CHAPTER I

INTRODUCTION

a. Overview of the Chapter

This chapter presents a general introduction of VOCs, sources and effects. The treatment methods employed with their limitations. An overview of the principle and mechanism of Advanced Oxidation Process, different methods with their limitations has been briefly explained. The current state of photocatalyst their applications in the present field is explained in detail.

b. General

Volatile organic compounds (VOCs) are the organic compounds which have high vapour pressure at room temperature and are also characterized by low water solubility (1-2). Rapid industrialization and urbanization has led to serious environmental pollution problems that impact on human health in major Asian developing countries. Studies on VOCs in relation to air and water qualities were initiated in the fifties and since then interest in VOCs has been steadily growing (3). VOCs play a critical role in photochemical reactions, which give rise to highly toxic secondary and intermediate pollutants. However, for the past few years, it has been realised that severe high impact of such VOCs disposed by anthropogenic activities on human health and environment (4). More recently, evidence is rapidly growing to show the potential health hazards associated with VOCs and their involvement with global climate change and some of the VOCs species were shown to be highly toxic, mutagenic, and carcinogenic (5). Apart from potential health impacts of the VOCs, they are also involved in photochemical reactions leading to the formation of oxidants which have serious deleterious effects on human health, agricultural crops, trees, natural vegetation, buildings, materials, etc (6–8).

c. Source of VOCs emission

The sources of VOCs emission are varied and scattered. Emission of VOCs into the environment from anthropogenic sources has rapidly increased with the growing use of fossil fuels, expansion of industries and transport sector. Identification and characterization of sources is an important aspect of developing a VOC emission inventor (9). The anthropogenic sources include fossil fuel combustion, industries, vehicular exhaust, and vaporization of gasoline during transportation, distribution and use, solvent usage, oil and chemical industries, storage and transportation of petroleum products, waste landfill sites, sewage treatment plant, food manufacture, agriculture, biomass burning, and livestock. Forests, grasslands, oceans, rivers, wetlands, soil and sediments, and peatlands constitute important natural sources of VOCs (5,9–11). The emission sources of VOC can be broadly classified into two main categories namely; a) anthropogenic and b) natural (Figure 1.1). Volatile organic source emitted to the atmosphere from natural source can be classified as geogenic and biogenic. Geogenic volatile organic compounds are emitted from earth’s crust and biogenic volatile organic compound are emitted mainly from flora (12). Globally the major VOCs sources are tropical forest which emit VOCs such as isoprene, monoterpenes, methanol in large quantities which accounts to around 1150 TgC (13-14). The primary anthropogenic sources in urban areas encompass vehicular emission, industrial processes, solvent usage, fuel evaporation, oil refining & degradation of waste (15–18). The minor sources are petrochemical industries, dry cleaning activities, coal powered fire plants, solvent industries, landfill sites, production, repository and handling of fossil fuels, though it is smaller source at global level, can dominate at regional level (14,18-19). The emitted
VOCs undergo four important processes. Dispersion is the transportation and dilution of the VOCs to the entire boundary of water or air. Physical transformation is the condensation of the gaseous VOCs or adsorption on the surface or solution. A chemical reaction is the process of change of VOCs into organic or inorganic molecules. Deposition is by the scavenging or sedimentation process on to the soil or water reserves (19).

d. Environmental consequences of VOCs

VOCs did not receive much attention, but caused serious threat to human health, vegetation and public welfare in recent days. In recent years, evidence is also rapidly mounting up to show potential health hazards associated with VOCs as well as their role in climate change globally. The effects of VOCs are complex and far-reaching, affecting the living organisms including human beings, animals and plants. Both direct and indirect effects of VOCs are important as well as distinct and they have been discussed separately (20).

Figure 1.1 Major emission sources of VOCs

(I) Direct Effects

The Direct effect is defined as the effect caused due to direct exposure to VOCs. It ranges from all the way from living organisms including man to global ecosystems. Exposure to VOCs through water and air pollution is believed to result in significant risks to human health, ranging from the minor effect such as a headache, fatigue to more serious effects such as cancer. Recent studies have shown that the VOCs affect the living systems
including the human being in various ways. This effect could be because of exposure to the ambient environment containing VOCs, largely because of the toxicity, mutagenicity, and carcinogenicity of some of the VOCs emitted into the environment.

(II) Toxic Effect

A large number of VOC species have been shown to be toxic, posing a serious threat to human health. The important aromatic compounds group such as benzene, ethylbenzene, toluene, and xylene can cause the health effects such as a headache, nausea, eye/throat/nose irritation, fatigue and if it prolongs for a longer duration it can damage liver, kidney and also central nervous system. Toluene, ethylbenzene, and xylenes can develop adverse health impacts on the respiratory and nervous system (21). Aldehydes, particularly formaldehyde and acrolein are potent irritants. Similarly, bromide, as well as CH$_3$Cl, is toxic to the living system. In addition, certain mono chlorobenzene(MCB) is also moderately reactive. The secondary products like benzaldehyde and phenols are also toxic (20). Such VOCs and organic solvents are highly toxic and affect the nervous system, reduce fertility, increase the risk of chronic obstructive pulmonary diseases and other respiratory problems, nasal and eye irritation, nausea, dizziness and headache in workers exposed to paints and adhesives. Acute exposure to benzene causes central nervous system depression, skin irritation, and removal of fat from the keratin layer which can cause erythema blistering and dry and scaly dermatitis (22). Some of the VOCs are highly toxic and belong to the category of hazardous chemicals. The worst ever industrial accident, at Bhopal, in India, resulted from the accidental release of deadly VOCs, namely, methyl isocyanate (MIC). An estimated 30 - 40 T of MIC got accidentally released into the atmosphere in the form of aerosol-cloud within a short period of 2 – 3 hour during the midnight of 2$^{nd}$ and 3$^{rd}$ December-1984, exposing over 0.5 million people killing at least 6000 people within the first week of the disaster. The current death toll is estimated to be well above 16000 (23–27).

(III) Carcinogenic Effect

A number of VOCs have been identified, which are supposed to be carcinogens and/or suspected carcinogens. The presence of these compounds in the environment poses serious threats to human health. A smaller group of VOCs are arguable of much more interests because they are known to be human carcinogens. These include C$_6$H$_6$, CH$_3$Cl, CCl$_4$, and chloroform. Benzene is classified as human carcinogen by group-1 of the International Agency for Cancer Research. Exposure to benzene at high concentrations is associated with leukemia, lymphomas and other types of cancers in the human being. A high level of benzene in the ambient air and water is a potential threat to public health. For example, the estimated lifetime risk of benzene is two times greater than that of vinyl chloride for equal exposure (1,20,28–30). Human and specifically children residing near highways or heavy traffic are at a higher risk of developing cancer such as leukemia (30-31).

(IV) Indirect Effects

The indirect effect of VOCs can be attributed to the creation of secondary and intermediated pollutants in the atmosphere and environment. VOCs in the atmosphere are available in two forms either as gas or particle phase. The form in which the organic compounds exist will have a strong influence on its lifetime and the impact on the troposphere layer. Most of the reactions are steered by sunlight and generally referred as photochemical pollutants. (12,32-33)

(V) Formation of Hazardous Secondary Pollutants
Volatile organic compounds influence the ecosystem indirectly through the formation of photochemical oxidants such as ozone and peroxyacetyl nitrate. Indirectly, VOCs also influence global climate by promoting global warming through the formation of radiantly active compounds like ozone and CO. It directly as well as indirectly exercise a controlling influence on the composition of the troposphere, via its role as sink and source of hydroxyl radicals as well as global warming (20). The formation of ozone in the troposphere is mainly attributed to the photochemical reactions of NOx, VOC and CO. Ozone, a secondary air pollutant, is a primary oxidizer of other highly reactive trace gases. Ozone has been implicated in respiratory problems in mammals and vegetation and is also a very strong greenhouse gas. Some halogen-containing VOCs are responsible for stratospheric ozone depletion. Chlorine, bromine, and fluorine-based VOCs are particularly effective in destroying the stratospheric ozone, leading to the higher influx of ultraviolet radiation (UV) to the earth surface. Increased UV radiation at the earth surface has adverse effects on human beings, animals, plants, and materials. Higher doses of UV at the ground level promotes skin cancer, eye damage, suppression of allergic reactions of the skin and affecting the immune system, increase in the formation of troposphere ozone, affects plants, materials, disrupts ocean life and marine food web. Secondary organic aerosols are formed in the atmosphere due to the oxidation of VOCs. These secondary organic aerosols can precipitate into existing particles or blend together to form a new particle. Secondary aerosols have an adverse effect on climate change, reduction in visibility and on health. VOCs affect the atmosphere by two ways. Direct effect by a halocarbon due to the infrared absorption and reflected by its higher global warming potential and higher atmospheric lifetime and as a hydrocarbon leading to the ground-level ozone formation. The second is mainly the release of CO2 from atmospheric degradation of VOCs or by incineration favoured by the combustion of fossil fuels (5,10,20,35–37).

e. Treatment of VOCs

VOCs removal techniques can be broadly classified into modification of equipment and process and the second one control techniques (35,38). Modification of equipment and process are usually the preferred method which is done by substituting of raw materials, change in the operating conditions and also monitoring and repair of the equipment. There are various technologies which have been currently used for the treatment or elimination of VOCs. Physical, chemical and biological treatments methods are available for the removal of VOCs present both in flue gas stream and also industrial wastewater either by recovery method or destruction method (8,10,39–42).

Control techniques can be complete destruction or recovery of VOCs from effluent disposed of by industries or anthropogenic sources. Recovery techniques are desirable when the cost of procuring VOCs is higher than the recovery cost; otherwise, the simple destruction technique is more feasible (38). Complete destruction is achieved by thermal and catalytic oxidation and microbial digestion. Oxidation with heat recovery is a good economic option for the destruction of VOCs. Incineration of the waste streams can be carried out in which the thermal oxidation of the VOCs compounds takes place. Thermal oxidation systems are designed to obtain 95 -99% of the destruction of all VOCs and also known as fume incinerators. Thermal oxidation system usually operates at a temperature range of 1300 - 1800° F. These systems can handle concentration of VOCs ranging from 100 to 2,000 ppm and has a capacity of 1000 to 500000 cubic feet per meter. Thermal oxidation requires proper design of the incinerator and specific operating condition. Longer retention time and higher temperatures are required for the complete destruction and increased removal efficiency. When halogenated compounds are combusted, they release acidic compounds that can corrode the pipelines and instruments. This necessitates the
application of costly corrosion resistant materials and scrubbers as additional gas controls. Operating at maximum temperature can release exalted levels of oxides of nitrogen. This is a secondary pollutant which further requires treatment and is inefficient for low VOCs concentration as complete oxidation requires more supporting fuel and not cost effective. The incoming gas stream can be heated by the heat content of the combustion exhaust flow and thereby the process becomes economical. Thermal oxidizers are not an economical method for treating very low concentration of VOCs as it requires a further supply of fuel to support continuous oxidation (8,10,35). Catalytic oxidation systems use the catalyst to oxide the VOCs at a lower temperature around 700 to 900° F. Catalytic oxidation is carried out at a lower temperature and thereby the process is economical by reducing the energy consumption requirements for complete oxidation. Efficiently designed catalytic combustion systems are able to handle VOCs concentration ranging from 100 to 2000 ppm. Catalytic oxidizers operate in a cyclic manner and are best suited for very low concentration of VOCs at an industrial level as well as indoor environment Catalytic oxidation system can be used to treat the effluent stream where the VOCs and flow rates are variable. Destruction efficiency of about 90 - 95% can be obtained by this method. Catalytic oxidation system produces secondary combustion waste and acidic compounds when halogen or sulphur compounds are oxidized by a catalyst. Acid-gas scrubbers are used to treat these acid compounds. The catalyst material is susceptible to poisoning from non-VOCs compounds and the spent catalyst material is a hazardous waste which needs proper disposal. The main limitation of the catalytic systems is the replacement of catalyst due to high cost. UV oxidation system is also used to oxidize organic compounds present in the wastewater and effluent streams With the UV radiation strong chemical oxidizers directly react with the organic contaminants. The end product of the UV oxidized technology is carbon dioxide and water(10,35,43).

Biological treatment techniques are designed on the capability of microorganisms to degrade the organic pollutants under aerobic conditions through oxidative and reductive reactions to water vapor, carbon dioxide, inorganic products and organic biomass. The biological techniques confide on two important fundamental mechanisms. One is the absorption of organic compounds to the media and the second one is the biodegradation. Volatile organic compounds are used by microbes as a carbon source for their growth and metabolic activities. The mechanism by which the biodegradation of pollutants is brought about by microbes in the biofilm is a consolidation of physico-chemical and biological action. Microorganisms are either supported or immobilized on organic media or inorganic structures or suspended in the liquid. They are proved to be a competent and reasonable method for the treatment of different types of industrial wastewater. Biological methods include Biofilter, Bio-trickling filters, bio-scrubbers, membrane and suspended bioreactors. Biofiltration is a process in which the flue gas or wastewater is allowed to flow over a porous packed medium that supports the thriving microbial population. Biofiltration is the oldest and the simplest method of biological treatment of wastewater. The biofilters are usually composed of simple packed bed structure surrounded with immobilized microorganisms. The wastewater or flue streams are allowed to flow through a packed bed supported by a mixed culture of microorganisms which have the ability to degrade the pollutant is immobilized on an inert material. The flow is usually maintained to be from the bottom of the reactor in the upward direction. The filter medium is composed of relatively inert materials such as compost, soil, peat, etc. The filter bed materials are selected based on the physical and mechanical properties such as void fraction, water retention capacity, structure, specific area, a degree of compaction and biological properties such as nutrient availability. A biofilter media must provide a favorable environment for the growth of microorganisms. Filter media provides a medium for microorganisms to attach, grow and metabolize the organic
contaminants present in the wastewater. Microbial activity is strongly dependent on the moisture content of the media, nutrient availability, temperature, microbial inoculum, pH, etc. Bio-filters are economical as the capital investment & operating costs are minimal, capable of operating a wide range of compounds. The major drawback of this method is that the efficiency decreases as the concentration of the pollutant increases and space constraints due to the large size of a bioreactor. Clogging of the medium is a common problem with the biofilters (44–46). Biotrickling filters have gas/wastewater flow on a fixed bed with immobilized microorganisms. Continuous recycling of the nutrient and can efficiently remove soluble VOCs. Bio-trickling filter systems can control the nutrient availability and pH. The advantages of a biotrickling filter is that it is able to handle the acid degradation product of VOCs, lesser operational and capital investments, higher output for lesser retention time. The major drawbacks of the system are accumulation of excess biomass, which can lead to the reduction in efficiency and uneven biomass distribution; skilled technicians for operations and production of a secondary waste stream (8,47). Bio-scrubbers comprises of a bioreactor and a absorption tower. The gaseous solutions are diffused through an aqueous solution. The treated gas is emitted from above and the liquid containing absorbed pollutants are pumped to an aerated bioreactor. A bioreactor is composed of microorganisms suspended in the nutrient-rich media. Biomass is allowed to deposit after complete degradation and then filtered Bio-scrubbers are able to deal with severe fluctuations in high flow rate. The major limitations with the use of bio-scrubbers are able to treat only water-soluble compounds with the production of liquid waste, along with the operational and maintenance complexity requires continuous air supply and sludge disposal problem (8,10). The Membrane bioreactors include a membrane separating the liquid and gaseous phase. The biomass growth and degradation take place in the aqueous phase. Limitations of membrane bioreactor are inefficiency at higher concentration of VOCs, higher construction cost, and operational cost, the operational problem such as the formation of excess biomass which leads to clogging of a membrane (8,10). Biotreatment offers many advantages such as lower capital and maintenance cost, efficient treatment, resistant to environmental conditions, minimal by-product generation, smaller carbon footprint and also for the lower concentration of VOCs. Certain complex compounds may not be biodegradable as microorganism lacks the enzymes to break the bond structure effectively, longer residence time, space constraint for the larger size of bioreactor, lesser life of packing media and chances of clogging and also undesirable secondary products are released, less treatment efficiency at higher concentration are some of the limitations of this method (5,6,12,15–17).

There are various techniques which are employed for the recovery of VOCs from the combustion gas and from the waste stream such as condensation, absorption, adsorption and membrane separation. Condensation is the best method for VOCs recovery. Condensation is usually achieved by cooling or pressurisation or both to the exhaust gas stream. For comparatively high concentration of VOCs above 5000 ppm and for VOCs with boiling point above 100°F, Condensation is recommended. The principle of condensation is partition technique in which volatile compounds are separated by saturation pursued by a phase change. The gas to liquid phase change can be achieved in two possible ways: (a) the pressure of the system can be increased with a constant temperature, or (b) the temperature is reduced at a given pressure. The method is best suited for mono solvent system. VOCs with lower boiling point will require extensive cooling or pressurization and thereby there is a sharp increase in the operation cost. The process generates liquid waste which needs further treatment. The limitations of the process is that compounds with lower boiling point especially non polar compounds require extremely low temperature and is applicable for higher VOC concentration in the exhaust stream and high operating cost.
The VOC absorption of the gas stream is affected by the interaction of the air contaminated with the liquid solvent. The soluble VOCs present in the contaminated air is transferred to the liquid solvent when the air stream is scrubbed with liquid solvent. Absorption is carried out in an absorption tower where air is brought in contact with the liquid to facilitate mass transfer. Absorption towers are able to handle VOC concentration ranges from 500 to 5000 ppm. Packed bed scrubber with packed material improves vapour liquid contact and thereby 95 to 98% removal efficiency can be achieved. Spray nozzles can be used to atomize the flow in small droplets using mist scrubbers. Mist scrubbers require a very little pressure drop but the incoming flue gas should be free of particulate matter to prevent the fouling. The process has the capacity to handle a broad range of concentrations, elementary equipment and process. Drawback with absorption technique generates wastewater which needs further treatment, high initial investment, difficult in design, startup time constraints, requires a precise maintenance of the system, and is not suitable method for lower concentrations of VOCs (8,35,48).

VOCs present in the exhaust gas and wastewater can be removed by adsorption. Adsorption processes are of two types physisorption and chemisorptions depending on the interaction between the adsorbate and the adsorbent. In the physical adsorption, the adsorbate is maintained on the surface of the adsorbent by the weak force of Vander Waals with a low adsorption heat and the adsorption equilibrium is usually reversible. There are a number of adsorbents currently used such as powdered and granular activated carbon, zeolites, alumina and silica gel. Adsorption by activated carbon is a common method employed for VOCs removal as they have a larger surface area, they are flexible and inexpensive to operate and lesser capital installment. Activated carbon adsorption has few limitations such as they are flammable; boost polymerization or oxidation with the release of few toxic compounds. Hydrophobic adsorbents such as zeolite have few advantages such as they are thermally stable, non-flammable and hydrophobicity. Zeolites have a crystalline structure and fixed pore sizes which prevent molecules of certain size. Hence, they are sometimes referred as the molecular sieve. Waste stream containing VOCs is allowed to pass through adsorbents so that the VOCs bind to it. Adsorption bed reactors can be of fixed bed reactors, moving or pulse bed reactors which are generally used for this process. This adsorption has few limitations such as limited effectiveness, higher capital investment and operating cost. Economic and logical problem arise when discarded or during the regeneration of carbon. Desorption and separation of VOCs from adsorbent increases the cost and complexity of the process. Hence adsorption is effectively used as a polishing treatment for the liquid waste stream containing the very low concentration of VOCs (10,35,39).

Membrane technology is a separation process where the effluent gas flue stream is allowed to pass through a semi-permeable membrane. Membrane separation is recommended for streams with highly loaded VOCs. Membrane technology is based on the concept of differences in size, shape, electrical charge, solubility, partial pressure, pollutant concentration in the exhaust gas or wastewater. For the recovery of VOCs gas permeation and reverse osmosis, techniques have been generally used. A major drawback is the high pressure and membrane fouling problem. The membrane-based recovery system is still in an experimental phase and the efficiency depends on few factors such as the cost and maintenance of the membrane and the possible chances of clogging of the membrane filter media (8,35,49).

f. Advanced Oxidation Process (AOP)

Oxidation is defined as the process where the electron acceptor or oxidant, having affinity for electrons gains an electron from the reductant (electron donor). Advanced oxidation process, by definition, is a process that associates the production of reactive
oxidizing agent such as hydroxyl radicals in sufficient quantity for the degradation of complex organic compounds present in both water and wastewater. The preeminent objective of AOP is to completely degrade the toxic organic pollutants to non-detectable limits from the ppb or ppm range without generating hazardous secondary pollutants. The OH\(^-\) insufficient yield can be utilized for wastewater treatment. In AOP, the hydroxyl radical being a very strong oxidizing agent has the ability to mineralize the organic compounds present in water and wastewater. AOPs are usually classified as chemical oxidation and photochemical oxidation (50). The basic principle of AOP is the generation of hydroxyl radicals that can be generated by photo-dissociation of hydrogen peroxide (H\(_2\)O\(_2\)/UV), photolysis of ozone (O\(_3\)/UV), Fenton reaction (Fe\(^{2+}\)/H\(_2\)O\(_2\)), Photo-Fenton reaction (Fe\(^{2+}\)/H\(_2\)O\(_2\)/UV), photocatalysis (TiO\(_2\)/UV), radiation chemical and sonochemical methods. Each method has its own merits and limitations, and efficiency of each process: depends on the ease with which it can be operated, the cost-effectiveness, the extent of mineralization achieved and finally the reaction time. Most of these methods are effective in bringing about the complete oxidation of organic pollutants, thus achieving the lowest level of pollution. The effectiveness and efficiency of AOP mainly rely on the water or wastewater characteristics and the treatment method chosen in the generation of hydroxyl radical (45,51–56). AOPs are employed for the destruction of toxic chemicals, pesticides, biorefactory compounds, pentachlorophenol, nitrophenols, aromatic compounds such as benzene, toluene, ethylbenzene, xylene and halogenated hydrocarbon such as trichloroethylene either partially or completely under ambient conditions of temperature and pressure. In general, AOP at a right place helps in the degradation of contaminants to less than ppb from several hundreds ppm. The high oxidation rate of radicals in the AOP significantly changes the chemical species after treatment (50,56-57).

(1) Degradation Mechanism of Advanced Oxidation Processes

The main mechanism that governs the AOP is the generation of highly reactive free radicals. AOP include processes in which the strong oxidant such as hydroxyl radical (OH\(^-\)) is generated for the degradation and destruction of pollutant materials using different methods. Hydroxyl radical are powerful reactive electrophiles (electron preferring) which react swiftly and non-selectively with approximately with all electron rich organic compounds. They show fast rate of oxidation reactions when compared to conventional oxidants with a high oxidation potential of 2.8V (49-58). The reaction pathway of hydroxyl radical with the organic compound undergoes in three steps. In the first step electrophiles addition of hydroxyl radical leads to the organic radical formation. In the second step of hydrogen abstraction, aliphatic compounds are reacted by the hydroxyl radical. In the last step electron transfer takes place with the reduction of hydroxyl radicals into a hydroxyl anion by a organic substances (54–56,59).

\[ \text{R} + \text{HO}^- \rightarrow \text{ROH} \]

\[ \text{R} + \text{HO}^- \rightarrow \text{R}^+ + \text{H}_2\text{O} \]

\[ \text{R}^n + \text{HO}^- \rightarrow \text{R}^{n-1} + \text{OH}^- \]

A chain of oxidative reaction is initiated by the OH\(^-\) radical in the presence of oxygen (51). The hydroxyl radical has the capacity to completely mineralize almost all classes of organic compounds into CO\(_2\), H\(_2\)O, inorganic salts or their conversion into simpler compounds. The exact sequence of these reactions is still unclear. Theoretically, the AOPs must oxidize the organic compounds to harmless end products such as carbon dioxide and water as illustrated in Figure 1.1. For example, the chlorinated organic compounds are completely oxidized to CO\(_2\), H\(_2\)O and chloride ion. Aldehydes and carboxylic acid are the
intermediate compounds which are formed during the oxidation process. In a similar manner, cyanide is oxidized first to cyanate and then finally to CO₂ and nitrate (51).

As a thumb rule, the rate of destruction is directly proportional to the rate constant of the OH⁻ radical. The rate constant of OH⁻ radical is in the order of 10⁶–10⁹ M⁻¹s⁻¹. The flexibility of AOP is that they offer several possible means for the production of OH radicals which allows a superior conformity with the definite treatment concern (60). The important factor which affects AOPs is the strength or the load of the wastewater. The presence of other chemical species or ions in the waste can also compete with the hydroxyl radical (54). There are different ways, which are employed for the generation of the hydroxyl radical by means of various processes such as ozone-based processes, Fenton based processes, sonolysis, photo Fenton based process and heterogeneous photocatalysis. Table 2.1 summarizes the various AOPs and the reactive species, which are generated during each process. From the table, it is clear that the HO⁻ is the highly reactive and is the most important reactive species and the efficiency is dependent on the method employed for the generation of hydroxyl radical (60-61). The AOPs can be classified as photochemical and non-photochemical depending on the use of radiation and also homogeneous and heterogeneous depending on various photocatalyst used in the processes (54).

**Table 1.1 Common AOP and reactive species produced in each process (61)**

<table>
<thead>
<tr>
<th>Sl. No</th>
<th>AOP</th>
<th>Reactive species</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Ozone Treatment</td>
<td>HO⁻, HO₂⁻, HO₃⁻, O₂⁻, O₃⁻</td>
</tr>
<tr>
<td>2.</td>
<td>O₃/H₂O₂</td>
<td>HO⁻, O₂⁻, O₃⁻</td>
</tr>
<tr>
<td>3.</td>
<td>Fenton Process</td>
<td>HO⁻, HO₂⁻</td>
</tr>
<tr>
<td>4.</td>
<td>Photo fenton Process</td>
<td>HO⁻</td>
</tr>
<tr>
<td>5.</td>
<td>UV/O₃, UV/H₂O₂, UV/ O₂/H₂O₂</td>
<td>HO⁻, HO₂⁻/ O₂⁻, O₃⁻</td>
</tr>
<tr>
<td>6.</td>
<td>V-UV</td>
<td>HO⁻, H⁺, e⁻</td>
</tr>
<tr>
<td>7.</td>
<td>Photocatalytic treatment: UV/Vis light using catalysts</td>
<td>HO⁻, h⁺, O₂⁻, e⁻, O₂, HO₂⁻, HOO⁻</td>
</tr>
<tr>
<td>8.</td>
<td>Ultrasonic Treatment</td>
<td>HO⁻, H⁻</td>
</tr>
<tr>
<td>9.</td>
<td>γ-Radiolysis</td>
<td>HO⁻, H⁻, e⁻</td>
</tr>
</tbody>
</table>
(II) Sonochemical method

In a sonochemical process, sound waves are used with a frequency range between 20 KHz and 500 MHz is used. When ultrasound propagates in the water or wastewater, alternate compression or rarefaction cycles results in the generation of bubble or cavity which ultimately collapses to release a huge amount of energy. Forces are generally strong which has the ability to corrode or wear and tear of the concrete or metal structures. The process will have a very high temperature in the range of 2000 to 5000°C and pressure greater than 500 atmosphere, which has the ability to drive many chemical reactions by pyrolysis. Bubble collapse is usually associated with physical and chemical effects. At higher frequency chemical ultrasonic effects lead to the generation of larger free radicals which react with the organic substance. These radicals react with the organic substance at a liquid-gas interface. Higher concentrations of free radicals recombine to form H₂O₂ and further assist in the degradation of organic pollutants. Sonochemical is a versatile process, has been employed for the degradation of several compounds. This technique can be combined with other AOP to obtain the desired results. The efficiency of the process mainly depends on optimizing the operating parameters such as intensity and frequency of radiation, physicochemical characteristics of medium, temperature and inlet pressure. They are widely used for the degradation of complex biodegradable compounds and the reactions occur in the near region of the cavity bubbles generated by the Sonochemical method. Research is being carried out in scaling up of the process from lab scale to a pilot plant. The main drawback of this technology is energy consumption which limits its applicability to the smaller volume (45,50,57,63).

(III) Ozonation

Ozone a selective oxidant used for oxidation of non-biodegradable compounds usually recommended after biological treatment of wastewater (50). Ozone may directly react with organic compounds or be being very unstable spontaneously decomposes with a complex set of reaction that implicate the hydroxyl radical (HO•) generation and superoxide radical (O₂•⁻). The disintegration is higher at alkaline levels of pH (51). Oxidation of organic compounds is brought about by a series of reactions with molecular ozone and hydroxyl radical. The efficiency of the process is mainly dependent on the gas-liquid mass transfer, contact time, ozone dose and pH. Ozone reacts slowly and directly with an organic substance has it has the high reduction potential of 2.07V (54,62). Oxidation of organic compounds occurs due to the reactions between molecular ozone and HO• as depicted below.

\[ 3O_3 + OH^- + H^+ \rightarrow 2HO^- + 4O_2 \]  

The efficiency of organic compound degradation can be increased by combining ozone with hydrogen peroxide, UV radiation or ultrasound. This results in the formation of hydroxyl radicals which increases the degradation rate. The degradation rate is increased when compared with the ozone alone (50,51,55). The mechanism clearly indicates the role exerted by H₂O₂, which is formed during the dissociation process of ozone in aqueous solution. Therefore it is fair by the H₂O₂ addition to the aqueous solution of ozone will increase the OH radicals formation by ozone decomposition process. It is evident that the speed of photolysis of aqueous H₂O₂ is dependent on pH as the active species concentration of OH⁻ is pH dependent. With the addition of hydrogen peroxide and alkaline pH with the aqueous solution of ozone will results in the oxidation of highly reactive substances and thereby enhances the degradation rate. Ozone technology can also be combined with UV radiation as the UV photons can also initiate the ozone molecules. Water
or wastewater system are saturated with ozone and then irradiated with a UV light of 254 nm in a reactor conducive to the reaction. Photolysis of ozone results in the production of H$_2$O$_2$ an intermediate, which later disassociate into highly reactive OH$^*$. This method is more effective than H$_2$O$_2$/O$_3$ and H$_2$O$_2$/UV or O$_3$ and H$_2$O$_2$ alone as the molar extinction coefficient of ozone is 3600 M$^{-1}$cm$^{-1}$ which is greater than hydrogen peroxide (60). The major limitations are that organic compounds present in the wastewater may absorb UV light irradiation, then the irradiation by UV does not have any additional effect to ozone and the method is energy intensive thereby increasing the operation cost (45,51,61,62). To accelerate ozonation reactions homogenous or heterogeneous catalyst such as Fe$_2$O$_3$, MnO$_2$, Fe$^{2+}$, Fe$^{3+}$ have been studied. Though the reaction mechanics is unclear a significant oxidation of the target pollutant has been achieved. O$_3$/Fe(II) and O$_3$/Mn(II) systems are more efficient in the degradation of organo chloride compound than ozonation at high pH alone (55,57). Ozone combined with H$_2$O$_2$ can also be combined with irradiation of UV in the wavelength range of 200-280nm. Smaller molar extinction coefficient of H$_2$O$_2$ allows relatively a very small portion of incident light to be utilized. The strong oxidizing power and short reaction time of ozone has the ability to treat a large quantity of water but it is a high energy consumption process with a high maintenance cost for the production of ozone. Ozone is unstable; hence it needs to be produced at the time of application. Ozonation leads to the formation of intermediate compounds such as bromated which interferes with the absorption of UV radiation by ozone (55).

(IV) Hydrogen Peroxide

Hydrogen peroxide is a strong oxidant but it is inefficient in oxidizing more complex organic compounds with a lesser reaction time. AOP encompasses the use of H$_2$O$_2$ with UV radiation. Photolysis of hydrogen peroxide results in the hydroxyl radical formation and latter on propagates the corresponding simultaneous reactions. The H$_2$O$_2$ photolysis to OH$^*$ is carried out by irradiation with UV light of wavelengths lesser than 280 nm (45,50). Irradiation by UV is used to hew the O-O bond present in H$_2$O$_2$ and thereby initiates the reaction to generate hydroxyl radical. The following equation illustrates the sequential reaction carried out when H$_2$O$_2$ is radiated with UV.

\[
\begin{align*}
H_2O_2 + HV & \rightarrow 2HO^* \quad \text{(5)} \\
H_2O_2 + HO^* & \rightarrow HO_2^* + H_2O \quad \text{(6)} \\
H_2O_2 + HO_2^* + H_2O + O_2 & \rightarrow \quad \text{(7)}
\end{align*}
\]

The equation-6 is the rate-limiting step which governs the oxidation of organic compounds. It is clear from the above equations that higher initial hydrogen peroxide concentration results in a large number of hydroxyl generation and thereby the complete oxidation of organic compounds. As depicted in the equation 3 surplus amount of H$_2$O$_2$ reacts with hydroxyl radical that leads to the HO$_2^*$ formation and thereby decreases the oxidation rate of organic compounds. Henceforth optimum dosing of H$_2$O$_2$ is crucial to obtain maximum efficiency by this method (53,54,58,61). Photolysis of H$_2$O$_2$ can be obtained by using mercury vapour lamps with high intensity and thereby results in the reduction of the amount of H$_2$O$_2$ required for the oxidation purposes. The factors, which governs the process are the initial pollutant concentration, optimum dosage of H$_2$O$_2$ to be used, aqueous solution pH and duration of the reaction. The advantages of H$_2$O$_2$/UV process is high reaction rate, complete solubility of H$_2$O$_2$ reagent in water hence there is no mass transfer limitation, flexible in the design of reactor, powerful source of HO$^*$, a separation process is not
necessary after treatment, feasibility; flexibility in operation, eco-friendly, effective source of HO\(^{-}\) and scaling up is easier. One of the major limitations of the method is the molar extinction coefficient of \(\text{H}_2\text{O}_2\) is \(18.6 \text{M}^{-1}\text{cm}^{-1}\) at 254 nm which enables to utilize just a small part of the incident light. If the aqueous solution has interfering compounds and suspended solids which absorb UV light energy, then the light absorbed by the reactor will be wasted and thereby the efficiency of the process decreases (55). The rate of photolysis is pH dependent and it is found to increase at a higher pH value. The reason for increased oxidation rate can be attributed to the molar absorption coefficient of peroxide anion at 254 nm in the alkaline pH increases from \(18.6 \text{ M}^{-1}\text{cm}^{-1}\) to \(240 \text{ M}^{-1}\text{cm}^{-1}\) (60). One of the major disadvantages of the process is that it is not possible to exploit sunlight as source of ultraviolet light as the appropriate energy for the oxidation of organic matter is not accessible in the solar spectrum. UV/\(\text{H}_2\text{O}_2\) can also be combined with ultrasonic (US) waves to enhance the degradation rate and is most effective in the removal of industrial dyes from various industrial wastewater (50,56,60,6354).

(V) Fenton Process

Fenton process reported by Fenton, where ferrous and hydrogen peroxide known as powerful oxidant is used for the generation of hydroxyl radical. Fe (II) is oxidized to Fe(III) within a fraction of minutes due to the presence of the excess of \(\text{H}_2\text{O}_2\) as depicted in the equation (8).

\[
\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{OH}^- + \text{OH}^- \tag{8}
\]

Hydrogen peroxide is oxidized catalytically by Fe(III) and hydroxyl radical is generated according to the following equation (9).

\[
\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{H}^+ + \text{Fe} - \text{OOH}^{2+} \tag{9}
\]

Then the hydrogen peroxide is catalytically decomposed by ferrous for the generation of hydroxyl radical (51). Fenton reagent has to ability to oxidize toxic compounds in the aqueous waste streams. Fenton process requires pH control to prevent the precipitation of iron. Hence a reactor is required for proper mixing of Fe(II) and \(\text{H}_2\text{O}_2\) and thereby the optimum number of hydroxyl radical is formed (55). Thus iron salts act as a catalyst for the decomposition of hydrogen peroxide which has the capability to destroy different volatile organic compounds both in water and wastewater. Fenton process is a simple method, which requires only chemicals like hydrogen peroxide and ferrous reagent without the need of special apparatus. Iron salts and hydrogen peroxide are readily available, non-toxic element, easier to handle and safe for environment. Advanced Oxidation pretreatment with the fenton reagent is effective to enhance the biodegradation of surfactants present in water. Acidic pH is required to prevent precipitation of iron thereby increasing the operation and maintenance cost. For the generation of fenton reagent, a reactor is required for the proper mixing of ferrous and hydrogen peroxide. Though fenton is effective in the hydroxyl radical generation, for the generation of one OH\(^{-}\) radical one molecule of Fe(II) is required demanding higher concentration of Fe(II) (51,55). The degradation by Fenton reagent is mainly dependent on the solution pH, initial concentration of ferrous ions, \(\text{H}_2\text{O}_2\) concentration, initial pollutant concentration and the presence of interfering ions (45,59). The rate of degradation can be increased with a Fenton reagent along with the UV light radiation at the wavelength of 280nm. When the pH of the aqueous solution is 3, Fe\(^{3+}\) disassociates to form Fe(OH)\(^{2+}\) which further degrades to form Fe\(^{2+}\) and OH\(^{-}\) as explained in the equation (10) and (11).
The process is called as photo Fenton oxidation. The photolysis of hydrogen peroxide is obtained with mercury vapour lamp, with a high intensity so as to reduce the amount of hydrogen peroxide needed for the process. Fenton reactions are driven by low energy photons and also ferric ion absorption spectrum is near the UV/visible region thus making photo-oxidation possible at the visible light region which can reduce the operational cost (59). Fenton and photo Fenton methods have a number of advantages such as flexibility in operation, simplicity in design and operation, both $H_2O_2$ and iron is abundant in nature, non-toxic, easy to handle and eco-friendly, lesser reaction time, toxic compounds can be effectively degraded and can be integrated with normal treatment units. The major drawback with this method is a large amount of sludge produced in the form of iron hydroxide, acidic pH range increases the operation and maintenance cost. At higher pH Fe$^{3+}$ is converted to Fe$^{2+}$, leading to the formation of complexes with hydroxyl, $H_2O_2$ loses its oxidative power (53, 59).

**(VI) Advantages & Disadvantages of AOP**

The advantages of AOP are briefed below:

1. AOPs are the complete destructive process.
2. Economically viable.
4. Lesser Carbon footprint.
5. Likely to decrease toxicity.
6. Complete mineralization of toxic organics pollutant.
7. Inhibits the generation of toxic residues.
8. Mild operating temperature and pressure.
9. No expensive oxidants needed.
10. AOPs also have disinfection capabilities.
11. It does not concentrate the waste for further treatment.
12. Does not produce materials where further treatment is not required for ex. for activated carbon absorption "spent carbon" needs to be treated.
13. Sludge is not generated as in the case of physical-chemical process or biological processes (wasted biological sludge).

Disadvantages of AOP:

1. Capital investment.
2. Primary treatment is essential to obtain maximum efficiency.
3. Specific application requires a complex chemistry.
4. Wastewater treatment requires quenching of excess peroxide.
5. Generation of oxidation by-products.
6. Radical scavenging by interfering compounds can reduce the effectiveness and also the efficiency of the process.

**g. Application of nanomaterials for AOP**

Photocatalyst is the solids, which can accelerate reactions in the presence of light without being consumed in the reaction. Photocatalysis is the excitation of a semiconductor under the photon sources (light sources). Under light irradiation, a semiconductor material excited by a photon creates an electron in the valence band and a hole in the conduction
band. These charge carriers carry out the oxidation and reduction reaction which occurs on the surface of the semiconductor \((51)\). The valence band and conduction band of a semiconductor must be arranged in specific way such that the hydroxyl radical oxidation potential and superoxide reduction potential should lie within the band gap. Photocatalytic oxidation provides a method for treating the assorted toxic and hazardous compounds present in water and wastewater. The photocatalytic process of a semiconductor is economical, environmentally friendly and viable treatment choice in environmental remediation. The semiconductor materials, which are commonly used, are \(\text{TiO}_2\), \(\text{WO}_3\), \(\text{ZnO}, \text{CdS}, \text{SrTiO}_3, \text{ZnS}, \text{SnO}_2, \text{Fe}_2\text{O}_3, \text{WSe}_2\), etc. Some of the photocatalysts such as \(\text{CdS}, \text{CdSe}\) and \(\text{PbS}\) does not exhibit long-term stability in the aqueous media as they undergo photoanodic corrosion. More research that is extensive is being carried out towards the development of metal oxide nanostructures as they are currently being used in optoelectronic devices, medicines, sensors etc., Semiconductor material prepared with particles of diameter less than 100nm are called as semiconductor nanomaterial. Crafting of the bulk material to nano-scale adds an advantage of an increment in the surface to volume ratio and also decrease the diffusion path length \((65)\). With the reduction to nano level in the size of materials convey the properties that are entirely disparate from the crystalline or bulk form, in addition, these nanoparticles exhibit the behavior of an isolated atom or molecule. In comparison with bulk, nanoparticles have lesser size with high surface/volume ratio. Reduction in the size of particles leads to the accumulation of atom on the surface of nanomaterial, which makes the nanomaterial highly reactive. Thus semiconducting metal oxide is more effective as they have to ability to produce charge carriers by simulating an amount of energy and they find application in environmental remediation as well as in the electronics field. When compared with other semiconductor photocatalyst nanomaterial has a preeminent property of biological inertness, photo-stability, cost-effective, surface area, quantum confinement consequence, low-cost production, high porosity, permeability, etc\((66)\).

\((\text{I})\) **Titanium dioxide**

Titanium is the ninth most sufficient stable element in the earth’s crust. It is one of the lightest metals that possesses an excellent mechanical and thermal property. Numerous investigations have revealed that titanium dioxide nanoparticles are much more effective than in bulk powder, as a photocatalyst. Titanium dioxide nanoparticles are more transparent and cling to their active UV absorption characteristics. It appears in three crystalline forms: anatase, brookite and rutile, Anatase and rutile forms are best suited for the photocatalytic process while anatase having higher efficiency as a photocatalyst as it has large negative conduction band edge potency or higher potential energy of photogenerated electron. Titanium dioxide is a promising catalyst with a wide number of advantages such as long-term stability, non-toxic, economical, photostable. In the presence of light, the electrons that are present in the valence band get excited to the higher level of conduction band producing a hole in the conduction band. These electrons and hole present on the particle surface react with the organic compound with suitable redox potentials or they can also recombine. The band-gap energy of anatase is 3.2 eV and for rutile and brookite it is 3.02 and 2.96 eV respectively. The outstanding application of \(\text{TiO}_2\) is strained by the broad band-gap energy and a fast rate of charge carriers and hole recombination. One of the major limitations of \(\text{TiO}_2\) is that its band-gap lies in the UV range of the electromagnetic spectrum. Hence, UV light can initiate the photocatalytic process by the creation of electron-hole pair. However, the solar spectrum consists of only 3 – 5% of UV light \((67–69)\). Hence, an extensive research is being carried out to change the \(\text{TiO}_2\) optical response from UV to the visible light region. Diversified studies are being carried out to decrease the band-gap energy and transfer the absorption to the visible light spectrum.
Extensive experiments have been carried out to extend the photoresponse and photoactivity of TiO$_2$ namely doping, synthesis of composite nanomaterials, surface modification, noble and non-noble metal deposition, etc. In order to improve the photocatalytic activity of TiO$_2$ doping with an sufficient amount of transition metal oxide is also been investigated. Recently doping with non-metal elements such as N, C, F, B, and S is been proved to be an effective method to increase photocatalytic activity in visible spectrum due to the decrease in the band-gap and redshift of the photocatalyst (69–75). In the present research work nitrogen-doped TiO$_2$, titanium nano composite and hydrothermally synthesized TiO$_2$ is studied for the complete oxidation of volatile organic compounds.

(II) Zinc oxide

Zinc oxide with the formula ZnO is an inorganic compound usually insoluble in water. The zinc oxide belongs to a group II-VI semiconductor or an n-type semiconductor material with broad band-gap energy of 3.37 eV, with the bond energy of 60 meV and possesses high mechanical and thermal stability. The semiconductor ZnO has a number of advantages such as larger surface area, high photocatalytic activity, induce reactive oxygen species, high chemical stability, the broad range of absorption, less toxic, antibacterial, and environment friendly. Electrical, optical and chemical property of ZnO semiconductor can be tuned when prepared in the nanometer size. Zinc oxide is available in one dimensional (1D), two dimensional (2D), and three dimensional (3D) structures. Three crystalline form of ZnO is hexagonal wurtzite, cubic zincblende, and cubic rocksalt among them the stable form is wurtzite at room temperature. For efficient UV emission, crystalline ZnO nanostructure is very much essential. Hence it is imperative to prepare fine ZnO structures with the near UV band edge emission for ZnO. ZnO has been recommended as an alternative photocatalyst to TiO$_2$ though the band gap energy is same as titanium, is that it has larger efficiency for absorption for an immense fraction of the solar spectrum at an ambient condition when compared to TiO$_2$. The preparation cost of ZnO is 75% lesser than TiO$_2$ (76). With the existence of the solar light, the ZnO is photoinduced with a photonic energy which excites the electron from the valence band to the conduction band, generating an empty hole in the valence band. This electron-hole pair migrates to the surface and they are involved in continuous oxidation and reduction reaction. ZnO is activated only by the UV light of wavelength less than 385 nm. In the solar spectrum the UV light is less than 5%, therefore, it is difficult to obtain symbolic photodegradation by nanomaterial during commercialization (77). The main restraint with ZnO is the brisk rate of electron-hole pair recombination, thereby reducing the rate of photodegradation. Efficient utilization of solar energy is dependent on optical absorption capability of ZnO and is correlated with the huge band gap energy. Hence profound exercises has been carried out to increase the optical property and reduce the band gap energy of ZnO and suppressing the rate of photogenerated electron and hole pair recombination (78–80). Dopants are important during the synthesis of nanomaterial. Microscopic dopants are imported into the crystal lattice of the semiconductor. Transition metal doping to ZnO nanomaterial activates more mismatch and defects in the crystal structure of ZnO. In the present research metal doped ZnO have been prepared and studied for the photodegradation activity of the photocatalyst.

(III) Composite materials

One of the important ways to enhance and improve the properties of nanomaterial is the development of composite nanomaterials. Composite materials are the one where materials are combined with the objective of obtaining more desirable combinations of properties. The properties of the composites are essentially the properties of constituent phases, the geometry of dispersed phase and their relative quantity. The composite
nanomaterials differ when compared to the conventional composite material with high surface to volume ratio. Composite nanomaterial has currently been used in biomedical, fuel cell, microfabrication, capacitor, catalytic, separation. Composite nanomaterials are complex of nanophase materials which optimise the performance of traditional nanomaterials (81). Photocatalytic performance of TiO$_2$ and ZnO can be increased by combining with other nanomaterials to accomplish visible light activation and also enhance the adsorption capacity. Research is being carried out to synthesize composite nanomaterials of TiO$_2$ and ZnO. The composite nanomaterial property depends both on the property of the individual parent material, morphology, and interfacial characteristics. Generally, composite nanomaterial is prepared by using nanoparticles which act as a building block and clay, polymer or carbon and sometimes even combinations of these materials are used. Nano-composite possesses exceptionally high surface to volume ratio that completely changes the individual properties and the pattern in which nanoparticles are bonded to the bulk material. This results in the formation of a nanocomposite, which is many a time better when compared to individual particle. (82–84)

(IV) Drawbacks in an application of nanomaterials in AOP

Although the use of nanomaterials in AOP has proved to be efficient in the abatement of a persistent organic compound, there is still room to improve. The rate of degradation or oxidation depends mainly on the hydroxyl radical generation and ion regeneration. In recent years, experiments have been conducted to increase the rate of hydroxyl radical generation. Semiconductor photocatalyst used in the AOP are either suspended or immobilized on a support media. The advantages of the suspended photocatalyst in the medium are the efficient mass transfer of a substrate from the effluent to the active surface sites of photocatalyst which provides a better stage both for adsorption and desorption of the pollutants in the medium and low pressure drop. The drawback of a slurry type reactor, where the photocatalyst nanomaterials are suspended in the reactor is the difficulty in the recovery of the photocatalyst. A separate additional step has to be designed to recover the photocatalyst, which adds up to the economy of the process. In order to reimburse the cost photocatalyst that employs solar radiation have to be developed as a more economic process that can be carried out without the use of an artificial and usually expensive irradiation source. Extensive research has been carried out to fabricate the photocatalyst to increase the efficiency and also to reduce the operation cost (80). Hence, there is a need to select appropriate photocatalyst fabrication method to get the desired size and dimension of nanomaterial depending on the application and effective at solar radiation or visible light spectrum and with a ease to scale up at a larger level. TiO$_2$ and ZnO nanomaterials use is still constrained by a broad band-gap energy and swift recombination rate of electron carrier and hole. Recent research consideration is mainly concentrated to improve the catalytic performance of TiO$_2$ and ZnO by the modification of surface through doping with metal ions oxide or metal cations. A comprehensive study has been carried out by my researchers to develop more efficient and economical photocatalyst for the treatment of wastewater. Hence, there is a need to develop an appropriate synthesis procedure for nanomaterial with proper doping to reduce the band gap energy and activate the photon generation (69,85–88).

h. Nanomaterial preparation methods

Intense research has been carried out to develop novel nanomaterials with improved properties, lower preparation cost and increase surface to volume ratio. Many physical and chemical methods of preparation have been developed mainly to reinforce the performance of nanomaterials with the objective of good control over the particle size, size distribution,
morphology, quantity and quality improvement by applying economic and environmentally friendly process is always a challenge for many researchers. Currently, there are various methods that have been recommended for the synthesis of TiO$_2$ and ZnO nanomaterials particularly chemical vapour condensation, micro emulsion, hydrothermal, sonochemical, sol-gel, solvothermal, facile hydrothermal method, laser pyrolysis, spray pyrolysis, precipitation, thermal evaporation, arc discharge, ball milling, etc. The properties of metal nanoparticle mainly depend on the synthesis procedure. As nanomaterial exhibit different physical and chemical properties which rely not only on morphological, synthesis method but also on the physical and chemical properties which is in need to be explored. The preparation of nanomaterial mainly depends on the application of the synthesized nanomaterial. Each preparation method stated above has few limitations, which needed to be addressed. The preferred synthesis method is an important factor in determining the performance of the synthesized nanomaterial. Therefore, one of the major objectives of the research is to synthesize nanomaterial in a most practical form (89–92).

(I) Hydrothermal and solvothermal method

Hydrothermal method of synthesis is generally carried out in a steel pressure vessel known as autoclaves with the reaction in an aqueous medium and carried out at a controlled temperature and pressure in the presence or absence of Teflon liners. The temperature rises above the water boiling point to reach the saturation of the vapor pressure. The internal pressure is determined by the temperature and the amount of aqueous solution present in the autoclave. The reaction is very sensitive to the experimental factors such as pH, temperature and reaction time or duration. Nanoparticles, nano-tubes, and nano-rods can be synthesized using this technique. A hydrothermal technique is an environmentally friendly technology carried out at low temperature and reaction in a closed system in aqueous solution where water is the reaction medium. The advantages of this technique are low energy requirement, high reactivity, simple equipment during preparation, easy to control the particle size, simple process, low reaction temperature, economical and nonpolluting sources (91,93–96). Solvothermal method is similar to the hydrothermal process except water other aqueous solvents are used in the process. The method is skill route for the preparation of different nanomaterials with a cramped size distribution. The method is usually employed when organic solvents of high boiling point are used in the preparation procedure. Solvothermal method regularly has a control over the size of the particles, shape distribution and crystallinity of the nanomaterials. This method is usually employed to synthesize TiO$_2$ nanotubes, nanorods.

(II) Sol-gel method (Soft-chemical)

This is a well-established technique for the preparation of various sizes of nanomaterials. The sol-gel method is a wet chemical technique of synthesis of nanomaterials. The principle of sol-gel is the chemical transformation to a gel state of a liquid followed by post-treatment and conversion into solid oxide material. In a sol-gel process, a formation of sol by the hydrolysis and polymerization reaction takes place with the precursors. Inorganic metal salts or metal organic compounds are generally used as precursors in the sol-gel technique. In sol-gel, the method there is four mechanisms involved. In the first step hydrolysis, the [OR] group is replaced by [OH-] group. This process can be accelerated by the addition of HCl and NH$_3$. In the second process, polymerization occurs due to the condensation reaction resulting in the formation of monomer, dimer. These molecules aggregate together to form a gel in the third step. The advantages of the process are lower temperature, effective control of size, shape, and properties, uniform
nanostructure, good homogeneity. The method allows molecular scale mixing, high purity of the precursors (97, 98)

i. Need for the Study

The traditional methods used for VOCs treatment such as adsorption on activated charcoal, bio-filtration and normal treatment methods are challenged by many factors such as energy requirements, expenses for scaling up large-scale applications, inefficient to degrade most of these organic compounds, generation of toxic organic by-products, reusability problem, generation of waste and waste disposal problem (99). Hence, for their complete removal from water or wastewater, a newer method needs to be developed. Carbon adsorption requires a large capital investment, maintenance costs and is not as effective as it determines the generation of solid sludge that must be removed. Most of these compounds proved to be resistant to biodegradation. Biological treatment is ineffective in most cases for the treatment of wastewater due to the toxicity of the chemicals. Therefore, this method is not preferred for wastewater treatment. Combustion using thermal or catalytic requires very high temperature for operation so more energy is needed. Absorption and condensation methods are employed only for the treatment of very low concentration of VOCs and they transfer the pollutant from one phase to another (100–102).

Recently, research focuses on the development of new technologies for the safe destruction of pollutants. It is believed that the oxidative degradation of organic pollutants in water with the help of hydroxyl radicals (OH-) is an efficient technique that can be used for the detoxification of water pollutants. Therefore, the reactions that generate OH- in the state of the solution at room temperature have gained great attention and such techniques are generally referred to as advanced oxidation processes (AOP). The AOP is highly effective in the treatment of industrial wastewater that not only increases the degradation rate but also without the production of secondary pollutants.

j. Direction of this work and thesis framework

The treatment methods employed for the removal of VOCs have a number of limitations and disadvantages as mentioned above. Photocatalysis is one of the methods of AOP that has been used widely for the pollutant treatment of water and wastewater. Numerous researchers have been carried out for the removal of pollutants from the environment viz water, wastewater and soil using heterogeneous photocatalysis. The VOC treatment systems are developed depending on the heterogeneous photocatalysis which is an area of great technical importance. The construction of nanomaterials has attracted interest because of the use of the nanomaterial for the photocatalysis. TiO2 and ZnO is a material of interest as a photocatalyst or the environmental purification. TiO2 and ZnO are extensively used as a photocatalyst because they are biologically and chemically inert, safe, economical and strong oxidizing power under light irradiation, high photostability and multifunctional material (78, 103–105). The photocatalytic activity of a semiconductor photocatalyst is guided by many factors such as semiconductor stability under illumination, the photocatalytic process efficiency and the wavelength of interest. Research is being carried out in heterogeneous photocatalysis for the development of a method, which is capable of utilizing natural sunlight for the degradation organic and inorganic pollutants present in water and wastewater. In the present research work, sol-gel and hydrothermal techniques were adopted to prepare novel photocatalytic materials for potential degradation of selected VOCs. Sol-gel is a wet chemical technique that utilizes a chemical solution or colloidal particles to synthesize the nanomaterial. The Sol-gel technique is effective because it is economical processing, energy efficiency, simple, high production rate and rapid productivity of homogeneous fine material. Hydrothermal soft chemical method of synthesis is carried out in autoclaves or steel pressure vessels with a controlled temperature and
pressure and the reaction in alkaline solution (106,107). The soft hydrothermal chemical synthesis method is carried out in an autoclave at controlled temperature and pressure with the reaction in an alkaline solution (105,106). The hydrothermal method is one of the best methods of synthesis for its advantages such as simplicity, economy, environmental harmlessness, lower energy consumption, mild reaction conditions, simple equipment, dimensions of crystalline and controlled particles (78,107,108). The most important limits of the photocatalytic process are the low efficiency under visible light (300 nm < \lambda < 600 nm). These limitations have really gained concerned in recent years. Research is being carried out to modify the optical and electronic properties of these metal oxides. Visible light activation can be introduced in TiO\textsubscript{2} and ZnO by doping with metals and non-metals or introducing co-catalysts into the core system. Doping the photocatalyst semiconductor with transition metals lead to an increased efficiency of the photocatalytic system. The main aim of doping is to decrease the band-gap energy or introduction of intra band-gap state, that results in adequate visible light absorption. The dopant ions can be adsorbed on the catalyst or on the semiconductor can be incorporated into the crystalline TiO\textsubscript{2} system or can form separate oxide phases. Doping agents can act as trap holes for electrons and can mediate the transfer of interfacial load. In the present research, TiO\textsubscript{2} was doped with nitrogen and ZnO is doped with Ag, Pb and Cd (108) under sol-gel techniques. The size of the nanoparticles, size distribution, morphological features, bandgap energy, shape and phase of the nanomaterial, functional groups requires a sophisticated characterization of the nanomaterial. A complete characterization of the prepared photocatalyst defines its possibility of use in large-scale applications. The main challenge is to design an efficient and effective photocatalytic reactor for the degradation of volatile organic compounds using potential nanomaterials.

k. Objectives of the research work

1. To novel synthesis of potential nanomaterials (architecture TiO\textsubscript{2} and ZnO nanoparticles) by adopting sol-gel and soft chemical methods
2. To characterize as-synthesized nanomaterials using analytical techniques such as UV-Vis spectroscopy, Powder XRD, FTIR, SEM, EDS, BET, DLS etc.,
3. To apply the nanomaterials for photocatalytic degradation of selected volatile organic compounds (VOCs) in aqueous media
4. To compare the photo-degradation efficiency with adsorption technique for the removal of VOCs
5. To design and demonstration of bench-scale photoreactor for photocatalytic degradation of VOCs using potential nanomaterials