CHAPTER 1 INTRODUCTION

1.1. GENERAL INTRODUCTION

This chapter covers a detailed outline of Volatile Organic Compounds (VOCs) and their impact on the environment, various treatment methods available & their disadvantages, outline of nanomaterials and their application in the degradation of VOCs. A brief survey of literature on various nanomaterials and support systems that can be used in VOC treatment is given. Towards the end of the chapter the research objectives of the thesis are defined.

1.1.1. Volatile Organic Compounds

Volatile Organic Compounds (VOCs) are organic compounds which have very high vapour pressure. Due to the high vapour pressure, they can readily evaporate or sublime even at low temperatures. Because of their very high vapour pressure they are capable of vaporizing even at normal atmospheric conditions, thereby they are easily miscible with atmospheric air and also in various water bodies, contaminating and affecting the whole ecosystem. VOCs are the major contaminants of the environment as they can cause various physiological and psychological disorders to living organisms especially humans and most of them are potential carcinogens. It is also reported that prolonged exposure to VOCs may cause many psychological disorders like depression, sick building syndrome etc. Increase in the atmospheric VOCs content also has an adverse effect on the environment as they lead to depletion of stratospheric ozone depletion, act as green house gases, smog formation etc. [1-2]. Over the past few decades, the emission of these VOCs is increasing exponentially because of the massive combustion of fossil fuels, production of synthetic dyes, pesticides, paints, thinners etc [3-5]. Due to their high miscibility, chemical stability
and high solubility many extremely harmful volatile reagents (VOCs) are being used by many industries since the early 1900s. Widespread emission of these VOCs into atmosphere via leakage from storage, accidental spills, natural calamities, leakage during transportation, inappropriate discharge methods, etc is reported all over the world.

Many of the VOCs like halogenated hydrocarbons; dyes etc. are dense non-aqueous phase liquids that form very stable suspensions with water. These VOCs are released into the environment by a number of industries in large quantities on a regular basis contaminating the soil and ground water. Many industries dilute these VOCs and release them instead of treating them. Cleaning-up these VOCs from contaminated soil and ground water is a challenging task, as these VOCs are very stable and very hard to separate.

1.1.2. Conventional treatment methods

Gradual accumulation of these VOCs in the environment poses a great threat to the ecosystem as they are very stable, non-biodegradable; affect the chemical oxygen demand (COD), highly toxic etc [6-7]. Many VOCs are benzene derivatives and are highly stable in almost all media. Conventional physio-chemical treatment methods such as adsorption [8-10], coagulation [11, 12], ion flotation [13], sedimentation [14], ozonation [15], UV photolytic technique [16-20], biodegradation [21, 22], etc. are being used for the past few decades, but their efficiencies are limited by various factors. This leads to a constant drive to develop efficient methods of degrading volatile organic compounds into small chain alkanes. But, the conventional methods mentioned above are extremely expensive or require high temperature or pressure or prolonged reaction times and the life time of the treatment materials are phenomenally small.

It is not possible to treat all the contaminants that are of different chemical nature by a single method. Moreover, many of these methods can only break bigger molecules into smaller molecules which can be much more harmful. In adsorption method the
contaminants are treated by adsorbing them on the materials like activated charcoal [2]. Adsorption is a surface driven phenomenon where the rate of adsorption is defined by the number of active sites available; due to this finding the life time of the adsorption material is very difficult. Methods like ion flotation, sedimentation etc are considerably effective in separating solutes from water, but these processes are very slow and take relatively longer time compared to adsorption. In ozonation, contaminants are treated with ozone gas in closed containers where the contaminants are oxidized vigorously forcing them to break down into small chain compounds. But, it a very expensive process as it requires extreme care to generate, store and transport ozone gas as it is extremely reactive and can be hazardous even at low concentrations.

UV photolytic process is a rapid process where organic molecules are degraded using UV radiation. But, it is an expensive procedure requiring power and is also risky as UV radiation is harmful to humans. Biodegradation is a very safe procedure involving degradation of contaminants using a wide range of microorganisms [22]. Biodegradation is a very slow process as it is a natural process and the process is very sensitive to factors like pH, temperature etc. Due to this there is a necessity for highly efficient treatment materials.

1.1.3. Nanomaterials

Nanotechnology is the engineering, manipulation or designing functional systems on the atomic or molecular scale. This branch deals majorly with the quantum mechanical effects of matter, where the properties of the matter change with change in size. Quantum effects of the matter become significant when the size of the matter is below 100 nanometres, typically called ‘Quantum realm’. Working at quantum-realm size has potential applications in broad fields of research like surface science, molecular biology, chemistry, catalysis, semiconductor physics, microfabrication etc.

Nanomaterials have attained a huge attention in the recent years and the term ‘nanoscale science and technology’ is attributed to development of methods that has
the ability to manipulate matter atom by atom [23, 24]. Due to their distinctive physical and chemical properties, these nanomaterials are found to have promising applications in design and development of catalytic, mechanical, optical, electronic and diagnostic devices with enhanced activities [25-30]. Due to their huge surface to volume ratio, nanomaterials exhibit quantum size effect [31]. As the size of the particle decreases, the surface atoms have a much stronger tendency to interact or react with the neighbouring atoms to attain surface stabilization [32].

Tailoring the characteristics of materials by controlling the size of the particles has been of great interest for material science. The change in characteristics of nanomaterials from their bulk counter-parts can be attributed to two major effects. Firstly, the number of surface atoms is in a large fraction compared to the total atoms. Surface atoms have a distinctive contribution to the total free energy, thermodynamic properties, surface Plasmon resonance etc [33]. Secondly, the intrinsic properties of the nanomaterials exhibit quantum size effects [34, 35]. When the size of the material falls below 100 nm, electronic and optical properties exhibit variation by a great extent [36, 37].

1.1.4. Porous Support systems

One of the major challenges faced in using nanomaterials for degradation of organic contaminants in water and air is, providing a base for the reaction to take place. Recovery of the nanomaterials used from the treated mixture (water or air) upon completion of the treatment is also very important. Porous support systems which are inert to nanomaterials and can adsorb various contaminants without any reactions are required for successful implementation of nanomaterials in environmental remediation.

The most suitable support system is polymer or ceramic based membranes. Membrane technology has been an area of interest over the past century. Ever since Loeb-Sourirajan published their method of membrane fabrication, there has been a lot of research going on in membrane fabrication and development [38]. There have
been a number of membrane systems developed and are classified into three types namely isotropic, anisotropic and solid membranes.

Isotropic membranes are further divided into sub groups based on the nature of the membranes namely microporous membranes, nonporous/dense membranes and electrically charged membranes. Microporous membranes usually have uniformly distributed pores, with pore diameters ranging from 0.001 to 10 μm all over the membrane. Nonporous/dense membranes are dense nonporous films which usually diffuse matter by a pressure, concentration or electrical potential gradient. Electrically charged membranes can be microporous or nonporous or dense membranes that carry fixed positive or negative charge predominantly throughout the membrane.

Anisotropic membranes polymer based membranes that are mechanically strong defect free films with varying pore diameters. Anisotropic membranes usually are composite films comprising of a thin functional surface layer that is supported by a thick, porous and strong substrate.

Solid membranes are a special class of porous membranes that are made of non conventional materials. Instead of the conventional polymers, clay or ceramic or metal/metal oxides are used for the fabrication of these solid membranes. Solid membranes have a distinctive advantage over other membranes for their enhanced mechanical strength and rigidity. These membranes are more suitable for sustaining pressure.

1.2. BRIEF SURVEY OF EARLIER WORK

Generally, chemical degradation of VOCs at room temperature can be achieved by different reaction pathways: (i) reduction (ii) oxidation or (iii) photocatalysis. Each pathway is effective in degrading different variety of contaminants. Reduction pathway is an efficient method for degradation of contaminants like halogenated hydrocarbons. Oxidation pathway is an efficient method for degradation of
contaminants like alcohols, carbonyl compounds, hetero compounds etc. Photocatalytic degradation involves degradation of many organic contaminants like aromatic compounds, dyes, pesticides etc. which are affected by free radicals, by a series of reaction that consists of initiation, propagation and termination steps. Reductive and oxidative pathways are affected mostly by the reaction temperature, $p_H^+$ of the medium etc. Influence of such factors on photocatalytic degradation is considered to be negligible.

1.2.1. Catalytic Reduction

1.2.1.1. Development

Reduction pathway involves addition of an electron or addition of hydrogen to reactants or removal of oxygen from reactants. Catalytic reduction of halogenated hydrocarbons is also referred to as dehalogenation reaction. Over the past few decades, zero valent metals ($Fe^0$, $Zn^0$, $Sn^0$, $Mg^0$ etc.) have been extensively reported in the literature as effective catalysts for dehalogenation of many halogenated hydrocarbons at room temperature [39-45]. Zero valent iron (ZVI) has been reported to be a very efficient catalyst for the dehalogenation and also considered to be a cost effective and benign environmental impact [41, 43, 46-51]. Many researchers worked extensively on dechlorination of contaminants like dichloroethane (DCE), trichloroethylene (TCE), perchloroethylene (PCE), polychlorinated biphenyls (PCBs) etc. [46, 50]. Reductive dechlorination with ZVI can be described by the following reactions [52]:

$$C_xH_yCl_z + zH^+ + zFe^0 \rightarrow C_xH_{y+z} + zFe^{2+} + zCl^- \quad (1.1)$$

$$Fe^0 \rightarrow Fe^{2+} + 2e^- \quad (1.2)$$

$$RCl + 2e^- + H^+ \rightarrow RH + Cl^- \quad (1.3)$$

$$RCl + Fe^0 + H^+ \rightarrow Fe^{2+} + RH + Cl^- \quad (1.4)$$
Reductive degradation by ZVI is based on corrosion of iron involving direct electron transfer and is driven by the number of halogen atoms present. The presence of dissolved oxygen in water enhances the corrosion of iron. Reduction potential of iron is -0.44 V and hence can efficiently reduce halogenated hydrocarbons which have reduction potentials in the range of 0.5 V to 1.5 V [53, 54].

\[
2H_2O + Fe^0 \rightarrow Fe^{2+} + H_2 + 2OH^- \quad (1.5)
\]

\[
O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \quad (1.6)
\]

\[
O^2 + 2H_2O + 2Fe^0 \rightarrow 2Fe^{2+} + 4OH^- \quad (1.7)
\]

But, it is also known that the dehalogenation efficiency on iron decreases with decrease in the number of halogen atoms, because of the reduced thermodynamic driving force for electron transfer from iron [55]. As the rate of electron transfer reduces, the reductive activity of ZVI reduces resulting in incomplete reactions [56, 57]. It is reported that incomplete reactions result in toxic intermediate products such as vinyl chloride (VC) are often formed [58, 59]. It is also reported in literature that complete dechlorination of PCB by ZVI does not take place at room temperature [60].

Many researchers conducted series of experiments to study the mechanism of dehalogenation and proposed two different pathways (i) hydrogenolysis, involving replacement of halogen atoms with hydrogen and (ii) reductive β-elimination, involving removal of halogens resulting in multiple bonds [39, 44, 54, 61-63]. But, both the pathways proposed are based on transfer of two electrons from iron. But, because of its slow reaction rate, rapid corrosion of iron and loss of reactivity within short time period resulting in incomplete reactions makes ZVI not so suitable for treatment of contaminated water over a long span. The proposed reduction pathway of dehalogenation by ZVI is given in figure 1.1 [54]. The whole mechanism is based on transfer of electron from the metal surface to the organic moiety through the medium. This mechanism is highly affected by factors such as pH of the medium as
the $p^H$ increases the OH$^-$ ions in the medium try to make an ionic bond with the metal resulting in aggressive corrosion of the metal. So it is very essential to maintain the $p^H$ of medium in a natural level.

![Reduction pathway of dechlorination from dichloroethylene by ZVI](Image courtesy Roberts et al., 1996) [54]

Many studies have been conducted to enhance the ZVI’s reactivity and reports have been made that introduction of a secondary, catalytic metal, results in increased life time of iron [52, 64-68]. Bimetallic combination of iron with catalytic metal such as palladium (Pd), copper (Cu), nickel (Ni), zinc (Zn) etc enhances the activity of iron by changing the electronic properties of the surface [69-74]. The presence of the secondary metal brings novel catalytic properties that are absent in the monometallic particles [75, 76]. It is believed that the presence of the secondary metal alters the reduction pathway from electron transfer (ZVI system) to catalytic hydrodechlorination and thus greatly increases the reaction rate [77, 78]. Furthermore, the formation of chlorinated intermediates is inhibited in the bimetallic system.
1.2.1.2. Limitations in Application

Li et al., studied the degradation potential of ZVI nanoparticles in water contaminated with a mixture of chlorinated hydrocarbons comprising of trans-dichloroethene (t-DCE), cis-dichloroethene (c-DCE), tetrachloroethylene (PCE), trichloroethylene (TCE) [31]. Studies are carried out in laboratory by adding 5 g of ZVI nanoparticles per 1 L water sample. Over a span of 120 hrs a total degradation of 95 % is reported. It is also reported that the sedimentation, settling and aggregation ZVI nanoparticles in ground water as well as soil may pose a major challenge for implementation of ZVI nanoparticles in contaminant degradation.

Zhang et al., used ZVI nanoparticles for environmental remediation by injecting the nanoparticle slurry (suspension with particles in the size range 10 – 100 nm) into contaminated water and soil [53]. The nanoparticles are found to be reactive in the medium for time periods of 4 - 8 weeks and a maximum of 99% degradation of TCE is reported. The nanoparticles are found to be well dispersed in ground water over distances up to 20 m. But, no possible way of recollection of the nanoparticles is reported.

Welch et al., reported the application of ZVI nanoparticles in degradation of 2,4,6-Trinitrotoluene (TNT) [68], a major ground water contaminant in military bases, ordnance manufacturing industries and testing facilities. The studies were performed by adding 0.05 g of ZVI nanoparticles to 10 ml water sample containing 0.75% TNT. The reaction temperature was maintained at 22°C and pH of the sample at 6.7. The author reports 60.7 % degradation in a time span of 30 min. But, it is not certain on the implementation of the nanoparticles in water purification as no efforts towards recovery of the nanoparticles were reported.

Li et al., [31] reported that there is a change in the activation energy required for degradation for iron-palladium (Fe/Pd) bimetallic nanoparticles, which was calculated to be 31.1 KL/mole. Where as the activation energy required for ZVI
nanoparticles is 44.9 KJ/mole. From this observation it is noted that bimetallic systems act as better reductive catalysts compared to zero-valent metal nanoparticles.

Schrick et al., reported the application of high surface area nickel iron nanoparticles in dehalogenation of TCE [67]. The author reports synthesis of bimetallic nickel-iron nanoparticles by borohydride reduction route. Degradation studies involve addition of 0.1 g of bimetallic nanoparticles to 40 ml of water sample containing 24 ppm TCE. After the completion of 120 min (2 hrs) the author reported that the concentration of TCE is reduced to 6 ppb. The author proposed that the rate of degradation can be changed to an appropriate degree by supporting or encapsulating the nanoparticles.

Zhang et al., reported the application of bimetallic palladium-iron (Pd/Fe) for catalytic dechlorination of 2,4-dichlorophenol (DCP) in presence of humic acid [69]. Pd/Fe nanoparticles were prepared by adding potassium hexachloropalladate to solution containing ZVI nanoparticles and reducing using borohydride. Degradation studies were performed by adding freshly prepared Pd/Fe nanoparticles to deoxygenated DI water containing DCP. The authors reported that humic acid acts as an inhibitor in the degradation reaction, accepting the electrons from the surface of the metals and acting as a reaction site for DCP to degrade. From this it is observed

1.2.2. Catalytic Oxidation

1.2.2.1. Development

Oxidative pathway involves removal of electron or addition of hydrogen from reactants or addition of oxygen to reactants. Treatment with ozone + hydrogen peroxide [79], Fenton's reaction [80, 81], etc. The main difference between oxidative and reductive processes is a complete reaction in the former leads to the formation of organic acids and CO₂, while the latter usually results in the formation of the hydrocarbon along with the parent compounds. Oxidative processes are usually based on the generation of free radicals as the oxidant (e.g. OH⁻ from Fenton’s
reaction). Among the different oxidants, radical is a non-selective oxidant with high potential energy. Oxidative process by free assisted radical reaction involves three pathways: (i) hydroxylation, involving substitution of hydrogen atoms by oxygen resulting in formation of multiple bonds (for eg. oxidation of alcohols into aldehydes), (ii) oxidation, involving removal of hydrogen or addition oxygen (for eg. Oxidation of alkanes into alkenes) and (iii) aromatic ring cleavage, reactions involving aromatic ring compounds cleavage into aliphatic compounds.

Catalytic oxidation using different oxidizing agents has been widely reported by many researchers. It has been reported that oxides of transition metal like chromium, iron, manganese, osmium, ruthenium, selenium, etc have proven to be good oxidizing agents [82]. But, many of these oxides are sensitive to the reaction conditions like pH, temperature, solvent etc. Potassium permanganate (KMnO₄), a very stable derivative of manganese, is an efficient oxidizing agent that is stable in both acidic as well as basic medium [83]. KMnO₄ is generally used in aqueous solution and by the end of the reaction manganese is reduced to Mn²⁺ or Mn⁴⁺ oxidation state from its initial Mn⁷⁺ oxidation state [84, 85]. But, as KMnO₄ is completely miscible in water, controlling rate of the reaction, recovering and regenerating the catalyst is not possible.

Manganese dioxide (MnO₂), a selective oxidizing agent is reported to have great efficiency in oxidation of specific organic compounds [86, 87]. Researchers have reported that the oxidation pathway is through radical intermediate; the reaction initiated by transfer of electron from the OH group in alcohol to manganese forming a co-ordination complex. Due to the transfer of electron manganese is reduced from Mn⁴⁺ state to Mn³⁺ state. Then Mn³⁺ is further reduced to Mn²⁺ state by transfer of another electron reducing manganese (IV) oxide MnO₂ to manganese (II) oxide MnO [88, 89]. The mechanism of alcohol oxidation by MnO₂ is shown in figure 1.2.
1.2.2.2. Limitations in Application

Lamaita et al., reported the application of $\beta$-MnO$_2$ in VOC abatement [86]. The catalytic activity was studied in oxidative degradation of ethanol. The author reported that there is an enhanced activity of the catalyst when the material is poorly crystalline. The author reported that the catalytic reaction is continued till ethanol is completely oxidized to CO$_2$, but $\beta$-MnO$_2$ is found to be reduced to MnO.

Sinha et al., reported the application of mesostructured manganese oxide/gold nanoparticle composites for extensive air purification. The authors reported that mesoporous $\gamma$-MnO$_2$ is capable of eliminating VOCs from ambient atmosphere [87]. The authors found and reported that mesoporous high surface-area $\gamma$-MnO$_2$ composite with gold nanoparticles efficiently eliminates a wide range of VOCs. Elimination of acetaldehyde is studied based on the rate of CO$_2$ formation. Under room temperature conditions the authors reported 18% CO$_2$ formation in a reaction given time of 1 hr. But, when the reaction temperature is raised to 60°C the CO$_2$ formation was also observed to raise up to 94%. But, it is highly tedious and expensive technique to implement in air purification as maintaining the reaction temperature at 60°C is not feasible.
Gemeay et al., reported the effect of polyaniline on the catalytic activity of $\beta$-MnO$_2$ [88]. The authors reported that the catalytic activity of $\beta$-MnO$_2$ is stable in the polyaniline/$\beta$-MnO$_2$ composite. But as the concentration of polyaniline is increased, there is an increase in the crystallinity and decrease in the thermal stability of the composite. At low concentrations polyaniline acts as the site of electron transfer, catalyzing the reaction.

Einaga et al., reported oxidation of benzene with ozone over supported manganese oxide [89]. Materials with high specific surface area such as alumina, silica, titania and zirconia were used as supports for manganese oxide. These supports with manganese oxides were studied for their catalytic conversion of benzene into carbon oxides reacting with ozone gas. The authors reported 67% carbon dioxide generation in a time span of 120 min (2 hrs) at 100°C. Though there is a potential application for manganese oxides supported with silica, the high temperatures that are required for the reaction makes it less feasible for practical implementation in air purification.

1.2.3. Photocatalysis

1.2.3.1. Development

In photocatalysis the mechanism of degradation involves the electrons in photocatalytic materials getting excited from valance band to conduction band. When the material absorbs photons having energy more than its band gap, there is formation of holes. The subsequent migration of electron towards the surface of the photocatalyst initiates redox reactions with the elements present in the surrounding environment in the presence of oxygen [90, 91]. The use of photosensitive semiconductor materials such as TiO$_2$, ZnO, CdS, ZnS etc. as a photocatalyst has been widely reported. In the mid 1900s there have been extensive studies towards developing photochemistry based on semiconductor materials [92-96].
Ever since Fujishima and Honda reported Photocatalytic splitting of water on TiO$_2$ electrodes [97], there has been a great interest in heterogeneous photocatalysis based on TiO$_2$. TiO$_2$ is considered efficient due to its high refractive index, thermal & chemical stability, exceptional optical & electronic properties and biocompatibility [98-101]. Due to this TiO$_2$ has been extensively used for its application in degradation of organic contaminants in water and air [102-103]. Studies reveal that the photocatalytic reaction of organic compounds such as benzene results in the formation of CO$_2$ and H$_2$O, via a series of oxidation reactions, which include formation of phenol derivatives and aromatic ring cleavage [104-109].

Photocatalysis in TiO$_2$ is initiated by generation of an electron-hole pair. When radiation with energy equal to or greater than the band gap of the material is absorbed, the material gets excited. Upon excitation, electrons in the valance band jumps into conductive band generation holes, the number of electron-hole pairs generated is based on the energy of the radiation absorbed. Upon the formation electron –hole pair, there are different pathways the electron transfer process takes place [110-116]. The electron-hole pair when comes into contact with chemical moieties that are in contact with the surface of TiO$_2$, there is electron transfer (donation/acceptation) based on the nature of the nature of the chemical moiety [117-119].

\[
\text{TiO}_2 \xrightleftharpoons{\text{hv}} \text{e}^- + \text{h}^+ \quad (1.8)
\]

\[
\text{TiO}_2 + \text{H}_2\text{O} \xrightleftharpoons{\text{hv}} \text{H}^+ + \text{OH}^- + (\text{e}^- + \text{h}^+) \quad (1.9)
\]

At the surface of TiO$_2$, there electrons will be donated to electron acceptor species like oxygen forming ion radicals, where as electrons will be accepted from electron donor species like hydroxides forming free radicals [120-122].

\[
\text{O}_2 + \text{e}^- \rightarrow \text{O}_2^- \quad (1.10)
\]

\[
\text{H}_2\text{O} + \text{h}^+ \rightarrow \text{OH}^- + \text{H}^+ \quad (1.11)
\]
\[
\text{OH}^- + h^+ \rightarrow \text{OH}^\cdot + e^- \quad (1.12)
\]

These reactions initiate a chain of reactions as long as there is a reactive species in contact with the surface of TiO$_2$ [123-125].

\[
\text{O}_2^\cdot - + H^+ \rightarrow \text{HO}_2^\cdot \quad (1.13)
\]

\[
\text{HO}_2^\cdot + \text{HO}_2^\cdot \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \quad (1.14)
\]

\[
\text{O}_2^\cdot - + \text{HO}_2^\cdot \rightarrow \text{O}_2 + \text{HO}_2^- \quad (1.15)
\]

\[
\text{HO}_2^- + H^+ \rightarrow \text{H}_2\text{O}_2 \quad (1.16)
\]

\[
\text{H}_3\text{O}_2 + \text{O}_2^- \rightarrow \text{HO}^\cdot + \text{HO}^- + \text{O}_2 \quad (1.17)
\]

\[
\text{H}_2\text{O}_2 + e^- \rightarrow \text{HO}^\cdot + \text{OH}^- \quad (1.18)
\]

The overall schematic mechanism of photoexcitation of TiO$_2$ is given in fig. 1.3.

Fig. 1.3: Schematic diagram of photo-excitation in TiO$_2$

Though TiO$_2$ is a very effective photocatalyst, due to the high band gap (~3.2 eV), it requires high energy UV radiation for the excitation of electrons. Hence many efforts
were made to improve the photocatalytic activity of TiO₂ towards visible light [126, 127]. To answer this limitation many researchers have come-up with many theories like synthesizing nanocrystalline TiO₂, TiO₂ with different crystalline phases & morphologies, mesoporous TiO₂, non-metal doped TiO₂, transition metal doped TiO₂, noble metal deposited TiO₂, etc. [128-136].

Extensive studies have been carried on doping TiO₂ with nitrogen using different wet-chemical methods like microemulsion, hydrothermal process etc involving organic compounds such as urea, hydrazine hydrate, thiourea etc as source of nitrogen [137, 138]. It was observed that doping TiO₂ with nitrogen resulted in a red shift in the absorption spectra of TiO₂ [137]. It has been reported that the absorption peak of TiO₂ shifted to the range of 397 to 404 nm [137-139].

Recent studies reveal that the introduction of transition metals or metal oxides into TiO₂ can reduce the band gap and thereby reduce the excitation energy of the material [134]. Initially introducing Platinum (Pt) [140-144] was widely studied; but it is an extremely expensive procedure involving utilization of high purity platinum precursors. Later introduction of other metals like Gold (Au), Silver (Ag), Iron (Fe), Chromium (Cr), Nickel (Ni) etc [145-150] has also been reported.

1.2.3.2. Limitations in Application

Hennezel et.al., reported the photocatalytic degradation of benzene and toluene using TiO₂ [104]. Degradation studies were performed on water samples contaminated with benzene and toluene by adding TiO₂ to the water in presence of UV light. The authors reported that the degradation pathway is by the formation of phenolic compounds due to the activity of OH radicals. The reaction is rapid but only in the presence of UV light. TiO₂ is found to be inactive in the absence of UV light.

Du et.al., reported the photocatalytic degradation of gaseous benzene using porous TiO₂ [125]. TiO₂ nanoparticles in the size range of 1 – 7 nm, with specific surface-area in the range of 159.4 – 265.4 m²/g were used for the study. The degradation
studies were performed in a hermetic stainless steel chamber with volume of 5 L with a UV lamp (wavelength ~365 nm) fixed in it. The authors reported 83% degradation of gaseous benzene in time span of 50 min.

Kozlova et al., reported the photocatalytic oxidation of dimethyl phosphonate using Pt/ TiO2 composite [144]. Pt/ TiO2 composite was prepared by impregnating H2PtCl6 onto TiO2 and then reducing to Pt using ammonia solution. Degradation studies were performed using gas phase samples in presence of a mild UV source (wavelength ~365 nm). The degradation efficiency was compared to that of TiO2 based on the CO2 generation. The authors reported an enhanced generation CO2 in the Pt/ TiO2 composite treated sample concluding that the photocatalytic activity in the composite is greater and is due to the introduction of Pt.

Tseng et al., reported the photocatalytic degradation of xylene vapours over nickel doped TiO2 [149]. TiO2 is doped with nickel (Ni) by refluxing nickel nitrate solution with commercially procured TiO2 nanoparticles. The degradation studies were performed in pyrex photo-reactors attached with a UV lamp (wavelength ~365 nm) with air samples mixed with known volume of xylene. The author reported an enhanced photocatalytic activity due to Ni dopant but no studies were performed in visible light.

1.2.4. Support systems

Membrane technology has been a major interest of research especially in separation and purification processes ever since the discovery of ‘osmosis’. Different types of membranes are being used by many industries based on the application such as microfiltration membranes (MF), ultrafiltration membranes (UF), osmosis membranes, reverse osmosis membranes (RO), nanofiltration membranes (NF), ion exchange membranes, gas separation membranes, pervaporation membranes, dialysis membranes etc. [151, 152]. The mechanism of transport in these membranes is either by sieving mechanism or by solution-diffusion mechanism [151].
Functionalized membranes for selective permeation or selective separation has been developed and being applied in various fields [153, 154]. Functionalized nanofiltration membranes for removal of heavy metals have been developed over the past few decades [155-157]. Recently reports have been made on metal and metal oxides immobilized membranes for selective separation [158-161].

Solid support systems coated with nanomaterials is also a field of interest for many researchers. Reports have been made on functionalizing various solid support systems such as silica, zeolites, activated carbon, metal oxides etc [162-165]. Alumina is found to be the most ideal choice for support because of its chemical inertness, adsorption capacity, thermal resistance and pressure tolerance.

1.3. MOTIVATION

Growing concerns of the VOCs and their impact on the environment, disadvantages of the conventional methods in removal of VOCs from contaminated bodies has attained a great interest in development of new methods for VOC treatment. Application of nanomaterials in VOC treatment has proven to be advantageous and from literature it is evident that certain nanomaterials and nanocomposite have been very efficient in VOC treatment. Efforts are made towards finding suitable support systems to immobilize nanoparticles and use them in treatment of contaminated water and air samples. So, the major challenges that are needed to be addressed are

i. Preparation of stable alloys and composites in nano meter size range that can be active catalysts under ambient temperature/pressure conditions.

ii. Finding composites that can tune the band gap of TiO$_2$ and bring its photo excitation energies into visible region.

iii. Fabricating suitable support systems for the nanomaterials so that the support system acts as an active site or a base platform for the reaction to occur.

iv. Find suitable methods for embedding the nanomaterials into support systems.
1.4. OBJECTIVES

From the literature survey it is found that, nanomaterials like iron-nickel bimetallic systems, manganese oxides, iron manganese composite oxides, titanium oxide and transition metal-titanium composite oxides have proven to be potential catalysts in degrading specific contaminants in water and air. The overall objectives of this thesis involves

- Synthesis of uniform sized, well defined catalytic nanoparticles such as iron nickel bimetals (Fe-Ni), iron manganese oxide composite (FMO), nickel titanium oxide composite (NTO) and copper titanium oxide composite (CTO).

- Characterization of these nanoparticles to study the crystalline structure, size, morphology and absorption properties.

- Fabrication of suitable support systems and immobilization of nanoparticles onto support systems

- Characterization of nanoparticle immobilized support systems to study the porosity of the support as well as the influence of both the nanoparticles and support systems on their characteristics.

- Testing the nanoparticle immobilized support systems for their VOC degradation efficiency.

Outline of the thesis is as follows

Chapter II: Synthesis and characterization techniques

In this chapter different types of synthesis methods and characterization techniques that were used for this research work are discussed. Highly sophisticated instrumentation techniques such as Atomic Force Microscopy (AFM), Field Emission Scanning Electron Microscopy (FE-SEM), Energy Dispersive Spectroscopy (EDS), X-ray Diffraction (XRD), Fourier Transform Infra Red
Spectroscopy (FTIR), UV-Visible spectroscopy (UV-Vis), Photoluminescence spectroscopy (PL), Transmission Electron Microscopy (TEM), BET Surface area analysis (BET) and Gas Chromatography Mass Spectroscopy (GCMS).

**Chapter III: Synthesis and Characterization of Nanocatalysts**

This chapter describes the synthesis and characterization of the nanocatalysts. Various synthesis techniques like mechanical alloying, simultaneous reduction, simultaneous oxidation, solvothermal are used to synthesize ZVI, Ni, Fe-Ni, MnO₂, FeO doped MnO₂ referred as FMO, TiO₂, NiO doped TiO₂ referred as NTO and Cu₂O doped TiO₂ referred as CTO nanocatalysts. The as synthesized nanoparticles are characterized using XRD, FESEM, HRTEM, AFM, BET, FTIR and PL and the results are discussed.

**Chapter IV: Fabrication and Characterization of Support Systems**

In this chapter, the necessity, importance, fabrication, working mechanism and characterization of support systems used are discussed. Two types of support systems, polymer membrane support as well as ceramic support (Clay based and alumina based) are fabricated and characterized to study their surface properties. Various techniques like dip coating, adding the nanoparticles during fabrication and in-situ immobilization are studied to immobilize the nanocatalysts onto the support.

**Chapter V: Catalytic Reductive and Oxidative Degradation**

This chapter is divided into two parts. Part one discusses the reductive degradation activity and its efficiency of the as synthesized Fe-Ni nanocatalyst immobilized on polymer membrane support against halogenated hydrocarbons such as trichloroethylene (TCE) and dichloroethane (DCE), which are chosen as probe compounds. The reduction activity of Fe-Ni nanoparticles is compared with that of ZVI nanoparticles. In addition to that, the change in catalytic activity of the nanoparticles with respect to the immobilization techniques is also discussed.
Part two discusses the oxidative degradation activity and efficiency of the as synthesized FMO nanocatalysts immobilized on ceramic support against alcohols such as ethanol and isopropanol, which are chosen as probe compounds. The catalytic activity of FMO nanoparticles is compared with that of MnO₂ nanoparticles.

Chapter VI: Photocatalytic Degradation

This chapter discusses the photocatalytic degradation activity and efficiency of the as synthesized NTO and CTO nanocatalysts immobilized on ceramic support against aromatic compounds such as benzene, toluene and chlorobenzene, which are chosen as probe compounds. The photocatalytic activity of NTO and CTO nanoparticles is compared with that of TiO₂ nanoparticles.

Chapter VII: Conclusions

This chapter reviews the research work carried out and its outcome. A brief scope of future work is also discussed.