CHAPTER 1
ORGANIC POLLUTANTS IN WATER AND THEIR REMOVAL

1.1 Introduction
Water is the most precious natural resource that exists on our planet as over 70% of the Earth’s surface is covered by water. When Neil Armstrong saw the Earth from the Moon, it appeared blue! This is because water covers more than two-thirds of the Earth’s surface. But fresh water represents less than 0.5% of the total water on Earth (Zacharia, 2004). Surface water is the resource for the provision of drinking water, irrigation water for agricultural activities, and process water for industrial activities. Every human activity affecting watershed components can have a strong impact on the surface water pollution. Water pollution occurs when water is adversely affected due to the addition of large amounts of materials to the water. The principal sources of water pollution are:

- Industrial discharge of chemical wastes and byproducts.
- Discharge of poorly treated or untreated sewage.
- Surface runoff containing pesticides.
- Surface runoff containing spilled petroleum products.
- Discharge of contaminated and/or heated water used for industrial processes
- Excess nutrients added by runoff containing detergents or fertilizers
- Acid rain caused by industrial discharge of sulfur dioxide (SEPA 2005).

The sources of water pollution are categorized as point sources and non-point sources of pollution. Point sources of pollution occur when the polluting substance is emitted directly into the waterway. A pipe spewing toxic chemicals directly into a river is an example. A non-point source occurs when there is runoff of pollutants into a waterway, for instance when fertilizer from an agricultural field is carried into a stream by surface runoff. The point sources include effluent outfalls from factories, refineries, and waste treatment plants, etc., that emit fluids of varying quality directly into water bodies. Non-point sources include contaminants that enter the water supply from soils/groundwater systems and from the atmosphere via rain water.
Wastewater from manufacturing or chemical processes in industries contributes to water pollution. Industrial wastewater usually contains specific and readily identifiable chemical compounds. During the last fifty years, the number of industries in India has grown rapidly. But water pollution is concentrated within a few sub-sectors, mainly in the form of toxic wastes and organic pollutants. Out of this a large portion can be traced to the processing industries.

The wastewater from various industries contains a high concentration of organic compounds. Many of these compounds, particularly the aromatic organic compounds are either carcinogenic or mutagenic in nature and they resist biological oxidation processes normally used by the industries for treating wastewater.

All toxins entering the environment can be regarded as environmental poisons. Certain pollutants can, acting over long periods, harm living organisms even in low concentrations. This means that pollutants that are stable and thus persistent have a great ability to act as environmental poisons. Their stability means not only that their effects are long-lasting, but also that they are dispersed over large areas before being broken. Many areas of surface water are now contaminated with heavy metals, POPs (persistent organic pollutants), and nutrients that have an adverse affect on health.

1.2 Organic pollutants in water

The source of organic matter in water is industrial effluents and domestic sewage. The organic matter is mainly responsible for depleting oxygen in the water column as it decomposes, stressing or suffocating aquatic life in the process.

Water contains aliphatic-, cycloaliphatic-, aromatic and polycyclic aromatic hydrocarbons. Small quantities of these compounds cause taste and odor problems in drinking water. Aromatic hydrocarbons, particularly the polyaromatic hydrocarbons (PAH) are generally carcinogenic in nature and have harmful health effects.

Many synthetic organic compounds can be found as trace contaminants in surface water. Even if they are present in very low concentration they can represent a long term hazard due to accumulation process either in food chain or in water sediment. Source of these organic compounds can be the agricultural activities (e.g. pesticide use), accidents (like spillage from oil pipeline) and the industrial discharges. Wastewater deriving from
chemical industries is the main source of surface water contamination with synthetic organic compounds, the type of pollution varying according to the type of processed material.

1.2.1 Natural Organic Matter

The decomposition of plant, animal and microbial material in soil and water produces a variety of complex organic molecules, collectively called natural organic matter. These compounds include carbohydrates, amino acids, proteins, fats and humic acids. Amino acids and proteins provide utility nitrogen for microorganisms in soil and water. Natural organic matter (NOM) occurs in all natural water sources and water high in NOM may be more costly to treat.

The variety of the components in NOM changes from water to water (seasonal changes, climate effects and drought) which leads to variation in the reactivity with chemical disinfectants such as chlorine, ozone and chlorine dioxide. Many of the disinfection by-products (DBPs) formed by the reaction of NOM with disinfectants, usually chlorine, are reported to be toxic, carcinogenic and mutagenic to humans if ingested over an extended period of time. Thus, natural organic matter creates problems in water disinfection and supply, requiring their removal to minimize color and odour in water, and also to prevent formation of potentially harmful chemical byproducts during chlorination. Through a process called "bio-fouling", natural organic matter is also a major culprit in degrading the performance of membrane filtration systems used for water purification and desalination.

Organic matter in groundwater plays important roles in controlling geochemical processes by acting as proton donors/acceptors and as pH buffers, by affecting the transport and degradation of pollutants, and by participating in mineral dissolution/precipitation reactions. Dissolved and particulate organic matter may also influence the availability of nutrients and serve as a carbon substrate for microbially mediated reactions. Numerous studies have recognized the importance of natural organic matter in the mobilization of hydrophobic organic species, viz., the metals (e.g. Pb, Cd, Cu, Zn, Hg, and Cr), and radionuclides (e.g. Pu, Am, U, and Co). Many contaminants that scientists view as virtually immobile in aqueous systems can interact with dissolved organic carbon or colloidal organic matter, resulting in migration of hydrophobic
chemicals far beyond distances predicted by structure/activity relationships. Although organic matter is often present in low concentrations in subsurface systems, this organic matter can exhibit significant reactivity with contaminants. In addition, these compounds are reactive substances that are potential precursors for the formation of disinfection by-products resulting from water treatment practices.

Organic matter in surface and groundwater is a diverse mixture of organic compounds ranging from macromolecules to low molecular weight compounds such as simple organic acids and short-chained hydrocarbons. Historically, organic matter in natural waters has been arbitrarily divided into dissolved (DOC) and particulate organic carbon (POC), based on filtration through a 0.45 μm filter. No natural cutoff exists between these two fractions and the distinction is arbitrary, based on the filtration of the sample. Overlapping the dissolved and particulate fractions is the colloidal fraction, which consists of suspended solids that are operationally considered solutes. Colloidal organic matter in natural waters is composed of living and senescent organisms, cellular exudates, and partially-to-extensively degraded detrital material, all of which may be associated with mineral phases. Generally, DOC is in greater abundance than POC, accounting for approximately 90% of the total organic carbon of most waters.

Microbial degradation of organic matter results in the formation of many of the compounds that comprise DOC, especially non-volatile organic acids that dominate the DOC in most aquatic environments. Many of these organic acids are considered refractory because the rates of subsequent biodegradation are slower than for other fractions or classes of organic matter. Organic matter derived from different source materials has distinctive chemical characteristics associated with those source materials. Organic matter derived from higher plants, for instance, has been found to have relatively large amounts of aromatic carbon, is high in phenolic content, and low in nitrogen content. Microbially-derived organic matter (from algae and bacteria), on the other hand, has greater nitrogen content, and low aromatic-C and phenolic content.

In ground water, there are 3 main natural sources of organic matter: organic matter deposits such as buried peat, kerogen and coal; soil and sediment organic matter; and organic matter present in waters infiltrating into the subsurface from rivers, lakes and marine systems. The relative contributions of these sources of organic matter varies between different water bodies, but there is presently no way to quantify this variation.
based on chemical characterization of the organic matter. Once in the system, microbial processes continue to slowly alter the structure and chemical reactivity of the organic matter.

A number of significant mechanisms can be responsible for the transport or retention of organic molecules in the subsurface. Once in the system, organic compounds, whether they can be anthropogenic or naturally derived, can be truly dissolved, associated with immobile particles or associated with mobile particles. Mobile particles include DOC, DOC-iron complexes and colloids. For an organic compound, each state is related to the other states through equilibrium partitioning and air/water exchange. The magnitude of the partitioning coefficients and the abundance of sorbents determine the mechanisms and enhancement of transport for a particular organic compound. Regardless of environment, chemical reactivity and speciation will be controlled by thermodynamics and reaction kinetics.

Organic particles in the water may harbor harmful bacteria and pathogens. Infection by the microorganisms may occur if the water is used for primary contact or as a raw drinking water source. Treated drinking water will not present the same health risks. In a potable drinking water plant, all organics should be removed from the water before distribution.

High organic inputs trigger deoxygenation. If excess organics are introduced to the system, there is potential for complete depletion of dissolved oxygen. Without oxygen, the entire aquatic community is threatened. The only organisms present will be air-breathing insects and anaerobic bacteria. If all oxygen is depleted, aerobic decomposition ceases and further organic breakdown is accomplished anaerobically. Anaerobic microbes obtain energy from oxygen bound to other molecules such as sulfate compounds. Thus, anoxic conditions result in the mobilization of many otherwise insoluble compounds.

Five-day Biochemical Oxygen Demand (BOD5) is defined as the amount of oxygen required by bacteria to decompose organic matter for a specified time (usually 5 days) under aerobic conditions. The amount of oxygen reported with this method represents only the carbonaceous oxygen demand (CBOD) or the easily decomposed organic matter. BOD5 is commonly used to measure natural organic pollution. Chemical Oxygen Demand (COD) is defined as the oxygen equivalent of the organic portion of
the sample that is susceptible to oxidation by a strong chemical oxidant. COD does not distinguish between refractory or "inert" organic matter.

1.2.2 Biodegradable organic matter

Biodegradable organic matter in water is broken down by the activity of microorganisms and the decomposition products enter into the biogeochemical cycles. They act as pollutants only when their quantity is large and they are not degraded at the right time. Examples of such pollutants are domestic waste products, urine and faecal matter, sewage, agricultural residue, paper, wood, cloth, etc.

Untreated or inadequately treated municipal sewage is a major source of biodegradable organic matter in surface and ground water in the developing and the under-developed countries where scientific treatment of sewage is almost absent. The biodegradable organic matter uses up substantial amounts of oxygen as the organics are being used by micro-organisms as food and in the process, upset the ecological balance of rivers and lakes.

1.2.3 Non-biodegradable Organic matter

Many aromatic hydrocarbons are both fat-soluble and persistent. If these compounds become halogenated (i.e. if their hydrogen atoms are replaced by chlorine, bromine or other halogens), their stability and their solubility in fat both tend to increase further. In some cases toxicity also increases. The majority of well-known persistent organic pollutants thus belong to the category of halogenated aromatic hydrocarbons (EPA, 2006). Chlorinated organic compounds are not natural.

Tap water contains halogenated organic compounds, polychlorinated biphenyls and chlorinated pesticides. These compounds are toxic to human health.

POPs or persistent organic pollutants represent the most harmful substances for the ecosystem and human health. These chemicals can accumulate in fish and cause serious damage to human health. Where pesticides are used on a large-scale, groundwater gets contaminated and this leads to the chemical contamination of drinking water.

The POPs are considered as hazardous because of four characteristics:
(i) they are toxic;
(ii) they are persistent, they resist normal processes that break down contaminants;
(iii) they accumulate in the body fat of people, marine mammals, and other animals
and are passed from mother to fetus; and
(iv) they can travel great distances with wind and water currents (Zacharia et al, 2004).

POPs have been linked to adverse effects on human health and animals, such as cancer,
damage to the nervous system, reproductive disorders, and disruption of the immune
system. Because they circulate globally via the atmosphere, oceans, and other pathways,
POPs released in one part of the world can travel to regions far from their source of
origin.

Another group of POPs is the pesticides, which were originally invented and used
effectively to better the human environment by controlling undesirable life forms such
as bacteria, pests, and foraging insects. Their effectiveness, however, has caused
considerable pollution. The persistent, or hard, pesticides, which are relatively inert and
non-degradable by chemical or biologic activity, are also bioaccumulative; that is, they
are retained within the body of the consuming organism and are concentrated with each
ensuing level of the biologic food chain.

Runoffs from farms, backyards, and golf courses contain pesticides such as DDT that
in turn contaminate the water. Leachates from landfill sites are another major
contaminating source. Their main effects on the ecosystem and health are endocrine and
reproductive damage in wildlife. Groundwater is susceptible to contamination, as
pesticides are mobile in the soil. It is a matter of concern as these chemicals are
persistent in the soil and water.

1.2.4 Water disinfection byproducts

Chlorine is added to the drinking water by municipal authorities to destroy disease-
causing bacteria. The following chlorination by-products are found in drinking water-
trihalomethanes (THM), chlorinated alkanes and alkenes, halogenated acetonitriles,
chlorophenols, chlorinated humic acids, aminoacids and benzoquinone. Of these, the
trihalomethanes are the most frequent chlorinated side products, deriving from methane,
where three hydrogen atoms are exchanged for three halogen atoms. Many trihalomethanes have mutagenic and carcinogenic effects.

1.3 Effects of Organic Pollutants

The effects of water pollution are not only devastating to people but also to animals, fish, and birds. Polluted water is unsuitable for drinking, recreation, agriculture, and industry. It diminishes the aesthetic quality of lakes and rivers. More seriously, contaminated water destroys aquatic life and reduces its reproductive ability. Eventually, it is a hazard to human health. Nobody can escape the effects of water pollution.

Toxicity of an organic pollutant is defined as its inherent ability to cause an adverse health effect, such as the ability to induce cancer, birth defects and other illnesses in animals and humans.

Among the many organic chemicals that exhibit acute toxicity are: polychlorinated and polybrominated biphenyls (PCBs and PBBs), a group of chemicals that are used in paints, electrical transformers, and insulators; and the pesticides aldicarb, paraquat, and DDT. Some of the acute effects from exposure to low doses of these compounds include diarrhea, nausea, respiratory distress, vomiting, convulsions, and blurred vision (ATSDR, 1999).

These and other POPs remain intact in the environment for long periods, become widely distributed geographically, and accumulate in the fatty tissue of living organisms and are toxic to humans and wildlife. The compounds circulate globally and can cause damage wherever they travel.

Chlorophenols with at least two chlorines either have been used directly as pesticides or converted into pesticides. Also, chlorophenols, especially 4-chlorophenol, have been used as antiseptics. In addition to being produced commercially, small amounts of some chlorophenols, especially the mono- and dichlorophenols, may be produced when waste water or drinking water is disinfected with chlorine, if certain contaminants are present in the raw water. They are also produced during the bleaching of wood pulp with chlorine when paper is being produced (ATSDR, 1999).
Chlorophenols can enter the environment while they are being made or used as pesticides. Most of the chlorophenols released into the environment go into water, with very little entering the air. Chlorophenols also rapidly enter the body through the skin. The monochlorophenols do not stay inside the body very long. They are changed to less harmful products, and most leave through the urine within 24 hours. The other chlorophenols (dichlorophenol, trichlorophenols, tetrachlorophenols), which also leave through the urine as less harmful chemicals, can stay in the body for several days.

Phenols can cause damage to the cells of the living organisms. It has been shown that a long-time intake of phenols by experimental animals leads to changes in the skin, lungs, liver, mucous membranes, oesophagus and in the kidneys (Bruce et al, 1987). As a result of phenol penetration through the man's skin, its darkening and weakening of the muscles are observed. Lethal doses cause structural and functional changes in the brain, necrosis of the liver, and emphysema (Roy et al, 1998). Poisoning caused by phenol compounds provoke such symptoms as headaches, dryness of the throat, dyspnoea, nausea, vomiting, diarrhoea, (Juhl et al, 2003). According to other reports phenols have cytotoxic effect on skeletal muscle and neurotoxic effect on piramidal neurones (Nikonorow, 1979). Phenol and its derivatives also show mutagenic effect by unbinding of the DNA helix, inhibition of DNA synthesis in the human cells, and induction of gene mutations.

The chlorinated phenols like 4-chlorophenol (4-CP), 2,4-dichlorophenol (2,4-DCP), etc., are found in waste effluents of iron and steel manufacturing industries, electrical component manufacturing units, photographic equipments, pharmaceuticals, pesticide industries, and paper and pulp manufacture (EPA, 1987). Other releases of 4-CP to water come from leather tanning and textile factories. Also, common pesticides such as lindane and hexachlorobenzene are metabolized to 4-CP by plants, animals and microorganisms. Some current research shows that 4-CP is carcinogenic in rodents, can induce chromosomal aberrations, and is associated with leukemia, malignant lymphoma and soft tissue sarcoma in humans (Exon, 1983). 4-CP is listed as hazardous for landfill disposal (Freedman et al., 1989).

2,4-dichlorophenol (2,4-DCP) has been reported to cause lethargy, tremors and convulsions in mice while workers who made pesticides or were exposed to chlorophenols developed acne and mild liver injuries (EPA, 2006). 2,4-dichlorophenol is
a key intermediate in the synthesis of chloride-based herbicides, such as 2,4-dichlorophenoxyacetic acid (2,4-D) and 2-(2,4-dichlorophenoxy) propionic acid (2,4-DP) (Mark, 1992). Not only the inhalation of dust containing 2,4-DCP can irritate the respiratory tract but the detrimental effects on kidneys, liver and blood-forming organs are known.

Physical, chemical and biological methods, including incineration, adsorption on activated carbon, chemical or enzymatic oxidation, solvent extraction, microbial degradation, incubation in the presence of microorganisms, etc., have been proposed for removing or degrading several chlorophenols from waste water (Debtaine 1996, Tong 1997, Polcaro 2001).

Factors affecting the toxicity of synthetic organic compound are molecular structure, water solubility, biodegradability, photodegradability and volatility. Halogen containing compound are considered as the most dangerous ones due to their persistence (resistance to biodegradation) and to their accumulation. Hazardousness of halogenated compounds seems to increase with the increase of the number of halogen atoms in the molecule.

Soluble chemicals are generally less dangerous than insoluble or fatty soluble substances as they scarcely accumulate in organisms, being removed by the regular turnover mechanisms. Also their accumulation in water sediments and on water particles is reduced. Biodegradable organic chemicals like detergents and surfactant show a low toxicity risk as they are decomposed by water microorganism and are therefore less susceptible to the accumulation process.

The EPA recommends that drinking water concentrations of 2-chlorophenol should not be more than 0.04 parts per million (ppm), and concentrations of 2,4-dichlorophenol should not be more than 0.02 ppm; these are levels that can be tested (EPA, 2006). In order for chlorophenols to be lower than levels that can be tested, the EPA recommends levels of 0.1 parts per billion (ppb; the amount of chlorophenols per billion parts of water) for monochlorophenols, 0.3 ppb for 2,4-dichlorophenols, and 1 ppb for 2,4,5-trichlorophenol and 2,3,4,6-tetrachlorophenol.

A wide range of adverse effects has been reported well documented human exposure to phenol by the dermal, oral or intravenous routes. Gastrointestinal irritation has been reported following ingestion. Local effects following dermal exposure range from
painless blanching or erythema to corrosion and deep necrosis. Systemic effects include cardiac dysrhythmias, metabolic acidosis, hyperventilation, respiratory distress, acute renal failure, renal damage, dark urine, methaemoglobinaemia, neurological effects (including convulsions), cardiovascular shock, coma and death. The lowest reported dose resulting in a human death was 4.8 g by ingestion; death occurred within 10 min. The potential for poisoning through inhalation of phenol vapours has long been recognized, but no cases of death following this route of exposure have been reported. Symptoms associated with inhalation of phenol included anorexia, weight loss, headache, vertigo, salivation and dark urine.

1.4 Techniques of removal

It is therefore very important to develop suitable techniques for treatment of water contaminated with the toxic and the persistent phenolic compounds. A few methods in use are described here.

1.4.1 Wet air oxidation (WAO)

Wet air oxidation (WAO) is the process of oxidizing organic matter in the presence of liquid water. Theoretically, any substance that is capable of burning can be wet oxidized in water.

Oxidation reactions take place in the aqueous environment where the water is an integral part of the reaction. Water provides a medium for the dissolved oxygen to react with the organics and can also react in part with the organics. It is theorized that the chemistry of wet oxidation involves free radical formation with oxygen derived radicals attacking the organic compounds and resulting in the formation of organic radicals (Teletzke 1966, Li 1991). Catalysts, such as homogeneous Cu$^{2+}$ and Fe$^{3+}$, their heterogeneous counterparts, or precious metal catalysts can be used to enhance the effectiveness of the WAO reaction. (Fortuny 1999, Ohta 1980, Maugans 1997, Sadana 1979).

It is an ideal process for pretreatment of wastes that are problematic to conventional biological facilities. The WAO process is suited to the oxidation of concentrated waste
liquors, slurries, and sludge's where the oxygen demanding organic matter is only a few percent of the predominantly water stream (Eletzke 1966).

Oxidation reactions take place in the aqueous environment where the water behaves much like a catalyst and is an integral part of the reaction. It is theorized that the chemistry of WAO involves free radical formation with the oxygen and/or water derived radicals attacking the organic compounds and encouraging the formation of organic radicals (Birchmeier 2000).

Wet oxidation processes can be carried out at conditions below or above the vapour-liquid critical point of water (374oC and 22.1 MPa). While a high temperature is required to attain a rapid rate of reaction, an increase in temperature will also increase the saturated water vapour pressure, which means that a higher pressure is required to maintain the liquid phase. Wet air oxidation (WAO) is carried out below the critical point of water, typically at 200–320oC and 2.0–20.0 MPa (Mishra et al., 1995). When compared to incineration, the WAO process creates minimal air pollution problems as the contaminants remain in the aqueous phase. The WAO process generally produces low molecular weight oxygenated compounds, like acetic and propionic acids, ethanol, etc. (Luck, 1999). Supercritical water oxidation (SCWO) processes are carried out at supercritical conditions. A recent review (Savage, 1999) on SCWO processes shows that complete and rapid oxidation of phenol as well as other organics can be achieved. Although higher efficiency for destruction of organic contaminants may be achieved in SCWO than in WAO, SCWO is usually an expensive process to install and operate.

Wet-air oxidation process is known to have a great potential for the treatment of effluents containing a high content of organic matter (chemical oxygen demand, COD 10–100 g/L), or toxic contaminants for which direct biological purification is unfeasible (Mishra et al., 1995). The WAO process has well-known capacities for breaking down biologically refractory compounds to simpler, easily treated materials before they are released into the environment. In general, this aqueous phase flameless combustion process takes place at severe reaction temperatures (473–593 K) and pressures (20–200 bar) by means of active oxygen species, such as hydroxyl radicals. Residence times of the liquid-phase in a three-phase reactor may range from 15 to 120 min, and the extent of COD removal may typically be about 75–90% (Luck 1999).
In the WAO processes, the organic contaminants dissolved in water are either partially degraded by means of an oxidizing agent into biodegradable intermediates or mineralized into innocuous inorganic compounds such as CO₂, H₂O and inorganic salts, which remain in the aqueous phase.

In contrast to other thermal processes, WAO produces no NOx, SO₂, HCl, dioxins, furans, fly ash, etc. (Luck 1999). One of the main drawbacks of the WAO process is its inability to achieve complete mineralization of organics, since some low molecular weight oxygenated compounds (especially acetic and propionic acids as well as methanol, ethanol, and acetaldehyde), originally present in a wastewater or accumulated in the liquid-phase during the oxidation process, are resistant to further transformation to carbon dioxide. For example, removal of acetic acid is usually negligible at temperatures lower than 573K (Mishra et al., 1995). Furthermore, organic nitrogen compounds are mostly transformed to ammonia, which is also stable in WAO operating conditions. Hence, the WAO process is considered as a pre-treatment step of wastewaters, which requires additional treatment, typically in a conventional biological treatment plant. WAO is not a new process. Its origins can be traced to the Strehlenert process of wood technology patented in 1911 and to the zinc sulfide oxidation process of hydrometallurgy patented in 1927 (Strehlenert, 1911).

Nevertheless, the WAO process may be prohibitively expensive when used to achieve deep oxidation of all organic material present to carbon dioxide. Consequently, it is considered as one of the most promising and simplest techniques for partial oxidation of parent pollutants into more biologically amenable intermediates. The efficiency of aqueous phase oxidation can be largely improved by the use of catalysts, either in the form of solids or as homogeneous catalysts.

1.4.2 Biological treatment

The aerobic genus *pseudomonas* is an attractive organism for use in wastewater treatment applications. Several types of phenol-degrading microorganisms, which have been isolated, harvested and tested on the substrates showed biodegradable efficiency comparable to Pseudomonas. This includes the fungi *phanerochaete chrysoporium*, *cryptococcus elinovii* yeasts, bacteria of genera *alcaligenes*, *bacillus*, *micrococcus*, *rhodotorulas*, and others.
A biological method for removal of chlorophenols in drinking water and wastewater is enzymatic detoxification using the horse radish peroxidase enzyme. The addition of this enzyme with hydrogen peroxide to solution causes enzymatic cross-linking of the substrate forming insoluble polymers, which then precipitate out of solution. This enzyme isolated from the roots of horseradishes, has been shown to be applicable for the treatment of several industrial wastewaters (Klibanov 1980, Klibanov 1983, Cooper 1996).

One-electron oxidation of aromatic substrates \( (\text{AH}_2) \) catalyzed by peroxidases is depicted by the Chance-George mechanism (Nicell 1994) as the following:

\[
\begin{align*}
E + \text{H}_2\text{O}_2 & \rightarrow E_i + \text{H}_2\text{O} & (1) \\
E_i + \text{AH}_2 & \rightarrow E_{ii} + \text{AH}^- & (2) \\
E_{ii} + \text{AH}_2 & \rightarrow E + \text{AH}^- & (3)
\end{align*}
\]

The native enzyme \( (E) \) is oxidized by peroxide \( (\text{H}_2\text{O}_2) \) to an active intermediate enzymatic form called compound I \( (E_i) \). Compound I accept an aromatic compound \( (\text{AH}_2) \) into its active site and carries out its oxidation. A free radical \( (\text{AH}^-) \) is produced and released into solution leaving the enzyme in the compound II \( (E_{ii}) \) state. Compound II oxidizes a second aromatic molecule, releasing another free radical product and returning the enzyme to its native state, thereby completing the cycle. The overall peroxidase reaction consists of the reactions described by Equations (1), (2) and (3). (Nicell 1994).

1.4.3 Photo-Fenton reaction

The treatment of industrial wastewater, which contains organic wastes, by biological processes, is often unsuitable due to their inherent toxicity to micro-organism. The use of traditional non-catalytic chemical processes or incineration may be too costly and energy intensive. Conventional wet air oxidation (WAO) processes usually require
higher pressures (0.5-20 MPa) and temperatures (423-598 K), which result in a high capital investment and a high energy consumption for operation. The application of homogenous and heterogeneous catalyst can improve the oxidation efficiency of organic wastes in water and reaction temperature can be reduced (Mishra 1995, Matatov-Meytal 1998). Homogeneous catalysts are reported to be more effective in increasing the rate of oxidation, but heterogeneous catalysts are preferred because the catalyst is present as a separate phase and therefore easier to separate.

The photo-Fenton reaction is also well-known in the literature (Kiwi 1993, Ruppert 1993) which is an efficient and inexpensive method for wastewater and soil treatment (Bauer 1997, Chen 1997, Kim 1996). Photo-Fenton is known to be able to improve the efficiency of dark Fenton or Fenton-like reagents, respectively, by means of the interaction of radiation (UV or Visible) with Fenton's reagent (Hislop 1999, Pignatello 1992). This technique has been suggested to be a feasible and promising process to remove pollutants from natural and industrial waters by increasing the biodegradability of chlorophenols and could be used as a pre-treatment method to decrease the toxicity of water (Fallmann et al., 1999a, 1999b).

In presence of Fenton reagent, photochemical reactions can be driven with photons of low energy, photons that belong to the visible part of the spectrum. Thus, photo-Fenton processes can be considered as low-cost techniques that can be run under solar irradiation (Klibanov 1983).

\[
\text{H}_2\text{O}_2 + \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{OH}^- + \text{OH}^- \quad (5)
\]

\[
\text{Fe}^{3+} + \text{H}_2\text{O} + \text{hv} \rightarrow \text{Fe}^{2+} + \text{H}^+ + \text{OH}^- 
\quad (6)
\]

Nevertheless applying Fenton's method has some drawbacks. The regeneration of ferric iron is slow. By applying irradiation the photo-Fenton reaction takes place, which accelerates the overall reaction rate by closing the catalytic cycle of Fenton and photo-Fenton reaction faster (Equations 5 and 6). This results in the advantage that another highly reactive hydroxyl radical is produced without consumption of hydrogen peroxide.
The photo-Fenton method has the advantage that it has high reaction rates and can be powered by sunlight. Furthermore hydrogen peroxide is a cheap oxidant compared for example to persulphate. The commonly mentioned disadvantage of the photo-Fenton method is the necessity to work at low pH (in literature normally a pH below 4 is considered to be necessary), because at higher pH ferric ions would begin to precipitate as hydroxide. Furthermore, the added iron has to be removed after the treatment (Klibanov 1980).

1.4.4 Adsorption of organic compounds onto activated carbon

Carbon adsorption is an advanced wastewater treatment method used for the removal of recalcitrant organic compounds as well as residual amounts of inorganic compounds such as nitrogen, sulfides, and heavy metals. This is a separation method in which the contaminant is transferred from a water phase, where it is dissolved, to the surface of active carbon where is accumulated for its subsequent extraction or destruction. The adsorption onto activated carbon is widely used for wastewater treatment. Thus, it is used in the control of color and odors, in the removal of organic compounds or trihalomethanes precursors, to remove chlorine and in general to remove toxic compounds.

The adsorption of nitrobenzene (NB) and phenol onto activated carbon has been widely studied. Both (NB and phenol) showed to be well adsorbable compounds onto activated carbon but in low concentration (Canizares et al., 1999; Sacher et al., 2001). This method has also been combined with others and a significant improvement has been obtained (Canizares et al., 1999). Many studies have been found in the literature regarding the treatment of textile wastewater by means of activated carbon (Roy and Volesky, 1977; Lin and Lai, 2000; Yeh et al., 2002). Most of them showed the high effectiveness of carbon activated adsorption process in the reduction of COD (Chemical Oxidation Demand) and color removal from textile wastewater.
1.5 Catalytic Wet Oxidation

1.5.1 General principles

Wastewater produced in many industrial processes contains organic compounds such as phenol and its derivatives, which cannot be treated by conventional biological oxidation. Other processes such as chemical oxidation, electrochemical treatment, photo-catalytic oxidation, photo-electrochemical oxidation, and wet oxidation processes under sub- and supercritical conditions and incineration have been tested in some countries (Mishra 1995). The application of a particular method depends on the nature of the pollutant, the concentration of the pollutant, the desired removal efficiency, effectiveness, ability to form secondary toxic product and cost.

The incorporation of a catalyst has also been considered in combination with all types of oxidants aiming to reduce the operating temperature and pressure, and/or to treat pollutants that cannot be destroyed during non-catalytic liquid phase oxidation processes. The classical Fenton’s reaction, which combines iron salts with hydrogen peroxide has also given good results for various organic pollutants (Bigda 1995). Nonetheless, the addition of a homogeneous catalyst has the inherent disadvantage of the posterior catalyst removal from the treated effluent, because the metal ions are pollutants themselves in the range of concentrations used. Heterogeneous catalysts, on the other hand, do not need any extra separation step and are thus more attractive.

A first attempt by (Lucking 1998, Andreozzi et al. 1999), led to the technology map in which WAO appears to be the most suitable technology for wastewater containing between 20 and 200 g/L of COD (Chemical Oxygen Demand). The suitability of WAO would be further reinforced if a heterogeneous catalyst is successfully incorporated in the process. Thus, particular emphasis has to be dedicated to the study of the Catalytic Wet Air Oxidation (CWAO) process.

Current literature shows that among the wastewater treatment techniques, catalytic wet oxidation (CWO) of organic wastes in water seems to be effective and promising (Mishra 1995, Luck 1999, Matatov-Meytal 1998).

Catalytic wet oxidation is a process involving an organic compound in water and oxygen over a catalyst. Heterogeneous oxidation involves intensive contacting of an organic compound in solution with oxygen over a solid catalyst. Heterogeneous systems
have the advantages over homogenous systems because the catalysts can be separated much more easily after the process.

Although homogeneous catalytic systems using transition metal catalysts (especially salts of Cu, Fe, Mn) are generally more effective than solid catalysts, the dissolved catalysts however, are in many cases toxic and their use requires a separation step such as precipitation to remove or recover the catalyst ions from the treated effluent. Heterogeneous oxidation involves intensive contacting of an organic compound in solution with oxygen over a solid catalyst. Due to this, heterogeneous catalyzed wet oxidation seems to be more promising since only one down-stream separation step, filtration, is required to remove the catalyst from the liquid phase.

Catalytic wet oxidation (CWO) of organic compounds and organic-containing wastewaters over homogeneous or heterogeneous catalysts can be carried out under much milder conditions than non-catalyzed processes. Catalytic wet oxidation (CWO) using solid catalysts, involves the following steps: diffusion of the reactants to the catalytic or support surface, adsorption of the reactants onto the surface, reaction on the surface, desorption of products off the surface, and diffusion of products from the surface. Because of these steps, heterogeneous processes are usually more complicated to control. Since the catalyst surface plays an important role in adsorption and desorption, appropriate selection of both the active part and the support of the catalyst therefore can have a remarkable effect on the reaction rate.

1.5.2 Mechanism of Catalytic Wet Oxidation

Various attempts have been made to study reaction mechanisms for pure organic compounds during liquid phase oxidation. For engineering purposes, it is important to quantify the reaction rate by identifying the major oxidation pathways as well as understanding the reaction controlling steps. Catalytic oxidations of organic molecules can proceed via different mechanisms, namely: [1] enzymatic oxidation; [2] free radical auto-oxidations initiated by transition metal cations; [3] metal ion oxidation of coordinated substrates; [4] oxygen transfer to the substrate mediated by metaloxo or peroxo complexes and [5] oxidative dehydrogenation on metal surfaces (Gallezot 1997). In alcohol oxidations, oxidative dehydrogenation on metal surfaces is commonly
reported (Gallezot 1997, Mallat 1994). The mechanism of alcohol oxidation on a noble metal catalyst involves the dehydrogenation of the organic substrate on the metal surface, while oxygen is needed to scavenge the adsorbed hydrogen from the surface.

Phenol and its derivatives has been the subject of many studies in CWO as a model reaction. Studies on the mechanisms for oxidation of phenol require some knowledge of the short-lived intermediates as well as the final reaction products. For transition metal oxide catalysts, the reaction is believed to occur by free-radical initiation on the catalyst surface, homogeneous propagation, and either a homogeneous or a heterogeneous termination process. Radical initiation could occur by dissociative adsorption of phenol or hydroperoxide decomposition on the catalyst.

Generally, the reaction intermediates reported on phenol oxidation catalyzed by supported metal oxides, like copper, zinc, manganese and other metal catalysts, are similar to those of non-catalysed phenol oxidation. The reaction products that have been reported from the oxidation of phenol by oxygen and ozone can be attributed to three classes: primary intermediates (hydroquinone, catechol, p-benzoquinone, o-benzoquinone), secondary intermediates (maleic acid, formic acid, pyruvic acid, oxalic acid, oligomers of primary intermediates), and end products (formic acid, acetic acid, carbon dioxide and water). Phenol supercritical water oxidation (SCWO) have been recently reviewed (Savage, 1999), in which the formation of dimers and other intermediates like single-ring compounds (e.g. hydroquinone), ring-opening products (e.g. maleic acid, glyoxylic acid, acetic acid and other organic acids) and gases (e.g. CO, CO₂) are reported. Some of these partial oxidation products and intermediates, especially the dimers, are relatively more toxic than phenol. The oxidation of phenol has in most cases involved oxidation, decarboxylation, dehydration and rearrangement of the molecules or some combination of these steps (Matatov-Meytal 1998, Pintar 1995).

**Fenton and Fenton like processes**

The Fenton reaction is a widely used and studied catalytic process based on an electron transfer between H₂O₂ and a metal acting as a homogeneous catalyst (Lucking 1998, Safarzadeh-Amiri et al 1996). By far, the most common of these ones is iron(Walling 1975, Bigda 1995). The reactivity of this system was first observed in 1894 by its inventor Fenton (Fenton 1894), but its utility was not recognized until the
1930s once a mechanism based on hydroxyl radicals (HO*) was proposed (Walling 1975, Prousek 1995). Fenton’s reagent can be employed to treat a variety of industrial wastes containing a range of organic compounds like phenols, formaldehyde, pesticides, wood preservatives, plastic additives, and rubber chemicals (Barbeni 1987, Bishop 1964, Flaherty 1994, Feuerstein 1982). The process may be applied to wastewaters, sludges, and contaminated soils (Lu and Huang 2000, Lu Chang 1997) with a reduction of toxicity, an improvement of biodegradability, and odor and color removal.

Fenton process has been well studied recently for its prospective applications in unmanageable wastewater treatment (Legrini 1993, Ollis1993, Prousek 1996).

The Fenton reagent (FR) is a mixture of hydrogen peroxide (H\textsubscript{2}O\textsubscript{2}) and an iron(II) salt (Fe\textsuperscript{2+}), which is frequently used for oxidation and degradation of organic substances owing to its high oxidizing power and simplicity. The oxidation of organic substances with FR is known as the Fenton reaction, which is in fact an induced chain reaction. The actual reagent in H\textsubscript{2}O\textsubscript{2}–Fe\textsuperscript{2+} mixtures is a highly reactive intermediate, but much controversy exists about it. In aqueous solutions, the most commonly accepted species has been the hydroxyl radical, \textbullet OH though the ferryl ion, FeO\textsuperscript{2+}, has also been proposed (Kremer 1999). If the hydroxyl radical is the key intermediate, the initiation step would be:

$$\text{H}_2\text{O}_2 + \text{Fe}^{2+} = \text{Fe}^{3+} + \text{OH}^- + \textbullet \text{OH} \quad (7)$$

Afterwards, \textbullet OH radicals may either oxidize another Fe\textsuperscript{2+} to Fe\textsuperscript{3+} (termination step):

$$\textbullet \text{OH} + \text{Fe}^{2+} = \text{Fe}^{3+} + \text{OH}^- \quad (8)$$

or they may react with H\textsubscript{2}O\textsubscript{2} (propagation step):

$$\textbullet \text{OH} + \text{H}_2\text{O}_2 = \text{H}_2\text{O} + \textbullet \text{OOH} \quad (9)$$

$$\textbullet \text{OOH} + \text{Fe}^{3+} = \text{O}_2 + \text{Fe}^{2+} + \text{H}^+ \quad (10)$$

Also, the \textbullet OH radical may oxidize other species (substrate) present in solution:
\[ \cdot \text{OH} + \text{RH} = \text{R}^* + \text{H}_2\text{O} = \text{products} \]  \hfill (11)

If the key intermediate is the ferryl ion, the first step would be:

\[ \text{H}_2\text{O}_2 + \text{Fe}^{2+} = \text{FeO}^{2+} + \text{H}_2\text{O} \]  \hfill (12)

Afterwards, the specie FeO\(^{2+}\) can undergo reactions similar to (8), (9) and (11); that are:

\[ \begin{align*}
\text{FeO}^{2+} + \text{Fe}^{2+} + 2\text{H}^+ &= 2\text{Fe}^{3+} + \text{H}_2\text{O} \\
\text{FeO}^{2+} + \text{H}_2\text{O}_2 &= \text{Fe}^{2+} + \text{H}_2\text{O} + \text{O}_2 \\
\text{FeO}^{2+} + \text{RH} &= \text{products}
\end{align*} \]  \hfill (13-15)

Both species are extremely reactive and some of their thermodynamic properties have been compared (Koppenol 1984). Whatever the intermediate species may be, owing to their high reactivity, poor selectivity should be expected when FR is used, and this has probably made an extra reason for the limited analytical use of FR so far.

The Fenton-like reagent is also capable of oxidizing organic substrates, but it is somewhat less reactive than Fenton's reagent. As iron (III) can be produced in applications of Fenton's reagent, Fenton chemistry and Fenton-like chemistry often occur simultaneously. Interestingly, Fenton and Fenton-like chemistry are generally believed to proceed via similar mechanisms as oxidation reactions with the aforementioned complex and bulky enzymes.

Fenton like reactions exploit the reactivity of the hydroxyl radical produced in acidic solution by catalytic decomposition of \( \text{H}_2\text{O}_2 \) in presence of \( \text{Fe}^{3+} \) ions. For the Fenton-like reagents, it is believed that initially no \( \text{O-O} \) bond breaking takes place, but instead an iron(III)hydroperoxo intermediate is formed as the first step via hydrolysis:

\[ \text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow [\text{Fe}^{\text{III}}\text{OOH}]^{2+} + \text{H}^+ \]

This intermediate might be able to react with organic substrates or break up in smaller active species in a second step. The iron(III)hydroperoxo may \textit{e.g.} homolyze at the Fe-O bond.
\[ [\text{Fe}^{III}\text{OOH}]^{2+} \rightarrow \text{Fe}^{2+} + \text{OOH}^- \]

generating iron(II) and producing the reactive OOH. radical, or at the O-O bond producing the ferryl ion and an OH radical.

\[ [\text{Fe}^{III}\text{OOH}]^{2+} \rightarrow [\text{Fe}^{IV}\text{O}]^{2+} + \text{OH}^- \]

Alternatively, O-O bond heterolysis could take place, producing the highly reactive Fe(V) species:

\[ [\text{Fe}^{III}\text{OOH}]^{2+} \rightarrow [\text{Fe}^{V}\text{O}]^{3+} + \text{OH}^- \]

Probably many of the proposed mechanisms compete with each other depending on the reaction conditions, such as the metal ligands, the solvent, the pH and the organic substrate to be oxidized. This is of course one of the reasons why Fenton-like chemistry still holds secrets. Another important reason is the very elusive nature of the active species, which live too short to have been definitively observed yet in experiments. Obviously, that is not a problem for computer simulations.

1.6 Case studies and literature review

Contreras et al. (2003) investigated the effect of ozonation on the biodegradability of 100-ppm aqueous solutions of 2,4-dichlorophenol. From this study it can be concluded that after the pre-ozonation step, 80% of TOC could be removed in the co-digestion of this solution with municipal wastewater by an aerobic biological treatment and 70% when feeding 100% of the pre-treated solution. Chu et al. (2005) also investigated the degradation of 2,4-dichlorophenol (2,4-DCP) by a photo-Fenton-like (Fe$^{3+}$/H$_2$O$_2$/UVC) process under various reaction conditions.

Sabhi and Kiwi (2001) carried out the degradation of 2,4-Dichlorophenol on Nafion–Fe (1.78%) in the presence of H$_2$O$_2$ under visible light irradiation. Nafion–Fe mediated photo-catalysis allows carrying out the degradation up to pH 11 avoiding the costly pH adjustment necessary during homogeneous photo assisted Fenton degradation.
István Ilisz et al. (2002) studied removal of 2-chlorophenol from water by adsorption combined with TiO₂ photocatalysis. With longer-wavelength and lower-intensity irradiation, either with or without the presence of the adsorbent, after 7 h of irradiation a 99% reduction in the 2-CP concentration was achieved by TiO₂ photocatalysis. No adsorbent damage was observed under these conditions.

Liu et al. (2001) dechlorinated three isomers of chlorophenols, (o-, m-, p-chlorophenols) by palladium/iron powder in water through catalytic reduction. The reaction rate constant increased with the decrease in the Gibbs free energy of the formation of chlorophenols, with the rate constant being 0.0215, 0.0155 and 0.0112 min⁻¹ respectively for o-, m- and p-chlorophenols with 0.048 % Pd/Fe.

Panizza and Cerisola 2001 investigated the treatment of an industrial wastewater mainly containing naphthalene- and anthraquinone-sulphonic acids, by electrogenerated Fenton's reagent. The maximum COD removal (87%) and colour fading (89%) were obtained with a Fe²⁺ concentration of 3 mM for the electro-Fenton treatment process. Thies (2004) studied Fenton's oxidation of Methyl-tert-butyl ether (MTBE) with zero-valent iron. Fenton's oxidation with Fe(0) removed over 99% of MTBE at pH 4 and 7 with H₂O₂: MTBE molar ratio of 220:1. Xu et al. (2003) have found that MTBE is readily and rapidly degraded in aqueous solution by Fenton's reagent. Under optimum conditions, 15 mM H₂O₂, 2 mM Fe²⁺, pH 2.8 and room temperature, the initial 1 mM MTBE solution was reduced by 99% within 120 min.

Huang and Lu (2001) examined the catalyzed decomposition of hydrogen peroxide and 2-chlorophenol (2-CP) in the presence of iron oxides. Granular ferrihydrite, goethite, and hematite were selected as catalysts in this study. The catalytic activity for hydrogen peroxide decomposition followed the sequence: granular ferrihydrite > goethite > hematite. Hematite exhibited the highest activity in catalyzing 2-CP oxidation. Cao Shengli et al. (2003) developed and examined noble metal catalysts on activated carbon (AC) (Pt/AC and Ru/AC) and base metal catalysts (Cu/AC, CoMo/AC, Mo/AC, Mn/AC, Ru/Al₂O₃) for the simultaneous removal of organic pollutants and ammonia from wastewater using the wet air oxidation (WAO) process in the liquid phase. The Pt/AC catalyst was able to remove ammonia (> 50%) and phenol (=100%) simultaneously from highly polluted wastewater containing up to 1500 mg/L of ammonia and up to 8000 mg/L of COD.
Stoyanova et al. (2003) studied catalytic activity of a new mixed Ni-Mn-oxide system in liquid-phase oxidation of phenol. With heterogeneous oxidation of phenol carried out under mild conditions ($T = 35 \, ^\circ \text{C}$, pH = 7.0, catalyst load = 2 g/L), the complete oxidation was achieved in 30 min. The following intermediates (their presence being proved using UV spectrometry and HPLC) are obtained in the course of the oxidation process: catechol, benzoquinone, hydroquinone, and hydroxyhydroquinone. The intermediates are further mineralized to CO$_2$ and carboxylic acids.

Ivanov et al. (2003) carried out benzene to phenol oxidation by nitrous oxide over the Fe-ZSM5 catalyst at 648 – 698 K and near atmospheric pressure using a bench scale plug flow reactor with a feed gas concentration of 30–80 mol% benzene, 1.5–5.0 mol% N$_2$O, and 0–4.7 mol% phenol. At these conditions, the selectivities of benzene and N$_2$O for phenol exceeded 98 and 95% respectively. Benzoquinone, hydroquinone, catechol, and carbon oxides were the main by-products. Arena Francesco et al. (2003), investigated the wet oxidation of phenol at 150°C on Cu-based solid catalysts and a direct relationship between Cu-leaching and activity was found. The induction time of the CWO reaction depends upon the rate of leaching of the active phase into reaction medium. The leaching process enables a faster kinetic regime during which a drop in pH to acidic values (< 3) promotes a further Cu dissolution and consequently both phenol and TOC conversion.

Guérou et al. (2003) performed phenol oxidation by hydrogen peroxide on iron containing clays pillared with Al or mixed Al-Fe complexes. The Al–Fe pillared clay has shown good performances towards the total phenol oxidation (80 % of TOC abatement at 70°C) and allows to use this kind of catalysts in a continuous process able to eliminate organic pollutants in industrial wastewater. Sotelo et al. (2003) studied the catalytic wet peroxide oxidation of phenolic aqueous solution over LaTi$_{1-x}$Cu$_x$O$_3$ perovskites and have shown a complete removal of aromatic compounds and high TOC reduction (ca. 90 %) under mild reaction conditions (temperature of 80°C and with initial peroxide concentration lower than the stoichiometric requirement).

Carriazoa et al. (2003) prepared Al–Fe or Al–Cu modified clays from two natural montmorillonites, which were employed in phenol oxidation with hydrogen peroxide in water. The clays were found to be very efficient catalysts for phenol oxidation to carbon dioxide under mild conditions. Catrinescu et al. (2003) presented an evaluation of the
catalytic performances of a Fe-exchanged Al-pillared synthetic beidellite for the wet hydrogen peroxide oxidation of phenolic aqueous wastes. The experimental results indicated that the use of this catalyst allowed a total elimination of phenol and a significant removal of chemical oxygen demand, without significant leaching of Fe ions. Thus, considering the lowest Fe concentrations in solution after oxidation at pH 5.0, 50°C and 180 min, the COD removal efficiency of 87.9% was remarkable.

Maugans and Akgerman (2003) carried out catalytic wet oxidation of phenol in a batch and a trickle bed reactor using 4.45 % Pt/TiO2 catalyst in the temperature range 150–205oC. The technology was able to achieve up to 80% TOC destruction in the tested configuration. Trawczynski (2003) investigated CBC supported noble metals as efficient catalysts for the process of phenol wet air oxidation in a continuous-flow fixed-bed reactor under relatively mild conditions of 393–433 K, 50–80 bar and LHSV=0.5–6 h\(^{-1}\). The activity of these catalysts depends both on the type of supported metal and on the adsorption capacity and decreases in the following order: Pt/CBC > Pd/CBC ≈ Ru/CBC >> CBC. Complete conversion of aqueous solutions of phenol can be achieved above 413 K. Masende et al. (2003) have studied the catalytic performance of graphite supported platinum (5 wt %) catalyst in liquid phase oxidation using a continuous flow stirred tank slurry reactor (CSTR) in a temperature range of 120–180oC and in a total pressure range of 1.5–2.0 MPa. Complete oxidation of phenol to CO\(_2\) and H\(_2\)O can be achieved at 150oC when the reaction proceeds within the range of weight specific oxygen loads of 0.15–0.35 mol s\(^{-1}\) kg(Pt\(^{-1}\)) and at stoichiometric oxygen excess in the range of 0–80 %.

Vaidya and Mahajani (2002) studied the kinetics of wet oxidation of phenol over a Ru/TiO2 catalyst in the temperature range of 175–200oC, oxygen partial pressure range of 0.34–1.38 MPa and a catalyst loading range of 0.5–1 kg m\(^{-3}\) at near neutral conditions (pH = 6.5). The catalyst used for the purpose was powdered 5% Ru/TiO2. This heterogeneous catalyst was found to be very effective for oxidation of phenol at near neutral conditions. The enhancement in the rates of reaction in the presence of this catalyst was even more pronounced in a strongly alkaline medium.

Cybulski and Trawczyński (2004) carried out CWAO of phenol using active platinum and ruthenium catalysts in a trickle bed reactor over temperatures of 393 and 473 K under total pressure of 5 and 8 MPa at LHV = 0.5–6 h\(^{-1}\). Chemical oxygen
demand for the lumped intermediates amount to $64 \pm 30$ g O$_2$/mol confirming the literature information that these are carboxylic acids, probably with predominant content of acetic acid that is most refractory at CWAO conditions. Reaction orders for phenol range from 0.94 to 2.0 and those for oxygen from 0.22 to 0.85.

Fenton’s oxidation of Methyl-tert-butyl ether (MTBE) with zero-valent iron could achieve over 99% removal of MTBE at pH 4 and 7 with H$_2$O$_2$: MTBE molar ratio of 220:1 (Bergendahla and Thies 2004). Yu and Savage (1999) used bulk MnO$_2$ as a catalyst for phenol oxidation in supercritical water at 380-420°C and 219-300 atmosphere pressure in a flow reactor. The rate of phenol disappearance over MnO$_2$ was consistent with a power-law rate equation that is of 0.83 order in phenol, 0.36 order in O$_2$, and zero order in water. Thus, the mechanism for product formation for catalytic SCWO is likely to be very similar to that for noncatalytic SCWO, with the key difference being the role of the catalyst in accelerating the rate of generation of reactive intermediates (phenoxy radicals).

1.7 Objectives of the present work

With the above background, the present work was formulated with the following objectives:

1. To prepare suitable oxidation catalysts for destroying organic pollutants with particular reference to phenol, 4-chlorophenol and 2,4-dichlorophenol in water, through wet oxidation with and without an oxidizing agent,

2. To characterize the catalysts with X-ray diffraction data, FTIR measurements, Scanning Electron Microscopy (SEM), Cation Exchange Capacity (CEC) measurement, etc.

3. To carry out the wet oxidation process under different sets of conditions (temperature, time, reactant mole ratio, catalyst load, etc.), and thus to find out the optimum reaction conditions for maximum oxidation,

4. To make a comparison of the effectiveness of the different oxide catalysts for the best possible removal of the phenolic compounds from water.