Chapter 1 Introduction



Jitendra Kumar Sahoo and Sourav Prusty

1.1 Introduction

Nanomaterials comprise the study of chemical materials or substances within the nanoscale, i.e. in the range of 1-100 nm. At this nanoscale, materials show inimitable properties based on their quantum phenomena (electron tunnelling, near fieldoptical methods, electron confinement ballistic transport, and quantum entanglement) or on the basis of subdomains (superparamagnetism and overlapping of double layers in the fluids) [1, 2]. In the present era, nanomaterials are regarded as the emerging advanced research domain in chemistry, physics, material engineering, and bioscience. In comparison with conventional materials, nanomaterials permit distinctive and unique physical, electrical, chemical, mechanical, and optical properties [3, 4]. Nanomaterials have a wide range of applications for various commercial purposes, for instance in semiconductors, cosmetics, catalysts, adsorbents, photocatalysts as carriers of drugs, fillers, antifriction coatings, storage, microelectronics, energy storage, etc. In addition, nanomaterials also have a broad range of applications in wastewater treatment, the production of energy, and sensing. In the preceding period, most of the research was focused on experimental and theoretical advancements in characterisation, novel synthesis, and an assortment of applications using a variety of nanostructures such as ceramics, nanocomposite materials, and metal oxides [5–10]. Among the widely available inorganic materials, metal oxide nanomaterials have gained significant attention, particularly in the fields of engineering and science. Metal oxide possesses exceptional physical and chemical properties due to its diminutive size and high density. Metal oxides also have large-scale applications in the treatment of wastewater, like degradation, catalysis, sensors, and adsorption [11, 12].

J. K. Sahoo (🖂) · S. Prusty

Department of Chemistry, GIET University, Gunupur, Rayagada, Odisha 765022, India e-mail: jksahoo@giet.edu

[©] The Author(s), under exclusive license to Springer Nature Switzerland AG 2024 H. Sahoo and J. K. Sahoo (eds.), *Iron Oxide-Based Nanocomposites and Nanoenzymes*, Nanostructure Science and Technology, https://doi.org/10.1007/978-3-031-44599-6_1

2

As the metals formed various types of oxide compounds, they showed several structural geometries through different electronic structures with semiconductor, metallic, and insulator characteristics. Metal oxides exhibit various properties such as magnetic, optical, photoelectrochemical, mechanical, optoelectronic, thermal, and catalytic [13, 14]. Metal oxides are small-scale-based nanomaterials that can augment the surface area-to-volume ratio and enhance their properties in comparison to vast materials. Additionally, metal oxide nanoparticles have been widely applied for the treatment of wastewater [11, 15]. For the treatment of wastewater and other functions, various metal oxides such as copper oxide (CuO), cerium oxide (CeO₂), magnesium oxide (MgO), manganese oxide (MnO₂), titanium oxide (TiO₂), iron oxide (Fe₂O₃, Fe₃O₄), and zirconium oxide (ZrO₂) have been extensively employed.

The past few years have drawn the attention of a variety of materials, such as metalorganic frameworks, molecularly imprinted materials, ionic liquids, and carbonaceous materials, in a wide range of techniques in order to diminish the amount of chemicals needed for sample preparation during extraction methods [12–14, 16]. In the middle of all this, magnetic nanomaterials have been found to gain special consideration as they possess special properties like being superparamagnetic due to the pressure of the thermal energy on a nanoparticle with ferromagnetic characteristics [7–10]. Apart from this, magnetic nanomaterials have a special characteristic in that they can separate themselves from the sample with the help of an external magnetic field and effortlessly coalesce with other materials, which shows their diverse functionality. The magnetic nanoparticles are mainly dependent on their surface effects and finite size. For magnetic nanoparticles, the configuration of spherical walls provides a state of high energy as a result of which particles combine together in the form of clumps or clusters. In order to avoid cluster formation, the magnetic nanoparticles are layered with different shells of polymer, carbon, metal oxide, and silica. Moreover, the magnetic nanoparticles have a large surface area, which enhances their catalytic activities [11, 13, 15, 17].

In the present circumstances, researchers are more aligned towards iron oxidebased nanoparticles as they show exceptional magnetic behaviour, a large surface area-to-volume ratio, exist in different oxidation states, can be separated easily from aqueous solutions, are cheap in comparison with other metal oxides, are small in size, have little toxicity, and are environmentally friendly in nature [18–20]. Iron oxide is found to exist in the form of hydroxides, oxides, and oxy-hydroxides. The majority of them include: Fe₃O₄, Fe₄O₃, FeO, Fe₄O₅, and polymorphic forms of Fe₂O₃ (γ -Fe₂O₃ and α -Fe₂O₃, FeOOH, and Fe(OH)₃). Amid the various available forms of iron oxide, basically three important phases can be categorised, such as magnetite (Fe₃O₄), hematite (α -Fe₂O₃), and maghemite (γ -Fe₂O₃), which are areas of greater interest due to their magnetic and opto-electrical properties [21]. These phases of iron oxide have practical applications in colour imaging, optical devices, drinking water, gas sensing, magnetocaloric refrigerant, ferrofluid technology, and as magnetic strong media. In the environmental condition, hematite $(\alpha - Fe_2O_3)$ was found to possess a stable form of iron oxide, but it is anti-ferromagnetic in nature as it demonstrates the weak magnetic property as well as being an n-type semiconductor with a band gap of 2.3 eV. Hematite shows a rhombohedral structure, which can be designated as its most common form, and it shows application in the photocatalyst driven by light in the visible range of 600 nm [17, 22–24]. Maghemite (γ -Fe₂O₃) shows a cubic structure with a band gap of $2.0 \, \text{eV}$ and possesses magnetic properties in every condition. Maghemite exemplifies a vast range of applications in the field of the fabrication of biocompatible magnetic fluids, in electronic devices, magnetic recorder media, and in MRI. Maghemite consists of 211/3 numbers of Fe³⁺ ions and 32 numbers of O^{2-} ions, and vacancy sites are 21/3, whereas the magnetite shows a cubic spinel-type structure and is found mainly in two oxidation states, such as Fe^{2+} and Fe^{3+} , whose stoichiometric ratio is found to be 1/2. Magnetite that is Fe_3O_4 can be operated as both an n-type and p-type semiconductor with a band gap of 0.1 eV [25, 26]. Magnetite proved to be an effective metal oxide for wastewater treatment due to its fast production rate, rapid uptake, high adsorption capacity, and easy separation. After adsorption, magnetite can be easily separated from an aqueous solution by using an external magnetic field [9, 27]. This iron oxide nanocomposite shows extraordinary efficiency towards wastewater treatment and the removal of dyes as well as toxic heavy metals with carcinogenic effects on aquatic biota.

1.2 Various Routes of Synthesis of Iron Oxide Nanoparticles

Nanoparticles of iron oxide can be synthesised using various physical, biological, and chemical methods. Among all these methods, the chemical method is widely preferred because, in the chemical method, the appearance of bulk material takes place with desirable morphology, tuneable sizes, and shapes possessing all the scientific properties [28, 29]. Iron oxide can be synthesised using various chemical synthetic methods such as coagulation, flocculation, co-precipitation, the sol-gel method, microwave irradiation, microemulsion, hydrothermal, and thermal decomposition techniques [13, 20].

1.2.1 Coagulation

Nanotechnology refers to the ability to produce and design nanoparticles by manipulating atoms as well as molecules at the nanoscale. Wastewater treatment is the most favourable environmental application of this technology. In the present era, iron oxide nanoparticles are studied by researchers as compared to other materials because of their wide utilisation, magnetic properties, low cost, very high adsorption capacity, and high surface area. In coagulation, iron oxide is used as a coagulant. Coagulation is the chemical process by which the electrostatic repulsive force among the particles changes in water. The main role of iron oxide NPs in this technology is due to their magnetic properties. The key term Fe_3O_4 nanoparticles shows innovative



Fig. 1.1 Methods of coagulation

research objects and a database for adsorption mechanisms. The colloidal α -Fe₂O₃ particles have a well-defined coagulation rate at constant temperature. The range of W values is from 1 to 10⁴, and pH values vary from 3 to 12. The results of iron oxides are specific for coagulation mechanisms. For anions, the stabilisation concentration of critical coagulation shows a range from 10^{-7} to 10^{-4} molar. With the help of the diffusion layer model, generally, the information regarding potential as well as charges of coagulation species can be known. Ferric sulphate, ferrous sulphate, and ferric chloride are the different forms of iron coagulants. Usually, ferric sulphate is treated as a coagulant in conjugation when it reacts with chlorine, and it refers to the hydrated form that is FeSO₄·7H₂O. During this period, polymeric ferric sulphates are also available, in which 12.5% w/w of iron is present [12, 30, 31]. Figure 1.1 shows the method of coagulation.

1.2.2 Flocculation

In mineral processing, flocculation is the most adequate technique for the separation of solids, which form larger flocs when removed from water. It is a very spontaneous process, with the help of chemical reagents. In the recent communication, an investigation is being conducted on the kinetics study of flocculation of Fe_3O_4 due to the variation in polyacrylamide's weight. This process was completely studied by taking PAM with the same pH, molecular weight, and ionic strength as the medium. It was observed that the percentage rate of flocculation is directly proportional to the molecular weight of the polymer. Polymers with a higher molecular mass have a higher adsorption capacity to adsorb a higher number of particles. According to the researcher, flocculation also depends on the electrostatic force of attraction. It was observed that the flocculation process is indirectly proportional to the percentage

1 Introduction



Fig. 1.2 Methods of flocculation

of pH. So, the pH differs from 1.5 to 8.5 range. Using the PAM, the test of flocculation technique is carried out by mixing kaolin and Fe_3O_4 at a ratio of 1:1. H_2O_2 , which is an oxidising reagent, can also be used for the preparation of modified iron coagulant, in which it was observed that its density is 1.43 g/mL and 9.47% iron is present [8, 16, 32]. Figure 1.2 shows the method of flocculation.

1.2.3 Co-precipitation

The co-precipitation method refers to the dissolution of materials in a solvent initially and then, after addition of a precipitating reagent, forming a homogeneous inorganic solid. The iron oxide nanoparticles show wide applications in catalysis, biomedicine, and wastewater treatment. Co-precipitation is an extremely ubiquitous method for the formation of Fe₃O₄ NPs, where the pH of the ferric and ferrous solutions depends upon the base added. In this technique, the pH range transits very slowly, i.e. in the range of 2-8. Whenever the divalent iron oxide reacts with the ammonia for the preparation of nanoparticles, by using the co-precipitation method, we get greater magnetisation properties. The co-precipitation method is eco-friendly, the most common, and a simple procedure for the preparation of iron oxide nanoparticles. According to this method, it holds cations very close to each other in the medium and decomposes at a lower temperature. The most common example of this method is the synthesis of metal oxide, i.e. FeCr₂O₄. At first, the Fe (III) ion dissolves, and the chromate ion, which is present in water, gets converted to Fe^{3+} and CrO_4^{-} ions. Then it gets precipitated by the NH₄⁺ solution to form a new complex. At last, the precipitate is decomposed at a higher temperature into FeCr₂O₄ [6, 17, 22]. Figure 1.3 shows the method of co-precipitation.



Fig. 1.3 Methods of co-precipitation

1.2.4 Sol–Gel Method

The most common chemical method for the synthesis of metal oxide nanoparticles is the sol-gel method. By stirring as well as heating, the dissolved molecules get converted into gel. This method follows parameters like nature, kinetics, pH, concentration, temperature, etc. Iron oxide nanocomposites can also be prepared by the sol-gel method. Commercially, Fe (III) is dissolved in aqueous medium and converted into gel format by heating for the generation of the final product. The formation of nanoparticles depends upon the reactivity, which is directly related to the surface area of iron oxide NPs. The synthesis of iron oxide NPs is also formed from ferric hydroxide gel, which is again subjected to this technique for 8 days at 100 °C to get the magnetite. Hematite, magnetite, and goethite are different forms of iron oxide NPs [33]. Figure 1.4 shows the method of sol-gel.

1.2.5 Microwave Irradiation

The microwave irradiation technique shows great potential as compared to other methods due to its high scaling rate of nanoparticles of iron oxide with a high specific absorption rate. The use of microwave irradiation has overcome a critical and



Fig. 1.4 Methods involved in sol-gel technique

perplexing issue during the preparation of iron oxide nanoparticles. Microwave radiation provides heating at a controlled rate with selective heating capability. Generally, in solution, the surface of the nanoparticles absorbs more radiation as compared to the core, which results in a change in their reactivity and surface energy. This feature attributes to the controllable exchange between the undesired adsorbed species and additional moieties such as coating agents. The best coating agent for this purpose is citric acid due to its biocompatibility. A mixture solution containing polyethylene glycol (PEG), urea, and FeCl₃·6H₂O was subjected to microwave irradiation for 10 min at 650 W. After cooling, the precipitate is subjected to centrifugation and air-dried by washing with distilled water. Then the product obtained is characterised using different characterisation techniques. Microwave radiation shows the greater advantage of a lower reaction temperature and a shorter reaction time [34, 35]. Figure 1.5 shows the method of microwave irradiation.



1.2.6 Microemulsion

In order to prepare iron oxide nanoparticles of ultrafine dimension, microemulsions are predominantly one of the striking reactive mediums. In microemulsions, it contains water droplets of nanosized that are continuously dispersed in the oil medium, and surfactants are used as stabilising agents that accumulate at the oil or water periphery. Microemulsions show less polydispersity, that is, droplet sizes are uniform in nature. Ionic reactants are subjected to the interior of an aqueous medium, as a result of which they can be precipitated initially to the droplet's dimension. This method is followed by the transport of precipitate from one droplet to another. During this process, large particles are formed, which can be termed as secondary growth. The reaction generally occurs in precipitating particles, which are of large size as compared to droplets in the aqueous core. A significant factor during the synthesis of microemulsion is the water-to-surfactant molar ratio, which is Wo and responsible for controlling the diameter of droplets of water. In a W/O microemulsion of oil and water, when particles of cadmium sulphide are synthesised, it is found that with Wo, the particle size goes on increasing. Particle size is independent of cadmium ion concentration. These consequences were construed in terms of an improved nucleation process and lesser secondary growth at an advanced concentration of metal salt. Fabrication of colloidal particles such as Pt, Pd, Rh, and Ir in a water-oil microemulsion resulted in particle sizes of 2-5 nm. An isooctane/water-based microemulsion system can be efficiently employed for the precipitation of ferrous oxalate, which is ultrafine in shape. Further, the ignition of ferrous oxalate in the presence of moist air at a temperature of 225–300 °C conferred a mixture of α -Fe₂O₃ and γ -Fe₂O₃. The γ -Fe₂O₃ synthesised during the microemulsion technique shows a higher yield as compared to the aqueous medium. The yield resulted from γ -Fe₂O₃ is mainly dependent upon the droplet size, due to which the precursor material can be precipitated [19, 36]. Figure 1.6 shows the method of microemulsion.

1.2.7 Hydrothermal

Hydrothermal serves as a brisk and incessant crystallisation novel method for the synthesis of fine particles of metal oxide, for example: NiO, Co₃O₄, ZrO₂, α -Fe₂O₃, etc. The aqueous solution of metal salt is taken, which is quickly heated in hydrothermal conditions, in which hydrolysis occurs followed by dehydration. With the growing resident time and feed concentration, the resulting particle size of α -Fe₂O₃ and Co₃O₄ goes on increasing. In the subcritical state, the reaction temperature will not show any momentous influences when a continuous flow reaction is performed. In this method, α -Fe₂O₃ can be synthesised by using activated carbon at 500 °C, as a result of which well-formed crystalline particles are formed. In this method, the dielectric constant of an aqueous solution plays a pivotal role in the properties of the solvent. With an increase in the hydrothermal temperature,



Fig. 1.6 Representation of microemulsion technique

the dielectric constant goes on decreasing. Declination takes place quickly as the temperature goes beyond the critical temperature, which leads to a considerable decrease in the solvent capability of water. When AlOOH is synthesised by the hydrothermal method at 350 °C, generally larger particles are obtained in comparison with synthesis at 400 °C. In the supercritical water when the reaction pressure increases, this results in the increase of particle size of AlOOH. But when the alcohol is added during the hydrothermal process, this largely exaggerates the crystallisation process. In hydrothermal method, iron oxide of superparamagnetic nature can be synthesised. Generally during synthesis process, anhydrous FeCl₃ was used as the precursor source of iron and ethylene glycol was used as solvent [37, 38]. Figure 1.7 shows hydrothermal method.



Fig. 1.7 Different steps involved in hydrothermal technique

1.2.8 Thermal Decomposition

Presently, various synthesis routes are available for the synthesis of nanoparticles of iron oxide. By using a salt solution of Fe (II) and Fe (III) with alkali-based metal hydroxide, particles can be synthesised by the co-precipitation method. But particles with a larger size and a narrower distribution can only be best prepared through the thermal decomposition method. Conventionally, certain batch methods are employed for the synthesis of magnetic-based nanoparticles. But these batch methods have various limitations, such as being limited to a smaller scale as it is difficult to maintain thermal control during the reaction. The heating rate, absolute temperature, and annealing time play a crucial role in the distribution of particle size at the nanoscale. When the batch is outsized, it is very complicated to maintain the temperature, as a result of which the particles are not compacted. To overcome all these problems, thermal decomposition proved to be a crucial method for the synthesis of magnetic-based nanoparticles. By decomposition of three precursors that are different from each other, iron oxide nanoparticles can be synthesised in the thermal decomposition method. Iron (III) oleate is used as an important reaction intermediate during this synthesis. By the adjustment of different parameters such as thermal rate, composition, and concentration of precursor particles, particle sizes of 2-30 nm were obtained. Initially, the iron particles were treated with oleic acid to form a complex of iron (III) oleate. Owing to the significance of the iron oleate composite, it is subjected to different thermal characterisations. Particle breakdown of iron oleate occurs at or above 250 °C. When the iron oleate complex is treated with 1-octadecene, it yields a larger particle size of up to 10 nm. But if the iron



Fig. 1.8 Technical set-up of thermal decomposition process

oleate complex undergoes dilution with a sufficient amount of oleic acid, the process of nucleation as well as the growth rate is slowed. By increasing the ratio of iron oleate from 5:1 to around 20:1, it results in a particle size of around 25 nm [25, 39]. Figure 1.8 shows thermal decomposition method.

1.3 Various Modification Techniques

Generally, iron oxide nanoparticles endure certain foremost issues, such as oxidation into the physiological atmosphere due to chemical reactivity, higher surface area, large surface energy, which results in magnetism loss, and rapid agglomeration. Therefore, to overcome these issues, surface modification of iron oxide is done to make it biocompatible. Modification of iron oxide nanoparticles not only thwarts agglomeration and oxidation but also provides a further route for functionalisation. The main advantages of surface modifications are: (1) to enhance the surface action of magnetic nanoparticles; (2) to improve or modify the diffusion of magnetic nanoparticles; (3) to augment the mechanical and physiological properties; and (4) to enhance the biocompatibility of magnetic nanoparticles. Here, iron oxide modification studies were done using metal oxide, bioadsorbents, polymers, and graphene [40, 41].

1.3.1 Metal Oxide

Iron oxide-based magnetic nanoparticles have superior magnetic properties, as a result of which iron oxide-based nanoparticles can be functionalised as well as modified with the help of different techniques. The progression of technology enabled the researchers to come up with the modification and functionalisation by incorporating various supporting materials that can be used as stabilising or capping agents, for example dopamine, cystein, trimethoxysilane, carboxylic acid, phosphonic acid, and amine. Basically, iron oxide-based magnetic nanomaterials are generally coated with layers possessing inorganic elements (gold, cobalt oxide, platinum, aluminium oxide, silica, and activated carbon) and with some organic layers (glycol, dextran, and polyethylene) in order to make them stable against different properties like oxidation, corrosion, and aggregation and to increase the efficiency of their adsorption capacity. For example, iron coated with sand can be eliminated between 1.34 and 1.10 mg/g Se (IV) and in the range of 1.10 and 1.026 mg/g Se (VI), which is more effective than iron oxide nanoparticles that are uncoated. Furthermore, the modifications of the surface of iron oxide, hydroxide nanoparticles, and oxyhydroxide facilitate colloidal activity and biocompatibility in the intricate environment when the modifications are carried out. The adaptation of these nanoparticles shows the removal of various potent pollutants such as Ni (II), Cd (II), Cr (III), Co (II), Cu (II), As (III), and Pb (II) from the wastewater [42, 43].

1.3.2 Bioadsorbent

For the past few years, the amalgamation of biochar has been extensively utilised for the adsorption of dyes such as cationic and anionic dyes, which are abundantly found in wastewater. It has been seen by various researchers throughout the world that the preparation technique involved for biochar is generally exorbitant. So for the deportation of basic as well as acidic dyes, low-cost and budget-friendly bioadsorbents, which contain numerous agricultural products and various by-products, are being put into practice in a sustainable manner. Numerous adsorbents of non-conventional nature, such as bagasse fly ash [44], modified rice husk, de-oiled soy, distinct peel neem sawdust, and rice straw-based iron humate sugarcane bases, are used for the removal of carcinogenic dyes. In conjunction with the bioadsorbents, scientists throughout the world have made significant considerations towards modifying the bioadsorbents with metal oxide-based nanoparticles. The adsorption process using metal oxide is being highly implemented due to its plentiful advantages, such as its small size and persuasiveness towards functionality as well as the adsorption process. So in this condition, iron oxide is being utilised as a considerable adsorption agent for decontaminating the deteriorated dye water [45-48].

1.3.3 Polymer

Among all the polymers that are naturally available, chitosan is found in profusion in seawater. It is non-antigenic, non-toxic, hydrophilic, biocompatible, and biodegradable. It contains the residue of hexosaminidase, which consists of two hydroxyl groups and one amino group. These functional groups that are present on the chitosan are responsible for the formation of complexes with the surface of iron oxide, making iron oxide nanoparticles stable, biocompatible, and hydrophilic. This has a wide range of applications in therapeutic gene delivery. Naturally available chitosan polymer is also responsible for providing better disparity in magnetic resonance imaging. When chitosan is coated with iron oxide nanoparticles, they form a complex in which the amine group is bonded to the desired particle and the hydroxyl group remains non-bonded. As a result of which the synthesised particle carries some positive charge. There is some repulsion in the form of Coulomb forces that remain in the colloidal state when no surfactant or organic solvent is used. The diameter of the synthesised particle was found to be 67 nm.

Polyethylene glycol is a water-soluble polymer that is extensively used for enhancing the water solubility of drugs. PEG coating diminishes the uptake and is responsible for increasing the efficiency of circulation timing. When iron oxide nanoparticles are coated with polyethylene glycol, they operate as an efficient adsorbent for attachment to various biomolecules. If antibodies and proteins are attached to iron oxide nanoparticles, the addition will be more target-specific in the area of interest. One problem associated with the PEG is that coating may result in the mixing of particles as a result of which particles are exposed to the cells. This problem can be overcome by mixing iron oxide with poly(ethylene glycol)-co-fumarate (PEGF). The role of fumaric acid is highly important as it is a macromer that is highly unsaturated. The hydrogel property of PEGF makes the iron oxide nanoparticles more stable, which makes them more efficient for absorption of water. Moreover, when the iron oxide nanoparticles are covered with crosslinked PEG starch, it is responsible for accelerating tumour imaging because it is a non-toxic coated material.

Dextran, which is a polysaccharide, has been successfully and extensively used for an assortment of applications. Iron oxide nanoparticles coated with dextran are commercially available and well-conventional methods for MRI and also in cancer treatment. The coating can be improved by the introduction of carboxymethyl groups, which improve functionality as well as stability. Epichlorohydrin is crosslinked with dextran to form crosslinked iron oxide nanoparticles.

Polyvinyl alcohol has a wide variety of applications in drug delivery, tendon repair, contact lenses, ophthalmic materials, and the biomedical field. Polyvinyl alcohol shows a high compatibility rate, and it serves as a water-soluble material and exceptional biocompatible agent when coated with iron oxide nanoparticles. When carboxylate groups are modified with PVA structures, they are strongly attached to metal oxide. The coated iron oxide nanoparticles are insoluble in water and are used as a phase transfer catalyst that replaces oleic acid and oleylamine acid. Moreover, when iron oxide nanoparticles are modified with PVA, they serve as an anti-cancer agent for drug delivery. Through hydrogen bonding, the polar functional group of PVA can adsorb successfully onto the oxide surface.

Poly(vinyl pyrrolidine) is extensively used in the field of biomedicine as it has a wide variety of applications due to its neutral charge, biocompatibility, and aqueous solubility. Iron oxide nanoparticles are generally coated with PVP, which increases their efficiency for MRI. Through the thermal decomposition method, the nanoparticle is successfully synthesised and is also soluble in buffer solution in addition to its water solubility capacity. Also, the coated nanoparticle possesses a high magnetic moment, which shows high relaxivity. In addition to that, when binding takes place through surface-initiated radical polymerisation, the nanoparticles are found to be superparamagnetic and possess the stability and dispersibility capacity of water for a long time [49–51].

1.3.4 Graphene

In the current scenario, hybrid materials can be synthesised by coating the iron oxide with graphene materials like nanosheets of graphene, reduced graphene oxide, and carbon nanotubes. Graphene shows a variety of applications in the fields of drugs, biomolecules, cells, metals, and other functional groups. Graphene oxide also attracted many researchers due to its unique combination of sp^3 and sp^2 carbons as well as various functional groups such as epoxy and hydroxyl and carboxyl groups. Graphene also possesses strong electrical conductivity, which is useful for the installation of electrochemical devices. When Fe_2O_3 is modified with graphene oxide, it shows a dominant magnetic property, which is used to prevent the stacking of graphene oxide and can also be used as a drug delivery agent for targeting a specific area.

When the iron salts are modified with reduced graphene oxide, the synthesised hybrid materials are used to improve the grafting efficiency and also increase the efficiency of the polymer matrix. When gelatin is mixed with graphene oxide, it improves the dispersion stability of the synthesised particle as well as prevents the oxidation of Fe_3O_4 . Coating of iron oxide with a graphene layer contains oxygen-based functional groups used in the nanofluid application. The synthesised nanoparticle is used to enhance the thermal conductivity. When graphene aerogel is successfully modified with iron oxide nanoparticles, it is used for the electro-Fenton system. The nanoparticle is prepared by using a natural drying method that has electrocatalytical and electrochemical performance with reusability and corrosion resistance properties for the treatment of wastewater containing organic pollutants.

When the iron oxide is coated with 3D foam-based graphene, the synthesised nanoparticle has a spherical shape with a particle size of 320 nm. These nanocrystals have a higher surface area, which shows exceptional electrochemical properties such as rate of capability, specific capacitance, and capacitance retention of around 89.8%. When the chemical reduction of iron oxide nanoparticles is done with graphene oxide, it shows a wide variety of applications in electrode applications, such as the

installation of supercapacitors, due to its good cycling capacity. Iron oxide is also modified with multi-walled carbon nanotubes through microwave-assisted Fenton's procedure via the green route. The synthesised nanoparticles improve the efficiency of the final material with high energy density and high capacitance in supercapacitors [52–54].

References

- 1. Taghipour F (2004) Ultraviolet and ionizing radiation for microorganism inactivation. Water Res 38(18):3940–3948. https://doi.org/10.1016/j.watres.2004.06.016
- Amodu OS, Ojumu TV, Ntwampe SK, Ayanda OS (2015) Rapid adsorption of crystal violet onto magnetic zeolite synthesized from fly ash and magnetite nanoparticles. J Encaps Adsorp Sci 05(04):191–203. https://doi.org/10.4236/jeas.2015.54016
- Wu R, Liu JH, Zhao L, Zhang X, Xie J, Yu B, Ma X, Yang S-T, Wang H, Liu Y (2014) Hydrothermal preparation of magnetic Fe₃O₄@C nanoparticles for dye adsorption. J Environ Chem Eng 2(2):907–913. https://doi.org/10.1016/j.jece.2014.02.005
- Stoia M, Pocurariu C, Istratie R, Nižňanský D (2015) Solvothermal synthesis of magnetic Fe_xO_y/C nanocomposites used as adsorbents for the removal of methylene blue from wastewater. J Therm Anal Calorim 121(3):989–1001. https://doi.org/10.1007/s10973-015-4641-x
- Fayazi M, Ghanei-Motlagh M, Taher MA (2015) The adsorption of basic dye (Alizarin red S) from aqueous solution onto activated carbon/γ-Fe₂O₃ nano-composite: kinetic and equilibrium studies. Mater Sci Semicond Process 40:35–43. https://doi.org/10.1016/j.mssp.2015.06.044
- Madrakian T, Afkhami A, Ahmadi M, Bagheri H (2011) Removal of some cationic dyes from aqueous solutions using magnetic-modified multi-walled carbon nanotubes. J Hazard Mater 196:109–114. https://doi.org/10.1016/j.jhazmat.2011.08.078
- Ranjithkumar V, Sangeetha S, Vairam S (2014) Synthesis of magnetic activated carbon/α-Fe₂O₃ nanocomposite and its application in the removal of acid yellow 17 dye from water. J Hazard Mater 273:127–135. https://doi.org/10.1016/j.jhazmat.2014.03.034
- Liu F, Jin Y, Liao H, Cai L, Tong M, Hou Y (2013) Facile self-assembly synthesis of titanate/ Fe₃O₄ nanocomposites for the efficient removal of Pb²⁺ from aqueous systems. J Mater Chem A 1(3):805–813. https://doi.org/10.1039/c2ta00099g
- Anbia M, Khoshbooei S (2015) Functionalized magnetic MCM-48 nanoporous silica by cyanuric chloride for removal of chlorophenol and bromophenol from aqueous media. J Nanostruct Chem 5(1):139–146. https://doi.org/10.1007/s40097-014-0145-7
- Zhang LH, Sun Q, Liu DH, Lu AH (2013) Magnetic hollow carbon nanospheres for removal of chromium ions. J Mater Chem A 1(33):9477–9483. https://doi.org/10.1039/c3ta10430c
- Zhang X, Wang Y, Chang X, Wang P, Pan B (2017) Iron oxide nanoparticles confined in mesoporous silicates for arsenic sequestration: effect of the host pore structure. Environ Sci Nano 4(3):679–688. https://doi.org/10.1039/c6en00514d
- Gwak GH, Kim MK, Oh JM (2016) Nanocomposites of magnetite and layered double hydroxide for recyclable chromate removal. J Nanomater 2016(V). https://doi.org/10.1155/2016/8032615
- Jafari Kang A, Baghdadi M, Pardakhti A (2016) Removal of cadmium and lead from aqueous solutions by magnetic acid-treated activated carbon nanocomposite. Desalin Water Treat 57(40):18782–18798. https://doi.org/10.1080/19443994.2015.1095123
- Wu Z, Li W, Webley PA, Zhao D (2012) General and controllable synthesis of novel mesoporous magnetic iron oxide@carbon encapsulates for efficient arsenic removal. Adv Mater 24(4):485– 491. https://doi.org/10.1002/adma.201103789
- Bayazit ŞS (2014) Magnetic multi-wall carbon nanotubes for methyl orange removal from aqueous solutions: equilibrium, kinetic and thermodynamic studies. Sep Sci Technol (Philadelphia) 49(9):1389–1400. https://doi.org/10.1080/01496395.2013.879595

- Egodawatte S, Datt A, Burns EA, Larsen SC (2015) Chemical insight into the adsorption of chromium(III) on iron oxide/mesoporous silica nanocomposites. Langmuir 31(27):7553–7562. https://doi.org/10.1021/acs.langmuir.5b01483
- Dwivedi MK, Agrawal R, Sharma P (2016) Adsorptive removal of methylene blue from wastewater using zeolite-iron oxide magnetic nanocomposite. Int J Adv Res Sci Eng 5(2):515–522
- Deligeer W, Gao YW, Asuha S (2011) Adsorption of methyl orange on mesoporous γ-Fe₂O₃/SiO₂ nanocomposites. Appl Surf Sci 257(8):3524–3528. https://doi.org/10.1016/j.aps usc.2010.11.067
- Jain N, Dwivedi MK, Agarwal R, Sharma P (2015) Removal of malachite green from aqueous solution by zeolite-iron oxide magnetic nanocomposite. IOSR J Environ Sci Ver I 9(6):2319– 2399. https://doi.org/10.9790/2402-09614250
- Yao S, Sun S, Wang S, Shi Z (2016) Adsorptive removal of lead ion from aqueous solution by activated carbon/iron oxide magnetic composite. Indian J Chem Technol 23(2):146–152
- Sahoo JK, Paikra SK, Baliarsingh A, Panda D, Rath S, Mishra M, Sahoo H (2020) Surface functionalization of graphene oxide using amino silane magnetic nanocomposite for chromium (VI) removal and bacterial treatment. Nano Express 1(1):010062. https://doi.org/10.1088/2632-959x/ab9e3f
- Kloster GA, Mosiewicki MA, Marcovich NE (2019) Chitosan/iron oxide nanocomposite films: effect of the composition and preparation methods on the adsorption of Congo red. Carbohydr Polym 221:186–194. https://doi.org/10.1016/j.carbpol.2019.05.089
- Chu JH, Kang JK, Park SJ, Lee CG (2020) Application of magnetic biochar derived from food waste in heterogeneous sono-Fenton-like process for removal of organic dyes from aqueous solution. J Water Process Eng 37:101455. https://doi.org/10.1016/j.jwpe.2020.101455
- 24. Amer R, Hadi H (2021) Application of CTAB-coated magnetic nanoparticles for solid-phase extraction of thiamine hydrochloride from pharmaceutical formulations and urine samples. Arab J Sci Eng 0123456789. https://doi.org/10.1007/s13369-021-05671-y
- Zhang J, Liu M, Yang T, Yang K, Wang H (2016) A novel magnetic biochar from sewage sludge: synthesis and its application for the removal of malachite green from wastewater. Water Sci Technol 74(8):1971–1979. https://doi.org/10.2166/wst.2016.386
- Schneider M, Ballweg T, Groß L, Gellermann C, Sanchez-Sanchez A, Fierro V, Celzard A, Mandel K (2019) Magnetic carbon composite particles for dye adsorption from water and their electrochemical regeneration. Part Part Syst Charact 36(6):1–11. https://doi.org/10.1002/ppsc. 201800537
- Borth KW, Galdino CW, Teixeira VDC, Anaissi FJ (2021) Iron oxide nanoparticles obtained from steel waste recycling as a green alternative for Congo red dye fast adsorption. Appl Surf Sci 546. https://doi.org/10.1016/j.apsusc.2021.149126
- Jia Z, Liu J, Wang Q, Li S, Qi Q, Zhu R (2015) Synthesis of 3D hierarchical porous iron oxides for adsorption of Congo red from dye wastewater. J Alloy Compd 622:587–595. https://doi. org/10.1016/j.jallcom.2014.10.125
- Abdullah NH, Shameli K, Abdullah EC, Abdullah LC (2019) Solid matrices for fabrication of magnetic iron oxide nanocomposites: synthesis, properties, and application for the adsorption of heavy metal ions and dyes. Compos B Eng 162:538–568. https://doi.org/10.1016/j.compos itesb.2018.12.075
- Othman NH, Alias NH, Shahruddin MZ, Abu Bakar NF, Nik Him NR, Lau WJ (2018) Adsorption kinetics of methylene blue dyes onto magnetic graphene oxide. J Environ Chem Eng 6(2):2803–2811. https://doi.org/10.1016/j.jece.2018.04.024
- Tan KB, Vakili M, Horri BA, Poh PE, Abdullah AZ, Salamatinia B (2015) Adsorption of dyes by nanomaterials: recent developments and adsorption mechanisms. Sep Purif Technol 150:229–242. https://doi.org/10.1016/j.seppur.2015.07.009
- 32. Lilhare S, Mathew SB, Singh AK, Carabineiro SAC (2021) Calcium alginate beads with entrapped iron oxide magnetic nanoparticles functionalized with methionine—a versatile adsorbent for arsenic removal. Nanomaterials 11(5). https://doi.org/10.3390/nano11051345

- Dai H (2019) Green and facile fabrication of pineapple peel cellulose/magnetic diatomite hydrogels in ionic liquid for methylene blue adsorption. Cellulose 6(381). https://doi.org/10. 1007/s10570-019-02283-6
- Wang H, Zhao W, Chen Y, Li Y (2020) Nickel aluminum layered double oxides modified magnetic biochar from waste corncob for efficient removal of acridine orange. Bioresour Technol 315:123834. https://doi.org/10.1016/j.biortech.2020.123834
- Ehsan A, Bhatti HN, Iqbal M, Noreen S (2017) Native, acidic pre-treated and composite clay efficiency for the adsorption of dicationic dye in aqueous medium. Water Sci Technol 75(4):753–764. https://doi.org/10.2166/wst.2016.435
- Rajabi M, Mahanpoor K, Moradi O (2019) Preparation of PMMA/GO and PMMA/GO-Fe₃O₄ nanocomposites for malachite green dye adsorption: kinetic and thermodynamic studies. Compos B Eng 167:544–555. https://doi.org/10.1016/j.compositesb.2019.03.030
- Zhang P, O'Connor D, Wang Y, Jiang L, Xia T, Wang L, Tsang DCW, Ok YS, Hou D (2020) A green biochar/iron oxide composite for methylene blue removal. J Hazard Mater 384:121286. https://doi.org/10.1016/j.jhazmat.2019.121286
- Kanwal A, Bhatti HN, Iqbal M, Noreen S (2017) Basic dye adsorption onto clay/MnFe₂O₄ composite: a mechanistic study. Water Environ Res 89(4):301–311. https://doi.org/10.2175/ 106143017x14839994522984
- Sehlleier YH, Hardt S, Schulz C, Wiggers H (2016) A novel magnetically-separable porous iron-oxide nanocomposite as an adsorbent for methylene blue (MB) dye. J Environ Chem Eng 4(4):3779–3787. https://doi.org/10.1016/j.jece.2016.08.018
- 40. Pramanik N, Ranganathan S, Rao S, Suneet K, Jain S, Rangarajan A, Jhunjhunwala S (2019) A composite of hyaluronic acid-modified graphene oxide and iron oxide nanoparticles for targeted drug delivery and magnetothermal therapy. ACS Omega 4(5):9284–9293. https://doi. org/10.1021/acsomega.9b00870
- 41. Rebuttini V, Fazio E, Santangelo S, Neri F, Caputo G, Martin C, Brousse T, Favier F, Pinna N (2015) Chemical modification of graphene oxide through diazonium chemistry and its influence on the structure-property relationships of graphene oxide-iron oxide nanocomposites. Chem Eur J 21(35):12465–12474. https://doi.org/10.1002/chem.201500836
- 42. Eren E, Cubuk O, Ciftci H, Eren B, Caglar B (2010) Adsorption of basic dye from aqueous solutions by modified sepiolite: equilibrium, kinetics and thermodynamics study. Desalination 252(1–3):88–96. https://doi.org/10.1016/j.desal.2009.10.020
- El Qada EN, Allen SJ, Walker GM (2008) Adsorption of basic dyes from aqueous solution onto activated carbons. Chem Eng J 135(3):174–184. https://doi.org/10.1016/j.cej.2007.02.023
- 44. Mall ID, Srivastava VC, Agarwal NK, Mishra IM (2005) Adsorptive removal of malachite green dye from aqueous solution by bagasse fly ash and activated carbon-kinetic study and equilibrium isotherm analyses. Colloids Surf A Physicochem Eng Asp 264(1–3):17–28. https:// doi.org/10.1016/j.colsurfa.2005.03.027
- 45. Shen D, Fan J, Zhou W, Gao B, Yue Q, Kang Q (2009) Adsorption kinetics and isotherm of anionic dyes onto organo-bentonite from single and multisolute systems. J Hazard Mater 172(1):99–107. https://doi.org/10.1016/j.jhazmat.2009.06.139
- 46. Nageeb M (2013) Adsorption technique for the removal of organic pollutants from water and wastewater. In: Organic pollutants—monitoring, risk and treatment. https://doi.org/10.5772/ 54048
- Bhatti HN, Jabeen A, Iqbal M, Noreen S, Naseem Z (2017) Adsorptive behavior of rice branbased composites for malachite green dye: isotherm, kinetic and thermodynamic studies. J Mol Liq 237:322–333. https://doi.org/10.1016/j.molliq.2017.04.033
- Demirbas A (2009) Agricultural based activated carbons for the removal of dyes from aqueous solutions: a review. J Hazard Mater 167(1–3):1–9. https://doi.org/10.1016/j.jhazmat.2008. 12.114
- 49. Santhosh C, Daneshvar E, Tripathi KM, Baltrénas P, Kim TY, Baltrénaité E, Bhatnagar A (2020) Synthesis and characterization of magnetic biochar adsorbents for the removal of Cr(VI) and Acid orange 7 dye from aqueous solution. Environ Sci Pollut Res 27(26):32874–32887. https:// doi.org/10.1007/s11356-020-09275-1

- 50. Wang L, Hu G, Lyu F, Yue T, Tang H, Han H, Yang Y, Liu R, Sun W (2019) Application of red mud in wastewater treatment. Minerals 9(5). https://doi.org/10.3390/min9050281
- 51. Samrot AV, Ali HH, Selvarani J, Faradjeva E, Raji P, Prakash P, Kumar SS (2021) Adsorption efficiency of chemically synthesized superparamagnetic iron oxide nanoparticles (SPIONs) on crystal violet dye. Curr Res Green Sustain Chem 4:100066. https://doi.org/10.1016/j.crgsc. 2021.100066
- McCoy TM, Brown P, Eastoe J, Tabor RF (2015) Noncovalent magnetic control and reversible recovery of graphene oxide using iron oxide and magnetic surfactants. ACS Appl Mater Interfaces 7(3):2124–2133. https://doi.org/10.1021/am508565d
- Yang X, Chen C, Li J, Zhao G, Ren X, Wang X (2012) Graphene oxide-iron oxide and reduced graphene oxide-iron oxide hybrid materials for the removal of organic and inorganic pollutants. RSC Adv 2(23):8821–8826. https://doi.org/10.1039/c2ra20885g
- Pham XH, Hahm E, Kim HM, Son BS, Jo A, An J, Thi TAT, Nguyen DQ, Jun BH (2020) Silicacoated magnetic iron oxide nanoparticles grafted onto graphene oxide for protein isolation. Nanomaterials 10(1):1–14. https://doi.org/10.3390/nano10010117