

CHAPTER 1

Introduction and Literature Review

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1.1. Water pollution: causes, effects and solutions

Water treatment is an ever-growing research area since pure and clean water is essential for human well being. Industrialisation, urbanisation, growing population and natural phenomena cause water pollution worldwide. According to UN reports, over 2 billion people live in a water-scarce area. Water treatment becomes essential due to the uneven and insufficient distribution of freshwater resources for the ever-expanding water requirements of the increasing world population. Providing safe drinking water is a fundamental human right and a responsibility towards future generations. Drinking potable water should be free from any physical, chemical and biological pollutants which otherwise cause water-borne diseases to human beings.

Every year, thousands of people die or become diseased by water-borne diseases such as cholera, diarrhoea, typhoid and dysentery by consuming contaminated water. Water treatment can only provide safe drinking water because preventing contamination of source water is not always possible due to the mixing of untreated industrial and sewage water and poor hygienic practices in developing and underdeveloped countries. Based on the nature of the contaminant, they are classified into physical, chemical and biological. The contaminants imparting odour, colour and turbidity to the drinking water are considered physical contaminants. The presence of sediments and organic compounds could adversely affect the aesthetic beauty of water, which is unacceptable for human consumption. Chemical and biological contaminants can also affect the colour and odour of water. Chemical contaminants consist of organic contaminants such as dyes, pesticides and inorganic contaminants are mainly heavy metals and radioactive elements. Sewage water and industrial effluents are significant sources of chemical contaminants. Biological contamination mainly happens due to the microorganisms like viruses, bacteria and parasites.

Different techniques or materials are used to inactivate or eliminate the different contaminants present in the source water in water treatment. Emerging pollutants and radioactive components act as barriers to the water treatment system. Generally, coarse

particles and turbidity can be removed from raw water through coagulation, pre-filtration and sedimentation techniques. Other common techniques employed in removing water contaminants include filtration, using a disinfecting agent, irradiation by UV and visible light, reverse osmosis, adsorption, electrolysis, electro dialysis, oxidation, ion exchange, precipitation, aerobic and anaerobic treatments. High operational cost and sophisticated operational systems make these techniques unappealing. Moreover, chemicals like chlorine compounds used in water treatment cause additional contamination in water. The untreated wastewater carrying rivers and channels cause groundwater pollution in the nearby areas. So it is essential to develop simple, environmentally compactable treatment techniques to treat raw water with low cost and more efficiency[1,2].

1.2. Nanotechnology: a small answer to bigger questions

The word "nanotechnology" infers the use and application of particles and materials in nanosize. In 1959, Richard Feynman, father of modern nanotechnology, proposed the idea "There's Plenty of Room at the Bottom". The idea of manipulating matter to atomic or molecular level traverse over the conventional subjects in science like physics, chemistry, biology and engineering[3,4]. Over the last few decades, the revolution in multidisciplinary nanotechnology has led to the invention of limitless engineered nanomaterials in diverse fields such as catalysis, electronics, drug delivery, monitoring and treatment of environmental pollution[5–12]. These applications were achieved by the distinctive chemical, magnetic, optical, mechanical, catalytic and electronic properties of nanomaterials with an extremely small size, surface and quantum effect[6,7].

Nowadays, nanomaterials demonstrate significant role in environmental protection by (i) pollution prevention, (ii) pollution detection and (iii) treatment/remediation of the pollutant[13]. Nanotechnology has an essential role in pollution prevention as it reduces/eliminates waste production and improves the effective use of resources like energy, raw materials and water. Nanocatalysts show high capability for the production of desired products in chemical engineering. For example, the high capacity and cycling constancy of Li-O₂ batteries can be attained by IrO₂ nanoparticles attached to N and Co co-doped reduced graphene oxide (Co-N-rGO)[14]. In another study, biodiesel was produced from waste cooking oil and methanol using calcium oxide (CaO) nanocatalyst[15]. Detection of pollutants has been done using nanomaterials that give more sensitive results at a low cost. For example, gold nanoparticles were used to detect

endosulfan pesticide in mg/L level[15] and Bi modified reduced graphene oxide was applied to detect Cd^{2+} , Pb^{2+} , Zn^{2+} and Cu^{2+} ions in water[16].

The most researched area of nanotechnology in environmental protection is the treatment of pollutants and the purification of contaminated air, water and soil. Nanomaterials can remove toxic gases in the air; for example, carbon nanotubes were used for the adsorption of dioxins, NO_x and CO_2 from the air. Porous structure and surface functional groups present in carbon nanotubes through chemical and thermal treatment are the reasons behind the specific properties of carbon nanotubes in pollutant adsorption[13]. Adsorption, filtration through nanomembranes, oxidative and reductive catalysis are the general mechanisms for removing air pollutants through nanomaterials. Different nanomaterials are used for different purposes, such as calcium-based nanomaterials used for CO_2 adsorption, TiO_2 nanomaterials used for Hg^0 removal and $\alpha\text{-Fe}_2\text{O}_3$ nanocubical catalyst for the conversion of CO to CO_2 at low temperature[17].

1.3. Nanotechnology in water treatment

The non-availability of clean drinking water is a critical environmental problem facing several countries[18]. Nanotechnology introduced novel methods for pollutant treatment which also improves the efficiency of conventional water treatment methods. High efficiency, small size, multifunctionality and high selectivity for specific contaminants make nanomaterials more attractive, along with the cost-effectiveness and simple instrumental setup involved[2]. The physical and chemical properties of nanomaterials vary with size, shape and composition. The nanoparticles interact more effectively with the contaminants compared to bulky composites. Nanomaterials have a large surface area, so a substantial fraction of atoms present on the surface will increase nanoparticle reactivity. The small particle size of nanoparticles also causes quantum confinement effect and localised surface plasmon resonance. Due to this, the search for more sustainable, efficient, affordable nanomaterials is a continual process in nanotechnology. Till now, different types of nanomaterials has been used for the remediation of water contaminants. They can be broadly classified into nanosorbents, nanofilters, nanomembranes, nano-based disinfectants, nanocatalysts and nanoparticles for reduction purposes. Furthermore, these nanomaterials are in various morphological forms like nanoparticles, nanotubes and nanosheets.

1.3.1. Nanosorbents

Adsorption is a surface phenomenon in which the adsorbate comes into contact with the adsorbent and accumulates on the surface of the adsorbent due to intermolecular forces of attraction. Depending on the nature of attraction between adsorbate and adsorbent, the adsorption process is broadly categorised into physisorption and chemisorption[19]. Chemisorption is more selective than physisorption due to the electron transfer occurred in the chemical process. Different types of nanomaterials such as carbon-based nanomaterials, metal and metal oxide based nanomaterials, nanoparticles and zeolites have been used for the adsorption of water contaminants

Carbon-based nanomaterials: Traditionally, activated carbon is used for the adsorption of heavy metals and dyes due to the large surface area and high porosity. Activated carbon has a low cost since it is prepared from readily available materials like coal, wood, coconut shells and agricultural waste. Even though activated carbon possesses a weak acidic ion-exchange character, they show difficulty to remove pollutants at parts per billion level. This drawback of activated carbon has been overcome by a new era of nanomaterials like carbon nanotubes, graphene and fullerenes. The unique chemical, structural, mechanical and physical properties of carbon nanotubes make them helpful in removing dyes and heavy metals. The functionalisation of carbon nanotubes with hydroxyl and carbonyl groups increases pristine carbon nanotubes' effectiveness for dye removal[19]. According to Gao et al., the carbon nanotubes show good efficiency for the adsorption of multiple metal ions (nickel, copper, zinc and cadmium) from an aqueous solution. The surface features, ion exchange process and electrochemical potential controlled the adsorption mechanisms[20].

Another nanomaterial used for the adsorption of water contaminants is graphene, a two-dimensional sheet material consisting of a single layer of carbon atoms. Graphene-based nanomaterials include graphene, graphene oxide, reduced graphene oxide and their modifications. Generally, graphene sheets have a hydrophobic surface and exhibit a strong adsorption capacity for organic pollutants. Different functional groups such as epoxides, alcohols and carboxylic acids in graphene oxide nanomaterials make them suitable adsorbents for organic and inorganic pollutants. Modifying with hydroxyl, carboxyl, sulfonate functional groups and incorporating other nanomaterials to pristine graphene-based nanomaterials improved its adsorption capacity[21]. The mechanism suggested for

the adsorption of pollutants by pristine graphene are p-p interaction and hydrophobic forces and that for graphene oxide are electrostatic, hydrogen and Lewis acid-base interactions[2].

Metal and metal oxide nanoparticles: These are common sorbents due to their high surface area, stability and reusability. Surface complexation, intraparticle diffusion and micropore active site interactions are the main forces behind the adsorption mechanism. Prevalent metal and metal oxide nanoparticles used for the adsorption process are Fe^0 , Fe_3O_4 , MnO , TiO_2 , ZnO , SiO_2 and Al_2O_3 [2,18,22]. Fe^0 is an excellent adsorbent for heavy metals and organic pollutants due to its high surface area, low cost, high reactivity, magnetic properties and environmental compatibility[2]. Recently Hasan et al. effectively used biocharcoal supported nanoscale Fe^0 to treat synthetic stormwater containing high concentrations of heavy metals (Cu, Cd and Zn)[23]. In another study, Abbas et al. synthesised surfactant modified maghemite nanoparticles and effectively removed different cationic dyes, including brilliant cresyl blue, thionine and janus green b from aqueous media[24].

Surface functionalisation of SiO_2 nanoparticles gives high effectiveness for the adsorption of dyes and heavy metals[2]. Rachel et al. successfully synthesised glycine functionalised SiO_2 nanoparticles and used them for effective absorption of malachite green dye from aqueous solution[25]. The $\gamma\text{-Al}_2\text{O}_3$ shows remarkable thermal stability and adsorption capacity and interacts with various chemical species such as heavy metals and dyes, using reactive sites[26]. Defluoridation of aqueous solutions have been studied by Sareh et al. using Al_2O_3 nanoparticles. The proposed mechanism of defluoridation is the complexation of Al_2O_3 nanoparticles with fluoride ions[27]. TiO_2 nanoparticles are significant in removing organic and inorganic pollutants due to their photocatalytic and adsorption mechanisms[2]. TiO_2 and TiO_2 -based materials are widely used to remove inorganic and organic arsenic species in water. The factors influencing the adsorption capacity of TiO_2 are specific surface area, degree of crystallinity and surface modification. The surface of TiO_2 -based materials makes inner-sphere complexes with inorganic and organic arsenic from water[28]. Another photocatalyst, ZnO also used for the adsorption of dyes and heavy metals[29]. Fan et al. studied the adsorptive removal of cationic and anionic dyes using ZnO nanoparticles and these nanoparticles show high adsorption capacity, good selectivity and reusability for removing malachite green, acid fuchsin and congo red dyes. Chemical

precipitation, electrostatic attraction and hydrogen bonds are the adsorptive mechanisms for dye removal[30].

1.3.2. Nanocatalysts and nanoparticles for reduction

The particle size of the catalyst has a significant impact on their activity in contaminant remediation. Materials with catalytic properties and at least one of the dimensions in the nanoscale are called nanocatalysts. Typically, nanocatalyst has high activity due to its high surface to volume ratio so that more pollutants can interact with the surface of the catalyst[31,32]. Different types of nanomaterials such as noble metal nanoparticles, nano-based photocatalysts, nano-based Fenton-like catalysts and transition metal nanoparticles are employed in the catalytic degradation of water pollutants[22].

Nanomaterials for the catalytic oxidation of pollutants: Nanomaterials like TiO₂ and ZnO act as photocatalysts for the oxidation via degradation of organic pollutants to nontoxic materials. The significant advantages of these materials are high photoconductivity, high photostability, low toxicity, low cost and easy availability. In photocatalysis, the charge transfer from the valence band to the conduction band results in the formation of hydroxyl radicals and these highly reactive radicals cause the oxidation of pollutants[22]. Recently, Krishnamoorthy et al. synthesised TiO₂ nanoparticles for the photocatalytic degradation of methylene blue and congo red dyes under UV–visible light. Their studies show that alkaline condition is favourable for methylene blue degradation and acidic condition for congo red degradation[33]. The modified entities of TiO₂ and ZnO photosensitive nanoparticles have also been studied for contaminant degradation[13].

Iron-based nanomaterials were used as Fenton-like catalysts in the presence of hydrogen peroxide to degrade organic pollutants by redox reactions, dehydrogenation and electrophilic addition. The hydroxyl radicals produced by the Fenton reaction result in the degradation of organic pollutants[21]. Kuang et al. reported the mineralisation of monochlorobenzene through oxidation using green synthesised iron nanoparticles as heterogeneous Fenton-like catalysts[34]. Irradiating UV-visible radiation with the Fenton system can improve the reaction process, known as the photo-Fenton reaction. Guadalupe et al. used Fe⁰ nanoparticles to degrade the 2-chlorophenol through the photo-Fenton reaction[35]. The efficiency of the Fenton system can be improved by ultrasonication. In the degradation of bisphenol A by Ruixiong et al., ultrasonication reduces the reaction's pH dependence and increases the degradation of bisphenol A[36]. Another important

category of Fenton reaction is the Electro-Fenton reaction, in which continuous electrogeneration of hydrogen peroxide occurs from the reduction of oxygen on a carbonaceous cathode.

Sebastian et al. studied the degradation of antibiotic nafcillin using bimetallic Fe/Cu nanoparticles. Their studies show that Fe/Cu bimetallic nanoparticles completely removed the drug at a lower duration of electrolysis than using individual Fe and Cu nanoparticles. The reaction intermediates and by-products of the drug degradation are oxalic, oxamic, formic and acetic acids. Electrocatalytic oxidation processes are a newly emerging technology for the degradation of organic pollutants through oxidation. In this method, reactive oxygen species were generated in situ at the anode surface at high current and these reactive species degraded the organic pollutant to mineralised form[37]. Electrocatalytic degradation of tetracycline in wastewater has been done by Wenhao et al., using electrospun iron/cobalt alloy nanoparticles on carbon nanofibers. This nanocomposite shows outstanding stability, recyclability and reusability and it also completely degrade the tetracycline into CO₂ and H₂O[38].

Nanomaterials for the catalytic reduction of pollutants: Metal nanoparticles were used for the catalytic reduction of organic and inorganic pollutants. Palladium based nanomaterials were used for the reduction of hexavalent chromium from water. Weixia et al. studied the reduction of Cr(VI) using two types of Pd based nanoparticles, PVP-stabilized Pd colloidal nanoparticles and the Pd-Fe₃O₄ magnetic catalyst. PVP acts as stabilising and capping agent for Pd nanoparticles, increasing the nanoparticle's Cr(VI) reduction capacity. The incorporation of Fe₃O₄ to Pd nanoparticles improved the nanoparticle's efficiency and recyclability due to their magnetic activity[39]. The catalytic degradation of nitrophenols and dyes was investigated by Soha et al., using two silver-based nanocomposites. The first was supported on cellulose acetate filter paper and the second was impregnated into titanium dioxide. In the presence of NaBH₄, these silver-based nanoparticles show high degradation efficiency for 4-nitrophenol, 2-nitrophenol, 2-nitroaniline, trinitrophenol, rhodamine B dye and methyl orange dye[40]. Metallic Ni and Cu nanoparticles embedded carbon sheets are useful for the NaBH₄-mediated reduction of 4-nitrophenol, methyl orange and methylene blue[41]. In another study, formic acid was used as a reducing precursor and Pd/Ag alloy nanoparticles supported on amine-functionalised SiO₂ were used as a catalyst for reducing nitrate in water[42].

Nanoparticles as reducing agents: Nanoscale zero valent metals were used to reduce water contaminants due to their strong chemical reducibility, high efficiency and large specific surface area[7,43]. The reactivity, mobility, longevity and toxicity of the zero valent metals are significant for selecting appropriate nanoparticles for water pollution remediation[6]. The most investigated nano zero valent metal as a reducing agent is Fe⁰ due to its low cost and high reduction potential. Fe⁰ can be used to reduce halogenated organic compounds, inorganic anions and heavy metals[44]. Hocheol et al. studied the reduction of eight chlorinated ethanes using Fe⁰ nanoparticles. They found that reductive β-elimination was the major pathway and reductive α-elimination and hydrogenolysis were concurrent pathways to form fewer chlorinated ethanes using Fe⁰ nanoparticles[45]. Other metals such as zero valent zinc and copper can also substitute Fe⁰ nanoparticles to remove contaminants. However, the toxic effect of zinc and copper at higher concentrations makes them less attractive for contaminant remediation[7]. Mario et al. compared the Cr(VI) reduction efficiency of Fe⁰ and zero valent copper nanoparticles and found that Fe⁰ nanoparticles are more effective than Cu⁰ nanoparticles[46].

1.3.3. Nanofiltration and Nanomembranes

Nanofiltration filters out the unwanted ions, organic molecules and heavy metals from water using pressure as a driving force with low energy input. Nowadays, it is one of the best methods for drinking water purification due to its high selectivity and availability of various nanomembranes[13]. These membranes are flexible, profitable and easy to prepare. Different types of membranes have a variety of properties. Ceramic membranes show good chemical, mechanical and thermal properties. Polymeric membranes show high water flux but have a high fouling rate and less chemical resistance[47]. The properties of nanomembranes have been improved through interfacial polymerisation, incorporating NPs, electron beam irradiation, UV grafting/photografting, plasma treatment and layer-by-layer modification[21]. Incorporating functional nanoparticles into the membrane makes them multifunctional materials for water treatment. For example, Hem et al. synthesised a stable silver-doped fly ash/polyurethane (Ag-FA/PU) nanocomposite multifunctional membrane with less bio-fouling. These membranes' specialities were spider-web-like nano-netting for nanoparticles separation, enhanced absorption capacity to remove carcinogenic arsenic and toxic organic dyes and antibacterial properties[48].

1.3.4. Nano based disinfectants

Antimicrobial nanotechnology is one of the emerging research areas in nanotechnology and different nanomaterials follow various mechanisms for antimicrobial activity. Chitosan nanoparticles inhibit the enzyme activity and DNA synthesis of bacteria[49,50]. Silver nanoparticles show different mechanisms such as i) they can penetrate in the bacterial cell wall, change the cell membrane texture leading to cell death, ii) the reactive oxygen species produced from Ag nanoparticles cause oxidative stress in the microorganism and Ag ions interrupt the replication of DNA[51]. The reactive oxygen species produced from photocatalysts like TiO₂ will damage the cell components of microorganisms. According to Sunanda et al., the photokilling of TiO₂ nanoparticles have two steps; in the first step, the outer membrane has disordered, which will ease the penetration of reactive species into the inner membrane and in the second step, the cytoplasmic membrane gets disordered and cause the death of bacteria[52].

Carbon nanotubes can also kill the bacteria and the reported mechanism for the destruction of bacteria are i) physical piercing, ii) oxidative stress, iii) length-dependent wrapping, iv) cell membrane damage by direct contact, v) penetration of the bacterial lipid membrane and vi) laser photothermal ablation[53]. The antibacterial activity of fullerene nanoparticles differs in gram-positive bacteria and gram-negative bacteria. In gram-negative bacteria, the proportion of unsaturated fatty acids decreases and the proportion of cyclopropane fatty acids increase in the bacterial cell wall and this will cause the inactivation of the bacteria. In gram-positive bacteria, the alterations in the phospholipid structure, increased permeability of the cell membrane and cell wall destruction causes the death of bacteria[54]. In water treatment systems, iron-based nanomaterials have a significant position compared to other nanomaterials mediated techniques due to their capacity for reduction, oxidation, complexation and adsorption of water contaminants.

1.4. Iron-based nanomaterials

Iron is a reactive metal and the fourth most abundant metal in the earth's crust[55]. Generally, iron exists as Fe²⁺ and Fe³⁺ in the earth's lithosphere. Fe⁰, bimetallic/trimetallic iron-based compounds and iron oxides are the major iron-based nanomaterials[56–58]. Fe⁰ symbolises iron in zero oxidation state or elemental state. Iron oxide is the common name

used to denote the oxides, hydroxides and oxy-hydroxides of Fe^{2+} and Fe^{3+} cations with O^{2-} and OH^- anions. Fe_2O_3 , Fe_3O_4 , FeO , $\text{FeO}(\text{OH})$, $\text{Fe}(\text{OH})_3$, $\text{Fe}(\text{OH})_2$ and $\text{Fe}_5\text{HO}_8 \cdot 4\text{H}_2\text{O}$ are the common iron oxides seen in the earth's crust. Most iron oxides have the Fe^{3+} oxidation state and low solubility[59]. Along with high reactivity, small particle size and large surface area, the iron nanomaterials also possess less toxicity, biodegradability, magnetic susceptibility and dual redox properties in water. The precursors used to synthesise iron-based nanomaterials have low costs and are widely available[60]. Fe^0 becomes a benchmark term among different iron-based nanomaterials due to its unique properties[61,62].

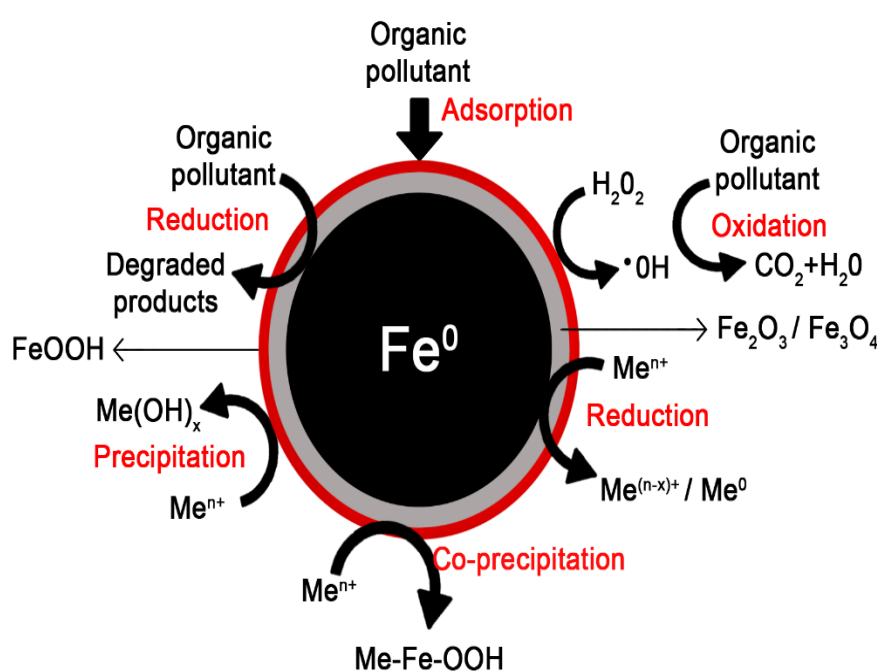
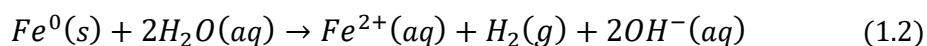
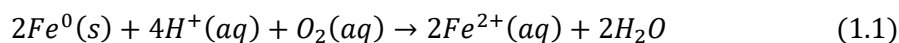


Figure 1.1 General mechanism of zero valent iron (Fe^0) nanoparticles for pollutant removal

1.5. Zero valent iron (Fe^0) nanoparticles and their properties

Around the last three decades, the Fe^0 or metallic iron nanoparticles were widely employed to remediate wastewater, drinking water and groundwater[63,64]. The standard electrode potential of $\text{Fe}^{2+}/\text{Fe}^0$ is -0.440 eV, which makes Fe^0 a strong reducing agent for oxidative pollutants. Reduction is the major mechanism carried out by the Fe^0 nanoparticles and adsorption and oxidation are the other mechanisms tailed by Fe^0 nanoparticles. The general mechanism of Fe^0 nanoparticles is shown in figure 1.1. Core-shell structure, large specific surface area and magnetic property are the three key influencing properties behind the high

reactivity of Fe⁰ nanoparticles[44]. Generally, Fe⁰ nanoparticles have a core-shell structure with a metallic iron core and iron oxide shell. The iron oxide/hydroxide shell formation is due to the oxidation/corrosion of the metallic (Fe⁰) iron core. The oxidation of iron with oxygen and water (equation 1.1 & 1.2) can be expressed as follows.



The core-shell structure contributes to the unique properties of Fe⁰. The core Fe⁰ have strong reducing power for organic pollutants. The iron oxide shell can improve/impede the electron transfer from Fe⁰ and/or molecular oxygen activation. The defect in the oxide shell can improve the reduction capacity of Fe⁰ nanoparticles. The physical and chemical composition of the oxide shell, such as porosity and electronic conductivity, can influence the mass transfer property and reactivity of Fe⁰ nanoparticles. For example, the conductive iron oxides like FeO and Fe₃O₄ allows electron transfer, but oxides like FeO(OH) inhibit the electron transfer from the iron core to the iron oxides shell. It may be due to the difference in bandgap energy of FeO(OH) and others since FeO and Fe₃O₄ have significantly less bandgap energy than FeO(OH). It is important to note that contaminant reduction was more thermodynamically favourable in oxide shell compared to iron core surface. However, it is greatly influenced by the porosity of the iron oxide. As the porosity decreases, oxide shell density increases with prolonged reaction time due to the formation of oxyhydroxides. Usually, molecular oxygen is undesirable for the reductive mechanism of Fe⁰ due to the reactivity loss by unwanted reaction with molecular oxygen. Nevertheless, this molecular oxygen can produce reactive oxygen species like hydrogen peroxide, hydroxyl radical and superoxide radical by reacting with the Fe⁰. Moreover, the reactive species can oxidise the contaminants to low molecular weight or complete mineralisation to CO₂. Another important thing is that the oxide shell of iron nanoparticles mainly mediates the adsorption mechanism. The pollutant adsorption to the shell of the iron nanoparticles improves the efficiency for the reduction of organic and inorganic pollutants[65]. The large specific surface area provides more reaction sites on the surface of Fe⁰ nanoparticles. It will increase the reaction between the contaminant and Fe⁰ nanoparticles. Along with large specific surface area, high-density reactive surface sites and greater intrinsic reactivity of surface sites contributed to the enhanced reactivity of Fe⁰

nanoparticles. The magnetic property of nanoparticles accelerates the aggregation of Fe⁰ nanoparticles, leading to a decrease in the reactivity of Fe⁰ nanoparticles[44].

In the 1990s, wang et al. applied nanoscale iron nanoparticles to treat trichloroethylene (TCE) and Polychlorinated biphenyl (PCB)[66]. In the years that followed, Fe⁰ nanoparticles were used for the degradation or removal of various water pollutants such as antibiotics[67], halogenated organic compounds[68,69], nitro compounds[70], explosives[71], pesticides[72,73], inorganic anions[74], heavy metals/metalloids[75], dyes[76–78] and radioactive elements[57]. Even though the major mechanism of Fe⁰ nanoparticles for pollutant removal is considered as adsorption, oxidation via Fenton reaction and reduction, the other mechanisms like complexation and co-precipitation also occur simultaneously and sequentially[79]. The electron transfer from Fe⁰ to pollutant reduces the pollutant and transforms the Fe⁰ to non-toxic Fe²⁺ and Fe³⁺ species[55]. The reductive properties of Fe⁰ were mainly due to the three reductive (Fe⁰, Fe²⁺ and H₂) species. Gotpagar et al. proposed three mechanisms for the dehalogenation of TCE, in that the most prevalent one is reduction of TCE by direct reduction of Fe⁰. Along with that, reduction by H₂ (produced during the corrosion process) and reduction by Fe²⁺ ion (produced by the corrosion process) improved the reductive dehalogenation of TCE[80]. Heavy metals or metalloids are removed by the absorption or chemical precipitation mechanism. Different heavy metals possess different mechanisms using Fe⁰ nanoparticles due to their difference in standard electrode potential since the standard electrode potential of Fe⁰ nanoparticle is -0.44 V. Reductive precipitation happens in metals with much higher standard electrode potential than Fe⁰. Sorption and partial chemical reduction occur in metals that have slightly more positive standard electrode potential than Fe⁰. Lastly, sorption/surface complexation occurs in metals with a more negative standard electrode potential than Fe⁰[62]. Another application of Fe⁰ nanoparticles is as a Fenton-like catalyst for the degradation of organic contaminants. Fe⁰ reacts with an oxygen molecule and produces H₂O₂, which is reduced to water by accepting two more e⁻ from Fe⁰. The resulting Fe²⁺ and H₂O₂, known as Fenton reagent and hydroxyl radicals produced during the Fenton's reaction, could act as the oxidising agent for organic compound degradation[81]. Generally, the removal/degradation mechanism by Fe⁰ nanoparticles depend on various parameters, including the type of pollutant, availability of oxygen and pH[82,83].

Large scale application of Fe⁰ nanoparticles is widespread in the USA compared to Europe and other countries[84]. In 2009, Namen et al. studied Cr(VI) removal in groundwater

using Fe⁰ filings, Fe⁰ powder and Fe⁰ nanoparticles and found that Fe⁰ nanoparticles are more efficient for Cr(VI) removal. Fe⁰ nanoparticles are also helpful for municipal wastewater treatment[85,86]. The laboratory-scale continuous flow system is tested for nitrate reduction using Fe⁰ nanoparticles and found that Fe⁰ nanoparticle reactivity is vulnerable to groundwater constituents[87].

Even though the Fe⁰ nanoparticles are highly effective for pollutant remediation, they also face practical application difficulties, including reactivity loss due to the intrinsic passive layer, aggregation tendency, less stability, reduced mobility, narrow working pH and low working pH selectivity for contaminants[88]. The oxygen and water molecules present in the environment reacted with Fe⁰ to create a passive layer on the surface of nanoparticles. The formed iron oxide layer on the surface of the Fe⁰ nanoparticles showed some ability for the adsorption of pollutants even though this iron oxide layer decreases the reduction capacity of Fe⁰ nanoparticles[59]. Despite the disadvantages of the Fe⁰ nanoparticles, their low cost, environmental compatibility and biodegradability make them a central attraction for water pollution remediation by researchers worldwide.

1.6. Synthesis of zero valent iron (Fe⁰) nanoparticles

Several methods for producing Fe⁰ nanoparticles include physical, chemical, and biological methods. For example, chemical reduction methods[89], electrochemical methods[90], ultrasound-assisted methods[56] and carbothermal reduction methods[91] etc. Generally, top-down and bottom-up approaches are followed widely to synthesise Fe⁰ nanoparticles. The size, shape and reactivity of the nanoparticles are influenced by the synthesis method adopted. In top-down approaches, micro/granular iron particles are crushed into nanosized particles through mechanical or chemical[92]. Ball milling, noble gas sputtering and laser ablation are the top-down methods commonly used for Fe⁰ nanoparticles production.

Ball milling: In ball milling, micro iron particles are broken down to Fe⁰ nanoparticles by the mechanical forces created on stainless steel beads in a high-speed rotary chamber[93]. The formed particles have an irregular shape and high surface energy to cause a strong aggregation tendency[92]. The milling process influences the size, shape and reactivity of Fe⁰ nanoparticles. The conventional ball milling process uses organic solvents like mono ethylene glycol to produce flattened iron nanoparticles. Ribas et al. established that

introducing fine alumina powder to the organic solvent containing ball milling system breaks the iron flakes into smaller particles[94]. Shaolin et al. verified that solvent-free Fe⁰ nanoparticles with particle size below 50 nm were formed after 8 hours of precision milling using micro iron as precursors[93]. Ball milling is helpful for large scale industrial production and it does not require any toxic and expensive chemicals.

Laser ablation: In this method, the iron metal target is locally melted and vaporised by the laser pulse. When the surrounding medium cools the hot metal atoms, the metal nanoparticles are formed from it[95]. It is a small scale synthesis method and the formed nanoparticles will easily get oxidised in the presence of oxygen and water. Yosmery et al. synthesised Fe⁰ nanoparticles with a mean particles size of 17 nm by laser ablation method and stabilised by surfactant sodium dodecyl sulfate. They used a medium with a high H⁺ concentration during the synthesis, which reduces the oxide shell thickness[96].

The bottom-up approach synthesises Fe⁰ nanoparticles from either iron oxide nanoparticles, iron-containing molecules or dissolved iron salt solution using various reducing agents. Reduction using chemical reducing agents like NaBH₄, carbothermal reduction, electrochemical deposition, chemical vapour deposition and reduction using biogenic compounds are bottom-up methods for Fe⁰ nanoparticle production[88,95].

Liquid-phase reduction: Reduction of the iron metal salt solution using a potent reducing agent like sodium borohydride under an inert atmosphere is the most commonly practised one. After the slow addition of NaBH₄, the formed black precipitate was washed with water, ethanol and acetone, then vacuum filtered and stored in airtight vials[92]. Good efficiency, the requirement of a short time for synthesis, high reactivity and easy to perform reaction are the advantages of sodium borohydride mediated synthesis of nanoparticles[97]. However, this method has shown some drawbacks due to the high cost and the toxic effect of potent reducing agents and less stability of nanoparticles[98]. According to Sungjun et al., NaBH₄ reduces the FeCl₃ salt solution and disintegrates the formed Fe⁰ nanoparticles to smaller particle sizes[99]. Heesoo et al. established that washing and drying conditions during the synthesis of zero valent iron nanoparticles influence the surface characteristics of Fe⁰ and reactivity towards contaminants. Fe⁰ nanoparticles reactivity can be improved using volatile solvents for washing and drying in anaerobic conditions[100].

Carbothermal reduction: In the carbothermal reduction method, high temperature and the presence of gas reducing agents like H₂, CO and CO₂ lead to the formation of Fe⁰ nanoparticles using iron oxide nanoparticles or aqueous salt solutions of Fe²⁺ precursors[92]. These gaseous reducing agents were formed by the thermal decomposition of carbonaceous materials like biochar and carbon black[88]. Lura et al. synthesised Fe⁰ on carbon black under argon atmosphere at a high temperature of 600-800°C[91].

Electrochemical deposition: Electrochemical deposition method uses electric current, electrodes (cathode and anode) and Fe²⁺/Fe³⁺ salt solutions for the Fe⁰ production through electrolysis. The atoms of iron deposited on the cathode have a high tendency for agglomeration and it can be overcome by introducing cationic surfactants and ultrasonic waves[88]. Chen et al. synthesised Fe⁰ nanoparticles by combining electrochemistry and ultrasonic vibration. Fe⁰ nanoparticles of 1–20 nm diameter and 25.4 m²/g specific surface area were produced using platinum as cathode and cetylpyridinium chloride as dispersion agent[90].

Chemical vapour deposition: In this method, pyrolysis of organoiron compounds like iron pentacarbonyl in the gas phase under inert conditions will give Fe⁰ nanoparticles[95]. Choi et al. synthesised Fe⁰ nanoparticles through the chemical vapour deposition method using iron pentacarbonyl [Fe(CO)₅] as iron precursor under flowing helium atmosphere. An increase in the decomposition temperature during the reaction causes an increase in the particle size of nanoparticles. The formed spherical core-shell nanoparticles have a particle size between 5 to 13 nm[101].

Biogenic synthesis: The toxic effect of chemicals and other drawbacks of conventional methods promotes the environment-friendly production of Fe⁰ nanoparticles. Biogenic materials were used for the green synthesis of nanoparticles and also it could act as both stabilising and reducing agents for nanoparticles.

The abundance and easy availability of plants make them a significant candidate for biogenic synthesis. The secondary metabolites, enzymes and other plant biomolecules are the factors behind the reducing capacity of plant biomaterials. Polyphenols, flavonoids, amino acids, terpenoids, reducing sugars, steroids, saponins, vitamins, alkaloids and organic acids are the main plant biomolecules used to reduce iron ions[102,103]. Different plant parts followed various mechanisms for reducing Fe⁰ nanoparticles due to the difference in bioactive components containing them. Extracts of leaves, seeds, fruits, bark

and flowers were applied to reduce Fe⁰ nanoparticles. Additionally, plant extracts' stabilising and capping property decreases the aggregation and controls nanoparticles' morphology. Researchers found that the green synthesis method for the Fe⁰ nanoparticles lessens the use of stabilising agents during synthesis. Low toxicity, more availability, simple and rapid synthesis route, more energy efficiency, low cost, faster reaction, good stability of nanoparticles, environmental compatibility and significant capability to control morphology, size and growth of the nanoparticles are also advantageous of plant-based synthesis Fe⁰ nanoparticles. The mechanism of phytogenic Fe⁰ nanoparticles for pollutant removal is almost similar to Fe⁰ nanoparticles. In some cases, plant extract itself shows some capacity for pollutant removal. Even though the plant-mediated Fe⁰ nanoparticles have tremendous advantages, they also have drawbacks. The significant issues are the incomplete reduction of Fe²⁺ ions to Fe⁰ nanoparticles by the plant components and lower reactivity and surface energy of phytogenic Fe⁰ nanoparticles compared to chemically prepared Fe⁰ nanoparticles[104–106].

Tea leaves are one of the most commonly used plant extracts to synthesise Fe⁰ nanoparticles. The tea extract contains many polyphenols and caffeine, which acts as a reducing, capping and stabilising agent during the preparation of Fe⁰ nanoparticles[34,107]. Typically, a single pot synthesis method is followed for the tea leaf extract based synthesis of Fe⁰ nanoparticles. The iron precursor (ferric chloride/ferric nitrate/ferrous sulphate) was treated with the tea extract at a specific volume ratio under room temperature and eventually, dark greenish/brown/black nanoparticles were formed within a few minutes. Hoag et al. used a 2:1 ratio for 0.1 M FeCl₃ and 20 g/L green tea extract and produced spherical nanoparticles of 5 to 15 nm particle size[107]. Creda et al. compared the properties of green synthesised and chemically (NaBH₄) synthesised nanoparticles. Different kinds of iron nanoparticles such as lepidocrocite, magnetite and Fe⁰ nanoparticle were produced by blueberry leaf extracts and this may be due to the presence of different phenolic compounds with different reducing and complexing capacities. Previous studies show that blueberry leaves have phenolic compounds (e.g. caffeic acid, chlorogenic acid and ferulic acid) with high reducing potential. Compared to chemically synthesised Fe⁰ nanoparticles, less agglomerated and more dispersible Fe nanoparticles are formed by blueberry leaf extract[108].

Different parts of fruit such as peel, albedo, pulp and seed were used to synthesise the Fe⁰ nanoparticles. Citrine fruit extracts are the most widely investigated fruit materials for

producing Fe⁰ nanoparticles. Machado et al. utilised the juice industry waste of citrine fruits such as orange, lime, lemon and mandarin to synthesise Fe⁰ nanoparticles. The peel, albedo and pulp of these fruits were collected and its bioactive ingredients were extracted using water. The green Fe⁰ nanoparticles are produced by the simple mixing of fruit extract and iron (III) solution. The fruit extract created Fe⁰ nanoparticles with diverse sizes, shapes and agglomeration. The concentration and chemical composition of the extract, temperature and reaction time are the parameters that influenced the size and shape of the Fe⁰ nanoparticles. The majority of the Fe⁰ nanoparticles except the orange pulp and albedo did not show any settlement, making stable dispersions in the aqueous medium. The authors professed that citrine fruits extracts could be used to synthesise Fe⁰ nanoparticles[109]. The unique chemical properties of flowers made them an appropriate material for generating various nanoparticles. Sravanthi et al. suggested a novel green method for preparing Fe⁰ nanoparticles using *Calotropis gigantea* (CG) flower extract as a reducing and capping agent and the *Pithecellobium dulce* seeds and chitosan as green stabilising agent and template. *Calotropis gigantea* flower extracts were prepared by boiling in an aqueous medium and it was mixed with Fe(NO₃)₃·9H₂O in a 1:1 ratio. The formed nanoparticles were mixed with chitosan and *Pithecellobium dulce* seed powder. A large number of polyphenols present in the flower extract helps the reduction of iron precursors. More phenolic groups provide more anti-radical capacity consecutively more antioxidant ability. Post grafting of iron nanoparticles using biomaterials and chitosan helped to prevent the oxidation and agglomeration of iron nanoparticles. The particle size of nanoparticles prepared by flower extract is between 50-90 nm and polydisperse[110].

The synthesis of Fe⁰ nanoparticles using root extract is rare. Green Fe⁰ nanoparticles were produced through the root extracts of *Ferula persica* as a reducing agent and FeSO₄·7H₂O as an iron precursor. *F. persica* is an essential medicinal plant since it contains a broad range of bioactive agents. Root extract was prepared by mixing the root tissue powder of *F. persica* with water and tailed by heating at 90°C for 1 hour. During the synthesis of green Fe⁰ nanoparticles (G-Fe⁰), the root extract was mixed with the iron sulphate solution for 2 hours at pH 8. The formed black precipitate was collected through centrifugation, washed with deionised water, and dried. These prepared nanoparticles showed the tendency for oxidation due to the high reactivity of Fe⁰. To overcome this problem, β-cyclodextrin (βCD) was applied as a stabilising and capping agent for iron nanoparticles. The primary antioxidant constituent of *F. persica* is ferulic acid and coumarins, forming

the resonance-stabilised phenoxy radicals. The reduction of metal ions through *F. persica* was assigned to the resonance stabilisation and ferulic acid/coumarin dimer formation[111].

1.7. Modification on Fe⁰ nanoparticles

Fe⁰ nanoparticles have a few drawbacks despite several advantages due to high surface energy and intrinsic magnetic interaction, which will cause chains like aggregation, rapid surface oxidation and microscale iron particle formation[112]. In order to reduce the aggregation and to improve the effectiveness and stability of the Fe⁰ nanoparticles, several modifications are implemented eventually during the synthesis. They are (i) encapsulation of Fe⁰ nanoparticles in a matrix/support like silica and activated carbon[83,113], (ii) emulsification of Fe⁰ nanoparticles using oils[114], (iii) doping the Fe⁰ nanoparticles with other catalytic metals such as Cu, Ag and Ni[115–117], (iv) coating the surface Fe⁰ nanoparticles with polymers[118], surfactants[119] and natural products[120]. The selection of stabilisation techniques depends on the intended application of Fe⁰ nanoparticles since the stabilising material influence the chemical and physical properties and morphology of the prepared nanoparticles. The nanoparticle production expense is related to the cost of reducing agents and stabilising agents. Some of the modification/stabilisation methods for the Fe⁰ nanoparticles are shown in figure 1.2.

1.7.1. Doping with catalytic metal

Bimetallic iron nanoparticles were synthesised by depositing a less active second catalytic metal onto the surface of the iron nanoparticle, improving the reactivity and functionality of Fe⁰ nanoparticles. Even though bimetallic nanoparticles are widely used to enhance the reactivity of Fe⁰ nanoparticles, the mechanism behind the enhanced reactivity is still not clear. One possible mechanism is that bimetallic nanoparticles act as a galvanic cell in which Fe⁰ act as an anode and the second metal (Pd, Ni, Cu, or Zn) acts as a cathode. Iron gets oxidised and the second metal remains unchanged. The electron transfer from Fe⁰ core to contaminant were permitted through doped catalytic metal. This will lead to the enhancement in reactivity of Fe⁰ nanoparticles[112]. Various bimetallic combinations such as Fe/Cu, Fe/Pd, Fe/Ni, Fe/Pt, Fe/Au, Fe/Al and Fe/Ag were prepared and applied for environmental remediation studies[116,117,121–124]. Tao et al. synthesised Pd/Fe nanoparticles and used them for dechlorination reaction. Doping of Fe⁰ with noble metal

Pd enhances the dechlorination reaction by utilising H_2 produced through iron corrosion with Pd as the cathode to allow electron transfer from Fe^0 core to contaminant[125]. Markova et al. reported novel air-stable bimetallic Fe/Ag nanoparticles with high antimicrobial efficiency and phosphorous removal potential. These nanoparticles were prepared by direct reduction of Ag^+ ions by commercially prepared Fe^0 nanoparticles. Silver nanoparticles were formed with particle sizes between 10-30 nm depending on the initial concentration of the $AgNO_3$ solution[117].

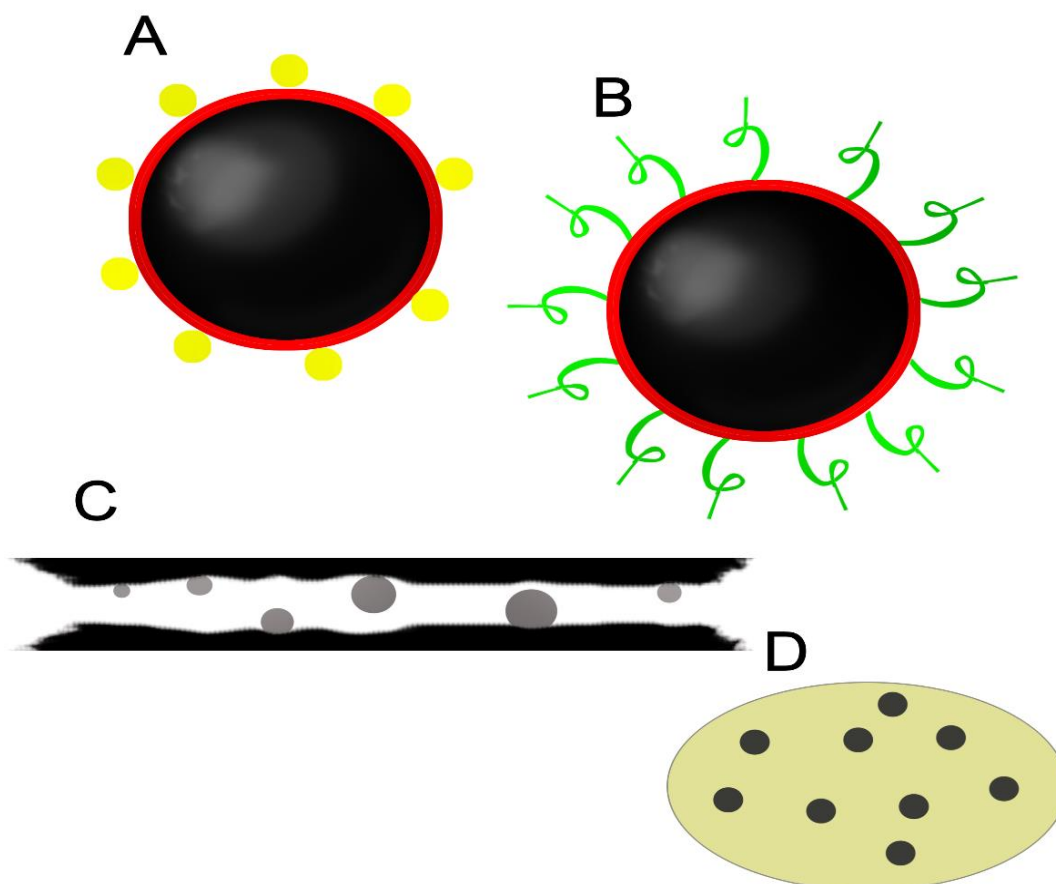


Figure 1.2 Modification of Fe^0 nanoparticles A) doping with catalytic metal, B) surface modification using polymers/surfactants, C) immobilisation onto a solid support and D) emulsification

1.7.2. Surface modification/coating

Surface modified Fe^0 nanoparticles were synthesised by coating a surface modifier on the Fe^0 nanoparticles surface to prevent aggregation and rapid oxidation. Proper surface modification of the nanoparticles improved the dispersibility in aqueous media and mobility in porous media. Through surface modification, the surface charge of the Fe^0 nanoparticles gets changed, which reduces the electrostatic attraction between Fe^0

nanoparticles and leads to the formation of nanoparticles with less particle size and less aggregation. Some surface modifiers use steric hindlers to separate the Fe⁰ nanoparticles through steric repulsion. An ideal surface modifier should have the capacity to get coated on the surface of Fe⁰ nanoparticles and become stable with the changes in the surrounding environment. Low cost and less toxicity are the additional requirements for the ideal surface modifier[88,112]. Different types of monomers, polymers, surfactants and polysaccharides are used for the surface modification of Fe⁰ nanoparticles and some of them are given below.

Polymers: Claudio et al. synthesised air-stable Fe⁰ nanoparticles coated with ethylene glycol at standard atmospheric conditions. Functionalisation with a short polymer chain like ethylene glycol gives high dispersibility to the Fe⁰ nanoparticles through steric repulsion between the grafted polymers[126]. Innocuous polymers like carboxymethyl cellulose (CMC) are commonly used to stabilise the Fe⁰ nanoparticles and reduce agglomeration. Feng et al. established that particle size and dispersibility of the Fe⁰ nanoparticles were manipulated using different types of carboxymethyl cellulose stabilisers. The size of the nanoparticles decreases with the increase in the CMC/Fe²⁺ molar ratio, degree of substitution to CMC and lowering the synthesising temperature. According to them, CMC accelerated the nucleation of Fe atoms during Fe⁰ nanoparticles formation and formed a negatively charged layer on the surface of Fe⁰ via sorption. This layer induces the electrosteric stabilisation of Fe⁰ nanoparticles[127]. Mohammad et al. reported that starch stabilised Fe⁰ nanoparticles show more capability to remove As(III, V) than CMC-Fe⁰ and bare Fe⁰[128]. Lin et al. studied the characteristics of polyacrylic acid stabilised zero valent iron nanoparticles (PNZVI) and carboxymethyl cellulose stabilised zero valent iron nanoparticles (CNZVI). The average particle size of PNZVI was 12 nm. In CNZVI nanoparticles, tens of nanoparticles with particle size 1–3 nm aggregate together to form a secondary particle. Through chemisorption, the two polymers adsorbed onto the Fe⁰ surface. Steric stabilisation by the polymers played a vital role in the dispersion of the synthesised nanoparticles[129]. Polyvinyl pyrrolidone (PVP) coated Fe/Cu bimetallic nanoparticles were synthesised by et al. to prevent the agglomeration of Fe⁰ nanoparticles. These nanoparticles show high dispersibility, confirmed by the high zeta potential value of 38.7 mV in distilled water at neutral pH. The result indicates that the static repellence of nanoparticles was the reason for high dispersibility and stability[130]. A detailed study on the stabilisation of Fe⁰ nanoparticles using natural hydrocolloid gum

karaya (GK) has been done by Vinod et al. In this study, the activated Fe⁰ nanoparticles were mixed with purified Gum Karaya to generate nanoparticles suspensions of Fe⁰-GK. The SEM images revealed the fibrous structure of the GK, which helped the Fe⁰ nanoparticles bound inside the GK scaffolds, leading to the formation of homogeneous dispersions of Fe⁰ nanoparticles. The GK's significant advantages are the presence of functional groups such as -OH, >CO, CH₃CO- and -COOH and its inherent high viscosity. The steric hindrance and negative surface charge of GK molecule through functional groups provided stability to the GK-Fe⁰ nanoparticles. Also the formation of gel networks and bidentate bridging between GK and Fe⁰ reduced the aggregation of nanoparticles. The GK exhibited several mechanisms (e.g. chemisorption, physisorption, ion-exchange and surface precipitation) to absorb the toxic heavy metals[120].

Surfactants: Surfactants are amphiphilic organic compounds that contain hydrophobic tails and hydrophilic heads. The surface of the Fe⁰ nanoparticles absorb the hydrophobic tail and the hydrophilic head hinders the aggregation of nanoparticles using steric or electrostatic repulsion forces. Anionic, cationic and nonionic surfactants were used to stabilise Fe⁰ nanoparticles[112]. Xiangyu et al. used three anionic surfactants such as methyl ester sulfonate (MES), anionic polyacrylamide (APAM) and sodium dodecylbenzene sulfonate (SDBS) to stabilise Fe⁰ nanoparticles. The surface coating of surfactant reduces the particle size and surface oxidation of the Fe⁰ nanoparticles. The presence of surfactant also increases the dispersibility and reactivity of Fe⁰ nanoparticles compared to pristine Fe⁰[131]. Peng et al. used polyacrylic acid (PAA) and three non-ionic surfactants (Tween 20, Tween 40 and Tween 60) to modify the Fe⁰ surface. Even though all modifiers show good dispersing ability, PAA based Fe⁰ nanoparticles exhibit more stability than surfactant-based Fe⁰ nanoparticles. In all surfactants, Tween 20 show better reactivity, better stability and better mobility through porous media[132].

1.7.3. Immobilisation onto supports

Immobilised Fe⁰ nanoparticles were synthesised to overcome the Fe⁰ nanoparticle's separation difficulty from the water after purification. Different materials such as clay, silica, activated carbon, zeolites, resins, membranes and metal oxides were used to synthesise immobilised/supported nanoparticles. The Fe⁰ nanoparticles get trapped on the pores or fixed on the surface of the supporting materials and these immobilisations affect the physicochemical properties of Fe⁰ nanoparticles[88]. Incorporation of a support control

growth reduce the aggregation and improve the reactivity of the Fe⁰ nanoparticles. Additionally, the supported Fe⁰ nanoparticles have a specific capacity to adsorb contaminants before degradation[112]. Augmented particle dispersion and applicability in a continuous flow system can be attained through solid support[133]. Some of the solid supports used to stabilise Fe⁰ nanoparticles are given below.

Clays and zeolites: Clays and zeolites are widely used to remove heavy metal ions through ion exchange and adsorption properties. Low cost, wide availability and high porosity are the additional advantages of clay minerals. Different clay minerals and zeolites are used to stabilise the Fe⁰ nanoparticles. Muath et al. prepared Fe⁰ nanoparticles with different iron/clinoptilolite ratios. Clinoptilolite is a natural zeolite with a large surface area, structural, chemical and thermal stability. Clinoptilolite crystals form physical barriers between the dispersed chains of iron nanoparticles, reducing the agglomeration of Fe⁰ nanoparticles[134]. Besides clinoptilolite, minerals like rectorite, sepiolite and kaolin have also stabilised the Fe⁰ nanoparticles[135–137].

Carbon-based materials: Carbon-based materials such as activated carbon[138], biochar[139], graphene-based compounds[140], carbon nanotubes[141] and carbon black[91] are used to stabilize the Fe⁰ nanoparticles. Due to the porous structure and mechanical strength, the carbon-based materials act as good supporting materials for Fe⁰ nanoparticles. Mahsa et al. prepared a novel nanoadsorbent based on the combination of zero valent iron, graphene oxide and active carbon and ultrasonication used to improve the physical properties of nanoparticles. Incorporation of the graphene oxide reduces the particle size and the crystallinity of the Fe⁰ nanoparticles. With respect to active carbon, the space between the graphene oxide becomes higher and more space is available for Fe⁰ nanoparticles accommodation at low graphene oxide concentration. The prepared nanocomposite show more Fe⁰ stability and graphene coupling improves reactivity through electron transfer and protects Fe⁰ from surface passivation[142].

Metal oxides: Metal oxides like Mg(OH)₂ and TiO₂ were used to stabilise the Fe⁰ nanoparticles. Minghui et al. synthesised novel Mg(OH)₂ supported Fe⁰ nanoparticles and applied them for Pb(II) removal. The synthesised Fe⁰ nanoparticles uniformly immobilised on the surface of flower-like petals of Mg(OH)₂ which reduced the aggregation of the nanoparticles. The reducing capacity of the Fe⁰ nanoparticles is enhanced by the hydroxides provided by Mg(OH)₂[143]. The efficiency of Fe⁰ nanoparticles can also be

enhanced by supporting them into a TiO₂ matrix. The porous TiO₂ matrix increase dispersibility and stability and decrease oxidation and agglomeration of Fe⁰ nanoparticles[144].

1.7.4. Emulsification

Emulsified Fe⁰ nanoparticles consist of food-grade surfactant, vegetable oil, Fe⁰ nanoparticles and water. During emulsification, the Fe⁰ nanoparticles were surrounded by an oil-liquid membrane. Emulsified Fe⁰ nanoparticles mainly focussed on the remediation of groundwater polluted by organic solvents. Fe⁰ nanoparticles degraded the contaminants in the solution sequestered by oil molecules. Enhanced stability due to the oil layer that results in limited oxidation and better mobility through porous media are the advantages of emulsified Fe⁰ nanoparticles. Jun et al. studied the degradation of nitrobenzene using emulsified Fe⁰ nanoparticles and found that adsorption and reductive reaction cause the removal of nitrobenzene. Usually, 1 % and 2 % oil concentrations are preferred to modify Fe⁰ nanoparticles for better performance[145]. Tao et al. used gum arabic to stabilise Fe⁰ nanoparticles in a soybean oil-in-water emulsion. Emulsification not only increases the shelf life of Fe⁰ nanoparticles but also limits the oxidation of Fe⁰ by water and non-target solutes during application[114].

1.8. Applications of zero valent iron-based nanomaterials

Implementation of appropriate methods/materials for water treatment is a difficult task. The selected method should fulfil the standard water quality parameters in the respective countries and be efficient, cost-effective and environmentally friendly. Simple treatment methods/materials and reusability of the materials made it economical in water treatment. Even though numerous materials are available, iron-based nanomaterials are widely investigated nowadays. Iron-based nanoparticles are extensively used for drinking and wastewater treatment and are also used for groundwater treatment. The ability of zero valent iron nanoparticles for environmental water treatment was established through laboratory and field-scale tests. The application of iron-based nanoparticles can be categorised based on the type of pollutant they remove since different mechanisms are followed during the removal of specific pollutants. The applications of Fe⁰ are shown in figure 1.3.

1.8.1. Removal of heavy metals/metalloids:

Industrial wastewater from electroplating, steel plants and tanning industries contains a large amount of toxic heavy metals such as Cr(VI), Pb(II), Hg(II), Cd(II), As(III), Ni(II) and Cu(II), wherein Cr(VI) is the most widely studied heavy metal for removal purposes. Usually, chromium is present in the environment in two oxidation states, Cr(III) and Cr(VI), in which Cr(VI) is more toxic compared to Cr(III). Conventional methods find it difficult for Cr(VI) precipitation since they are typically found as oxyanions (CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$). Surprisingly, the Fe^0 nanoparticles gave a new solution to this problem due to their large surface area and high reactivity. In recent years, treatment of Cr(VI) has been accomplished with Fe^0 nanoparticles. The Cr(VI) removal process involves three major mechanisms: adsorption, reduction and co-precipitation[146]. Typically, the Cr(VI) concentration has been analysed through UV-visible spectroscopy using the 1,5-diphenylcarbazide method. During the Cr(VI) removal, the hexavalent chromium was reduced into Cr(III) along with the oxidation of Fe^0 to Fe^{2+} and Fe^{3+} . According to researchers, the initial pH of the solution is the major influencing factor for the removal of the Cr(VI). Even though the optimum pH range showed some differences, the Cr(VI) removal preferred the acidic pH. The predominant Cr(VI) form at pH in between 2-6 was HCrO_4^- and the major Cr(VI) form at $\text{pH} > 6$ was CrO_4^{2-} . The HCrO_4^- formed was more susceptible to adsorption compared to CrO_4^{2-} form[147]. In acidic pH, iron corrosion was accelerated by H^+ ions which increases the removal rate of Cr(VI). The H^+ ions also helped to maintain the reactivity of the iron nanoparticles by removing the passive oxide layer on the iron surface. At a higher pH range, surface passive layer formation prevents the electron transfer from Fe^0 to Cr(VI)[148]. At $\text{pH} < \text{pH}_{\text{zpc}}$, the primary mechanisms for Cr(VI) removal was redox reaction and electrostatic attraction, but at $\text{pH} > \text{pH}_{\text{zpc}}$, redox reaction and ion exchange reaction were the predominant mechanisms, even though at higher pH, redox reaction was not preferred. In the ion-exchange mechanism, $-\text{OH}$ was substituted by chromate anions[147]. While evaluating the other parameters influencing the Cr(VI) removal, it is evident that the percentage of removal was directly proportional to the contact time and amount of adsorbent and inversely proportional to the initial concentration of Cr(VI) solution[149–151].

Vinod et al. stabilised the chemically synthesised Fe^0 nanoparticles by Gum karaya (GK) and examined them to remove chromium completely. They discovered that the reduction of Cr(VI) to Cr(III) by Fe^0 -GK and followed adsorption of the remaining Cr(III) onto gum

karaya were the possible mechanism behind the Cr(IV) removal. This leads to the total removal of Cr(VI) from the contaminated water[120]. According to Quian et al., the major and final product of Cr(VI) reduction by carboxymethyl cellulose-stabilised Fe⁰ nanoparticles was iron hydroxide and chromium hydroxide since the precipitation of Cr(OH)₃ and mixed Cr(III)/Fe(III) hydroxides onto the iron surface was confirmed through spectroscopic data[152]. Jiao et al. compare the Cr(VI) removal capacity of agar stabilised Fe⁰ nanoparticles with bare Fe⁰ nanoparticles and found that agar stabilised Fe⁰ nanoparticles have outstanding Cr(VI) removal capacity in various conditions. 100 % removal efficiency of 50 mg/L Cr(VI) was attained within 2 hours using Cr(VI)/agar-Fe⁰ nanoparticles at a molar ratio of 0.025 and optimum pH 3[153]. Dong et al. synthesised biochar and modified biochar supported Fe⁰ and analysed their capacity to remove Cr(VI). They found that acid-treated biochar based Fe⁰ has the highest Cr(VI) removal efficiency. They also noticed that low biochar to Fe⁰ ratio causes the aggregation of iron nanoparticles and high biochar to Fe⁰ ratio blocks the active sites of the Fe⁰ nanoparticles[154]. In another study, Soroosh et al. inferred that activated carbon stabilised Fe⁰ has a 33 times higher adsorption capacity and a greater affinity for Cr(VI) than activated carbon[155]. According to Xiao et al., temperature and pH are the variables that strongly affect the Cr(VI) removal and some anions such as CO₃²⁻ and HCO₃⁻ can also influence it[146]. According to Xiangyu et al., the effect of temperature on Cr(VI) removal was complex due to various factors. With increased temperature, the adsorption capacity increases upto a certain point whereas the surface complexation and electrostatic interaction may decrease after an optimum temperature[131]. The stabilising agent of Fe⁰ has an important role in the Cr(VI) removal. For example, amino-functionalised vermiculite-supported nanoscale zero-valent iron showed high efficiency and reusability for Cr(VI) removal compared to bare Fe⁰. Electrostatic attraction between the negative species of Cr(VI) and protonated amino groups on the stabilising agent of Fe⁰ influence the removal of Cr(VI)[156]. Feglian et al. studied the removal of Cr(VI) and Cr(III) from water using resin supported Fe⁰ nanoparticles. The removal of Cr(VI) was accomplished by chemical reduction. Cr(III) removal was done by ion exchange at pH below 6.3 and precipitation at pH greater than 6.3[157]. Yaru et al. prepared the heteroaggregates of montmorillonite microparticles with nanoscale Fe⁰ to study the Cr(VI) removal efficiency from water. The Cr(VI) removal followed the pseudo-second-order kinetics and Langmuir equilibrium model. The authors suggested that Cr(VI) removal was mainly by chemisorption and is spontaneous and exothermic[158]. The complete removal of 100 mg/L Cr(VI) was

achieved within 30 minutes by 0.2 g/L of green nanoparticles, which was synthesised using the leaf extracts of *Rosa damascene* (RD), *Thymus vulgaris* (TV) and *Urtica dioica* (UD). The higher pore volume on the nanoparticles leads to higher Cr(VI) removal. Since the prepared nanoparticles are susceptible to agglomeration, the nanoparticles in the agglomerates show multilayer adsorption along with adsorption into the internal adsorption site of small pores[159].

The high affinity of arsenic for proteins makes them a toxic contaminant in groundwater and wastewater. As(III) is more toxic than As(V) due to the neutral character of the oxyanions (H_3AsO_3 , H_2AsO_3^- and HAsO_3^{2-}) of As (III). So, the neutral character of As(III) (Arsenite) does not prefer adsorption, but the oxyanions of As(V) can be adsorbed onto solid minerals. Hence for the effective removal of arsenic, the researchers practised the conversion of As(III) to As(V)[160,161]. The Fe^0 nanoparticles showed multiple mechanisms for removing arsenic, such as adsorption, absorption, precipitation, co-precipitation, oxidation and reduction. It may be due to the core-shell structure of iron nanoparticles in which the shell consists of iron oxides and iron hydroxides and the core consists of metallic iron[108]. The metallic iron can reduce the As(V) into As(III) and As(0) due to its fast kinetics. The oxidation and complexation of the As(III) have been done by iron oxide/hydroxide shell, formed during the oxidation of Fe^0 . The removal mechanisms depend on the redox nature of the pollutant and the nature of the medium, such as pH, ionic strength and redox potential[161]. Tandon et al. synthesised Fe^0 nanoparticles supported on the montmorillonite clay particles using tea liquor as a reducing agent. The authors revealed that 99 % As(III) could be removed from the water within 30 minutes by green montmorillonite clay- Fe^0 nanoparticles. The removal efficiency depends on the amount of Fe^0 nanoparticles loaded on montmorillonite clay particles and the maximum removal efficiency was obtained at both low and high pH. It was also found that as time increased, the Fe^0 nanoparticles were agglomerated due to the expulsion of Fe^0 nanoparticles from the clay cage, leading to the decrease in the elimination of As(III)[161]. Rana et al. suggested a new mechanism for the oxidation of As(III) to As(V) using green Fe^0 nanoparticles which are synthesised using guava leaf extract. In batch experiments, 2-propanol was used as a hydroxyl radical scavenger to determine the possible reaction mechanism of As(III) oxidation via leaf extract stabilised Fe^0 nanoparticles. The decrease (70 % to 26 %) in the oxidation of As(III) at acidic pH 3 indicated that oxidation was not only mediated by the $\cdot\text{OH}$ radicals produced by green Fe^0 . Some oxidants originating from

guava leaf extracts was also responsible for the oxidation. More than 70 % of As(III) was oxidised into As(V) using prepared nanoparticles within 10 minutes and the optimum pH for the reaction was pH 3 and pH 7[160].

The Fe⁰ nanoparticles were also used to eliminate the divalent heavy metals such as Co, Pb, Hg, Ni and Cu[162,163]. Wen et al. found that Fe⁰ nanoparticles are efficient for removing Zn²⁺. Hydroxide shell on the surface of Fe⁰ nanoparticles exhibits a major role in the adsorption and co-precipitation of Zn²⁺[164]. Ye et al. used calcium alginate encapsulated Ni/Fe nanoparticles beads to remove Cu²⁺ through adsorption and reduction[165]. The elimination of Pb(II) and Hg(II) ions from the water was investigated using *Azolla filiculoides* modified Fe⁰ nanoparticles. The XRD results reveal that these heavy metals were reduced into metallic forms or other possible insoluble forms. The reduction of heavy metal cations is energetically favourable due to the differences in the standard electrode potential of Fe(II)/Fe(0) (-44 eV) with Pb(II)/Pb(0) (-0.12 V) and Hg(II)/Hg(0) (+0.86 V). The metallic core in the Fe⁰ nanoparticles exhibited a crucial role in the Pb(II) and Hg(II) reduction. The uptake efficiency was increased with increasing temperature and the time required for the maximum uptake was around 20 minutes[166].

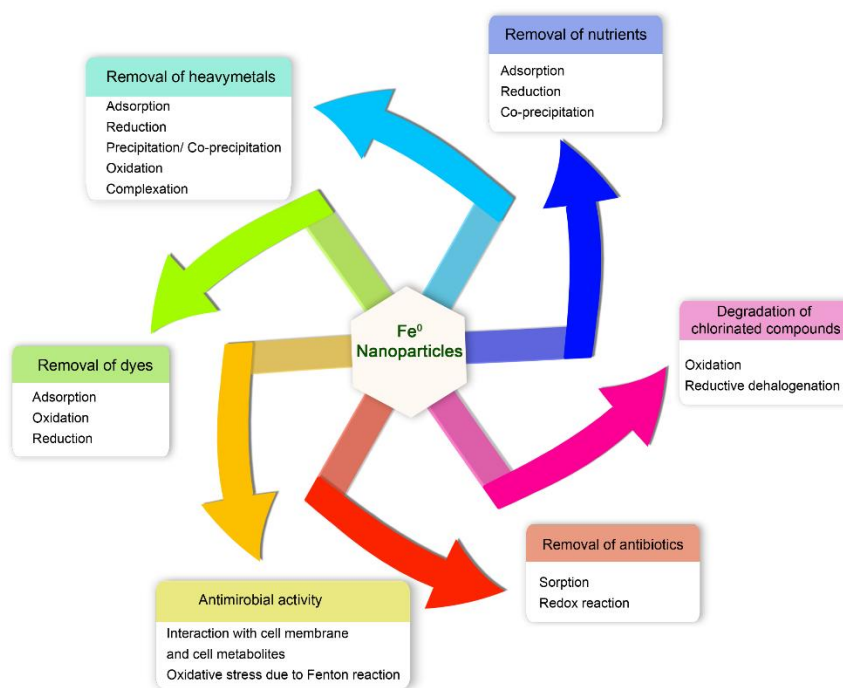


Figure 1.3 Application of Fe⁰ nanoparticles in water treatment

1.8.2. Removal of nutrients:

Contamination due to nutrients such as nitrates and phosphates significantly affects the water bodies since they lead to eutrophication[167]. Wang et al. compared the nitrate removal efficiency from an aqueous medium using green-Fe⁰ nanoparticles and chemically synthesised Fe⁰ nanoparticles. Green Fe⁰ nanoparticles were prepared using green tea and eucalyptus leaf extracts. The authors found that chemically synthesised nanoparticles are more efficient than green nanoparticles, but on the other hand, the green nanoparticles have high stability even after two months of air storage. The Fe⁰-iron oxide/polyphenols core-shell structure of green nanoparticles favoured nitrate removal by adsorption, co-precipitation and reduction[168]. Yu-Hoon et al. established that during reaction with the Fe⁰ nanoparticles, nitrate was degraded into ammonium ion followed by ammonia stripping under high pH, which reduces the nitrogen amount in the solution[169].

1.8.3. Degradation/removal of dyes:

A large amount of dye wastewater from the industries reduces the light penetration to the water bodies and leads to the formation of toxic contaminants. The significant contribution of textile dye pollution was from azo and triarylmethane dyes[110]. The Fe⁰ nanoparticles have been used to remove various dyes in the last few years. Reduction, adsorption and oxidation via advanced oxidation process are the major mechanisms for dye removal. In the presence of hydrogen peroxide, the Fe⁰ nanoparticles acted as Fenton-like catalyst, producing hydroxyl radicals and eventually leading to the oxidation of pollutants in water. Nanoparticle size and lifespan are the limiting factors in the advanced Fenton-like reactions[170].

Yang et al. compared the efficiency of Fe⁰ nanoparticles to remove three different dyes, including azo dye (Reactive brilliant red), triphenylmethane dye (Malachite green) and anthraquinone dye (Reactive brilliant blue). The results indicated that pH has a negligible effect on dye removal. They suggested that the dye decolourisation process is mainly due to the chromophore destruction and transformation of some functional groups such as amino and aromatic rings[171]. Chen et al. used kaolin stabilised Fe⁰ nanoparticles to degrade triphenylmethane dye crystal violet. Crystal violet adsorbed onto the surface of the Fe⁰ nanoparticles, then transformed into leuco crystal violet. Finally, reduction by Fe⁰ nanoparticles caused the cleavage of the C=C bond[136]. The polyacrylic acid modified filter paper was used as a matrix to stabilise Fe⁰ nanoparticles by Pingping et al. and these

novel nanoparticles were applied to remove cationic methylene blue and anionic methyl blue dyes. Decolourisation of the methylene blue dye is attributed to the cleavage of -C=N- and -C=S- bonds, while the decolouration of methyl blue is attributed to the cleavage of -C=C- and -C=N- bonds by Fe⁰ nanoparticles[172].

Fe⁰ nanoparticles act as heterogeneous Fenton-like catalysts for the degradation of organic dyes. Degradation of the azo dye, Direct Black G, was studied by Jiajiang et al. using kaolin supported Fe⁰ nanoparticles. In the degradation process, firstly, the dye molecules are adsorbed onto the surface of nanoparticles, then the azo bond is scavenged by the strong reduction of Fe⁰ nanoparticles which leads to the formation of reduced product of dye molecules. H₂O₂ in the solution caused the formation of ·OH radicals by reacting with the iron nanoparticles. The ·OH radicals formed are potent oxidising agents that react with the dyes and oxidise and mineralise them into CO₂ and H₂O[173].

Fe⁰ nanoparticles can perform the decolourisation of azo dyes through the oxidation of dye molecules by hydroxyl radical. Hydroxyl radicals are generated by the reaction between the excited surface electrons from the nanoparticles and dissolved oxygen molecules. Harshiny et al. compared azo dye, methyl orange (MO) removal efficiency using green Fe⁰ nanoparticles synthesised using *Amaranthus dubius* leaf extract and chemically synthesised Fe⁰ nanoparticles using sodium borohydride. The green synthesised Fe⁰ nanoparticles (81 %) show slightly less removal efficiency than chemically synthesised ones (90 %), which may be due to the surface stabilisation of Fe⁰ nanoparticles[174]. Radini et al. incorporated UV irradiation technique with green Fe⁰ nanoparticles for the effective removal of MO. Iron nanoparticles are used as a photocatalyst for MO removal. The MO dye molecules are degraded into smaller molecules due to the photodegradation of dye on the reactive surface of Fe⁰ nanoparticles. The hydroxyl radical produced by the UV-irradiation on iron nanoparticles is the reactive agent behind the removal of MO[175].

Huang et al. compared the malachite green (MG) dye removal using three types of iron nanoparticles synthesised by tea leaves such as green tea (GT), oolong tea (OT) and black tea (BT). The green tea stabilised Fe⁰ nanoparticles showed higher removal efficiency with 81 %, following OT-Fe⁰ nanoparticles (75 %) and BT-Fe⁰ nanoparticles (67 %). A large amount of polyphenols/caffeine content in GT-Fe⁰ nanoparticles make them a beneficial removal agent for dyes. The dye removal increased with temperature since the dye degradation process by GT- Fe⁰ nanoparticles is an endothermic process. The authors

proposed two possible mechanisms for MG removal using tea leaf stabilised Fe⁰ nanoparticles. The first one is the reduction of contaminant using Fe⁰, which involves the cleavage of the -C=C- and =C=N- bond linked to the benzene ring. The second one is the adsorption of dye molecules onto iron/iron oxide and tea extract components[176].

1.8.4. Degradation of chlorinated compounds:

The removal of volatile organic compounds such as cis-1,2-dichloroethene, perchloroethene and trichloroethene was studied by Vinod et al. They used gum karaya to stabilise the chemically synthesised Fe⁰ nanoparticles for the removal of chlorinated compounds. The enhancement of surface reactivity per unit area of the Fe⁰ nanoparticles and growth in the sorption area of the prepared nanoparticles were the significant advantages of gum karaya stabilised Fe⁰ nanoparticles. The major mechanism for reducing chlorinated hydrocarbon using the prepared nanoparticles was β -elimination. The Fe⁰ nanoparticles act as an electron donor for the reductive dehalogenation of chlorinated compounds. The chlorine number was calculated to estimate the possibility of direct removal of chlorinated compounds and the results indicated that the simultaneous degradation of all chlorinated hydrocarbons has occurred without any lower chlorinated hydrocarbon formation[120].

Kuang et al. suggested a mechanism for removing monochlorobenzene (MCB) using green Fe⁰ nanoparticles synthesised from tea leaf extract (GT). GT-Fe nanoparticles were used as heterogeneous Fenton-like catalysts for the oxidation of monochlorobenzene. The authors proposed a three-step mechanism for the mineralisation of the monochlorobenzene in which the first step is the adsorption of the pollutant to the iron/iron oxide surface of the adsorbent. In the next step, the hydroxyl radicals were generated through the reaction of iron species with hydrogen peroxide. Finally, hydroxyl radicals attacked the MCB, which was mineralised into CO₂ and H₂O on the surface of iron nanoparticles. The favourable MCB removal conditions using GT-Fe nanoparticles were optimized as 0.6 g/L GT-Fe nanoparticles, 0.045 mol/L H₂O₂ and initial pH 3[34].

1.8.5. Degradation/removal of antibiotics:

Pharmaceutical products in the aquatic ecosystem have been a concern for researchers in the last few years due to their environmental and health effects. Fe⁰ nanoparticles were used for the removal of pharmaceutical products. Machado et al. prepared green Fe⁰

nanoparticles (gnFe⁰) using oak leaf extract and studied its antibiotic amoxicillin elimination capacity. They investigated the possibility of gnFe⁰s as a reductant and a Fenton-like catalyst to remove the amoxicillin (AMX) from soil and water. 100 % degradation of the amoxicillin was attained by gnFe⁰ as a reductant after 95 min with a 1:15 AMX/gnFe⁰ molar ratio in water. At the same time, 100 % removal efficiency of amoxicillin was attained by gnFe⁰ as a Fenton-like catalyst in 15 minutes with a molar ratio of 1:13:1 AMX/H₂O₂/gnFe⁰. The gnFe⁰ degraded the amoxicillin by physical sorption, redox reactions and biological degradation methods. The application of natural extract on prepared nanoparticles has boosted the biodegradation of amoxicillin. The mechanism of amoxicillin degradation included the transformation of amoxicillin into undetectable amoxicillin penicilloic acid through the b-lactam ring-opening reaction[177].

1.8.6. Antimicrobial activity:

Fe⁰ based nanoparticles show superior antimicrobial activity. Khan et al. synthesised iron nanoparticles using flower extract of *Hibiscus sabdariffa roselle* as a reducing agent. The authors studied the antifungal and antibacterial activities of bio fabricated iron nanoparticles in fungus (*Candida albicans*, *Candida glabrata* and *Candida tropicalis*) and bacteria (*Escherichia coli* and *Staphylococcus aureus*) through the disk diffusion method. The flower extract capped iron nanoparticles displayed a significant inhibition zone for all the pathogenic microorganisms. The mechanism of the antimicrobial activity of iron nanoparticles includes the interaction between the iron nanoparticles and cell membrane of the microbes, bonding between the iron nanoparticles and metabolites present inside the microorganisms, deformation and structural changes in the bacterial cell wall and membranes eventually, death of microorganisms[178]. Iron nanoparticle's antibacterial effect was studied on gram-positive and gram-negative bacteria by Radini et al. Antibacterial efficiency was analysed by agar well diffusion method and found that iron nanoparticles have more zone of inhibition in *Escherichia coli* (gram-negative, 16 mm) than *Staphylococcus aureus* (gram-positive, 12 mm). The interaction between iron nanoparticles and bacterial cell membranes influenced the antibacterial activity of iron nanoparticles. The differences in the cell membrane structure of the bacteria lead to different inhibition zone for different bacteria. A thick peptidoglycon layer was present in the cell wall of gram-positive bacteria, whereas a thin peptidoglycon layer was seen in gram-negative bacteria. It makes gram-negative bacteria more vulnerable to iron nanoparticles, and its growth was significantly prevented[175]. Recently vitta et al. studied

the antibacterial activity through the agar diffusion method on *Bacillus subtilis*, *Escherichia coli*, *Staphylococcus aureus* and *Pseudomonas aeruginosa* using iron nanoparticles prepared by leaf extracts of *Eucalyptus robusta*. Even though the iron nanoparticles exhibit antibacterial activity, the leaf extract of *Eucalyptus robusta* boosted the capability of iron nanoparticles since the phytochemical components of the *Eucalyptus robusta* have some antibacterial activity. The authors proposed two mechanisms for the antibacterial activity of newly synthesised nanoparticles. In the first one, they suggested that the accumulation of particles in the cytoplasmic region causes the rupture of the membrane and eventually leads to the bacteria's death. The reaction between nanoparticles and biomolecules inside the bacteria caused the conformational changes in protein structure and DNA molecule, leading to bacteria-killing. In the second mechanism, the authors proposed the production of reactive oxygen species through the Fenton-like reaction, where the bacteria produces hydrogen peroxide as a metabolic product. The reactive oxygen species causes oxidative stress on bacteria, leading to bacterial death[179].

1.9. Objectives of the present study

- Synthesise Fe⁰ and bimetallic Fe based nanoparticles using chemical reduction method.
- Prepare chitosan stabilised Fe⁰ and Fe/Ni nanoparticles.
- Develop TiO₂ and zeolite based novel composites as supporting and stabilising material for Fe⁰ nanoparticles.
- Prepare Fe nanoparticles using plant extracts as green reducing agents.
- Evaluate the efficiency of synthesised nanoparticles in the removal of toxic hexavalent chromium under different reaction conditions such as initial Cr(VI) concentration, nanoparticle dosage, contact time and solution pH.
- Study the effectiveness of synthesised nanoparticles regarding the removal of toxic dyes under various reaction conditions, including initial dye concentration, nanoparticles dosage, contact time and solution pH.

1.10. References

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