Research in composite materials has blossomed over the past twenty years. The primary driving force for the composite material research is to synthesize stronger, tougher, lighter, and efficient materials that aspire to elevate the comfort of life in general. Many new materials have been developed by mimicking the natural composite materials such as diatoms, radiolarian [1], and bone [2]. Nanocomposite materials are the materials of 21\textsuperscript{st} century. They comprise of organic polymer and inorganic fillers and exhibit significantly improved properties in comparison to conventional composite materials. The composites hybridized at nanometer scale are of rising interest in view of their uniqueness and enhanced properties such as conductivity [3], toughness [4], optical activity [5], catalytic activity [6], chemical selectivity [7] etc. Such materials have shown good results in many applications such as drug delivery, water remediation, and enzyme immobilization etc. The study and investigation of the multifunctional properties of nanocomposites are the inspiration of this thesis.

**Organic/inorganic nanocomposite**

Organic/inorganic composite materials have been investigated for a long time. They can be broadly defined as composites of organic polymer and inorganic component with a characteristic length scale on the nanometer
size. Properties of composite materials comprise of individual contributions from both the components like inorganic phase having rigidity, and thermal stability and the organic phase with flexibility, dielectric properties, ductility, and processability. But the role of nanoscale dimensions of inorganic building blocks is predominant which leads to an incredible increase in the interfacial area. Inorganic nanoscale building blocks include nanotubes, layered silicates (e.g., montmorillonite, saponite), nanoparticles of metals (e.g., Au, Ag, Fe), metal oxides (e.g., SiO$_2$, TiO$_2$, Al$_2$O$_3$), and semiconductors (e.g., PbS, CdS) etc.

**Biopolymer based nanocomposites**

Out of various kinds of inorganic/organic nanocomposites, biopolymer based nanocomposites are most important. They have attracted considerable attraction in recent years and have been utilized in various fields. Biopolymers are the polymers produced by living organisms. They contain monomeric units that are covalently bonded to form larger structures. There are three main types of biopolymers based on the differing monomeric units and their structures, i) Polynucleotides- long polymers which are composed of 13 or more nucleotide monomers; ii) Polypeptides- short polymers of amino acids; and iii) Polysaccharides- which are often linearly bonded
polymeric carbohydrate structures. While synthesizing high performance macromaterials, the use of natural polymers is more attractive than using the conventional synthetic polymers. Natural polymers are nontoxic or less toxic and renewable materials and thus their use may provide better sustainability. There has been recent trend to use them in their native and various modified forms. Biopolymers such as polysaccharides can be suitably modified by chemical and physical means, like grafting [8], chemical derivatization [9], nanoparticle formation [10], oxidation [11], hydrolytic degradations [12], hydrogel formation [13], and conjugate formation with metal nanoparticles. Polysaccharide hydrogels are 3D cross linked network structures which are formed by the involvement of -NH₂, -COOH, -OH, -CONH₂, and -SO₃H groups of the polymer network. They have been widely used in various fields because of their high water retention capacity such as materials for protein separation and contact lenses, dies for encapsulating cells, and devices for controlled release of proteins and drugs.

Polysaccharide nanoparticles can be synthesized through variety of techniques such as covalent crosslinking, polyelectrolyte complexation, self-assembly of hydrophobically modified polysaccharides, solvent evaporation, spontaneous emulsification or solvent diffusion, and dialysis. Polysaccharide nanoparticles show excellent use in drug delivery.
Grafted polysaccharides have shown improved mechanical strength, better oil/water repellant behavior, and resistance to heat or abrasion etc. Modified polysaccharides have been used in various applications e.g. as potential carrier for pH sensitive drug delivery, as heavy metal and dye adsorbing agent, and as flocculating agent etc.

Low mechanical properties and low water resistance of natural polymer can be significantly enhanced by using nanocomposite technology. Different types of polysaccharides and proteins are being used to form biopolymer particles for food industry [14,15]. Many polysaccharides find use in green synthesis of metal nanoparticles [16-18]. Polysaccharides have been used in controlled drug release e.g. tamoxifen citrate, a non-steroidal antiestrogenic drug loaded guar gum nanoparticles, cross-linked with glutaraldehyde have been prepared for treatment of breast cancer [19]. Polysaccharides can template silica polymerization and hybrid silicas have shown high surface area, porosity, and thermal stability. There has been recent focus on enhancing the properties of biopolymers by preparing nanocomposites. In the present thesis development of polysaccharide based nanocomposites has been undertaken and the synthesized materials have been evaluated for dye removal and catalysis.
Broad literature is available on polysaccharide derived materials. Polysaccharide templated sol gel materials are especially attractive as they possess numerous potential applications. The term "hybrid" has been used to express materials that have two moieties blended on the molecular scale. Commonly, the term “nanocomposites” is used if materials comprise of various phases with different compositions and one of the phases has one or more dimensions of less than 100 nanometers. The organic part can be introduced as (i) A monomer or oligomer precursor, (ii) a preformed linear polymer that may be in molten, solution, or emulsion state, or (iii) a polymer network, physically or chemically thermoset or cross-linked. The inorganic component can be incorporated as, a precursor e.g. tetraethylorthosilicate (TEOS) or preformed nanoparticles. In general, polymerization (organic or inorganic) is a compulsory step if at least one of the preliminary moieties is a precursor.

Different synthetic strategies have been proposed for the preparation of polymer/silica nanocomposites. These include (i) blending, (ii) sol-gel process, and (iii) in situ polymerization.

(i) **Blending** - One of the easiest techniques for fabricating polymer/silica nanocomposites is blending. In a typical synthesis, polymer is dissolved in a good solvent to obtain a homogeneous
solution followed by the addition of inorganic nanoparticulates. The nanoparticle dispersion is prepared via stirring or ultrasonication. The resulting polymer-based nanocomposites can then be simply processed to generate a new class of material.

(ii) **Sol-gel process** - This route involves polymerization of inorganic precursor in presence of a preformed organic polymer.

(iii) **In situ polymerization** - In situ polymerization is a simple and efficient way of nanocomposite synthesis. In this case, the nanoparticles are grown inside the monomer(s) which can be polymerized later.

In recent years, significant efforts have been devoted to the design and controlled synthesis of organic/inorganic nanocomposite. These nanocomposites have been utilized in water remediation, separation, enzyme immobilization, sensor, and biomedical fields.

Bionanocomposites are generally synthesized under mild conditions using soft chemistry e.g. sol-gel reaction. Polysaccharides act as template and silicate solutions or silica alkoxides perform as the inorganic precursors. Polysaccharides being abundant, biodegradable, renewable, and polyfunctional are appropriate for the synthesis of silica nanocomposites.
Silica bionanocomposites can be easily obtained from silica precursor/biopolymer mixed solutions or by the silicification of a preformed biopolymer-based material [20-22]. Typical sol-gel precursors such as silicon alkoxides are preferred for synthesizing gel like diphasic system than the aqueous silicates [23,24]. Sol-gel derived silica materials are mechanically robust, chemically inert, porous with high surface area, and resistant to thermal degradation and photochemical degradation and they find use in a variety of fields such as separation [25,26], enzyme immobilization [27,28], sensor [29], environment remediation [30], coating [31], and biomedical application [32]. Judicious selection of polysaccharides can considerably change the properties of nanocomposites in terms of porosity, crystallinity, morphology, and particle size. Chemistry of silica precursors, additives, and processing conditions e.g., pH, ionic strength and catalyst can also change the surface area, surface charge, and porosity of the final material. Depending upon the requirement for the target application, different synthetic strategies have been used for the controlled synthesis of bionanocomposites of different morphologies (such as monoliths, powders, thin films, and fibers).
The sol-gel chemistry

The sol gel process is a wet-chemical technique which involves transformation of colloidal liquid sol phase into solid gel phase. This method can be used for designing biopolymer based nanocomposites with required properties. The properties of the nanocomposites can be easily tuned by controlling the precursor chemistry, surfactants, chelating agents, solvents, pH, aging time, reaction temperature/time, and inorganic electrolyte properties. The sol gel processing of metal oxide gel includes the sequential hydrolysis, polycondensation, gelation, and densification of a precursor solution.

A precursor has ligand surrounded metal or metalloid element. A metal alkoxide precursor is denoted as [M(OR)\_x], where M is a complex forming element such as Si, Ti, Zr, Al, and B, and R is an alkyl group (typically CH\_3 and C\_2H\_5). In sol gel process, precursor undergoes hydrolysis and subsequent polycondensation to form M-OH-M or M-O-M bridges. The common silica precursors are tetraethylorthosilicate (TEOS) [33] and tetramethylorthosilicate (TMOS) [34]. Some other precursors are tetrakis(2-hydroxyethyl) orthosilicate, γ-glycidoxypropyltrimethoxysilane, methyltrimethoxysilane and 3-aminopropyltrimethoxysilane. The chemical steps involved in sol gel polymerization are the hydrolysis and condensation
of metal alkoxide precursors which result in the formation of colloidal phase (sol phase) of polymeric intermediates of relatively higher molecular weight. The polycondensation of the reactive intermediates results into oligomers and polymers having cross-linked three-dimensional gel. The sol gel method is extensively applied to the field of material science and engineering in synthesizing metal oxides, composites, and organic-inorganic hybrids [35,36]. The key advantages of sol gel technique are summarized below:

i) It can be carried out at low temperature.

ii) It allows an easy control on the chemical composition of the final product.

iii) It is capable of fabricating fine powders.

iv) It produces different compositions which are not possible by solid state fusion.

The advantages associated with metal alkoxide precursors are:

i) The reactions are carried out under mild temperature.

ii) Simple vacuum extraction techniques can be used to separate the byproducts (alcohol and water) formed in this reaction.

iii) The metal-organic precursor sols can be easily shaped into a variety of
morphologies (such as monolithic ceramics, glasses, fibers, membranes, aerogels, nanospheres as well as microspheres) with the use of appropriate mould.

iv) Dopants can be incorporated at the sol stage to obtain novel materials with improved environmental performance and characteristics.

Nanocomposite produced using sol gel technique find application in various fields such as in electronics, energy, space, optics, bio-sensors, medicine, and metabolite separation (e.g. chromatography) [37].

Silicate gels involve the hydrolysis and polycondensation of tetrafunctional alkoxide precursors and a mineral acid (HCl) or base (NH₃) as a catalyst. At first the alkoxide is diluted in a solvent, usually the alcohol of the alkoxy group, because water and alkoxy silanes are immiscible in each other. If the precursor is tetraethylorthosilicate, the best choice of mutual solvent is ethanol. Firstly, the addition of water to the silicon alkoxide should produce intermediate Si-OH groups, which are known as silanols. The silanol groups condense and form an oxide cluster or siloxane group (Si-O-Si). The ratio of H₂O to Silica is an important parameter for controlling the hydrolysis reaction. In general when H₂O/Silica ratio is <<2, the alcohol forming condensation mechanism is preferential but when H₂O/Silica ratio is ≥2, water producing condensation becomes preferential. The ligand present at
silica precursor has considerable control on the mode of condensation process.

Silicon alkoxides have lesser reactivity than titanium alkoxides due to their electrophilic nature \([\delta (\text{Si}) = +0.32, \delta (\text{Ti}) = +0.60]\). They react very slowly in water and alcohol and the addition of a catalyst is necessary. The hydrolysis becomes faster in the presence of catalyst. In general mineral acids or ammonia are used as the catalysts. While the non-silicate alkoxides hydrolyze in absence of catalysts as they possess high reactivity. The hydrolysis reaction proceeds via pentacoordinate intermediate or through transition state intermediate.

The bimolecular nucleophilic substitution (SN\(_2\)) reaction is the key mechanism for the process of hydrolysis of metal alkoxides.

The leading factor for the hydrolytic stability of organosilanes is the branching of the alkoxy groups. Rate of hydrolysis decreases with the increase in the bulkiness of the alkoxy groups. TEOS is considerably more inert than TMOS, it does not easily hydrolyze in sol gel reaction due to retarding effect of bulkier ethoxide group.

Liquid-liquid phase separation can be done by the addition of solvents. Most important solvents, such as water, alcohol, formamide, THF, dioxane are used to control the solubility of metal alkoxides. Aprotic solvents (THF or
dioxane) are relatively inert (as compared to water and alcohol) in sol-gel process. The sol gel reaction kinetics can be manipulated by decreasing the potency of electrophile or increasing the potency of the nucleophile. Firstly the addition of water to the silicon alkoxide produces intermediate Si-OH groups, which further condense to form continuous gel network of Si-O-Si bonds. The different texture and morphologies of porous silica can be obtained by acid and base catalyzed sol-gel processes which have been displayed in scheme 1 and 2.

**Reactions in basic environment**

Hydroxyl anion or silanolate ions perform a nucleophilic attack at the central silicon atom. Water or Si-OH dissociates to form the OH\(^-\) and Si-O\(^-\) species. Reactions is a type of bimolecular nucleophilic substitution (SN\(_2\)) reaction where OH\(^-\) replaces OR\(^-\) (hydrolysis) or Si-O\(^-\) replaces OH\(^-\) or OR\(^-\) (condensation). Base catalyzed hydrolysis promotes more discrete, highly branched and weakly cross-linked clusters [39].
Scheme 1: Base catalyzed reaction

Reactions in acid environment

The acid catalyzed mechanism is preceded by protonation of oxygen atom in Si-OH or Si-OR for generating H-OH or H-OR as better leaving groups. The electron density is shifted from the Si atom, making it more available for reaction with water (hydrolysis) or silanol (condensation). Acid-catalyzed hydrolytic reactions (nucleophilic substitution) result linear or randomly branched chains in the silicate sol which undergoes gelation (when a solution gradually loses its fluidity) to form silicate gel (appearance of an elastic fluid).
\[
\equiv\text{Si}-\text{OX} + H^+ \rightleftharpoons \equiv\text{Si}-\text{O}_X^+ \quad X= R, H
\]

\[
Y-\text{OH} + \equiv\text{Si}-\text{O}_X^+ \rightarrow Y-O-Si\equiv + H-OX
\]

\[Y= H, \equiv\text{Si} \]

**Hydrolysis reaction** : \( X=R, Y= H \)

**Condensation reaction** : \( X= R \ or \ H, Y= Si \equiv \)

**Scheme 2: Acid catalyzed reaction**

As the sol aggregates, the thickness of the solution increases until a continuous 3D network (gel) is formed. The object is known as monolith if the smallest dimension of the gel is greater than few millimeters. The term aging involves the progression of change in structure and properties after gelation. The process of spontaneous shrinkage of gel is termed as syneresis which involves network contraction and eviction of fluid from the pores. Silica gels can also be prepared by using sodium silicate (Na\(_2\)SiO\(_3\)) and potassium silicate (K\(_2\)SiO\(_3\)) metal salt precursors [39] but with these NaCl or KCl are produced as the by-products which are not easy to remove and hence the purity of silica gel is adversely affected.
Metal nanoparticles

Metal nanoparticles are attracting huge concern from all fields of science since they possess magnificent properties and diversity of applications. Nanoparticle science has encouraged new materials with improved properties that are considerably diverse from their bulk counterparts. Material properties change considerably when they are in the nano-range of 1-100 nm. Nanoscaled materials generally show fascinating and even astonishing properties due to their high surface energy, large fraction of surface atoms, reduced imperfections, and spatial confinement. Nanoparticles dominate over bulk materials due to their Surface plasmon light scattering, Surface Plasmon Resonance (SPR) [40,41], Surface Enhanced Rayleigh Scattering and Surface Enhanced Raman Scattering (SERS) properties. Because of these properties metal nanoparticles find extensive use in the field of chemical sensing, enzyme catalysis, electronics, optics, and environmental biotechnology [42-47]. Metal nanoparticles can be synthesized and stabilized by physical and chemical methods. Chemical methods include chemical reduction, electrochemical techniques, and photochemical reduction [48,49]. Experimental conditions can prejudice the properties of metal nanoparticle in terms of size, morphology, stability etc. [50].
Zerovalent iron nanoparticles

Among the metal nanoparticles, the use of zerovalent iron nanoparticles (Fe\textsuperscript{0}Nps) is most popular because they have large surface area [51], low cost, high reactivity [52], fast kinetics, small particle size, magnetic property [53], good reducing property [54], and high degradation capability since they are capable of generating highly reactive oxidizing species (OH\textsuperscript{—}) during Fenton reaction [55,56]. Due to these properties, application of Fe\textsuperscript{0}Nps is gaining interest in several different directions of research and applications. Potential applications of zerovalent iron nanoparticles provide new opportunities to remediate environmental pollution.

Zerovalent iron is very much reactive in water under ambient conditions, and it behaves as an outstanding electron donor. Using this property it is used in remediation of chlorinated solvents, organochlorine pesticides (lindane and DDT), PCBs, organic dyes, inorganic pollutants (such as perchlorate, nitrate), heavy metal ions (like Pb(II), Cd(II), Cu(II)), trichloroethene (TCE), carbon tetrachloride, and energetic munitions such as TNT and RDX etc. [57-66].
Catalytic properties

Zerovalent iron nanoparticles (Fe⁰Nps) are effective as catalyst due to their high surface area to volume ratio, surface exposure of atoms, cost effectiveness, abundance, stability, recyclability, and environmental friendliness. Zerovalent iron in the quantum dot range has been used in reduction of substituted aromatic ketones to alcohols with NaBH₄ [67]. Fe⁰Nps have been used as catalyst for Fischer-Tropsch (F-T) synthesis [68,69] and in the fabrication of both single and multi-walled carbon nanotubes by chemical vapor deposition (CVD) method [70]. Fe⁰Nps are suitable alternative for Fenton catalyst. Fe⁰Nps/H₂O₂ system is reported to be heterogeneous Fenton-like system. Zerovalent iron, a two-electron donor is reported to be an effectual catalyst which catalyzes general oxidants (like O₂, H₂O₂ and persulfate) to produce reactive radicals of high redox potential such as hydroxyl radicals (OH⁻) and sulfate radicals [71-77]. These radicals can effectively oxidize many organic pollutants [71,72]. Iron usually occurs in nature as iron (II) and iron (III) oxides and zerovalent iron is a manufactured material. Numerous physical and chemical methods have been adopted for the synthesis of iron nanoparticles.
Scheme 3: Methods of preparation of zerovalent iron

The reduction of ferric salt to iron nanoparticles is an attractive technique for obtaining iron nanoparticles because of the reasons summarized as below:

1) Cost effectiveness
2) Simplicity
3) Easy replication on large scale
4) No special equipment or materials are required
5) Environmental friendliness

Most of the techniques of nanomaterial synthesis are not reasonable or commercial for industrial large scale fabrication [78]. Less toxic, water soluble, and eco-friendly leaf extracts (polyphenols) have been successfully used for the reduction of iron salt to zerovalent iron [79]. The
mango leaves were boiled in water and then the extract was poured drop-by-drop to aqueous iron salt to reduce iron salt to nanoscale zerovalent iron. The leaf extract was utilized as a reducing agent as well as capping agent for zerovalent iron nanoparticles. The capping polyphenols prevented zerovalent iron nanoparticles from oxidation and also served as scavenging agent for free radicals [80].

**Challenges pertaining to zerovalent iron**

The anaerobic conditions prevent oxidation of zero-valent iron, but in presence of aerobic conditions it rapidly transforms into iron oxides [81]. The major challenges to the use of nanoscale zero-valent iron include mainly- fast aggregation of the particles, quick oxidation, sorption to materials, and rapid sedimentation. These properties consequently limit the mobility of nanoparticles in the aquatic environment [82,83]. The long term storage of Fe\(^0\)Nps is not feasible hence they are used soon after the production unless they are stabilized on a support to inhibit the oxidation [84].

**Carriers for zerovalent iron**

In order to overcome the problem of aggregation and oxidation of iron nanoparticles, modification of the surface charge of the particles is needed
There are two ways to resolve this problem, first is electrostatic repulsion and the second one is steric stabilization [82,83]. Electrostatic repulsive forces between nanoparticles in aggregates are needed to overcome the magnetic attraction between the iron nanoparticles. In steric stabilization, iron nanoparticles are covered with water loving polymers and surfactants whose long loops and tails extend out into solution [86]. It is found that coats used can be organic or inorganic molecules which play an important role in steric stabilization [87]. To prevent the aggregation and leaching of metal nanoparticles (NPs), stabilization of the metal nanoparticles on a support has been done [88]. The stabilization of the zerovalent iron has also been done by coupling with other metals such as palladium or nickel, yielding bimetallic nanoparticles [89]. Alternatively, some of the inorganic substances such as silica, metal, nonmetal, metal oxides, and sulfides etc. are used as a support or carrier to decrease the oxidation of zerovalent iron due to their good adsorption properties, surface ions, and good ion exchange capacity. Fe⁰Nps modified with organic carriers offer both electrostatic stabilization and steric stabilization which reduce the aggregation. Guar gum [90], xanthan gum [91], starch [92], zeolite [93], polyvinylpyrrolidone (PVP) [94], polyvinyl alcohol-co-vinyl acetate-co-
itaconic acid (PV3A) [95], polyacrylic acid (PAA) [96], bentonite [97], oyster shells [98], clay [99], kaolin [100], and biochar (BC) [101] etc. prevent aggregation of nano scale zerovalent iron and serve as the effective supports for iron transport.

A number of carriers have been used to overcome the fast agglomeration and oxidation of Fe\(^0\)Nps. The selection of a support needs cautious consideration because some carriers can decrease the reactivity of the nanoparticles, specifically if the optimum ratio between the support and the Fe\(^0\)Nps is not perfectly well.

**Water pollution**

There is an ancient saying “Water is an Elixir of Life”, and is essential only next to air for the survival of life. Less than 1% of the earth’s surface is covered with fresh water resources of the total water [102,103]. Water pollution is being focused worldwide, since it changes the physical, chemical, and biological properties of water and therefore adversely affects the human health and water ecology [104,105]. The main source of water pollution is the water from untreated sewage, storm drains, septic tanks, run off from farms, and industrial effluents. Certain natural phenomena such as volcanic eruptions, soil erosion, landslides, decay and decomposition of
flora and fauna render the water inappropriate for drinking and for the use in other domestic pursuits. The consumption of contaminated water can seriously affect the human health [106] and produce numerous water borne diseases such as typhoid, gastroenteritis, hepatitis, jaundice, cholera, amoebiasis, giardiasis, cryptosporidiosis, and ascariasis. Water pollution causes serious metabolic disorders, hormonal problems, abnormalities in reproductive system, failure of nervous and cardiac system, malfunctioning of kidneys, development of malignant tumors, cancer and in extreme cases may even lead to death [107]. Water pollution also leads to significant destruction of floral and faunal life, and fatally upset overall functioning of the water ecology [108]. Thus the protection and preservation of the natural water resources is necessary.

**Classification of water pollutants**

The water pollutants can be classified into five major categories namely [109]: (1) Sediments and suspended solids, (2) Biological pollutant, (3) Radioactive pollutant, (4) Inorganic pollutant, and (5) Organic pollutant

**Organic pollutants**

The organic pollutants can be further categorized into two categories: Natural and Synthetic. The natural organic compounds enter to the
ecosystem through domestic, municipal, industrial processing, slaughter houses, paper, pulp mills, tanneries, and agricultural field in form of run-off [110]. Synthetic organic matters are usually released from industrial and agricultural activities [111]. Synthetic organic compounds include mineral oils, phenols, food additives, pharmaceuticals, paints, solvents, plasticizers, fertilizers, pesticides, polychlorinated biphenyls, surfactants, and dyes [112].

**Dyes**

Various pollutants are present in the industrial waste among which synthetic dyes are most important. It has been estimated that water bodies are generally contaminated from wastewater from textile industry which holds approximately 10-15% of the synthetic dyes [113]. According to Witt (1876), dye molecules contain chromophores (for imparting color to the substrate) and auxochromes (for intensifying these colors). A few important chromophores are C=C, C=N, C=O, N=N, NO₂, and quinoid rings. Some of important auxochromes are -COOH, -SO₃H, -NR₂,-NHR, -NH₂, -OH, and -OR etc.

**Classification of dyes**

Dyes can be classified on the basis of their chemical structure, color, and mode of application [114,115]. On the basis of method of application they
can be classified as Acid dyes; Basic dyes; Direct dyes; Disperse dyes; Reactive dyes; Mordant dyes; Vat dyes; Sulphur dyes; Solvent dyes; Azoic or Ingrain dye; Pigment dyes; Fluorescent brightners; and Food dyes etc. Dyes are also classified on the basis of their chemical composition e.g. Azo dye; Anthraquinone dye; Diphenylmethane dye; Nitro dye; Nitrosodye; Indigoid dye; Phthalein dye; Thiazine dye; Thiazone dye; Triphenylmethane dye; and Xanthene dye etc.

**Azo dye**

Azo dyes are aromatic compounds having one or more \(-\text{N}=\text{N}-\) bond. The electron deficient nature of azo dyes contributes electron deficiency in the molecules (dyes), making them opposed to degradation [116]. Azo dyes and their break down products, such as benzidine, naphthalene, and other aromatic compounds are carcinogenic to living organisms. Azo dyes are regularly used in textile, dyeing, hair colorings, food technology, cosmetics, photo electrochemical cells, and paint industries etc. [117]. They are quite stable and possess low bio-degradibility towards light, temperature, and chemical treatment due to their complex structure and large molecular size. The dye contamination in wastewaters can be easily detected even if they are present in small quantities. They inflict damaging effect on aquatic biota and
limit photosynthesis by blocking the sunlight [118-121]. Wastewater contaminated with azo dyes has toxic effects such as burning sensation in eyes, damage to respiratory system, difficulty in breathing, nausea, vomiting, abnormal functioning of liver, spleen, kidney, hypersensitivity, immunosuppressive, tumor promoting, mitotic poisoning, induces teratogenicity, carcinogenicity, mutation, and several allergic reactions [122-127]. Hence dye remediation of industrial effluents is necessary before it is finally discharged to water bodies.

**Treatment technologies currently used for dye removal**

In an attempt to remove dyes, many methodologies can be applied such as membrane filtration related to nanofiltration, biological treatment, coagulation/flocculation, reverse osmosis, electro-dialysis, ion exchange, and sorption techniques [107, 128-130]. Treatment process can be done by using any of the three methods such as biological, chemical, and physical.
None of these treatment methods got widespread acceptability due to their inherent limitations. Fenton’s process is one of the most promising methods for dye removal. Fenton’s reaction is a chemical process which has many attractive properties such as:

1) Effective for degrading all kinds of dyes

2) Results into complete degradation of dyes to form low molecular weight compounds

3) Generation of negligible solid secondary pollutants
Fenton’s process

As an example of the advanced oxidation processes (AOPs), Fenton’s oxidation is one of the well-known processes which can be effectively used in the field of wastewater remediation. It eliminates the color or results into complete mineralization of organic pollutants. Fenton’s reagent is a solution of iron (II) (commonly FeSO₄) and H₂O₂ [131]. Fenton process proceeds via a free radical chain reaction to generate the hydroxyl radicals with very high oxidizing ability. It can oxidize organic compounds to harmless compounds (CO₂, water and inorganic salts) in a short time [132]. Firstly, H₂O₂ is decomposed by ferrous ion (Fe²⁺), forming a hydroxyl radical. On the other hand, the newly generated ferric ion (Fe³⁺) catalyzes the decomposition of H₂O₂ into water and oxygen (forming ferrous ions and radicals).

\[
\begin{align*}
\text{Fe}^{2+} + \text{H}_2\text{O}_2 & \rightarrow \text{Fe}^{3+} + \text{OH}^{\cdot} + \text{OH}^{-} \\
\text{Fe}^{3+} + \text{H}_2\text{O}_2 & \leftrightarrow \text{Fe} \cdot \text{OOH}^{2+} + \text{H}^{+} \\
\text{Fe} \cdot \text{OOH}^{2+} & \rightarrow \text{HO}_2^{\cdot} + \text{Fe}^{2+} \\
\text{Fe}^{2+} + \text{H}_2\text{O}_2 & \rightarrow \text{Fe}^{3+} + \text{OH}^{\cdot} + \text{OH}^{-}
\end{align*}
\]

The above reactions are attributed as Fenton-like reaction. The Fenton process requires acidic pH i.e. low pH (2 to 5). The chemical reaction is slow at pH < 2 because of the formation of oxonium ion [H₃O₂]⁺ [133] and
complex iron species while at pH values >4.0, the reaction slows down due to the generation of ferric-hydroxo complexes [134]. Hence, the initial pH value has to be in acidic range (between pH 2-4) to produce the highest amount of hydroxyl radicals which can effectively catalyze the oxidation of organic compound [135,136]. However, generation of large amount of sludge in the coagulation phase, and loss of Fe ions in water remains a problem for this mechanism [137]. Heterogeneous Fenton oxidation is a better alternative to homogeneous catalysis as it affords recyclable use of Fe catalysts.

In the past few years, progress has been made towards the development of various Fe-based catalysts such as zerovalent iron (Fe$^0$) [138], Fe$_3$O$_4$ [139], and Fe$^0$/Fe$_3$O$_4$ [140]. Fe$^0$Nps can be used in the reduction of contaminants like nitroaromatic compounds, heavy metals, pesticides, halogenated organics, nitroaromatic compounds, and nitrates [141]. The high remediation efficiency of nanoscale zerovalent iron is mainly due to its large surface area and high surface reactivity [141]. Nanoscale zerovalent iron acts as a good Fenton-like heterogeneous catalyst. Fe$^0$Np is quite reactive in water and also behaves as a slow-releasing source of dissolved Fe$^{2+}$ ions in acidic medium, which further react with H$_2$O$_2$ to generate most reactive chemical species (OH$^-$) in the Fenton system. The produced hydroxyl
radicals (HO\textsuperscript{·}) are the major reactants involved in the Fenton oxidation of organic contaminants [142,143]. Fenton reaction involving Fe\textsuperscript{0}Nps can be represented by the following equations:

\[ \text{Fe}^0 + \text{H}_2\text{O}_2 + 2\text{H}^+ \rightarrow \text{Fe}^{2+} + 2\text{H}_2\text{O} \]

\[ \text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{HO} \cdot + \text{HO} \]

\[ 2\text{Fe}^{3+} + \text{Fe}^0 \rightarrow 3\text{Fe}^{2+} \]

The advantages of using Fe\textsuperscript{0}Nps in Fenton like oxidation over classical Fenton oxidation (Fe\textsuperscript{2+}/H\textsubscript{2}O\textsubscript{2}) [143] are:

a) Fe\textsuperscript{0}Nps may attach or coat on large particles and Fe\textsuperscript{0}Nps coated particles can treat contaminated water by passing through a sand filter or other type of filtration systems.

b) Fe\textsuperscript{0}Nps can be immobilized in/on soil grains of contaminated aquifers.

c) Increased reaction rate in the reductive degradation.

d) Small reductant dose is required.

e) Release of toxic intermediates can be controlled.

f) Nontoxic end products are generated.
Characterization of composite Materials

In order to analyze various physical and chemical properties as well as molecular and nanometer structure of the as-synthesized composite, a range of characterization techniques have been used. In the following section, a brief description about all instrumentation techniques including, X-ray Photoelectron Spectroscopy (XPS), Energy-dispersive X-ray Spectroscopy (EDX), Field Emission Scanning Electron Microscopy (FE-SEM), Transmission Electron Microscopy (TEM), High Resolution Transmission Electron Microscopy (HR-TEM), Field Emission Scanning Electron Microscopy (FE-SEM), Vibrating Sample Magnetometer (VSM), X-Ray Diffractometry (XRD), Fourier Transform Infrared Spectroscopy (FTIR), and UV-Visible Spectroscopy is being furnished.

X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy is surface-sensitive quantitative spectroscopic technique and is also known as ESCA (Electron spectroscopy for chemical analysis). This technique helps in analyzing the elemental composition, chemical state, and electronic state of the elements that exist within a material. It provides information about spatial distribution by scanning the micro focused X-ray beam across the sample. XPS spectra are
obtained by irradiating with a mono-energetic Al kα X-rays due to which the electrons present at the surface of the sample are ejected and with the help of electron energy analyzer, energy of the ejected electrons can be measured. The emitted electron’s binding energy can be determined by measuring its kinetic energy. Binding energy and intensity of a photoelectron peak gives the information regarding the elemental identity, chemical state, and quantity of a detected element.

**Energy-dispersive X-ray Spectroscopy**

Energy-dispersive X-ray spectroscopy (EDX) is useful technique for providing chemical composition of materials. It informs about the abundance of specific elements. The interaction of an electron beam with a solid specimen results in a variety of emissions, including X-rays. An energy-dispersive spectrometer is used to examine the energy of the emitted X-rays which is a characteristic of atomic structure of the element.

**Field Emission Scanning Electron Microscopy**

Field emission scanning electron microscope produces high resolution 3-D images of a sample’s surface and thus provides micro structural information, spatial variation in chemical composition, qualitative chemical analysis and crystalline structure of material. The two major components of an instrument
are: an electron column and an electron detector. The electron column generates electron beam from a field emission source and is accelerated under the influence of a high electrical field gradient. The liberated primary electrons are focused and deflected by electromagnetic condenser lens to generate a narrow scan beam that strikes on the sample’s surface. As a result, each spot on the specimen starts producing secondary electrons and back-scattered electrons. The emitted secondary electrons are captured by the detector and thereby produce an electronic signal. These signals are amplified for obtaining the valuable information in terms of composition, surface topography as well as size of the samples under investigation.

**Transmission Electron Microscopy**

Transmission electron microscopy (TEM) produces high resolution two dimensional image of the inner structure of the specimen. The electron source at the top of the microscope emits the electrons beams (30-300 KV) that are passed through the column in vacuum environment. These transmitted electrons (scattering phenomena) contain valuable information that is employed to examine the samples at molecular level. Image is magnified and recorded onto an imaging device, such as a fluorescent screen, photographic plate and light sensitive sensor such as a CCD (charge-coupled device) camera. Fundamentally TEM provides a
great resolution image of the microstructure of a thin sample by which we can get a magnification of million times or more. The electron beam can damage the organic components of the sample and to avoid this Cryo-TEM technique is used in which the sample is kept at liquid nitrogen or liquid helium temperatures to avoid this problem.

HR-TEM is a powerful technique to study the atomic structure of the sample, such as semiconductors, metals, nanoparticles, graphene, and carbon nanotubes etc. Highest point resolution observed in HR-TEM is around 0.5 angstroms (0.050 nm). HR-TEM image-interference patterns come from diffracted (transmitted) and forward-scattered electron waves. The information about the atomic resolution and lattice image of crystals is contained in the HR-TEM. Angular distribution of scattering can be observed in the form of diffraction patterns which is generally attributed as selected area electron diffraction (SAED). It is used in order to get the information about the crystallinity and to know the d-spacing of the crystal planes.

**Vibrating Sample Magnetometer Study**

The vibrating sample magnetometer (VSM) can measure the magnetic behavior of materials. Principally it is based on Faraday's law of induction and the magnetic hysteresis loops of the specimen. When a sample is placed
in a uniform magnetic field between two inductive coils and made to undergo sinusoidal motion (i.e. mechanically vibrated), a changing magnetic flux is observed and the produced electric current is proportional to the saturation magnetization. This information gives a hysteresis curve. Magnetic moment of sample is measured by hysteresis loop as an alternating magnetic field is applied. Magnetic materials became demagnetized when the magnetizing field is applied in opposite direction. The path from magnetization to demagnetization is traced by hysteresis loop. Magnetic moment at which all the dipoles in the sample are aligned with the magnetizing field direction refers to saturation magnetization. Coercivity describes the magnetization required to reduce the magnetization to zero after a sample has reached the saturation. SANS (Small Angle Neutron Scattering) samples and VSM samples are prepared at the same time and they are placed directly into VSM sample screw top capsules. Samples are cured for two hours at 37°C after vortex mixing and then are stored in a refrigerator.

**X-Ray Diffractometry**

X-ray diffraction is a powerful nondestructive tool used to examine the crystalline composition and the phase purity. The technique also gives
information about structures, phases, preferred crystal orientation (texture), and other structural parameters such as average grain size, crystallinity, strain, and crystal defects. Fine crystallite peaks represent crystalline nature of the material whereas broadening of the peaks exhibit its amorphous nature. Electronic databases such as the “JCPDS-International Centre for Diffraction Data” are generally consulted to differentiate different crystallographic phases of a material. Constructive interference is obtained when monochromatic X-rays interact with the sample. This interference (and a diffracted ray) is possible when conditions satisfies Bragg’s law ($n\lambda = 2d \sin\theta$). It is possible to determine an average crystallite size by the Debye–Scherrer equation that is given as:

\[ d = \frac{0.9\lambda}{fwhm\cos\theta} \]

where $d =$ crystallite size (nm), $\lambda =$ wavelength of monochromatic X-ray beam, fwhm= full width at half-maximum for the diffraction peaks (rad), and $\theta =$ diffraction angle (degrees).

This technique can be used to determine the degree of crystallinity in a crystalline material. The presence of broad hump in the diffractogram is an indication of semicrystalline or amorphous materials.
Fourier Transform Infrared Spectroscopy

Fourier transform infrared spectroscopy is an analytical technique which measures the IR radiation absorbed by sample. The technique can be employed to identify the chemical bonding and molecular structure of the samples. Spectrum appears only when chemical bonds tend to vibrate and produce a change in the permanent electric dipole moment of the molecule. Wavelengths that are absorbed by the sample are a unique reflection of their molecular structure. This technique measures the absorption of infrared radiation as a function of frequency or wavelength due to its interaction with a sample.

UV-Visible Spectroscopy

UV-visible spectrophotometry is widely used to quantitatively characterize organic and inorganic nanosized molecules by irradiating a beam of visible or ultraviolet radiation through the sample. This technique can identify the constituents of a substance and determine their concentrations. The UV-visible spectra are usually presented as plots of wavelength of absorbed radiations as a function of intensity of absorption in terms of optical density. The spectrophotometer works on the principle of Lambert-Beer’s law. The fraction of incident monochromatic radiation is proportional to
the number of absorbing molecules. The linear expression for the Lambert-Beer’s law is given in the following equation:

\[
\log_{10} \frac{I_0}{I} = A = \varepsilon cl
\]

Where \(I_0\) is the intensity of the incident light on the sample solution, \(I\) is the intensity of the transmitted light, coming out of the sample, \(A\) is the absorbance of optical density, \(\varepsilon\) is the molar extinction coefficient, \(c\) is the concentration of the compound in the solution (mol L\(^{-1}\)) and \(l\) is the path length of the cuvettes containing the sample (cm). A beam of monochromatic light from the source is split into two beams of equal intensity. One of them travels through the sample and the other passes through the reference (a solvent in which the sample is dissolved). After passage from the sample and reference cell, the resulting two beams are directed back to the detectors where they have been compared. Concentration of the target analyte in the sample can be calculated at wavelength of maximum absorbance (\(\lambda_{\text{max}}\)) form double beam UV-visible spectrophotometer.

**Literature survey**

The following section deals with the literature survey on zerovalent iron nanocomposites. Silica, montmorillonite, sepiolites, and zeolite have been mainly used as the matrix material for embedding zerovalent iron
nanoparticles (Fe⁰Nps). Many biopolymers have been integrated with Fe⁰Nps to derive novel composites for various end applications. Among various biopolymers, use of polysaccharides is most attractive because of their abundant, biodegradable, and renewable nature. Polysaccharide templated silica matrices embedded with Fe⁰Nps have emerged as the promising nanocomposite materials for wastewater treatment.

**Silica**

SiO₂-coated iron nanocomposites (Fe@SiO₂) have been developed using borohydride reduction method in combination with modified Stöber method. The core-shell Fe@SiO₂ behaved as more effective reductant than the uncoated Fe⁰Nps. This composite was used for the removal of Cr(VI) (from its aqueous solution) under ambient conditions [144]. SiO₂-FeOOH-Fe core-shell hybrid has been synthesized by using a versatile reduction method. This hybrid has been utilized for nitrate removal from aqueous solutions [145]. The core-shell Fe@SiO₂ nanocomposite haas been successfully synthesized by a Stöber method using tetraethylorthosilicate (TEOS) as the silica precursor. SiO₂ shell significantly decreased their agglomeration and thus increased the catalytic performance of the composites. The core-shell Fe@SiO₂ nanocomposite behaved as the potential candidate for Cr(VI)
reduction [146]. A highly stable nanoscale zerovalent iron composites derived from tetraethylorthosilicate (TEOS) and hexadecyltrimethoxysilane (HDTMOS) were prepared. The composite was used for the effective removal of Cr(VI) [147]. Silica fume-nanoscale zerovalent iron (SF-Fe\textsuperscript{0}) composite was prepared by borohydride reduction of an aqueous iron salt in the presence of commercial silica fume as a support. SF-Fe\textsuperscript{0} could efficiently remove Cr(VI) in groundwater [148]. Nanoscale iron/silica composite have been prepared from nanoscale iron and spherical silica particles via aerosol-assisted process and subsequent reduction. This composite has been used for trichloroethylene remediation. The use of silica particles could overcome the mobility and settlement problems associated with bare Fe\textsuperscript{0}Nps [149]. Porous silica particles containing nanoscale zerovalent iron particles were fabricated through an aerosol-assisted process. Silica matrix prevented their aggregation as it served as the effective carrier for nanoscale zerovalent iron transport. These systems were therefore of interest in developing in situ remediation of trichloroethylene [150]. Mesoporous silica MCM-41/Fe\textsuperscript{0}Nps composite have been synthesized facilely. Nanoscale zerovalent iron nanoparticles have been incorporated into porous silica particles to reduce the problem of Fe\textsuperscript{0}Nps aggregation. The study paying attention on the adsorption performance of Pb(II) ions on MCM-41/Fe\textsuperscript{0}Nps composite from
aqueous solution has been reported [151]. New nanocomposites (APS-Fe\textsuperscript{0}Nps) were synthesized on the basis of nanoscale zerovalent iron particles (Fe\textsuperscript{0}Nps) and 3-aminopropyltriethoxysilane (APS). APS-Fe\textsuperscript{0}Nps had the potential to become a promising adsorbent for the removal of Pb(II) from its aqueous solution [152]. Fe\textsuperscript{0}Nps immobilized on mesoporous silica microspheres covered with FeOOH have been successfully prepared and their efficiency in the degradation of decabromodiphenyl ether (BDE209) has been evaluated [153].

**Montmorillonite**

Organo-montmorillonite supported nanoscale zerovalent iron particles were synthesized by liquid phase reduction of FeSO\textsubscript{4} using NaBH\textsubscript{4}. It acted as the carrier support and Fe\textsuperscript{0}Nps dispersant. Organic modification of sodium-montmorillonite has been done via ion exchange method. These hybrid materials behaved as effective catalyst for the degradation of decabromodiphenyl ether (BDE-209) [154]. Montmorillonite (Mt) and zerovalent iron were used to prepare Mt-Fe\textsuperscript{0}Nps composites with nanoscale zerovalent iron (Fe\textsuperscript{0}Nps) at different montmorillonite ratios. Mt-Fe\textsuperscript{0}Nps has been successfully produced by loading Fe\textsuperscript{0}Nps onto Mt through chemical reduction of ferric ions by NaBH\textsubscript{4}. Highly functional Mt-Fe\textsuperscript{0}Nps surface
provided fast removal kinetics for both As(III) and As(V) [155]. Montmorillonite (Mt) and hexadecyltrimethylammonium modified montmorillonite (HDTMA-Mt) were used to synthesize Mt/iron and HDTMA-Mt/iron particles. Mt-Fe\(^0\)Nps showed increased stabilization of reactive iron particles against aggregation. The synthesized material behaved as an effective reductant for Cr(VI) in aqueous solution [156].

**Sepiolites**

SEP or AAS/Fe\(^0\)Nps nanocomposite of varying compositions have been designed using natural sepiolites (SEP) and partially acid-activated (AAS) sepiolites and were used for cadmium adsorption [157]. A series of sepiolite-supported nanoscale zerovalent iron superabsorbent composites were prepared by sodium borohydride reduction method. These were evaluated for an advanced treatment technique to remove aqueous \(\beta\)-blockers (i.e. metoprolol (MPL)) [158].

**Zeolite**

Zeolite supported nanozerovalent iron copper bimetallic composite (Z-Fe\(^0\)Nps-Cu) has been prepared by an ion exchange method. The agglomeration of zerovalent iron nanoparticles (Fe\(^0\) NPs) was significantly decreased by Zeolite. Ion exchange derived Zeolite-Fe\(^0\)Nps-Cu hybrid
materials behaved as an effective heterogeneous catalyst for the removal and degradation of trichloroethylene (TCE) [159].

**Starch**

The nanoscale zerovalent iron particles/starch hybrid sorbent for separation of As(III) from its aqueous solution is reported where zerovalent iron nanoparticles (Fe$^0$Nps) were prepared by in situ reduction of Fe$^{3+}$ ions onto a mesoporous carbon matrix (Starch-derived mesoporous carbonaceous composite) [160]. Starch and CMC (Carboxymethyl cellulose) stabilized Fe$^0$Nps showed faster degradation (1.8 and 3.3 times) of perchlorate than those prepared without a stabilizer (in both contaminated water and brine) [161].

**Chitosan**

A series of 3D honeycomb-like structured nanoscale zero-valent iron/chitosan composite was developed by a facile freeze-drying method. These hybrid matrices were used for the effective removal of inorganic arsenic from water [162]. Chitosan-Fe$^0$Nps have been fabricated and utilized for the effective removal of As(III) and As(V) from water [163]. Chitosan-stabilized nanoscale zero-valent iron nanoparticles (CS-Fe$^0$Nps) have been prepared by means of liquid-phase reduction technology using chitosan as a
stabilizer material. CS-Fe\(^0\)Nps was used for the remediation of acid fuchsine (AF) from aqueous solution with the assistance of ultrasound [164]. Fe\(^0\) nanoparticles have been successfully entrapped in chitosan-carboxymethyl-cyclodextrin complex which yielded chitosan-Fe\(^0\)Nps-carboxymethyl-cyclodextrin beads (CS-Fe\(^0\)Nps-CM-CD). Batch adsorption studies showed that CS-Fe\(^0\)Nps-CM-CD beads were effective in removal of both Cr(VI) and Cu(II) [165]. The significantly enhanced removal of As(III) and As(V) with fast kinetics has been achieved using CS-Fe\(^0\)Nps-CM-CD beads as an adsorbent [166]. Fe\(^0\)Nps entrapped chitosan (CS) beads were reported as a suitable material for removal of Cr(VI) under ambient conditions [167]. Fe\(^0\)Nps-chitosan composite beads have been prepared by simple entrapment method [168]. The beads could efficiently remove chromium from waste water. They also behaved as an excellent material for the remediation of heavy metals from electroplating wastewater [169]. Chitosan fiber-supported zero-valent iron nanoparticles have been prepared by liquid phase borohydride reduction of FeCl\(_3\) [170]. They had shown efficiency in removing inorganic arsenic from aqueous solution. Zerovalent iron incorporated polyvinyl alcohol-chitosan nanofibrous material was fabricated by electro-spinning method. Glutaraldehyde was used as crosslinker to improve the stability of the electrospun nanofiber material and the material synthesis was optimized for arsenic removal [171]. Introduction of an
innocuous stabilizer such as chitosan could significantly improve the performance of zerovalent iron nanoparticles for remediation process [172].

**Cellulose**

Preparation and removal properties of novel nanoscale zerovalent iron-carboxymethyl cellulose biocomposite are reported. The composite played a significant role in uranium (VI) removal from aqueous systems [173]. Carboxymethyl cellulose (CMC) or poly(acrylic acid) (PAA) supported zerovalent iron nanoparticles are reported for the removal of Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) [174]. CMC stabilized Fe$^0$Nps synthesis was done by chemical process using NaBH$_4$. Nano zero-valent iron (Fe$^0$) particles were nucleated at the surface of water soluble carboxymethyl cellulose (CMC). The zerovalent iron nanoparticles were spherical in shape and their size ranged from 20 nm to 100 nm. CMC-supported Fe$^0$ nanoparticles were used in the reduction of hexavalent chromium from aqueous systems. CMC acted as innocuous stabilizer to prevent agglomeration and gave a large reactive area [175]. In recent years, dye degradation using zerovalent iron (Fe$^0$) nanoparticles has received much consideration. Hydroxyethyl cellulose (HEC) and hydroxypropylmethyl cellulose (HPMC) stabilized Fe$^0$ nanoparticles displayed much less
agglomeration and led to high degradation efficiency for dye wastewater [176]. Nanoscale zerovalent iron was coated with carboxymethyl cellulose to obtain a modified surface with decreased toxicity and oxidizing capacity [177]. A pilot scale injection of nanoscale zerovalent iron (Fe\textsuperscript{0}Nps) stabilized with carboxymethyl cellulose (CMC) were examined and used as the most promising material for chlorinated volatile organic compounds (cVOC) removal [178]. Nanoscale zerovalent iron (Fe\textsuperscript{0}Nps) stabilized with carboxymethyl cellulose (CMC) or starch was used for reductive removal of selenite ion from water [179]. Carboxymethyl cellulose (CMC)-stabilized Fe\textsuperscript{0}Nps (with a trace amount of Pd catalyst) was prepared and used for the removal of chlorinated ethenes such as perchloroethylene (PCE) and trichloroethylene (TCE) and polychlorinated biphenyls (PCBs) [180]. Carboxymethyl cellulose-stabilized iron nanoparticles were synthesized for the chemical degradation of toxic RDX explosive in soil [175]. The removal of arsenite ions from aqueous solution has been accomplished using zerovalent iron stabilized in carboxymethyl cellulose solution [182].

**Alginate**

Macroporous alginate substrate-supported Fe\textsuperscript{0}NPs (Fe\textsuperscript{0}NPs/MAS) were prepared using two distinct steps: (1) synthesis of a macroporous alginate
substrate (MAS), (2) chemical reduction of iron salts to produce zerovalent iron nanoparticles which were covalently attached to the surface of alginate. This hybrid was efficient in the removal of nitrates from an aqueous solution [183]. The Ca-alginate-Fe$^0$Nps fabrication was done by chemical method using NaBH$_4$ solution. Calcium alginate provided both electrosteric stabilization and steric stabilization. The alginate entrapped Fe$^0$Nps beads showed combined effects of highly dispersed Fe$^0$Nps particles and highly functional alginate biopolymer. The Fe$^0$Nps entrapped calcium-alginate beads were used as a potential material for remediation of nitrate [184]. A composite material derived from nanoscale zerovalent iron particles supported on the calcium (Ca)-alginate beads has been characterized. Fe$^0$Nps doped alginate beads were suitable for the removal of trichloroethylene from an aqueous solution [185]. Fe$^0$Nps were entrapped within Ca-alginate. The entrapment did not compromise with the reactivity of Fe$^0$Nps. Ca-alginate entrapped Fe$^0$Nps behaved as the potential material for remediation of arsenic [186]. Highly reactive Fe$^0$Nps immobilized in alginate beads were synthesized and these beads exhibited the potential for Cr(VI) removal [187].
**Gum acacia**

Gum acacia has been used to effectively stabilize Fe\(^0\)Nps in oil-in-water emulsions. Fe\(^0\)Nps within the emulsion was utilized as a promising nanomaterial for degradation of trichloroethylene (TCE) and H\(_2\) production [188].

**Guar gum**

Guar gum has been used as stabilizing agent for reactive iron nanoparticles against aggregation and sedimentation. The synthesized zerovalent iron nanoparticles were potentially used for remediation of contaminated ground water aquifers. Guar gum prevented aggregation of Fe\(^0\)Nps even at very high salt concentrations (0.5M NaCl and 3 mM CaCl\(_2\)) [90].

**Gum karaya**

Fe\(^0\)Nps-Gum karaya composites have been prepared. The composite was effectively used for the removal of VOCs (cis-1,2-dichloroethene, perchloroethene and trichloroethene) and chromium from water [189].

**Agar agar**

Agar coated zero-valent iron nanoparticles were synthesized using a rheological phase reaction method. They had potential use in the remediation...
of hexavalent chromium [190]. Agar agar-stabilized milled zerovalent iron particles have been fabricated and applied for the degradation of chlorinated aliphatic hydrocarbons in groundwater [191].

**Xanthan gum**

Xanthan gum-Fe\(^0\)Nps composite was synthesized. Zervalent iron nanoparticles stabilized on xanthan gum were smaller in size with no aggregation. The Xanthan gum-Fe\(^0\)Nps synthesis was done by sonication method [91].

**Different applications of zerovalent iron nanoparticle**

Methyl 2-Br-2-Cl-carboxylates on reacting with terminal alkenes yielded 2-alkyl-2-Cl-4-Br-carboxylates in fair to good yields. It is noteworthy that the reactions occurred under mild conditions through a radical process promoted by CuBr/Fe\(^0\) in DMF/CH\(_2\)Cl\(_2\) [192]. The functionalized 3-aminopropyltriethoxysilane (APTES) coated Fe/Fe\(_3\)O\(_4\) nanoparticles have been successfully synthesized to catalyze the ring opening of epoxidized methyl oleate for potential soy based polyols applications with low energy consumption and excellent atom economy and environment factor. Soy based polyols were produced by acid-catalyzed ring opening of expoxidized soybean oil by nucleophilic SN\(_2\) attack of methanol [193]. Alkenes, alkynes,
aromatic imines, and aldehydes were hydrogenated with interesting chemoselectivity using amphiphilic polymer-stabilized Fe\textsuperscript{0} nanoparticle catalyst in ethanol or water in a flow reactor [194]. The halogen atom transfer radical additions (HATRA) of methyl 2,2-dichlorocarboxylates or trichloro acetic acid derivatives to alkenes were proficiently promoted by iron filings at 50°-100°C in N,N-dimethylformamide (DMF)/1,2-dichloroethane (DCE). These reactions resulted into γ-haloester which was used for the synthesis of butyrolactones. Butyrolactones are the precursor of biologically active compounds [195]. The halogen atom transfer radical additions (HATRA) of methyl 2-Br-2-Cl-carboxylates to alkenes have been achieved by catalytic amounts of iron filings in dimethylformamide (DMF)/1,2-dichloroethane (DCE) at 800°C under Ar atmosphere [196]. Carboxymethyl cellulose, polyethylene glycol, and poly N-vinyl pyrrolidone stabilized iron nanoparticles were fabricated and applied as catalysts in the hydrogenation reaction of different substituted aromatic ketones to alcohols. The reaction has been done under mild and eco-friendly experimental conditions. Iron nanoparticles were synthesized by reducing FeCl\textsubscript{3} salt with strong reductant like THF with alkyl Grignard’s or alkyl lithium’s. The fabricated nanoparticles were evaluated as excellent catalyst for the hydrogenation of olefins and alkynes [197]. Fe\textsuperscript{0}Nps were synthesized from
FeCl₃ and EtMgCl in THF and have been evaluated as cost effective and non-toxic catalyst for the hydrogenation of alkene and alkyne (norbornene and 1-Hexyne) under moderate conditions [198]. Zerovalent iron nanoparticles prepared by the decomposition of {Fe(N[Si(CH₃)₃]₂)₂} under dihydrogen were effective catalyst for the hydrogenation of unsaturated C–C, C=X and C=O bonds [199]. Iron-iron oxide core-shell nanoparticles were prepared by reducing of FeSO₄ using NaBH₄. These nanoparticles have been utilized for the hydrogenation of olefins and alkynes, under mild conditions in ethanol and aqueous ethanol [200].

The thesis entitled “SYNTHESIS AND CHARACTERIZATION OF BIOPOLYMER BASED NANOCOMPOSITES” deals with the sol-gel synthesis and characterization of polysaccharide-Fe⁰Nps-silica nanocomposites. The polysaccharides such as acacia gum, starch, and aloevera have been used for designing their composites with silica and Fe⁰Nps. The three composites designed during this study have been evaluated for the same application, dye degradation. For evaluating the nanocomposites, Remazol Brilliant Violet (RBV) dye was selected as a model dye. The experimental conditions for the degradation have been optimized and the kinetic studies were also done. These composites may be
utilized for metal separation, pesticide removal, enzyme entrapment, and catalysis. To fully understand the catalytic behavior of the synthesized nanocomposites, an attempt has been made to use Aloevera-Fe$^0$Nps-Silica as a catalyst in the synthesis of thiourea coupled oxazole nucleus. The material exhibited good catalytic performance and nearly doubled the yield of the heterocyclic product while the reaction time for the catalyzed reaction was just the half of the time consumed in uncatalyzed reaction.
References


