Ozone | 44 |
| 2.11 | Ozone And UV Light | 46 |
| 2.12 | E-Beam Treatment | 49 |
| 2.13 | Marketing Strategy | 50 |
| 2.13.1 | Targeting | 51 |
| 2.13.2 | Positioning | 51 |
| 2.14 | Pricing Strategy | 52 |
| 3 | METHODOLOGY | |
| 3.1 | Introduction | 53 |
| 3.2 | Materials and Equipments | 53 |
| 3.2.1 | Preparation Synthetic Wastewater | 54 |
| 3.2.2 | Preparation Hydrogen Peroxide | 55 |
| 3.2.3 | Preparation Granular Activated Carbon | 55 |
| 3.3 | Bench Scale Experimental | 55 |
| 3.3.1 | Oxidation Process | 55 |
| 3.3.2 | Adsorption Process | 55 |
| 3.4 | Experimental Rig Design | 56 |

| | | |
|----------|--|----|
| 3.4.1 | Experimental Procedure | 58 |
| 3.4.1.1 | Testing Method | 58 |
| 3.5 | Analytical Analysis | 58 |
| 3.6 | Technologies involved in the Invention | 59 |
| 4 | RESULTS AND DISCUSSION | |
| 4.1 | Bench Scale | 61 |
| 4.1.1 | Calibration standard curves of the Methyl Tert-Butyl Ether (MTBE) | 61 |
| 4.1.2 | Adsorption Process | 64 |
| 4.1.3 | Oxidation Process | 65 |
| 4.2 | Experimental Rig | 67 |
| 4.2.1 | Short Cycle Pulsation Time with Air Flow Rate at 4L/min | 67 |
| 4.2.2 | Short Cycle Pulsation Time Rate with Air Flow Rate at 6L/min | 68 |
| 4.2.3 | Long Cycle Pulsation Time with Air Flow Rate at 6L/min | 70 |
| 4.2.4 | Contact Time for Adsorption Process | 71 |
| 4.2.5 | Contact Time for Oxidation Process | 72 |
| 5 | MARKETING STRATEGY | |
| 5.1 | Products and services | 73 |
| 5.1.1 | Products and services description | 73 |
| 5.1.2 | Competitive Comparison | 74 |
| 5.2 | Sales Literature | 75 |
| 5.3 | Processes Adopted | 75 |
| 5.4 | Future Services | 76 |
| 5.5 | Marketing Analysis Summary | 76 |
| 5.6 | Marketing Segmentation | 77 |
| 5.7 | Target Market Segment Strategy | 77 |
| 5.7.1 | Market Needs | 78 |
| 5.7.2 | Market Trends | 78 |
| 5.8 | Main Competitors | 78 |

| | | |
|----------|---------------------------------------|----|
| 5.9 | Strategy and Implementation Summary | 79 |
| 5.9.1 | Value Proposition | 79 |
| 5.9.2 | Competitive Edge | 79 |
| 5.10 | Market Strategy | 80 |
| 5.11 | Promotion Strategy | 80 |
| 5.12 | Distribution Patterns | 80 |
| 5.13 | SWOT Analysis | 80 |
| 5.13.1 | Strengths | 81 |
| 5.13.2 | Weaknesses | 81 |
| 5.13.3 | Opportunities | 81 |
| 5.13.4 | Threats | 81 |
| 5.14 | Sales Strategy | 82 |
| 6 | FINANCIALS | |
| 6.1 | Start-Up Summary | 83 |
| 6.2 | Company Location and Facilities | 85 |
| 6.3 | Sales Forecasts | 85 |
| 6.4 | Personnel Plan | 86 |
| 6.5 | Financial Plan | 87 |
| 6.6 | General assumptions | 87 |
| 6.7 | Break-even Analysis | 87 |
| 6.8 | Projected Profit and Loss | 88 |
| 6.8.1 | Pro Forma Profit and Loss | 88 |
| 6.8.2 | Projected Cash Flow | 89 |
| 6.8.3 | Projected Balance Sheet | 91 |
| 6.9 | Business Ratios | 92 |
| 7 | CONCLUSIONS AND RECOMMENDATION | |
| 7.1 | Conclusions | 95 |
| 5.2 | Recommendation | 97 |

REFERENCES

98

APPENDIX

109

LIST OF TABLES

| TABLES NO | TITLE | PAGE |
|-----------|---|------|
| TABLE 1.1 | Properties of Methyl tertiary butyl ether (MTBE) | 16 |
| TABLE 1.2 | Overview on Methyl tertiary butyl ether (MTBE) Treatment process | 17 |
| TABLE 2.1 | Air Stripping Technology | 32 |
| TABLE 2.2 | Characteristics of Typical Low Pressure (LP), Medium Pressure (MP), and Pulsed UV (P-UV) Lamps | 39 |
| TABLE 2.3 | Advanced oxidation processes wastewater treatment | 48 |
| TABLE 3.1 | The function of each component in the experiment setup | 54 |
| TABLE 4.1 | Standard curve of Methyl tert-butyl ether at various Wavelengths | 61 |
| TABLE 4.2 | Percentage removal of MTBE for adsorption process | 109 |
| TABLE 4.3 | Percentage removal of MTBE for oxidation process | 109 |
| TABLE 4.4 | Percentage removal of MTBE with different cycle Pulsation time at air flow rate, 4 L/min | 110 |
| TABLE 4.5 | Percentage Removal of MTBE with different cycle Pulsation time at air flow rate, 6 L/min | 110 |
| TABLE 4.6 | Different cycle pulsation time and contact time for Adsorption column | 111 |
| TABLE 4.7 | Different cycle pulsation time and contact time for Oxidation column | 111 |

LIST OF FIGURES

| FIGURES NO | TITLE | PAGE |
|-------------------|---|-------------|
| Figure 1.1 | Molecular structure of MTBE | 14 |
| Figure 3.1 | Schematic diagram of Experimental Rig design | 57 |
| Figure 4.1 | Standard calibration curve at wavelength, $\lambda = 300\text{nm}$ | 62 |
| Figure 4.2 | Standard calibration curve at wavelength, $\lambda = 400\text{nm}$ | 62 |
| Figure 4.3 | Standard calibration curve at wavelength, $\lambda = 450\text{nm}$ | 63 |
| Figure 4.4 | Standard calibration curve at wavelength, $\lambda = 550\text{nm}$ | 63 |
| Figure 4.5 | Effect of contact time on the percentage of removal with different concentration of MTBE | 65 |
| Figure 4.6 | Effect of contact time on the percentage of removal with different molar ratio of MTBE to hydrogen peroxide | 66 |
| Figure 4.7 | Effect of time on the percentage of removal with different cycle pulsation time at air flow rate 4 L/min | 68 |
| Figure 4.8 | Effect of time on the percentage of removal with different cycle pulsation time at air flow rate 6 L/min | 69 |
| Figure 4.9 | Effect of time on the percentage of removal with different cycle pulsation time at air flow rate 6 L/min | 70 |
| Figure 4.10 | Effect of contact time on the percentage removal of MTBE at adsorption column | 71 |
| Figure 4.11 | Effect of contact time on the percentage removal of MTBE at oxidation column | 72 |

LIST OF ABBREVIATIONS

| | | |
|-------------------------------|---|---------------------------------------|
| MTBE | - | Methyl Tertiary Butyl Ether |
| EPA | - | Environmental Protection Agency |
| CAA | - | Clean Air Act |
| NAAQS | - | National Ambient Air Quality Standard |
| RFG | - | Reformulated Gasoline |
| AOPs | - | Advanced Oxidation Processes |
| FR | - | Fenton Reagent |
| COD | - | Chemical Oxygen Demand |
| BOD | - | Biochemical Oxygen Demand |
| DOC | - | Dissolved Organic Carbon |
| NOM | - | Natural Organic Matter |
| DBP | - | Disinfection by-Products |
| VOCs | - | Volatile Organic Compounds |
| GAC | - | Granular Activated Carbon |
| H ₂ O ₂ | - | Hydrogen Peroxide |
| UV Light | - | Ultraviolet Light |
| EBCT | - | Empty Bed Contact Time |

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF THE STUDY

Water is a resource that is inevitable in life, the supply, usage, consumption and the roles played by water in our daily activities, domestic purposes and industrial cannot be overemphasized, this makes the need for continuous water supply in every aspect of the Human existence, very important because we cannot do without water.

In addition, as the needs for water increases daily, this in turn increases the rate of water contaminants and in turn makes the water polluted, it is on this note that, demands for the treatment of water is of importance, so that there could be a continuous flow and supply of water to the teeming population as well as for the sustenance of water to all and sundry. Thus, measures were taken, studies as well as researches which led to the introduction of this type of water treatment that works on a trio effect for the water treatment majorly for small scale, domestic purposes and rural areas water supply means.

The design is aimed at producing a plant based on high technology using a trio effect water treatment methods for removing pollutants (contaminants) from wastewater and industrial water(MTBE from petroleum wastewater) from the industries, ground water as well as other sources, treat it and supply to rural and urban areas which could be used for drinking purposes as well as other domestic usages, unlike the other methods that only adopts one of these at a time making the plant a cost effective one and affordable even to the rural areas inhabitant.

It should be noted here however that, there have been several measures and techniques that have been put in place for the treatment of this so called MTBE, nevertheless, none of these have proved to be effective as they all have only succeeded in removing part from the whole of the percentage of contaminant present in the water. In lieu of this, the design should be introduced which combines three technologies in one for the effective removal of MTBE from waste water.

Over the years, efforts have been made to remove methyl tertiary butyl ether (MTBE), a chemical compound having a molecular formula $C_5H_{12}O$ or $(CH_3)_3COCH_3$. It is an organic compound, volatile, flammable, and colorless liquid that is sparingly soluble in water. It has a minty odor vaguely reminiscent of diethyl ether, leading to unpleasant taste and odor in water. MTBE is a gasoline additive, used as an oxygenate to raise the octane number. Due to its high solubility, low adsorption to soil and poor natural biodegradation, MTBE is a highly mobile and persistent contaminant in groundwater.

It benefits air quality by making gasoline burn cleaner, thus reducing automobile emissions. But it can also find its way into groundwater supplies and give drinking water an unpleasant taste and odor, the health effects of MTBE are uncertain as it is classified as a possible human carcinogen. As a result of this, the removal from drinking water is of great importance because of its side effects on human beings.

Existing technologies for its removal includes air stripping, granular activated carbon (GAC) and advanced oxidation, other type of removal are resins and biological processes, the bacteria strains or natural isolations under aerobic condition, but this last method can be unreliable as the bacteria grows slowly with low yields of bio mass. Thus the plant shall be designed in such a way that it combines all these first three techniques in one plant for the removal of these contaminant as a single process is found to be ineffective.

It should be noted here that, those properties that make MTBE a major contaminant in groundwater are those that hardened its control, making it not easily removable contaminant compared to other common organic contaminants. As stated above, there are various treatment techniques, which may occur sometimes at centralized facilities that treat water for either reinjection or immediate portable use or at point of entry (POE) locations at individual residential or business locations.

Activated carbon has been a reliable and the most historical technology of choice due to many reasons such as, its ease of installation and use for organic contaminant removal, thus, often considered for MTBE applications.

As it is a known fact, that MTBE has poor adsorption characteristics and drinking water applications requires very low ppb concentrations, application of activated carbon in its removal has been a serious challenge. Thus to effectively do this, activated carbon needs relatively high percentage of "high energy" adsorption pores in its pore structure, which have the strongest adsorption forces to remove low concentrations of MTBE from water. The difficulties posed by these materials could be dependent on their pore structures, if not properly made.

1.1.1 Adsorption Process

Adsorption can be referred to as the adhesion of atoms, ions, or molecules from a gas, liquid, or dissolved solid to a surface. This usually creates films of the adsorbate on the surface of the adsorbent. It differs from absorption, in which a fluid (the absorbate) permeates or is dissolved by a liquid or solid (the absorbent). One should be reminded here that adsorption is a surface-based process while absorption involves the whole volume of the material. The term sorption encompasses both processes, while desorption is the reverse of adsorption. It is a surface phenomenon.

In comparison with surface tension, adsorption is as a result of surface energy. In a bulk material, all the bonding requirements (such as ionic or

Electrovalence, covalence, or metallic bonding) of the materials present in the atoms of the material are filled by other atoms in the material. However, atoms on the surface of the adsorbent are not fully surrounded by other adsorbent atoms and therefore can attract adsorbates. The exact nature of the bonding is dependent of the details of the species involved, but the adsorption process is generally classified as physisorption (characteristic of weak van der Waals forces) or chemisorption (characteristic of covalent bonding). It may equally be as a result of electrostatic attraction.

Adsorption is present in many natural physical, biological, and chemical systems, and is widely used in industrial applications such as activated charcoal, capturing and using waste heat to provide cold water for air conditioning and other process requirements (adsorption chillers), synthetic resins, increase storage capacity of carbide-derived carbons for tunable nanoporous carbon, and water purification. Adsorption, ion exchange, and chromatography are sorption processes in which certain adsorbates are selectively transferred from the fluid phase to the surface of insoluble, rigid particles suspended in a vessel or packed in a column. Lesser known, are the pharmaceutical industry applications as a means to prolong neurological exposure to specific drugs or parts thereof. It should be noted here that, adsorption can take place in different media, such as the liquid and in solids.

i) Adsorption in liquids

In this case, water molecule present on the surface is attracted inwards by the molecules of water present in the bulk. This results in surface tension. While the molecule of water present within the bulk is equally attracted from all the sides and the net force experienced by the water molecule in bulk is zero. This clearly shows that particles at surface and particles at the bulk are in different environment.

ii) Adsorption in solids

In case of solid state these residual forces arise because of unbalanced valence forces of atoms at the surface. As a result of cleavages of a big crystal into smaller units arising from this, residual forces or vacancies get generated on the surface of the solid. Occupancy of these vacancies by some other molecular species results into adsorption.

There are many factors that are responsible for adsorption, such as the free energy of the system, entropy etc.

iii) Adsorption is a spontaneous process

For reaction or process to be spontaneous, there must be decreases in free energy of the system i.e. ΔG of the system must have negative value.

Also we know,

$$\Delta G = \Delta H - T\Delta S \quad (1)$$

And during this process of adsorption, randomness of the molecule decreases which ΔS is negative. We can rewrite above equation as

$$\Delta G = \Delta H + T\Delta S \quad (2)$$

Therefore for a reaction to be spontaneous ΔH has to be negative and

$$|\Delta H| > |T\Delta S| \quad (3)$$

iv) Adsorption is an exothermic process

Adsorption process takes place by adsorbate getting adsorbed on adsorbent. Forces of attraction exist between adsorbate and adsorbent and due to these forces of attraction, heat energy is released. So adsorption is an exothermic process.

1.1.2 Factors on which Adsorption Depends

There are lots of factors upon which adsorption can depend on, some of which are highlighted below:

i) Temperature

Adsorption increases at low temperature conditions.



Adsorption process is exothermic in nature. According to Le Chateleur principle, low temperature conditions would favor the forward direction.

ii) Pressure

In an adsorption Isotherm, increases in pressure, gives rise to adsorption increasing up to a certain extent till saturation level is achieved. After saturation level is achieved, it stops and no adsorption takes place no matter how high the pressure is applied.

iii) Surface Area

Adsorption is a surface phenomenon therefore it increases with increase in surface area and it has been clearly stated above that it is dependent of surface energy.

iv) Activation of Adsorbent

Activation of adsorbent surface is carried out so as to provide more number of empty sites on surface of adsorbent. This can be achieved by breaking solid crystal in small pieces, heating charcoal at high temperature, increasing the surface area or other methods suitable for particular adsorbent.

v) Surface Area of Adsorbent

As adsorption is a surface phenomenon, surface area offered by adsorbent becomes important factor for consideration as it provides sensitivity or the ease of adsorbent.

1.1.3 Types of Adsorption

Adsorption can be classified into two categories as described below:

(a) Depending upon the concentration: In adsorption the concentration of one substance is different at the surface of the other substance as compared to adjoining bulk or interior phase.

(i) Positive adsorption: If the concentration of adsorbate is more on the surface as compared to its concentration in the bulk phase then it is called positive adsorption. Example: When a concentrated solution of KCl is shaken with blood charcoal, it shows positive adsorption.

(ii) Negative adsorption: If the concentration of the adsorbate is less than its concentration in the bulk then it is called negative adsorption.

Example: When a dilute solution of KCl is shaken with blood charcoal, it shows negative adsorption.

(b) Depending upon the nature of force existing between adsorbate molecule and adsorbent: Forces of attraction exist between adsorbate and adsorbent. These forces of attraction can be due to Vander waal forces of attraction which are weak forces or due to chemical bond which are strong forces of attraction. Adsorption is classified majorly into two types, based on the type of forces of attraction taking place between adsorbate and adsorbent, they are: Physical Adsorption or Chemical Adsorption.

(i) Physical Adsorption or Physisorption

This occurs when the force of attraction existing between adsorbate and adsorbent are weak Van der Waal forces of attraction, the process is called Physical Adsorption or Physisorption. It takes place with formation of multilayer of adsorbate on adsorbent and has low enthalpy of adsorption i.e. ΔH adsorption is 20-40KJ/mol. It takes place at low temperature below boiling point of adsorbate. As the temperature increases, process of Physisorption decreases.

(ii) Chemical Adsorption or Chemisorption

This on the other hand as the name implies, takes place when the force of attraction existing between adsorbate and adsorbent are chemical forces of attraction or are of chemical bonding, the process is called Chemical Adsorption or Chemisorption. Chemisorption takes place with formation of unilayer of adsorbate on adsorbent having high enthalpy of adsorption.

It can occur at all temperature. With the increases in temperature, Chemisorption first increases and then decreases.

This usually take place where some surfaces, especially catalysts, which are sufficiently reactive to form chemical bonds with certain gases, unlike the physisorption, chemical adsorption (chemisorption) involves the formation of strong bonds between adsorbate molecules and specific surface locations known as active site.

Thus, they are primarily used to evaluate quantitatively the number of surface active sites which are likely to enhance (speed up) chemical reactions.

Some basic characteristics of chemisorption include:

- formation of strong chemical bond between adsorbate and chemically active surface sites
- often have a high activation energy
- generally irreversible except at high temperatures
- due to the high adsorption energy the assumption of monolayer adsorption works well, although some multilayer adsorption or spillover is possible

It is widely used in catalysts characterization for investigating:

- active metal surface area, particularly in heterogeneous catalysis where transition metals are used
- characterization of metal dispersion
- acid site distribution
- crystallite size
- heats of adsorption
- adsorption kinetics

There are some important features which are useful in recognizing chemisorptions, some of which include:

- (a) The phenomenon is characterized by chemical specificity;

- (b) Changes in the electronic state may be detectable by suitable physical means (e.g. u.v., infrared or microwave spectroscopy, electrical conductivity, magnetic susceptibility);
- (c) The chemical nature of the adsorptive(s) may be altered by surface dissociation or reaction in such a way that on desorption the original species cannot be recovered; in this sense chemisorption may not be reversible;
- (d) The energy of chemisorption is of the same order of magnitude as the energy change in a chemical reaction between a solid and a fluid: thus chemisorption, like chemical reactions in general, may be exothermic or endothermic and the magnitudes of the energy changes may range from very small to very large;
- (e) The elementary step in chemisorption often involves activation energy;
- (f) Where the activation energy for adsorption is large (activated adsorption), true equilibrium may be achieved slowly or in practice not at all. For example, in the adsorption of gases by solids the observed extent of adsorption, at a constant gas pressure after a fixed time, may in certain ranges of temperature increase with rise in temperature. In addition, where the activation energy for desorption is large, removal of the chemisorbed species from the surface may be possible only under extreme conditions of temperature or high vacuum, or by some suitable chemical treatment of the surface;
- (g) Since the adsorbed molecules are linked to the surface by valence bonds, they will usually occupy certain adsorption sites on the surface and only one layer of chemisorbed molecules is formed.

It should be noted here that, the adsorption process takes place in three steps:

- i. Macro transport:** The movement of organic material through the macro-pore system of the active carbon (macro-pore >50nm)

- ii. **Micro transport:** The movement of organic material through the meso-pore and micro-pore system of the active carbon (micro-pore < 2nm; meso-pore 2-50nm)
- iii. **Sorption:** The physical attachment of organic material on the surface of active carbon in the meso-pores and micro-pores of the active carbon.

Adsorption, ion exchange, and chromatography are sorption processes in which certain adsorbates are selectively transferred from the fluid phase to the surface of insoluble, rigid particles suspended in a vessel or packed in a column. It can adsorb the following soluble substances:

1.1.4 Advanced Oxidation Processes (AOPs)

This refers to a set of chemical treatment procedures designed to remove organic (and sometimes inorganic) materials in water and waste water by oxidation through reactions with hydroxyl radicals (.OH). In real-world applications of wastewater treatment, however, this term usually refers more specifically to a reasonable percentage of such chemical processes that uses ozone (O₃), hydrogen peroxide (H₂O₂) and/or UV light. One such type of process is referred to as in situ chemical oxidation.

These processes involve in situ generation of highly potent chemical oxidants such as hydroxyl radicals in sufficient and maximum quantities to significantly affect the oxidation and destruction of wide range of organic pollutants in contaminated water and air. It has gained noticeable and growing attention as a promising clean and efficient technology in air and water treatment as it has a significant advantage of completely or partially destruction of organics at ambient temperature by modifying them into various harmless intermediates and end products like carboxylic acids, carbon dioxide and halide ions.

It can be described as near ambient temperature treatment processes based on highly reactive radicals, especially the hydroxyl radical ($\cdot\text{OH}$), as the primary oxidant (Glaze 1987). Although oxidation processes involving $\cdot\text{OH}$ have been in use since late 19th century (such as in Fenton reagent, which, however, was an analytical reagent at that time), the utilization of such oxidative species in water treatment did not receive adequate attention until Glaze et al. suggested the possible generation of $\cdot\text{OH}$ “in sufficient quantity to affect water purification” and defined the term “Advanced Oxidation Processes” for the first time in 1987 the $\cdot\text{OH}$ radical is among the strongest oxidizing species used in water and wastewater treatment and offers the potential to greatly accelerate the rates of contaminant oxidation. The generation of $\cdot\text{OH}$ radicals is commonly accelerated by combining ozone (O_3), hydrogen peroxide (H_2O_2), titanium dioxide (TiO_2), heterogeneous photocatalysis, UV radiation, ultrasound, and (or) high electron beam irradiation. Of these, $\text{O}_3\text{-H}_2\text{O}_2$, $\text{O}_3\text{-UV}$, $\text{H}_2\text{O}_2\text{-UV}$, and heterogeneous photocatalytic processes hold the greatest promise to detoxify water and wastewater. Ozone at elevated pH will be decomposed into hydroxyl radicals. Thus, ozonation itself can be considered as one of the AOPs. In addition, the knowledge about many AOPs is based on the initiation of ozone decomposition in water.

Consequently, $\cdot\text{OH}$ reacts unselectively once formed and contaminants will be quickly and efficiently fragmented and converted into small inorganic molecules. In general, when applied in properly tuned conditions, AOPs can reduce the concentration of contaminants from several-hundred ppm to less than 5 ppb and therefore significantly bring COD and TOC down, which earned it the credit of “water treatment processes of the 21st century”.

Contaminants are oxidized by four different reagents: ozone, hydrogen peroxide, oxygen, and air, in precise, pre-programmed dosages, sequences, and combinations. These procedures may also be combined with Ultra Sound reactors, UV irradiation and specific catalysts. This results in the development of hydroxyl radicals.

There are various advantages of AOPs, some of which are:

AOPs hold several advantages that are unparalleled in the field of water treatment:

- It could effectively eliminate organic compounds in aqueous phase, rather than collecting or transferring pollutants into another phase.
- Due to the remarkable reactivity of $\cdot\text{OH}$, it virtually reacts with almost every aqueous pollutants without much discrimination. AOPs could therefore be applicable in many, if not all, scenarios where many organic contaminants are expected to be removed at the same time.
- Some heavy metals could also be removed in forms of precipitated $\text{M}(\text{OH})_x$.
- In some AOPs designs, disinfection could also be achieved, leading AOPs to an integrated solution to some of the water quality problems.
- Since the complete reduction product of $\cdot\text{OH}$ is H_2O , AOPs theoretically do not introduce any new hazardous substances into the water.
- AOPs represent alternative drinking water treatment option to air stripping, GAC adsorption, and resin sorption.

1.1.5 Methyl Tert-Butyl Ether (MTBE)

Methyl *tert*-butyl ether (MTBE), also known as methyl tertiary butyl ether, is an organic compound with molecular formula $(\text{CH}_3)_3\text{COCH}_3$, a volatile, low viscosity clear liquid at room temperature with an ether odour; having boiling point of 55.2°C ; and melting point -109°C . It is flammable and can form explosive mixtures with air. It is slightly soluble in water and very soluble ethers and alcohol and in most organic solvents including hydro carbons. MTBE is an ether which contains an oxygen atom bonded to two carbon atoms. It is a colourless liquid having minty odor vaguely reminiscent of diethyl ether, leading to unpleasant taste and odor in water. MTBE is a gasoline additive, used as an oxygenate to raise the octane number.

This (MTBE) gets into drinking water whenever there are opportunities for it to leak into the environment (and potentially get into drinking water sources) which might be from wherever gasoline is stored, spilled whenever fuel is transported or transferred, underground and above ground fuel storage tanks, pipelines, refueling