CHAPTER 1

Introduction and literature survey

1.1 Introduction

Various types of artificial pollutants (inorganic, organic, and radioactive) from domestic and industrial wastewater cause water pollution. Toxic organic pollutants include resins, dyes, pesticides, fertilizers, hydrocarbons, phenols, plasticizers, biphenyls, detergents, greases, explosives, tanning agents, pharmaceuticals, lubricating oils, etc. [Pang & Lei (2016), Bae et al. (2016), Köhler et al. (2006)]. Among these, phenols and phenolic compounds are ultimately valuable and common by-products in dyes, paper, antioxidants, plastics, drugs, pesticides, and petrochemical industries. A major disadvantage of phenolic derivatives is that they are toxic in higher concentrations and cause severe skin disorders, kidney and liver damage [USEPA (1986)]. The Central Pollution Control Board (CPCB) has reported that industrial waste produces ~70 lakh tonnes of phenols annually. The United States Environment Protection Agency has declared eleven phenolic compounds like phenol, *p*-nitrophenol (PNP), *p*-chlorophenol (PCP), etc. [USEPA (2014)] as priority pollutants. These are common organic pollutants and very stable in groundwater and soil [Ju & Parales (2010)].

Dyes such as azo, nitro, nitroso, anthraquinone, triarylmethane, and indigo [Benkhaya et al. (2020)] are another set of organic pollutants frequently encountered in industries like textile, leather, food, cosmetic, paper, pharmaceutical, etc. Textiles are the largest consumer of dyes and pigments and produce large amounts of effluents after the dyeing process [Nidheesh et al. (2018)]. Many of these dyes are stable in an aqueous medium and, therefore, persist long in the environment [Suteu & Bilba (2005)]. The effluents containing dyes are one of the significant threats to the environment. Even in low concentrations, they affect the aquatic life and food chain [Malik (2003), Namasivayam & Kavitha (2002)].

Removing such toxic pollutants from industrial effluents is imperative before releasing wastewater into the aquatic environment. Various water remediation processes such as adsorption, coagulation, filtration, membrane, filtration, ion-exchange, photocatalysis, sonolysis, ozonization, Fenton process, etc., have been used to remove pollutants from wastewater. According to the pollutant removal mechanisms, these processes can be divided into separation methods (physical and physicochemical) and degradation methods (chemical and biological). Figure 1.1 displays a schematic diagram of various techniques used for pollutant removal.

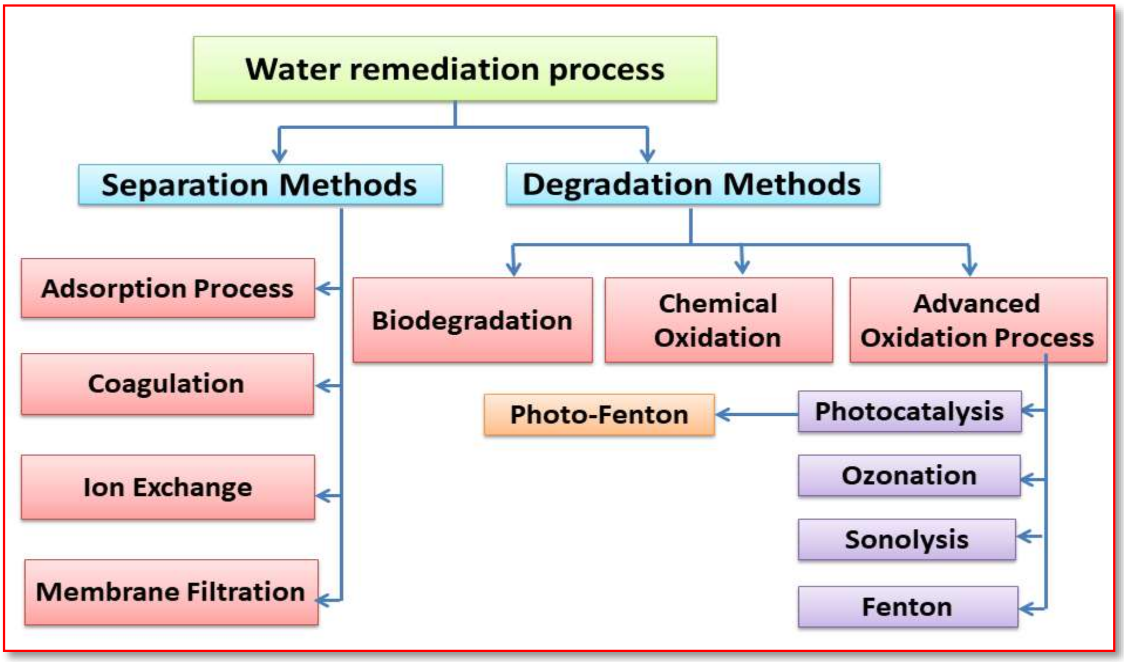

Figure 1.1 Schematic diagram of the various methods used for pollutants removal.

Separation techniques include coagulation, membrane filtration, ion-exchange processes, and adsorption. The main disadvantage of separation methods is the disposal of pollutants. For instance, the disposal of pollutants containing sludge in coagulation processes, pollutants concentrated on adsorbent surfaces, and concentrated pollutant solution, as in membrane processes. Among these, adsorption methods are practical and cost-effective. Critical concerns with the adsorption process are the separation and the recyclability of the adsorbent particulates. One way of tackling this issue is by fabricating effective superparamagnetic adsorbents. Superparamagnetic nanoparticles can be separated by a magnetic field and then re-dispersed by simple sonication without any magnetic field.

Degradation methods, on the other hand, degrade pollutant molecules into harmless end products. They include chemical oxidation, biodegradation, and advanced oxidation processes (AOP). From these, AOPs are a class of highly efficient oxidation methods well-suited for the large-scale treatment of contaminants in water. This class of techniques involves using reactive oxygen species (ROS) such as hydroxyl radical ($^{\bullet}OH$), superoxide radical ($O_2^{\bullet-}$), hydroperoxyl radical ($^{\bullet}OOH$), and peroxy radical ($^{\bullet}OOR$) for oxidative degradation of organic pollutants. Hydroxyl radicals are the second most potent oxidant species (after fluorine) with a high reduction potential (E^0 = 2.8 V v/s SHE) capable of oxidizing all classes of organic compounds [Pera-Titus et al. (2004)]. They can cause the complete mineralization of organic pollutants. In most cases, the final products of AOP methods are carbon dioxide, water, and various inorganic ions (which contain heteroatoms present in the starting organic pollutants) [Andreozzi et al. (1999), Bolton et al. (1996), Pignatello (1992)]. AOPs can reduce the concentration of contaminants from several hundred ppm to less than five ppb [Munter (2001)], making them the treatment processes of the twenty-first century. Most AOPs involved the production of $^{\bullet}OH$ at near-ambient temperature and pressure conditions in a reaction system [Glaze et al. (1987), Méndez-Arriaga et al. (2009)]. Ozonation, Fenton reaction, sonolysis, photocatalysis, electro-Fenton, ultraviolet irradiation (H_2O_2/UV) process, and photo-Fenton oxidation processes that involve $^{\bullet}OH$ radicals as oxidants belong to advanced oxidation methods. These AOPs are all green processes because they use H_2O_2 as the reagent for the generation of $^{\bullet}OH$ radicals. Given this, the design and the development of more efficient heterogeneous catalysts/photocatalysts for the Fenton process are critical. In this context, catalysts or photocatalysts that are superparamagnetic can ensure easy recyclability because of the reasons stated earlier.

From the above discussion of different wastewater remedying techniques, one can see that pollutant separation by adsorption or degradation by the Fenton process are the most techno-economically feasible processes among those listed. Thus, the present thesis first investigates the adsorption properties of magnetite nanoparticles, a magnetic iron oxide phase, towards organic pollutants. The emphasis is on understanding the nature of adsorbate-adsorbent molecular interactions in the presence of a large number of solvent molecules. In general, experimental investigations have not addressed the molecular interaction featured during the adsorption process. Thus, the thesis examines this aspect extensively using classical large-scale molecular dynamics (MD) simulations. The subsequent chapters of the thesis investigate the Fenton catalytic/photocatalytic properties of magnetite and its composites through a combination of experimental and computational investigations. Given this, the following sections introduce the main adsorption concepts and the issues involved in a heterogeneously catalyzed Fenton process.

1.2 Adsorption process

An increased concentration of the adsorbate (adsorbed molecule) on the solid adsorbent particle surfaces relative to its concentration in the bulk liquid (solution) or gaseous phase describes adsorption. The concentration of the solute species (i.e., adsorbed on the adsorbent) in the bulk fluid is called the adsorptive. Adsorption requires the presence of a solid surface (adsorbent) in contact with another liquid or gaseous phase.

The component in the liquid or gaseous phase that accumulates on the surface of the adsorbent is called the adsorbate [Dąbrowski (2001), Yang (2003)]. Adsorption is classified as physisorption or chemisorption depending on the strength of the adsorbate-adsorbent interaction. Physical adsorption or physisorption occurs through non-specific weak Van der Waal forces interaction between adsorbate molecules and the adsorbent surface. It has small heat of adsorption and is reversible. If there is a specific bond between the adsorbate molecule and the adsorbent surface, the adsorption process is irreversible. Such adsorption occurs with a relatively higher heat of adsorption and is referred to as the chemical adsorption (chemisorption) process.

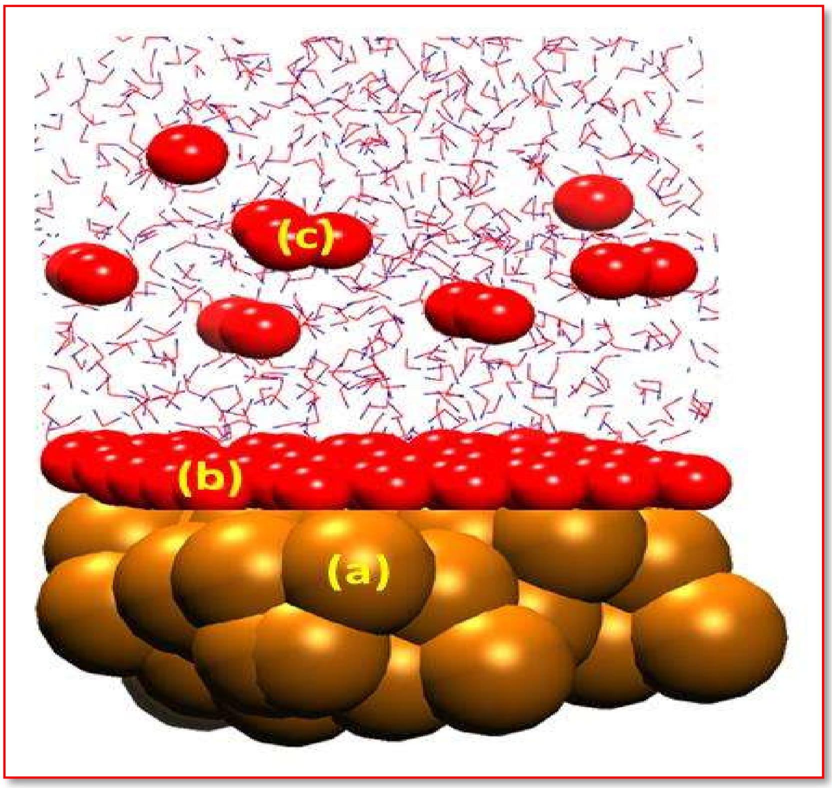

Figure 1.2 Model picture represents adsorption of adsorbate onto an adsorbent surface. Here a) represents the surface of the adsorbent, b) the adsorbed solute molecules (adsorbate), and c) the solute molecules that are not adsorbed.

Figure 1.2 describes the adsorption process; it shows the adsorption of adsorbate onto an adsorbent surface. Various interactions possible during the adsorption phenomenon are as follows:

1) Adsorbate-adsorbate interaction, 2) Adsorbate-adsorbent interaction,

3) Adsorbate-solvent interaction, 4) Adsorbent-solvent interaction,

5) Solvent-solvent interaction

For efficient adsorption, adsorbate-adsorbent interaction should be more potent than adsorbate-adsorbate and adsorbate-solvent interactions. But there are other entropic considerations as well due to the size and morphology of adsorbate molecules. Since the present thesis is concerned with organic pollutant water remediation, all discussions hereafter will only consider water as the solvent.

1.3 Overview of adsorption isotherm models

An adsorption isotherm is an equilibrium relationship between the adsorbate (the adsorbed molecule quantity) and its (adsorptive) concentration in the bulk fluid phase at a constant temperature [Dąbrowski (2001)]. Equilibrium adsorption isotherms involve plotting the adsorbate concentration on the adsorbent surface versus the adsorptive concentration in the bulk liquid phase. It can usually be described by one or more of a series of adsorption isotherm models or equations that help to analyze the experimental equilibrium adsorption process. These include the Freundlich (Freundlich 1906), Langmuir (Langmuir 1916), BET (Brunauer, Emmett and Teller 1938), Temkin (Temkin 1940), Sips (Sips 1948), Langmuir-Freundlich (Sips 1950), Hill-de Boer (Hill 1946, De Boer 1953), Koble-Corrigan (Koble 1952), MacMillan-Teller (MacMillan 1951), Frenkel–Halsey-Hill (Hill 1952), Redlich-Peterson (Redlich 1959), Dubinin-

Radushkevich (Dubinin 1960), Tóth (Tóth 1971), Flory-Huggins (Jnr 2005), Radke-Prausnitz (Vijayaraghavan 2006). An isotherm equation is based on an adsorption model. The latter may or may not be derived from a particular adsorption mechanism model. The most popular adsorption isotherms applied to solid-liquid interface systems are the Langmuir and Freundlich adsorption models. The subsequent sub-sections introduce these two isotherm models. Note that the Langmuir isotherm is derived from an adsorbate-adsorbent interaction model, whereas the Freundlich isotherm is empirical.

1.3.1 Langmuir isotherm model

The Langmuir isotherm (1916) is the first and the oldest adsorption model [Langmuir (1916)]. It assumes monolayer adsorption and no interaction between neighboring adsorbed molecules. Additionally, it considers that all active sites as identical (or the adsorbent surface is homogeneous).

Equation 1.1 gives the Langmuir adsorption isotherm expression:

$$\boldsymbol{Q_e = \frac{K_L \times Q_{max} \times C_e}{1+(K_L \times C_e)}} \tag{1.1}$$

Here, $\boldsymbol{Q_e}$ = amount of adsorbate adsorbed on the adsorbent (mg/g),

$\boldsymbol{C_e}$ = concentration of adsorbate present in the solution at equilibrium condition (mg/L),

$\boldsymbol{Q_{max}}$ = maximum adsorption capacity of the adsorbent (mg/g),

And $\boldsymbol{K_L}$ = Langmuir adsorption isotherm constant (L/mg).

1.3.2 Freundlich isotherm model

The Freundlich isotherm is an empirical model that describes the solutes' adsorption from a fluid to a solid surface [Freundlich (1906)]. This isotherm is generally applicable to multilayer adsorption, where the adsorbent surface has sites with non-uniform adsorptive affinities or heterogeneous sites. The Freundlich isotherm equation describes the adsorption process as being one in which the stronger binding sites are occupied first, and the adsorption energies decrease exponentially with the adsorption process [Foo & Hameed (2010)]. Equation 1.2 expresses the Freundlich adsorption isotherm.

$$\boldsymbol{Q_e = K_F \times Q_{max} \times C_e^{\frac{1}{n}}} \tag{1.2}$$

Here, $\boldsymbol{K_F}$ = Freundlich isotherm constant (describes adsorption capacity)

and $\boldsymbol{n}$ = the heterogeneity factor (describes adsorption efficiency).

These Freundlich constants are empirical constants that are affected by several environmental factors. The degree of non-linearity between solution concentration and adsorption is shown by the value of 1/n, which varies from 0 to 1. The adsorption process is linear if the value of 1/n is equal to unity; if the value is less than unity, the adsorption process is chemical; if the value is more than unity, adsorption is a favorable and physical process; the more heterogeneous the surface, the closer the 1/n value is to 0 [Foo & Hameed (2010)].

Adsorption is critical not only for its pollutant separation properties but also because it is a primary requirement for the efficacy of a heterogeneous catalyst. All heterogeneous catalysis mechanisms depend on the nature of reactant adsorption on the catalyst in some way or other. Therefore, the following section introduces the basic heterogeneous catalytic reaction mechanisms from this perspective.

1.4 Heterogeneous catalysis

In the chemical industry, heterogeneous catalytic processes contribute much more than homogeneous catalytic processes. In the former, the catalysts are solid, and the reactants (or substrates) are in the liquid or gaseous phases. As a result, the interfacial phenomena during heterogeneous catalysis is vital [Whitby (2015)]. Adsorption is the primary (first) step in heterogeneous catalysis. There are mainly two catalyst surface reaction mechanisms. These are the Langmuir-Hinshelwood and the Eley-Rideal mechanisms.

1.4.1 Langmuir-Hinshelwood Mechanism

The Langmuir-Hinshelwood mechanism of heterogeneous catalysis involves the following steps. These are schematically illustrated in Figure 1.3.

1. Both reactants (i.e., A and B) adsorb on the catalyst surface.
2. They may adsorb on adjacent active sites or can diffuse to adjacent positions on the catalyst surface.
3. Being on adjacent sites, they react and form a product.
4. The product desorbs from the catalyst surface, and the catalyst's active site is regenerated. Excess adsorption of one reactant can impede the reaction or poison the catalyst surface.

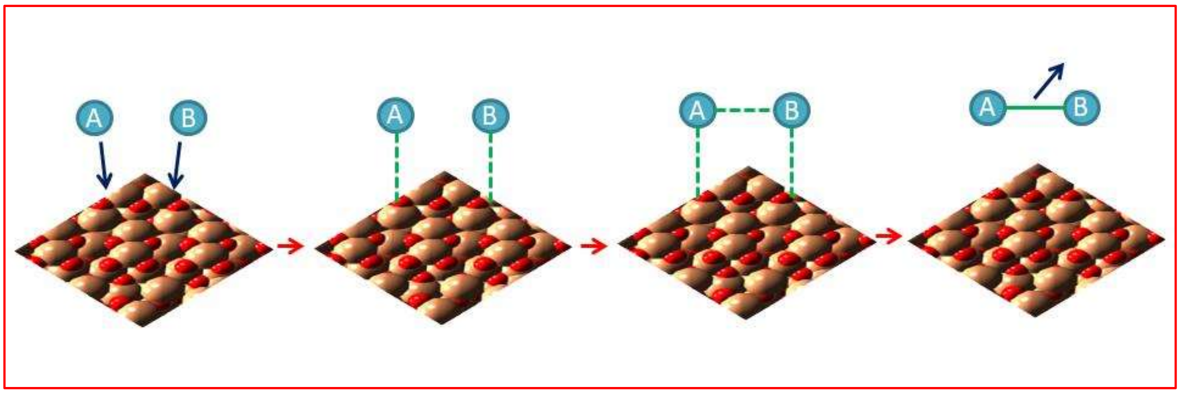

Figure 1.3 Illustration of Langmuir–Hinshelwood mechanism

1.4.2 Eley-Rideal Mechanism

Figure 1.4 illustrates the scheme of the Eley-Rideal mechanism. Only one of the reactants is adsorbed to the catalyst surface in this mechanism. Then, the second reactant in the solution phase interacts with the adsorbate molecule on the surface and forms a product. The product desorbs from the catalyst surface and produces a vacant active site for further adsorption and reaction.

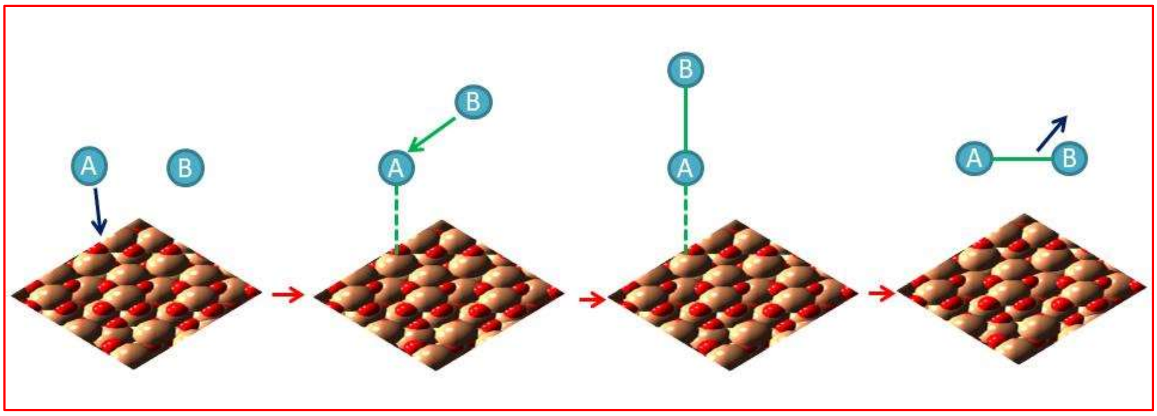

Figure 1.4. Illustration of Eley-Rideal mechanism

1.5 Heterogeneously catalyzed Fenton reaction

The brief discussion on the essentials of heterogeneous catalysis mechanisms was a necessary prelude for introducing heterogeneous Fenton reaction mechanism issues discussed in this section. The original Fenton reaction, discovered by Henry John Horstman Fenton in 1819, was homogeneous. It consists of quick generation of hydroxyl radicals by the reaction between ferrous ions and hydrogen peroxide (H_2O_2) in an acidic medium (the reaction shown in equations (1.3)) [Fenton (1894)]. The first step, therefore, is a fast reduction of H_2O_2 by the Fe^{2+} ions. Consequently, the latter gets oxidized to Fe^{3+} ions. The second step requires the regeneration of the catalyst Fe^{2+} ions. But relative to the first step, the second part is much slower (Equation 1.4). In fact, the rate constant of the first step (generation of hydroxyl radicals) is many times that of the second step, resulting in the concomitant generation of sludge (the accumulated Fe^{3+} salt). Furthermore, it also requires the continuous addition of the Fe^{2+} salt to sustain the reaction.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^-, \ k = 40\text{-}80 \ M^{-1}s^{-1} \tag{1.3}$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\bullet} + H^+, \ k = 0.001\text{-}0.01 \ M^{-1}s^{-1} \tag{1.4}$$

H.R. Eisenhaner first applied this reaction for degrading organic matter in wastewater effluents in 1964 [Eisenhauer (1964)]. Later, many researchers used the classical homogeneous Fenton reaction to degrade organic pollutants [Babuponnusami & Muthukumar (2014), Neyens & Baeyens (2003), Pignatello et al. (2006)]. However, as mentioned earlier, this process shows two significant drawbacks: catalyst loss (Fe^{2+} salt) and a large amount of sludge generation.

Fenton reactions on heterogeneous catalysts have been classified as heterogeneous Fenton or Fenton-like reactions [Cai et al. (2016), Diao et al. (2017), García-Rodríguez et al. (2017), Li et al. (2018c), Lyu & Hu (2017), Pignatello et al. (2006), Tyre et al. (1991), Velichkova et al. (2017)]. The heterogeneous Fenton reaction [Ruales-Lonfat et al. (2015), Wang et al. (2016)] replaces dissolved iron salt in the classical Fenton approach with solid iron-based catalyst particles or nanoparticles. The solid catalyst particles have active sites that help activate the H_2O_2 molecules to generate reactive oxygen species (ROS) for organic contaminant degradation in the wastewater. While the hydroxyl radical is the dominant ROS species, there is the generation of other reactive species (like superoxide radicals, hydroperoxyl radicals, and higher-valent iron species) as well [He et al. (2016)]. Furthermore, the heterogeneous catalysis processes are feasible over a wider range of pH conditions.

He et al. published a review article in 2016 on the interfacial mechanisms during heterogeneous Fenton reactions [He et al. (2016)]. The primary step in a Fenton reaction is the generation of powerful hydroxyl radical oxidants. This requires the adsorption and activation of H_2O_2 on the heterogeneous catalyst surface. They mentioned that $^{\bullet}OH$ could be produced by two possible mechanisms. One mechanism could be because of iron ions leached from the catalyst surface. The Fenton reaction can proceed by the outer-sphere reaction mechanism between Fe^{2+} ions and H_2O_2 at pH 3, resulting in the reaction depicted by equation 1.5. This scheme is analogous to the homogeneous Fenton reaction mechanism. The more frequently observed process is the generation of hydroxyl radicals by a true heterogeneous catalytic mechanism on an iron-based material surface (Equation 1.6) which involves electron transfer from Fe^{2+} ions on the catalyst surface to H_2O_2 to form the $\equiv Fe^{3+}$ surface species. Hence, most iron oxide-based heterogeneous Fenton catalysts are quite stable, even under acidic conditions.

$$Fe^{2+} + H_2O_2 + H^+ \rightarrow Fe^{3+} + {}^{\bullet}OH + H_2O \qquad (1.5)$$

$$\equiv Fe^{2+} + H_2O_2 \rightarrow \equiv Fe^{3+} + OH^- + {}^{\bullet}OH \qquad (1.6)$$

Where, $\equiv Fe$ indicates surface iron

As mentioned earlier, besides hydroxyl radicals, other ROS species, such as $^{\bullet}OOH$ and $O_2^{\bullet-}$ have also been detected. Hydroperoxyl radicals are generated from the reaction between surface-complexed ($\equiv Fe^{3+}$-OH) and H_2O_2, reactions between $^{\bullet}OH$ and H_2O_2, and reactions between carbon-centred free radicals and O_2 (Equations 1.7-1.10) [Lin & Gurol (1998), Pignatello et al. (2006), Kakavandi & Babaei (2016)].

$$\equiv Fe^{3+}\text{-}OH + H_2O_2 \rightarrow \equiv Fe^{2+} + H_2O + {}^{\bullet}OOH \qquad (1.7)$$

$$\equiv Fe^{3+}\text{-}OH + {}^{\bullet}OOH \rightarrow \equiv Fe^{2+} + O_2 + H_2O \qquad (1.8)$$

$$^{\bullet}OH + H_2O_2 \rightarrow {}^{\bullet}OOH / O_2^{\bullet-} + H_2O \qquad (1.9)$$

$$R^{\bullet} + O_2 \rightarrow R(-H^+) + {}^{\bullet}OOH \qquad (1.10)$$

Note that $^{\bullet}OOH$ and its conjugate base O^{2-} species are less reactive than $^{\bullet}OH$ radicals [Navalon et al. (2010), Xue et al. (2009)]. The $^{\bullet}OH$ radicals may also be produced in a reductive environment [Cao et al. (2013), Le et al. (2011), Vilardi et al. (2018)].

1.6 Heterogeneous photo-Fenton process

The heterogeneous photo-Fenton process driven by visible light energy has raised considerable interest recently. Since nearly 45% of the solar radiation is in the visible range, the photocatalytic processes that utilize visible light energy are of prime importance. The photo-Fenton process involves a photocatalytic mechanism for hydroxyl radical generation from H_2O_2. The photocatalyst should have a finite band gap in the UV-visible range. On irradiation of the photocatalyst by light energy exceeding the band gap it results in the formation of photo-excited electrons and holes. In a photo-Fenton process, the excited electron in the conduction band (CB) should be able to reduce H_2O_2 molecules for hydroxyl radical generation. The following equations summarize the photo-Fenton mechanistic possibilities.

$$\text{Iron oxide} + h\vartheta \rightarrow \text{Iron oxide}\ (h^+ + e^-) \qquad (1.11)$$

$$e^-(cb) + H_2O_2 \rightarrow Fe^{3+} + OH^- + {}^{\bullet}OH \qquad (1.12)$$

Depending on the valence band (VB) position, one of the following reactions may take place for regeneration of Fe^{2+} ions from the oxidized Fe^{3+} ions on the photocatalyst surface.

Thus, $h^+(vb) + OH^- \rightarrow {}^{\bullet}OH$ results in the following

$$\equiv Fe^{3+} + OH^- + h\vartheta \rightarrow Fe^{2+} + {}^{\bullet}OH \qquad (1.13)$$

Another pathway: $h^+(vb) + {}^{\bullet}OOH \rightarrow O_2 + H^+$ resulting in

$$\equiv Fe^{3+} + {}^{\bullet}OOH + h\vartheta \rightarrow Fe^{2+} + O_2 + H^+ \qquad (1.14)$$

The third option is: $h^+(vb) + H_2O \rightarrow H^+ + {}^{\bullet}OH$, which results in

$$\equiv Fe^{3+} + H_2O + h\vartheta \rightarrow Fe^{2+} + H^+ + {}^{\bullet}OH \qquad (1.15)$$

Note that the VB position of the photocatalyst should be more positive (or higher) than the $^{\bullet}OH/OH^-$ (1.99V) reduction potential for successful execution of the first pathway. Similarly, the VB position of photocatalyst needs to be higher than the $O_2/{}^{\bullet}OOH$ reduction potential (0.10V). The third option is rare because of the very high $^{\bullet}OH/H_2O$ (2.38V) reduction potential value [Fadillah et al. (2020)]. Figure 1.5 shows the general mechanism involved in the heterogeneous photo-Fenton process.

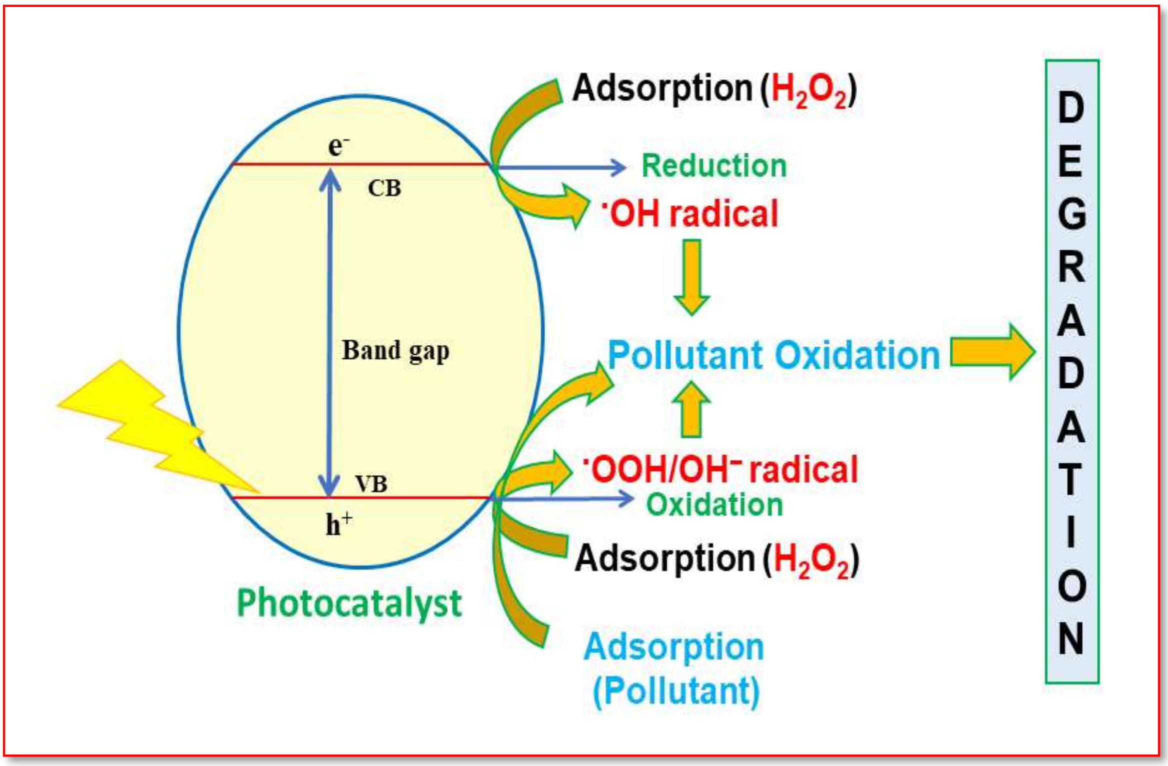

Figure 1.5 The general mechanism involved in the heterogeneous photo-Fenton process.

An iron oxide-based photo-Fenton catalyst contains iron ions or iron hydroxide or oxides or redox species which can serve as the active centres for activation of HO-HO bond in the H_2O_2 molecules. Essentially, light irradiation plays a significant role in promoting $\equiv Fe^{3+}/Fe^{2+}$ circulation. The photo-excitation populates more electrons on specific regions of the catalyst surfaces that can accelerate the reduction of H_2O_2 and simultaneously enables the reduction of the oxidized $\equiv Fe^{3+}$ to $\equiv Fe^{2+}$ to enhance Fenton reactivity. As mentioned earlier, this thesis investigates the adsorption, Fenton and photo-Fenton properties of magnetite and its composites. Hence, the next section introduces the basic features and properties of magnetite particles/nanoparticles.

1.7 Literature review and Research Gap

In recent years, researchers have focused on magnetic adsorbents as well as magnetic catalysts. These have been used for water remediation [Xu et al. (2012), Zhang (2003)], biomedical [Mahmoudi et al. (2011), Soenen et al. (2011)], construction [Foley & Wiek (2014), Smith et al. (1990)], electronics [Tuharin et al. (2020), Wang et al. (2020)], healthcare [Ali et al. (2016), Rodner et al. (2019)], automotive [Mayer et al. (2010)], textiles [Xiao et al. (2009)] and agriculture and food packing [Kamzin et al. (2018)] applications. Several iron oxides like magnetite (Fe_3O_4), hematite (α-Fe_2O_3), maghemite (γ-Fe_2O_3), etc., have been used as catalysts in different reactions. From these, magnetite is an inverse spinel iron oxide with permanent magnetic properties. Nano-sized magnetite particles have a finite band gap due to quantum size effect and are photostable. Magnetite is an effective adsorbent for many pollutants and it has also been found to be a capable heterogeneous catalyst for degrading some organic pollutants in waste effluents by Fenton reactions [Ambashta & Sillanpää (2010), Hongping et al. (2015), Munoz et al. (2015)]. The magnetite crystal structure consists of an FCC lattice of oxygen anions with Fe(III) ions occupying equal number of octahedral and tetrahedral sites, and Fe(II) cations occupying only the octahederal sites. This iron oxide is relatively cheap compared to other oxide nanoparticles (such as gold, silver, ceria, etc.) and is less toxic to the human body [Singh et al. (2010)].

Magnetite nanoparticles (MNPs) are easily recoverable by magnets than other non-magnetic catalysts because they show superparamagnetic properties. But the high surface energy and hydrophobic nature of MNPs cause the formation of larger aggregated particles with lesser surface areas, surface energies, and inhibited catalytic activities [Wei et al. (2012)]. Surface stabilization (or coating) with an organic molecule can stabilize the MNPs against aggregation. Besides stabilization against aggregation, such surface coating can also provide more functional groups for reactants adsorption [Avella et al. (2005), Deng et al. (2002), Huang & Tang (2004), Lee et al. (2004), Liu et al. (2003), Xu et al. (2004), Zhang et al. (2003)]. Stabilized magnetic nanoparticles can be re-dispersed into a new system after removing the external magnetic field and efficiently reused several times. Various researchers have used many supporting materials on iron oxide nanoparticles such as organic moieties, surfactants, polymers, biomolecules, inorganic compounds, and carbon materials to alter the surface properties of nanostructures [Wu et al. (2008)] and to prevent iron leaching problems.

1.7.1 Computational approaches to adsorption studies

Many experimental reports have proclaimed magnetite as an effective adsorbent for organic pollutants such as phenol, *p*-chlorophenol, thiazine dye, congo red, trinitrotoluene, pentachlorophenol, *p*-nitrophenol, etc. [Ambashta & Sillanpää (2010), Giri et al. (2011)]. These reports have explained the adsorption phenomena by the thermodynamic and kinetics parameters. Generally, experimentalists optimized adsorption experiments and obtained adsorption equilibrium data. These data sets were then fitted to different adsorption isotherm equations. As mentioned earlier, most experimental studies have reported fitting their data to Langmuir and Freundlich isotherm models. It seems, in many cases, the adsorption data fit both isotherm equations almost equally well. For example, Yoon et al. (2016) reported that their experimental data for adsorption of phenol on magnetite nanoparticles fits both Langmuir and Freundlich isotherms. However, Langmuir and Freundlich model's assumptions are different. Thus, such fitting exercises do not give any insight into the adsorption mechanism.

Very few experimental research papers are interested in understanding the adsorption mechanism based on the interaction between adsorbate and adsorbent. Earlier literature discusses interactions such as covalent bonding, π–π stacking interactions, electrostatic interactions, hydrogen bonding, acid-base interaction, complexation, chelation, hydrophobic interactions, microprecipitation, proton displacement, oxidation/reduction, and ion-exchange [Catherine et al. (2018), Chowdhury & Balasubramanian (2014), Crini et al. (2019), Crini & Badot (2008), Sasaki & Tanaka (2011), Wang et al. (2014)]. These mechanisms are not fully understood because they involve many simultaneously occurring interactions [Crini et al. (2019)].

Some spectroscopic studies like Ultraviolet-visible spectroscopy (UV-Vis) [Farahani et al. (2016)], Fourier Transform Infrared (FTIR) [Sabna et al. (2016)] and Raman [Song et al. (2016)], X-ray photoelectron spectroscopy (XPS) [Song et al. (2016)] have been used to investigate adsorption mechanisms and give structural information. However, these investigations involve many complicated facets due to the involvement of many coupled variables during the interfacial phenomenon. These techniques have proven to be less effective in explaining the system's dynamical behavior at the molecular level. Considering the drawbacks of experimental methods, some researchers came up with mathematical modeling, a statistical tool to design the adsorption system. Linear regression is a statistical technique that is preferably used to estimate adsorption coefficient parameters [Allen et al. (2004), Crini & Badot (2010), El-Khaiary & Malash

(2011)]. The adsorption data of phenol, 2-chlorophenol, and 4-chlorophenol onto magnetite nanoparticles were analyzed by the Langmuir and Freundlich isotherms using the statistical techniques [Tural et al. (2016)]. Unfortunately, this statistical tool also falls short of explaining the adsorption mechanism.

In the above matter, computational approaches are a powerful tool for describing the inter/intramolecular interactions in the system. The computational methods such as quantum mechanical approaches (Density Functional Theory (DFT)), ab-initio molecular dynamics (AIMD), and classical molecular dynamics (MD) simulations can provide complementary pieces of information on molecular aspects of adsorption phenomena. DFT is a quantum mechanical method that is used to calculate adsorption energy (E_{ads}, i.e., the difference between the energy of the adsorbent with the single-molecule adsorbed and the separated components), structural parameters of minimum energy configurations, electronic and spectroscopic properties [Ruiz et al. (2016); Tang et al. (2015)]. A couple of researchers used the quantum mechanics approach to investigate pollutant molecules' interactions with carbon material such as graphene and graphene oxide model sheets [Cortés-Arriagada et al. (2013), Tang et al. (2018)]. Another study investigated the removal mechanism of heavy metal complexes (zinc (Zn^{2+}), nickel (Ni^{2+}), and chromium (Cr^{6+})) onto the prepared magnetite-graphene oxide (MGO) composite. They estimated the metal hydrates' adsorption binding energy and geometries with oxygen functional group (i.e., hydroxyl, epoxide, carboxylic, carbonyl groups) and magnetite on the MGO surface. These authors also investigated the adsorption phenomena in the absence of solvent conditions because DFT is not applicable for larger systems.

The AIMD method uses DFT to obtain the inter and intramolecular forces and then compute the system's dynamical behavior [Botu & Ramprasad (2015)]. These calculations are typically performed on replicated supercell structures with periodic boundary conditions (PBC). For instance, the Li group investigated the polycyclic aromatic hydrocarbon adsorption mechanism on graphene sheets by first principle DFT calculations and AIMD simulations [Li et al. (2018a)]. They successfully concluded that physical adsorption takes place on the surface of adsorbents from the density of states and electron density data. Water was used as an implicit solvent in their study; therefore, they could not figure out the entropic effect of solvent on adsorption.

In this respect, classical MD simulations are feasible to calculate adsorption free energies in the presence of many explicit solvent molecules. MD results interpret various adsorption properties such as radial distribution function (RDF), coordination number, potential mean force, time-dependent properties (mean square displacement, residence time, diffusion coefficients) surface accessible area. The MD simulation is based on the laws of classical mechanics and uses force-field parameters for calculations. The force field describes the intramolecular and intermolecular interactions in the chosen system [Cramer (2013), Frenkel (2001)]. Various force fields like PCFF [Sun et al. (1994)], Drieding [Mayo et al. (1990)], CHARMM [Huang & Mackerell (2013), Lee et al. (2014)], AMBER [Dickson et al. (2014), (Cornell et al. (1995)], GROMOS [Pechlaner et al. (2017)], etc. are commonly used in the MD simulations. It can provide dynamic adsorbate-adsorbent data that cannot be accessed through experimental methods [Comer et al. (2015)]. This approach can yield adsorption isotherms in good agreement with experimental data and capture adsorption mechanisms to see their molecular interactions when used with proper force field parameters.

Previously, some researchers have applied molecular modeling techniques to study environmental phenomena, such as the adsorption mechanisms of organic contaminants adsorbed onto clays and minerals, carbon nanomaterials, carbon nanotubes, surfactants [Boateng et al. (2013), Ding et al. (2016), Greathouse et al. (2015), Liu et al.

(2015), Peredo-Mancilla & Dominguez (2016)]. For example, the Liu group in 2015 studied that methylene blue cations quickly congregate around graphene oxide in water by MD simulations. They checked interaction with pollutant dye by Material Studio software using a COMPASS force field in an explicit aqueous environment. Their findings provided a better understanding of the interaction of graphene oxide with organic pollutants. Some MD research articles focus on oxide-type adsorbents such as titanium oxide for adsorption studies [Wahab & Koutselos (2009)]

While many experimental studies have investigated the adsorption of organic pollutants on iron oxide-based adsorbents, there is less understanding of competitive adsorption between reactants on these adsorbents by computational methods. From the theoretical point of view, a deep investigation is required to understand the mechanism of adsorption. Mentioned below are the questions that need answers to explain the interfacial mechanism during the adsorption process.

1. How are the adsorbate molecules adsorb on the adsorbent surface in the presence of large numbers of explicit water molecules?
2. How is each atom of the organic pollutant molecule (adsorbate) interacting with specific atoms on the adsorbent surface?
3. The orientation of the reactant molecules relative to the adsorbent surface?

These questions have been investigated in the present thesis using the MD approach.

1.7.2 Fenton and Photo-Fenton catalytic properties of magnetite and its composites

As mentioned earlier, pure MNPs, without any stabilizers or organic surface modifiers, or other supports, suffer from several disadvantages. The organic surface coating of MNPs not only prevents aggregation but also changes their adsorption properties. The latter is critical for both Fenton and photo-Fenton effectiveness of a catalyst. Thus, various iron oxide nanoparticles have been combined with stable support (zeolites, metal-organic frameworks, clays, graphene oxide, silica), which can provide more surface area for adsorption in heterogeneous Fenton catalysts [Nidheesh (2015, 2017)], Ahmad et al. (2020), Del Campo et al. (2005), Saikia et al. (2014), Yuan et al. (2009), Zhang et al. (2018), Zubir et al. (2014), Navalon et al. (2010)]. For instance, investigators have used soluble starch to stabilize the MNPs since the former is inexpensive, hydrophilic, and environment-friendly [Robinson et al. (2019)].

The heterogeneous Fenton mechanism has two main aspects. The first one is to identify the catalyst sites responsible for the activation of bonds in H_2O_2 for the generation of $^{\bullet}OH$ radicals. The second one is to know the adsorption/interaction/distribution of H_2O_2 and organic substrate on the catalyst surface in the presence of a solvent. The reductive cleavage of H_2O_2 needs its effective interaction with nucleophilic sites on the catalyst for optimum $^{\bullet}OH$ generation for organic pollutant degradation. Maximum hydroxyl radical generation is desired. But hydroxyl radicals have very short lifetimes ($\sim10^{-9}$s). Hence, the substrate or the organic pollutant molecule should be located nearby. It is necessary to know the optimum distance and orientation of the substrate or the pollutant molecule from the catalyst surface.

In this context, some authors have proposed a Langmuir-Hinshelwood type mechanism; others have suggested an Eley-Rideal type pathway. Hu, Liang, and Yang investigations indicated that the surface produced ROS only attacking the adsorbed organic molecules on the iron-based material surface and proposed a Langmuir-Hinshelwood mechanism [Liang et al. (2012), Hu et al. (2011), Yang et al. (2009)]. Liang et al. (2012) and Furman et al. (2009) proposed an Eley-Rideal mechanism where ROS generated on the catalyst surface oxidizes unadsorbed organic substrates. He et al. (2014) found that catechol adsorbs to the iron oxide surface during oxidation in their in-situ flowcell ATR-FTIR studies. As a result, they assumed that ROS would primarily target unadsorbed parent compounds near the interface region. They concluded that $^{\bullet}OH$ radicals should be close to catalyst surface and organic molecules as it has a short lifetime [He et al. (2014)]. Xue et al. (2009) found that excess adsorption of organic molecules blocks the active catalyst sites for H_2O_2 interaction. It leads to the reduction of ROS production. Lucking and Oliveira implied that the competition between the target organic moiety and H_2O_2 molecules for active sites might impede the Fenton reaction. The proposed path indirectly supports an Eley-Rideal type mechanism [Lücking et al. (1998), Oliveira et al. (2007)]. However, the optimum distribution of organic pollutant and H_2O_2 molecules relative to each other and the catalyst surface resulting in the best possible pollutant degradation remains uncertain.

Most experimental studies using iron-based composites as the heterogeneous Fenton/photo-Fenton catalyst do not give enough attention to the mechanism involved. Careful catalyst design requires in-depth knowledge of the interfacial reaction mechanism. Therefore, the purpose of investigating the surface adsorption mechanism is to design the particular catalyst that accelerates the rate of Fenton activity. It is well known that stabilization by a particular molecule of the nanoparticle surface can increase its Fenton activity for a specific organic pollutant in different pH conditions [Bulánek et al. (2019), Wang et al. (2014)]. Thus, proper understanding of the catalyst interface mechanism is essential for designing nanoparticles decorated by a specific stabilizer (or forming its composite) that can enhance its Fenton activity towards a specific organic pollutant.

Density functional theory (DFT) approaches only provide data for adsorption of a single reactant on the catalyst surface by giving information regarding bond breaking or bond-forming in a chemical reaction. Some theoretical researchers have used DFT calculations to investigate the Fenton mechanism for homogeneous catalysts [Buda et al. (2001), Ensing & Baerends (2002), Lu et al. (2018), Petit et al. (2014), Ramos et al. (2015), Yamamoto et al. (2012)]. Minfeng Huo and co-workers proposed a heterogeneous catalytic Fenton reaction mechanism via plane wave-DFT calculations using Vienna ab Initio Simulation Package (VASP). They predicted that H_2O_2 could be readily adsorbed and dissociated on a single atomic iron nanocatalyst [Huo et al. (2019)]. Another study used DFT calculations to predict the adsorption of one H_2O_2 molecule on bare and functionalized iron-containing perovskites. It concluded that functionalized perovskites formed hydrogen bonds with H_2O_2 molecule, which is mainly responsible for the weakening of the O-O bond and the generation of $^{\bullet}OH$ radicals [Wang et al. (2011)]. From the available approaches, DFT does not shed light on the competitive aspect of the problem. This drawback of DFT can be overcome by using classical MD simulations, which can bring out the competition and the entropic nature of the problem. MD techniques can provide more insight into the working mechanism of heterogeneous Fenton reactions. The present thesis combines MD simulations and experimental studies to understand better the Fenton interfacial mechanism on the nanoparticles and the surface functionalization required for improving pollutant degradation.

1.7.3 Heterogeneous Photo-Fenton reaction

Bare MNPs are semiconducting and have visible range bandgap [Liu & Di Valentin (2017), Shamaila et al. (2017)] but suffer from rapid recombination. Coating MNPs with a water-soluble organic moiety with semiconducting properties can provide enhanced charge separation with better dispersibility. The formation of such composites can improve the photo-Fenton activity of a catalyst. For instance, graphene oxide (GO) has a visible bandgap region, and making a composite with it can enhance electron-hole charge separation. Recent magnetite/GO nanocomposite investigations have demonstrated effective photo-Fenton catalytic activity towards specific organic pollutants under visible light [Baptisttella et al. 2020, Yu et al. 2016].

For an effective photocatalytic procsess, band gap, band edges position, recombination rate, and reactant adsorption are the critical factors of any photocatalyst. Generated hole and photoinduced electron perform oxidation and reduction reactions and produce oxidized/reduced products only when concerned species adsorb on the photocatalyst surface. If the nature of reactant molecules is reducing then it should adsorb on the electrophilic (electron deficient) sites, and reactants that are oxidising in nature should interact effectively with the nucleophilic (electron rich) sites of a photo-excited photocatalyst. Hence, for photo-Fenton reactions, it is necessary to know whether, in the photo-excited state, the nucleophilic part of the photocatalyst has active interaction with H_2O_2 or not.

The knowledge of the relative location and interaction of the organic pollutant molecules with photocatalyst sites are also critical because of the short lifetimes of •OH radicals. Ground state DFT and time-dependent density functional theory (TDDFT) calculations can locate the nucleophilic and electrophilic functionalities in the ground and photo-excited states of any model catalyst [Hosseini et al. (2022), Verma et al. (2020), Verma et al. (2021)]. As mentioned earlier, MD simulations in an aqueous medium can tell us how different reactants interact with the catalyst surface and adsorb on it. These simulations can help to locate the positions of H_2O_2 and organic pollutants near the catalyst surface using the radial distribution function analysis. Another task of the present thesis is to combine MD simulations and DFT calculations with the proper experimental investigation to propose the interfacial phenomena during a photo-Fenton reaction mechanism over the catalyst surface. Carrying out parallel experimental investigations will help to validate computational predictions appropriately.

1.8. Objectives of the thesis

The detailed literature survey in the preceding section shows that a substantial number of experimental investigations have used magnetite and magnetite-based composite as adsorbent/catalysts to degrade various organic pollutants. Nevertheless, the interfacial phenomena during adsorption and heterogeneous Fenton catalysis on such materials are still unexplored. Furthermore, an appropriate combination of experimental and computational investigations is needed for understanding these interfacial interactions. Given this perspective, this thesis investigates the following objectives

i) The first problem tackled in the thesis is the adsorption of some organic pollutants on magnetite (111) surface in the presence of many water molecules by large-scale classical MD simulations. This study does not have any experimental parts. It is entirely an MD study. The results of these investigations are qualitatively compared with the experimental results available in the literature.

ii) The next objective is to investigate the mechanism of Fenton catalysis of *p*-nitrophenol (PNP) degradation on starch stabilized magnetite nanoparticles. Both magnetite and starch stabilized magnetite nanoparticles are prepared experimentally following earlier reports. Then Fenton reactions for PNP degradation are carried out on the prepared nanocatalysts. Simultaneously, MD simulations investigate and elucidate the interfacial distribution of reactants on magnetite, and a starch stabilized magnetite cluster during the Fenton reaction.

iii) The following objective was to understand the photo-Fenton degradation of orange-G dye on GO. This study was a necessary prelude to investigate the next goal about the Fenton and photo-Fenton activities of Fe_3O_4/GO nanocomposites. Two GO samples with different degrees of oxygen functional groups were prepared by variations of the modified Hummer's method. Parallelly, GO models with different degrees of oxygen functionalities were also constructed. A combination of experimental studies, MD simulations, DFT, and TD-DFT calculations were used to understand the Fenton and photo-Fenton mechanisms operating on these nanomaterials.

iv) The final objective was to understand the mechanism of Fenton and photo-Fenton degradation of PNP on the magnetite-GO nanocomposite. As earlier, here also experimental, MD, DFT, and TD-DFT results were combined to arrive at the operating mechanism.

The nanomaterials prepared in thesis work were magnetite, starch functionalized magnetite, and magnetite-graphene oxide composite by variations of precipitation method. Besides this, graphene oxide was prepared by a modified Hummer's method [Hummers & Offeman (1958), Hayes et al. (2015)]. These nanomaterials were characterized by X-ray diffraction, Fourier transforms infrared spectroscopy, Scanning electron microscopy, Raman spectroscopy, Transmission electron microscopy, and UV-visible spectroscopy, solid-state UV-visible diffuse reflectance spectroscopy.