2.1. Catalysts used in the present work

In the present investigation, seven different catalysts have been selected for evaluating their suitability for oxidative degradation of phenol, 4-chlorophenol and 2,4-dichlorophenol in presence and in absence of hydrogen peroxide as the oxidizing agent. The catalysts are

A. Hematite (Fe$_2$O$_3$)
B. Goethite (FeOOH)
C. MnO$_2$
D. TiO$_2$
E. Fe$_2$O$_3$ + MnO$_2$ (1:1 mixture)
F. Fe$_2$O$_3$ + TiO$_2$ (1:1 mixture)
G. MnO$_2$ + TiO$_2$ (1:1 mixture)

A brief description of the catalysts along with their important physical characteristics is given below.

A. Hematite

Hematite, with its high iron content is a very useful mineral. Its chemical composition contains a high percentage of Iron (70%) and it is the primary ore used to create Iron. The ore sometimes contains a small amount of titanium. It is soluble in concentrated hydrochloric acid. Hematite is harder than pure iron, but much more brittle. The red powdered hematite is used as a pigment and as rouge in polishing. When shaped into ornaments, it is often called black diamond. Hematite is an antiferromagnetic material below 260 K, and is weakly ferromagnetic above this temperature.

Hematite in this work is obtained from Howards of Ilford Limited, England and it has the following characteristics
Color = reddish brown.
Systematic name = Hematite
Chemical Formula = Fe$_2$O$_3$
Molar mass = 159.69 g
Density and phase = 5.26 g/cm$^3$, solid
Crystal System: Trigonal-Hexagonal Scalenohedral
Cell Parameters: $a = 5.0317$, $c = 13.737$, $a : c = 1 : 2.73009$

B. Goethite

The catalyst goethite was prepared in the laboratory by ageing ferric hydroxide precipitates produced from ferric nitrate solution at pH 13 and 343 K for 60 h. The final synthesized goethite was separated from suspension by centrifugation; washed with deionized water till the pH value of supernatant was reduced below pH 7 and then dried at 313 K for 48h. Goethite has the following physical characteristics:

Color: Yellowish brown
Chemical Formula = Fe$^{3+}$O(OH)
Molar mass = 88.85 g
Density and phase = 4.27 g/cm$^3$, solid
Crystal System: Orthorhombic
Cell Parameters: $a = 4.6$, $b = 9.95$, $c = 3.02$; $a : b : c = 0.462 : 1 : 0.304$

C. Manganese (IV) oxide (MnO$_2$)

MnO$_2$ was used for production of chlorine in the eighteenth century, before being displaced by electrolytic methods. This blackish solid occurs naturally as the mineral pyrolusite, which is the main ore of manganese. It is also present in manganese nodules. The principal use for MnO$_2$ is for making dry-cell batteries such as the alkaline batteries and it is also used for production of permanganates. Manganese dioxide is used extensively as an oxidant in organic synthesis. MnO$_2$ catalyses the decomposition of hydrogen peroxide to oxygen and water.

\[2 \text{H}_2\text{O}_2 (aq) = \text{O}_2 (g) + 2 \text{H}_2\text{O (l)}\]
In pyrolusite (P-MnO₂), single chains of edge-sharing Mn(IV)O₆ octahedra share corners with neighboring chains to form a framework structure containing tunnels with square cross sections that are one octahedron by one octahedron on a side.

Manganese dioxide used in the present work is obtained from BDH, England and has the following characteristics:

- **Color:** Black
- **Systematic name:** Manganese (IV) dioxide
- **Chemical Formula:** MnO₂
- **Other name:** Pyrolusite
- **Molar mass:** 86.94 g/mol
- **Density and phase:** 5.026 g/cm³, solid
- **Solubility in water:** insoluble
- **Melting point:** 535 °C

D. **Titanium (IV) dioxide (TiO₂)**

Titanium dioxide (also called titanium(IV) oxide, titanium white, or even titania) is cheap, nontoxic, readily available in bulk, and very widely used as a white pigment in paint, enamel, lacquer, plastic and construction cement. TiO₂ powder is chemically inert, resists fading in sunlight, and is very opaque: this allows it to impart a pure and brilliant white colour to the brown or gray chemicals that form the majority of household plastics. Paint made with titanium dioxide does well in severe temperatures, is somewhat self-cleaning, and stands up to marine environments. Pure titanium dioxide has a very high index of refraction and an optical dispersion higher than diamond. In nature, this compound is found in the minerals anatase, brookite, and rutile.

Titanium dioxide (TiO₂) is a wide band gap semiconductor, crystallizing as rutile, anatase or brookite. Due to its physical properties (including high refractive index and dielectric constant) as well as its chemical behaviour in photosensitive reactions, TiO₂ is a highly attractive material for a wide variety of industrial applications, such as photocatalysis, catalysis, charge separating devices, chemical sensors, solar cells,
microelectronics and electrochemistry (Alexandrescu et al, 2004). It has the physical characteristics as given below:

- **Color:** White
- **Systematic name:** Titanium (IV) dioxide
- **Chemical Formula:** TiO$_2$
- **Molar mass:** 79.87 g/mol
- **Density and phase:** 4.23 g/cm$^3$, solid
- **Solubility:** insoluble
- **Melting point:** 1850 °C

### 2.2 Catalyst characterization

Four independent techniques, viz., X-ray diffraction (XRD), FT-Infra-red spectroscopy (FTIR), scanning electron microscopy (SEM) and cation exchange capacity (CEC) determination are utilized for a reliable characterization of the metal oxide catalysts.

#### 2.2.1 Characterization by XRD

X-ray powder diffraction is the most common technique used to study the characteristics of the crystalline structure of the catalysts. As a method, X-ray diffractometry is attractive because of its speed and ease of performance, and because it requires only small amounts of material, and also it is nondestructive. In this analysis, two parameters are determined (Brindley and Brown, 1980) as follows:

a. The spacing between the planes of atoms or groups in the crystal and,
b. The intensities of the X-ray reflections from the corresponding planes.

Bragg’s diffraction law is used to determine these two parameters, viz., $n \lambda = 2d \sin \theta$, where $\lambda$ = wavelength of the X-rays, $d$ = lattice spacing, $\theta$ = angle of diffraction, and, $n$ = order of reflection. One-dimensional XRD patterns for the clay minerals give information about Peak position, Peak intensity, Peak shape and Peak breadth. In the
present work, XRD measurements of all the catalysts were done at the Sophisticated Instruments Facility, Gauhati University with Phillips Analytical X-ray spectrometer (PW 1710) using Cu anode.

X-ray diffractogram of Hematite is shown in Fig 2.1. The d-spacing (Å) obtained from the diffractogram is 2.02 which compares well with the reported values. The most intense peak is obtained at 2θ = 44.72°. More reflections have also been observed. Since the material is crystalline at the atomic level, reflections at higher angles are also observed. It is thus not possible to quantify the purity of the material from XRD measurements.

The XRD pattern of TiC is shown in Fig. 2.2, which gives a 2θ angle of 25.32 and a d-spacing of 3.51 Å for the most prominent reflection. Similarly, the XRD pattern of goethite in Fig. 2.3 reveals 2θ of 36.64 with d-spacing of 2.45 Å for the most prominent reflection.

2.2.2 Characterization by FTIR

FTIR spectroscopy is well known as a complementary technique of XRD analysis for identification of catalysts. This method has been extensively used for the qualitative determination of the major constituents of catalysts and can be considered as a fingerprint for identification. Following the standard procedure (Farmer, 1964), the IR spectra of catalysts have been taken by Perkin-Elmer FTIR Spectrometer (Model Spectrum RXI, range 4000-500 cm⁻¹) at the Department of Chemistry, Gauhati University.

The infrared spectrum above 400 cm⁻¹ of powdered Fe₂O₃ samples has two major bands, attributed to lattice vibrations. Published values for the position of these two bands differ by up to 30 cm⁻¹. Several reasons for these variations have been suggested in the literature, but it is generally accepted that variations among the spectra are most often caused by differences in the size, and more importantly the shape, of the Fe₂O₃ particles (Wilson, 1994). Fe₂O₃ in which the particles have a fairly equivalent shape, produces an infrared spectrum with bands at approximately 559.5 and 464.8 cm⁻¹, with the more intense band at 560 cm⁻¹ (Fig. 2.5)
Fig. 2.1. XRD pattern of Hematite

Fig. 2.2. XRD pattern of Goethite
Fig. 2.3. XRD pattern of MnO$_2$

Fig. 2.4. XRD pattern of TiO$_2$
Fig. 2.5. FTIR spectra of Hematite
The infrared spectrum of goethite has a characteristic hydroxyl stretch at approximately 3150 cm\(^{-1}\) and the hydroxyl deformation bands near 900 and 800 cm\(^{-1}\), these lower energy bands being attributed to lattice vibrations (Cambier, 1986). Studies of synthetically prepared goethites have shown that factors such as crystallinity, adsorbed water, and isomorphous substitution of iron by aluminum influence the position of these bands. For example, in a series of synthetic goethites of varying crystallinity, the hydroxyl stretch shifted from 3130 cm\(^{-1}\) in the most crystalline sample to 3170 cm\(^{-1}\) in the sample with the least amount of structural order (Schwertmann, 1985). Goethite hydroxyl stretch is partially obscured by the presence of water, adsorbed on the goethite. The bands at 900 and 800 cm\(^{-1}\) can certainly be attributed to goethite, but because of possible overlaps, it is difficult to assign exact peak positions (Fig. 2.6).

Manganese dioxide, MnO\(_2\), used in the present work shows an infrared spectrum as shown in Fig. 2.7. Titanium dioxide powder used in the present work gives an infrared spectrum as shown in Fig. 2.8.

### 2.2.3 Cation Exchange Capacity (CEC) measurement

The cation exchange capacity (CEC) is the number of equivalents of exchangeable charge per mass of a mineral, which is equivalent with the layer charge. The CEC is one of the basic properties of minerals. It has two origins (Lagaly, 1981):

- One origin is isomorphic substitution. Substitution of a cation by a lower-valent cation leads to a net negative charge and vice versa. This part of the CEC is considered to be constant.
- The second origin is dissociation of some groups like M-OH on the edges. This part of the CEC may not be constant and will depend on factors such as pH.

Several methods to determine the CEC have been developed. Some of these are by using ammonium acetate (Schollenberger, 1927; Chapman, 1965), metal-organic complexes (Pleysier, 1975), BaCl\(_2\) Compulsive Exchange (Gillman and Sumpter, 1986;
Fig. 2.6. FTIR spectra of Goethite
Fig. 2.7. FTIR spectrum of MnO$_2$
Fig. 2.8. FTIR spectra of TiO$_2$
Hendershot and Duquette, 1986), copper bisethylenediamine (Bergaya and Vayer, 1997), copper triethylenetetramine (Meier and Kahr, 1999), cationic surfactants (Janek and Lagaly, 2003), isotope dilution method (Brouwer et al., 1983; Baeyens and Bradbury, 2004), etc.

In the present work, the CEC of the catalysts was estimated by using the copper bisethylenediamine cation method (Bergaya and Vayer, 1997, Ammann, 2003). The procedure is as follows: 1 molar solution of CuCl₂ was prepared by dissolving 26.89 g CuCl₂ (0.2 mole) in distilled water to give 0.2 liter. 1 molar solution of ethylenediamine was prepared by dissolving 33.39 ml of ethylenediamine in distilled water to yield 0.5 liter. The complex was formed by adding 50 ml of the CuCl₂ solution to 102 ml of the ethylenediamine solution. The slight excess of the amine ensured complete formation of the complex. The solution was diluted with water to one liter to give a 0.05 molar [Cu(en)₂]²⁺ solution. 0.5 g of dry catalyst was weighed in a 100 ml conical flask. 2 to 5 ml of the complex solution was diluted with distilled water to 25 ml and added to the catalyst. The mixture was shaken for 30 min in a thermostated water bath and then centrifuged. The concentration of the complex remaining in the supernatant was determined by iodometry. For this, 5 ml of the supernatant was mixed with 5 ml of 0.1 N HCl to destroy the [Cu(en)₂]²⁺ complex. 2 ml of 0.5 g/ml KI solution was added, and the sample was titrated with 0.02 M Na₂S₂O₃ solution with starch as indicator. The CEC was calculated from the following formula:

\[
\text{CEC (meq/g)} = \frac{MSV(x-y)}{10m}
\]

where, \(M\) = molar mass of the complex,
\(S\) = strength of the thio solution,
\(V\) = volume (ml) of the complex taken for iodometric titration,
\(m\) = mass of catalyst taken (g),
\(x\) = volume (ml) of thio required for blank titration (without the catalyst),
\(y\) = volume (ml) of thio required for the titration (with the catalyst).

The CECs of all the catalysts, as determined above, are given in Table 2.1.
### Table 2.1: Cation exchange capacity (CEC) of catalysts

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Fe$_2$O$_3$</th>
<th>Goethite</th>
<th>MnO$_2$</th>
<th>TiO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CEC (meq/100g)</td>
<td>0.007328</td>
<td>0.014656</td>
<td>0.065952</td>
<td>0.003664</td>
</tr>
</tbody>
</table>

#### 2.2.4 Characterization by Scanning Electron Microscope (SEM)

The Scanning Electron Microscope (SEM) is one of the most versatile and widely used tools of modern science as it allows the study of both morphology and composition of biological and physical materials. The SEM provides an image of surfaces and is capable of both high magnification and good depth of field, so that even at low magnifications it is often more useful than an optical light microscope. The SEM has a large depth of field, which allows a large amount of the sample to be in focus at one time. The SEM also produces images of high resolution, which means that closely spaced features can be examined at a high magnification. The combination of higher magnification, larger depth of focus, greater resolution, and ease of sample observation makes the SEM one of the most heavily used instruments in research areas today. Morphological structure and particle size distribution were studied with a scanning electron microscope (SEM).

The SEM images of TiO$_2$ and goethite were taken (LEO-1430 VP, IIT Guwahati) and are given in Fig. 2.9 and 2.10. The SEM image for TiO$_2$ samples demonstrate that the particles have an almost spherical shape with a particle size of 30-160 micron, while the XRD analysis indicated that these TiO$_2$ microspheres still had a crystal size of 8.1 nm. Since these TiO$_2$ microspheres have a porous structure with higher specific surface area and pore volume than normal TiO$_2$ powders, they appear to have strong adsorption ability in its aqueous suspensions (Li et al., 2003).

#### 2.3. Reactants

Phenol is obtained from E Merck (Mumbai, India). 4-Chlorophenol is obtained from B.D.H, England and 2, 4-dichlorophenol (2, 4-DCP) from Merck-Schuchardt, Germany. Hydrogen peroxide H$_2$O$_2$ is from E. Merck, Mumbai. Other chemicals used are Ferrous ammonium sulphate (E Merck, Mumbai, India), Potassium dichromate (Qualigens, India), Silver sulphate (E Merck, Mumbai, India).
Fig. 2.9. SEM photographs of TiO$_2$ at two different magnifications.
Fig. 2.10. SEM photographs of goethite at two different magnifications.
2.4. Reaction Procedure

Water spiked with reactants was used as the synthetic effluent contaminated with the chlorophenol in this work. The synthetic effluent was prepared by dissolving measured quantities of reactants in deionized water.

All the reactions with and without H$_2$O$_2$ were carried out in a batch reactor with 100 ml conical flasks. After mixing the reactants (phenol, 4-clorophenol, or 2,4-dichlorophenol) and the catalyst in appropriate amounts, the flasks were capped and the contents were agitated in a water bath shaker (NSW, INDIA) at a constant temperature of 300 K for a predetermined time interval. After the reaction was over, the reaction mixture was centrifuged (Remi Research centrifuge, R24) and the centrifugate was analyzed to determine the amount of phenol and its derivatives remaining unconverted with a UV-Visible spectrophotometer (Hitachi 3210). The total conversion of phenol and its derivatives into various oxidized products was computed from the decrease in concentration of phenol, 4-CP and 2,4-DCP.

The percentage conversion is calculated according to the relation

\[
\% \text{ conversion} = \left(\frac{C_0 - C_t}{C_0}\right) \times 100
\]

where $C_0$ is the initial concentration (mol/L), $C_t$ the concentration at any time after the reaction starts, $t$ the time (min$^{-1}$).

COD estimation

The chemical oxygen demand (COD) is a measure of the oxygen equivalent to that portion of organic matter present in the waste water sample that is susceptible to oxidation by potassium dichromate. This is an important and quickly measured parameter for stream, sewage and industrial waste samples to determine their pollution load.

For following phenol oxidation by monitoring of COD, the reactions of phenol ($1 \times 10^{-3}$ M) were carried out in 250 ml double necked round bottom flask with a magnetic stirrer at 423 K. One neck of the flask was fitted with a condenser and the other was capped from which samples were withdrawn at different time intervals. The progress of the reactions was monitored by measuring the COD of the reaction mixture using the
standard dichromate reflux method (APHA, 1985). In this method, 10 ml of reaction mixture brought out from time to time was refluxed in a 250 ml round bottom flask with 5 ml $K_2Cr_2O_7$ (0.25 M), 15 ml concentrated $H_2SO_4$ using silver sulphate as a catalyst. The solution is refluxed for 3 h, and then allowed to cool down to room temperature. 40 ml distilled water was added to the solution, which was then titrated with 0.1 M ferrous ammonium sulphate (FAS) using Ferroin indicator. COD was computed from the following expression:

$$ COD = [(B - S) \times M \times 8000] / \text{ml of sample taken} $$

where, \( B \) = titration reading for water.
\( S \) = titration reading for sample.
\( M \) = molarity of FAS.

The procedure was repeated with the standard phenol solution and the COD of the same was estimated similarly.

**Phenol conversion in stirred reactor**

The reactions of phenol ($1 \times 10^{-3}$ M) were carried out in batch reactor stirring at 172 rpm at 353 K under atmospheric pressure. Using a UV-Visible spectrophotometer (Hitachi 3210), phenol remaining unconverted after the reaction was monitored and the percentage conversion was calculated. The products were analyzed by High performance liquid chromatography (Shimadzu HPLC Model LC-10AT).