Chapter

Magnetic Iron Oxide Colloids for Environmental Applications

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Abstract

This chapter deals with magnetic colloids with catalytic properties for the treatment of polluted waters and the efficient production of fuel alternatives. This kind of materials presents great advantages such as high surface/volume ratio, reproducibility, selectivity, ability to be magnetic harvested, functionalizable surfaces (e.g. with tunable pores and selective chelators deposited on them), high efficiencies and reusability. In particular, this chapter will consider the case of magnetic iron oxide colloids, which can be easily synthesized at low cost, are biocompatible and presents a well-developed surface chemistry. The most common techniques for the synthesis and functionalization of these magnetic nanoparticles will be reviewed and summarized. The iron oxide nanoparticles present outstanding properties that can be exploited in different aspect of the wastewater treatment such as heavy metals and organic pollutants removal by ionic exchange or adsorption, and degradation of the contaminants by advanced oxidation processes, among others. In the field of alternative energies, they have also been used as catalysts for biofuels production from oil crops, in Fischer-Tropsch reactions for liquid hydrocarbons and many other processes with potential environmental impact.

Keywords: magnetic colloids, iron oxide nanoparticles, renewable energies, water remediation, biofuels, pollutant, degradation, adsorption

1. Introduction: Environmental challenges

The incessant deterioration of the environment caused by anthropogenic activities, including industrial ones, has been an issue of great concern over the last few decades. The modern society demands the development of novel technological solutions able to create a more efficient and eco-friendly industry. Nanotechnology has the potential to improve traditional environmental remediation technologies through cleaner processes at a reduced cost. This global “nanorevolution” has located engineered nanomaterials and in particular, magnetic iron oxide colloids, under the spotlight for environmental applications such as water treatments and renewable energies solutions.

1.1 Water management

Water management has emerged as a global issue while the governmental agencies in many countries are stepping up to combat climate change. Pollution of oceans, water sources eutrophication, pollution of effluents by heavy metals and industrials wastes, the spread of desserts and the restricted access to drinking water are all challenges that demand the development of alternative treatment techniques and cleaner industrial processes [1].

Water and wastewater treatment generally includes up to four different stages that encompasses chemical, physical and biological processes [2]. Usually, wastewater needs to go through a preliminary treatment aimed to easily separate large residues, and in some cases a pre-aeration process. Once pretreated, the following stage known as primary treatment consists on processes of sedimentation and smaller sieving. The secondary treatment comprises more complex biological and physicochemical techniques. Finally, in a tertiary treatment, water is disinfected and processed to adequate the biologic oxygen demand and heavy metals concentrations by simple methods like adsorption or filtration [3]. Magnetic iron oxides colloids are a well-known alternative for adsorption processes mentioned in ternary treatments, since they present a high relative surface area and ease of functionalization that increase their adsorption capacity, selectivity and facilitate the separation by magnetic harvesting [4, 5].

Typically, the secondary water treatment stage requires more efforts and presents more challenging inconveniences [6]. Depending on the wastewater effluent composition, this stage may comprise different processes either physicochemical or biological. Biological treatments like aerobic and anaerobic processing are usually implemented to efficiently eliminate and remove organic matter by transforming it into harmless compounds. These treatments may fail when the effluent is not biodegradable with a relation between chemical oxygen demand and biological oxygen demand above 4 (COD/BOD>4) [7]. In those cases, a physicochemical alternative results more convenient, being advanced oxidation processes (AOPs) the most promising and exploitable ones [8]. These AOPs are based on the in-situ generation of highly oxidative hydroxyl radicals or other oxidative species able to purify water by mineralizing the harmful organic matter into CO_2, water, salts or inorganic acids. The oxidative species can be generated with the help of oxidizing agents, irradiation or with a catalyst [9, 10]. In the last years, many efforts have been place to improve these AOPs by combining them with photochemical, electrochemical and catalytic techniques and looking for cheaper, eco-friendly and more efficient agents that enable the transference of these technologies to industrial processing of wastewater [11]. In this sense, iron oxide colloids have been proposed as a very interesting catalyst for the degradation of contaminants by AOPs, through the Fe-mediated Fenton and Fenton-like reactions [12].

1.2 Fuels and alternatives

Fossil fuels are a non-renewable energy resource produced by organic matter from different living beings accumulated hundreds of millions of years at the bottom of lakes or sees with very little oxygen and covered with several layers of sediment. Humanity has known about the existence of fossil fuels since ancient times, becoming the main energy source during the industrial revolution [13]. At present, fossil fuel along with natural gas, are still fundamental for modern's society economy and alternative sources have not yet been found to replace them. The current energy model, based on these fuels, presents serious concerns of sustainability, either due to the emissions of polluting greenhouse gases or the economic and political tensions and therefore, there is a need to search for new alternative energies [14, 15]. In the last decade, different resources have been used to overcome the problematic carried out by fossil fuels, among these are solar, wind, water, natural gas, coal and biomass. **Figure 1** shows how some alternative fuels can be processed

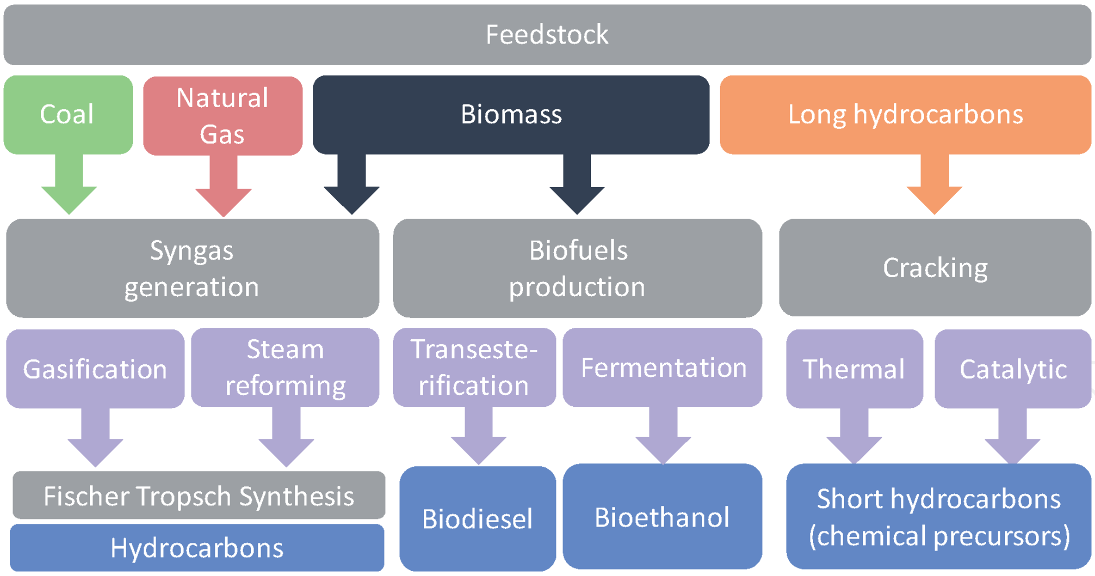

Figure 1.
Different feedstock for alternative fuels.

from different feedstock. The idea of waste valorization comes as a strong alternative for fuel and bio-fuels production. It is possible to reuse, recycle and compost waste materials and convert them into fuels. This is a way to overcome the environmental impact of common fossil fuels while taking advantage of useless wastes like food and wood residues, agricultural and municipal waste and used engine oil, among others [16, 17].

Biodiesel is a synthetic fuel obtained from natural components such as vegetable oils or animal fats through a transesterification reaction. It is mainly used for the preparation of diesel substitutes and can be mixed with it for commercial purposes. The use of biodiesel offers many advantages against traditional fossil fuels. As this combustible is synthesized from vegetable sources, such as rape, soy or sunflower seeds, it can be considered as an environmentally friendly fuel. It is even possible to manufacture it from recycled oils produced by different food industries [18–20]. Moreover, biodiesel generates less emissions of polluting gases and harmful substances like soot or benzenes. During the last decade the efficient production of biodiesel has been of great importance, and novel catalytic pathways, using for example nanocatalysts, are currently explored to increase the production yields [21].

Another alternative for fuel production comes from the waste valorization for hydrocarbons synthesis. Fischer-Tropsch process obtains gasoline from synthesis gases (syngas). This process was developed in the early 20's to obtain liquid fuels from coal as raw material as an alternative for fossil fuels [22]. But the syngas can be obtained from more sustainable sources, being biomass the one with the less environmental impact. The Fischer-Tropsch alternative process consists in transforming dry biomass into hydrocarbons via gasification with oxygen and using the syngas generated in the process as organic source [23]. As any chemical reaction, an efficient catalyst could lead this process to better yields of the desired product.

Finally, a third strategy to obtain alternative fuels consist on taking advantage of highly pollutant wastes such as used engine oils to produce liquid hydrocarbons. By thermal cracking, it is possible to break down the long, branched and cyclic chains, to obtain less heavy hydrocarbons that are in the order of the 15 to 20 carbons, which are usually the compounds of diesel [24].

Two important parameters play a fundamental role in the enhanced production of alternative fuels: the efficient heating and the catalyst separation. Both of them are usually expensive and time consuming and there is still a lack of efficient processes to provide a profitable alternative. The use of nanocatalysts in all these processes has been extensively studied since they make possible to work at moderated temperatures and increase mass transfer. Recent works in this area have shown that magnetic nanoparticles based on iron oxide could be a powerful tool to address many of the limitations exposed for the efficient waste valorization for fuels production [25, 26].

1.3 Magnetic colloids as alternative materials

In both applications, wastewater treatment processes and catalytic biodiesel production at industrial scale, it is crucial the use of efficient and inexpensive materials. This is the case of magnetic iron oxide nanoparticles (IONPs) that, as mentioned before, can be used in the former case as adsorbents for heavy metals or organic compounds and for the advanced oxidation of organic matter, and for the latter case, they have demonstrated a high-performance as reaction catalysts [5, 27].

It is essential to design and produce an efficient colloid for the mentioned environmental processes taking into account parameters such as the particle size and the colloidal stability. It should be emphasized that in the case of these colloids, the magnetic properties of the nanoparticles provide important advantages over other commonly used materials as it is the possibility of easy separation by using a magnetic gradient and heating them under an alternating magnetic field [28, 29]. However, magnetic properties are also responsible for the formation of aggregates and agglomerates due to the magnetic interactions inter-particles that reduce the specific surface area and the colloidal stability, limiting the efficiency and possible re-use of the particles [30]. Therefore, it results crucial to design colloids with nanoparticle sizes in the nanometer range (<100 nm) and coatings that provide them electrostatic and, if possible, steric repulsion, to keep magnetic interactions at the minimum and assuring in this way long term colloidal stability.

2. Environmental applications of magnetic iron oxide colloids

Figure 2 summarizes in a schematic way some of the applications of IONPs colloids that can be beneficial for environmental conservation. Compared to conventional macroscale materials such as activated carbons or zeolites, IONPs can achieve similar performance with minimum masses reduction on materials and energy costs. To understand how important IONPs are turning out to be, in this section the most recent works on this field will be reviewed.

2.1 Wastewater treatment agents

IONPs have been extensively studied for water purification and remediation of wastewaters. The three most important properties for these applications are the surface area/volume ratios, the possibility of magnetic harvesting and their surface reactivity. Among the possible uses of IONPs in this field, some of the most highlighted are the adsorption for the removal of contaminants and, less-known is the advanced oxidation processes (AOPs) for its degradation [31–33].

Adsorption is a surface phenomenon where the molecules of a sorbate are bound to the solid surface of the sorbent. In this phenomenon, mass transfer has a remarkable significance in the three steps involved: external diffusion, pore diffusion and surface reaction. In the first step, the adsorbate is transported from the bulk phase to the external surface of the sorbent. The pore diffusion refers to the transport through the sorbent pores so it can get to the final step were the sorbate molecules are attached to the internal surface, for the surface reaction [34]. Once

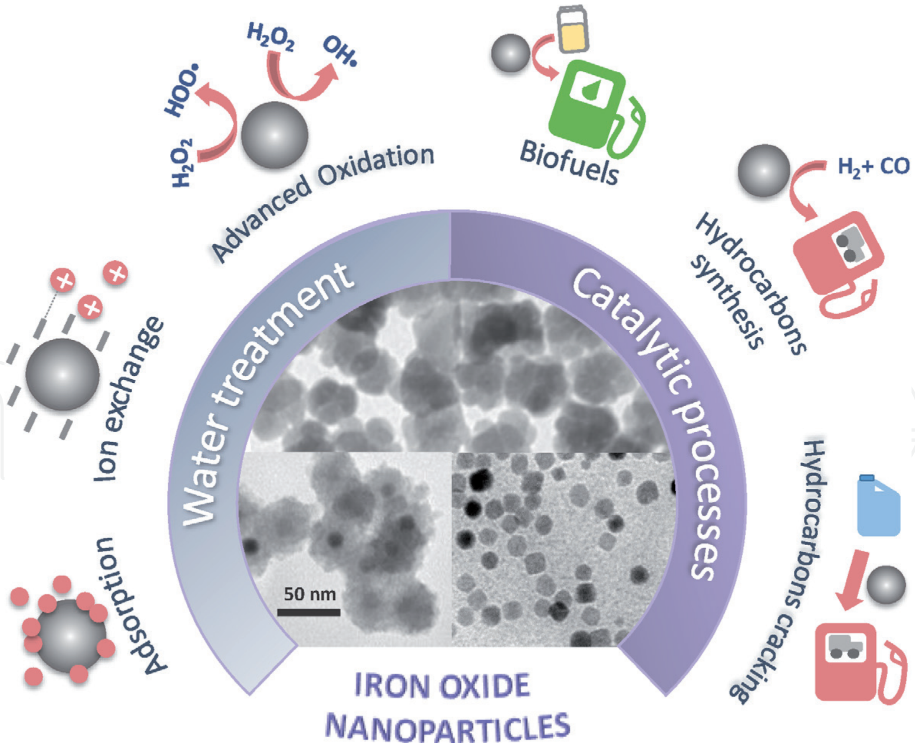

Figure 2.
Examples of applications of magnetic iron oxide colloids with positive impact on the environment.

adsorbed, the pollutants can be removed by magnetic collection using permanent magnets or alternatively degraded by the characteristic surface chemistry of iron oxide. As mentioned before, AOPs are based on physicochemical processes capable of producing profound changes in the chemical structure of pollutants. The concept was initially established by Glaze and collaborators, who defined AOPs that involve the generation and use of powerful transient species, mainly the hydroxyl radical (HO•) [35]. This radical, and others like HO•, OOH• can be generated by photochemical means (including sunlight) or by other forms of energy and are highly effective for the oxidation of organic matter. Some toxic pollutants that are not very susceptible to oxidation, such as metal ions or halogenated compounds, requires the use of chemical catalyst such as iron oxide [36]. An additional advantage of AOPs, is that they do not only change the pollutant phase but transform it chemically by its complete mineralization with no sludge generation [37].

Table 1 summarizes some recent works in the field of adsorption and AOPs using different iron oxide nanoparticles formulations. As it can be observed, IONPs are widely used in this matter due to their unique properties. Their applications for water remediation range from the elimination of inorganic and organic pollutants to the elimination of bacteria, proving that IONPs are materials with great versatility. Between the inorganic contaminants that can be removed by magnetic colloids, the most common are arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb) and zinc (Zn), which can cause, above their maximum levels in water, adverse health effects [38]. On the other hand, organic compounds like azo dyes, which present ecological hazardous effects due to their capacity of obstruct light within streams causing distress in aquatic environments, can also be removed using magnetic colloids [39]. Another class of organic pollutants that have been intensively studied for many researchers in the last decade are the emerging contaminants [40]. IONPs have demonstrated their ability to successfully remove many of these novel contaminants like for example pharmaceutical active chemicals, pesticides, personal cleaning compounds and others proving to be an efficient tool for environmental remediation [41, 42].

Material	**Process**	**Highlights**	**Ref.**
Fe_3O_4 immobilized on sand	Chromium adsorption	Supportive matrix for nanoparticles to avoid agglomeration and enhance adsorption.	[43]
Fe/La oxide microspheres	Arsenic adsorption	SiO_2 template used for the microsphere synthesis and a double shell material composed of Iron oxide and Lanthanum oxide	[44]
Resin-based hydrated iron oxide	Organic and inorganic compounds	Simultaneous removal of ρ-arsanilic acid and adsorption of arsenic.	[45]
Pristine γ-Fe_2O_3 nanoparticles	Arsenite adsorption	Material presented binding affinity to arsenite when coexisting with arsenate.	[46]
Fe_3O_4/Douglas fir biochar	Pharmaceuticals adsorption	Byproduct waste of syn-gas production was used for developing the adsorbent. Caffeine, ibuprofen and acetylsalicylic acid were removed in a fast equilibrium process.	[47]
Zr metal organic framework immobilized onto Fe_3O_4@SiO_2	Fungicides adsorption	Adsorbent with maximum adsorption capacities for triclosan and triclocarban (476 and 602 mg/g). Material recycled up to 11 times.	[48]
Chitosan-polyglycidol coated iron oxide	Methylene blue adsorption	Interactions between the coating molecules where analyzed. It was proved that this material can be used for dye removal	[49]
α-Fe_2O_3/lignosulfonate composite (no-magnetic)	Cadmium adsorption	The incorporation of organics onto magnetic sorbent can improve the adsorption process of heavy metals	[50]
Fe_3O_4 grafted with β-cyclodextrin	Bacteria adsorption	Pathogenic bacteria in water can be adsorbed and removed by magnetic harvesting processes.	[51]
Fe_3O_4/activated carbon	Combined adsorption and Fenton oxidation of chlorophenol	Iron oxide was impregnated over porous activated carbon. Adsorption followed the intraparticle diffusion model and 90% degradation was achieved. 5 times recycled.	[52]
Fe_3O_4 immobilized on graphene oxide	Fenton-like degradation of emerging pollutants and arsenic	Simultaneous degradation of ρ-arsanilic acid and adsorption of arsenic.	[53]
Fe_3O_4/SiO_2 coated with Polyethylene and polyacrilyc acid	Photo-Fenton for bacteria inactivation	*E. coli* bacteria photo-Fenton inactivation was achieved at natural pH	[54]
(Ag_3PO_4)-(Fe_3O_4)@ activated biochar	Sonocatalytic degradation of Rhodamine B and Bisphenol A	H_2O_2 production was achieved by pyrolysis of water molecules on catalyst surface. Degradation of synthetic dyes, endocrine-disrupting compounds/pharmaceutical active chemicals, and chlorinated compounds was tested.	[55]

Table 1.
Different iron oxide nanoparticles as adsorbents or catalysts for water remediation (references taken from recent works).

To maximize the adsorption capacity of the magnetic colloids, several parameters can be adjusted to the compound to be removed, that include the surface chelated molecules, the surface charge and the surface area available for the adsorption, being the later one determined by the nanoparticle size and the porosity of the coating.

IONPs can be efficiently chelated with certain molecules like (3-Aminopropyl) triethoxysilane (APTES) to modify the surface charge and promote the heavy metals adsorption process. Gallo et al. showed how the efficiency of IONPs increased with the increasing positive surface charge [56]. Moreover, the way IONPs are chelated can influence their selectivity for certain compounds. Removal of uranium from nuclear power polluted wastes has become a major issue in water processing since it can cause severe health and ecological problems. Helal et al. developed and efficient IONPs nanosorbent coated with APTES and succinyl-β-cyclodextrin molecules to increase its selectivity for uranium [57]. For other heavy metal ions such as chromium usually found in its anionic form ($HCrO^{4-}$, $Cr2O_7^{2-}$), the ionic attraction with its sorbent is an important parameter to be considered.

Silica coating of magnetic nanoparticles is an innovative way to modify the porosity of the sorbents surface and has been widely tested for the adsorption and degradation of different pollutants. Gallo *et al.* designed an interesting mesoporous silica coated IONPs for the adsorption of heavy metals and organic compounds [58]. They observed an interesting remark in which mesopores, growth with porogenic agents (e.g. octadecyltrimethoxysilane), present more affinity for the adsorption of organic compounds than heavy metals, in spite of having larger molecules. In this sense, it is not only possible to optimize the IONPs surface area but also their selectivity for specific compounds. On the other hand, as proved by Wu, *et al.* it is possible to grow the IONPs by spontaneous infiltration over a mesoporous SiO_2 template, which results in a much faster and easy way of producing these hybrid materials for the degradation of harmful azo dyes [59]. Even though the active sites available where occupied by IONPs and the adsorption decreased, they observed that the removal was enhanced by the Fenton-like degradation, proving that the hybrids are efficient agents for dyes remediation. Likewise, an interesting approach for wastewater treatment using IONPs@SiO_2 is to chelate the shell to increase selectivity for certain compounds. Uranium selectivity of cobalt ferrite nanoparticles coated with SiO_2 was studied by Huang *et al.* where they decorated the shell with 2-Phosphonobutane-1,2,4-tricarboxylic acid to increase the affinity sorbent/sorbate [60]. The SiO_2 coating was performed by the Stöber method and by coexisting ions tests they proved that the silica matrix can be efficiently chelated to improve selectivity. These examples show the importance of the physico-chemical nature of the coating on the stability, adsorption capacity and catalytic activity of the IONPs [61].

2.2 Catalysts for alternative energies

The use of magnetic iron oxide nanoparticles as catalyst supports dates back to the 70's when Robinson *et al.* reported the synthesis of enzymatic biocatalysts supported over magnetic iron oxides. The initial interest for the use of iron oxide was to facilitate the catalyst recovery and the immobilization of the catalyst in the reactor with magnetic fields [62]. Since then, the interest for IONPs as catalyst has emerged for an extensive list of chemical reactions including the ones that contribute to diminishing environmental harmful effects triggered by anthropogenic activities. Some of these reactions are based on developing alternatives to the highly pollutant use of fossil fuels, *e.g.* biodiesel production, Fischer-Tropsch synthesis and catalytic cracking of used engine oil, among others.

The design of IONPs for this application, should prevent mechanical breakdown of the catalyst and increase its lifetime by avoiding the possible particle growth or sintering during the process. One way is by introducing IONPs in mesoporous materials, assuring better catalytic process due the relatively large pores with high surface area that facilitate mass transfer and increase the concentration of active sites per mass of material. A recent study of Wei, *et al.* consisted in the Fischer-Tropsch synthesis catalyzed by a mesoporous iron oxide nanoparticle-decorated graphene oxide [63]. Here, they showed that the designed hierarchically mesoporous material can hinder the contact of the syngas with the active sites, highlighting that the improved mesoporous structure of the IONPs is extremely beneficial for reactants access and products release. Zhang *et al.* postulated that maybe metals atoms with multiple valences, including Fe and their oxides, result partially reduced during pyrolysis processes and generate oxygen vacancies that might transform some volatile biomass compounds into bio-oil [64]. The high specificity in the catalytic cracking of spent engine oils, reducing the undesired aromatics and high molecular weight constituents in a produced diesel-fuel, has been demonstrated also for simple natural magnetite particles in the micrometer range [65].

More complex nanostructures, like CaO@Fe_3O_4 composites have been shown to increase yields in the transesterification reaction of vegetable oils with no need of additional base compounds. It is also possible to improve the biodiesel production by immobilizing enzymes like lipase over IONPs. In this way there will be no need of purification after the reaction as these catalysts decrease yields of toxic byproducts [66]. Furthermore, Teo *et al.* prepared a highly recyclable $CaSO_4/Fe_2O_3\text{-}SiO_2$ catalyst for biodiesel production, showing its efficiency in the reaction [67].

In spite of the promising results in the use of magnetic colloids in this area, the literature is quite limited, and it is needed to strengthen the efforts in the years ahead to evaluate the potential of these catalysts in the efficient production of alternative fuels. It should be mentioned that besides the benefits of high surface areas, high selectivity and specificity and the ability to be functionalized, IONPs can offer a selective heating at the nanoparticle surface under an alternating magnetic field that may enhance the reaction rate and yield as will be described in Section 4.

3. Preparation of iron oxide magnetic colloids

The past two decades have seen tremendous advances in the synthesis and application of IONPs that take advantage of their distinct properties and functionalities. As seen in **Figure 3**, the economical perspectives for the market of magnetite nanoparticles is in continuous growth mainly boosted by their use in biomedical applications but also in fields like energy and wastewater treatment. As the interest for IONPs in different applications rises, the demand of new ways and technologies to produce them also increases.

Iron is one of the most abundant elements in nature presenting multiple crystalline phases with different structural and magnetic properties. Specifically, magnetite

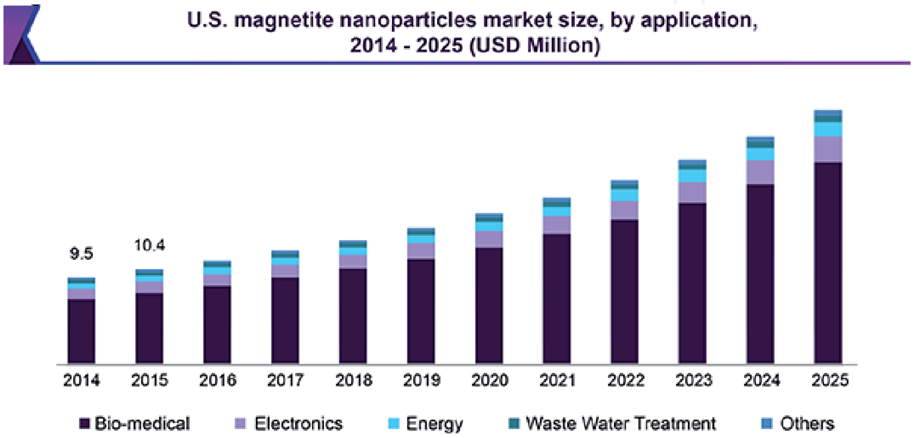

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Figure 3.
U.S. market perspectives on the application of magnetite nanoparticles [68].

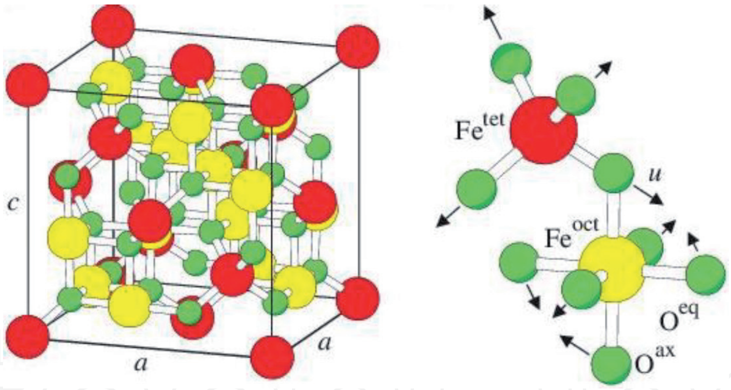

Figure 4.
Typical inverse spinel crystalline structure of magnetite [70]. © IOP Publishing and Deutsche Physikalische Gesellschaft. Reproduced by permission of IOP Publishing. CC BY-NC-SA.

(Fe_3O_4) and maghemite (γ-Fe_2O_3, the oxidized form of magnetite) have an interesting magnetic crystalline structure that can be described as a cubic inverse spinel structure with O_2 shaping an fcc structure and Fe cations in the tetrahedral and octahedral sites, as presented in **Figure 4**. These are the two most common phases used in environmental applications due to their high magnetic susceptibility and good chemical stability. Other iron oxides like hematite (α-Fe_2O_3) or goethite (α-FeOOH) frequently found in nature, present poor magnetic properties although they present unique and different advantages for other specific applications [69].

Different methods of synthesis have been studied and optimized so far in order to improve the physicochemical features of the magnetic iron oxide colloids. By selecting the proper method and controlling their key parameters (solvent, temperature, reaction time...) it is possible to generate IONPs of specific morphologies, size distributions and to control their colloidal stability. Each synthesis method presents specific advantages and drawbacks, therefore none of them can be declared as the universal method for producing IONPs. Between top-down or bottom-up approaches, the last ones are the most commonly used for large scale production because they offer a better control on the production of uniform nanoparticles with less defects, more homogeneous in shape, and better short and long range ordering (better crystallinity). This bottom-up category can be subclassified as a function of the reaction media, as aqueous synthesis (coprecipitation, hydrothermal and electrochemical, among others) or organic synthesis (thermal decomposition, polyol process, etc.) [71, 72]. In this section we will focus our attention in three different methods for comparison purposes: coprecipitation, thermal decomposition and polyol-based hydrothermal method.

3.1 Synthesis techniques

3.1.1 Coprecipitation

This is probably the most common and simplest method of synthesis of IONPs. Magnetic nanoparticles of magnetite or maghemite can be produced by coprecipitation of a stoichiometric mixture of Fe (II) and Fe (III) salts in an alkaline medium such as sodium hydroxide or ammonium hydroxide, for example. It is possible to obtain particles with diameters between 5 and 15 nm by controlling the synthesis key parameters like pH, temperature, addition rate of iron precursors and concentration of precursors [73]. For magnetite formation the overall reaction can be described as Eq. (1):

$$Fe^{2+} + 2Fe^{3+} + 8OH^{-} \rightarrow Fe_3O_4 + 4H_2O \tag{1}$$

The complete precipitation of magnetite is obtained in pH ranging from 8 to 14 with Fe^{3+}/Fe^{2+} ratios of 2:1, usually in an oxygen free environment to avoid premature Fe^{2+} oxidation. As magnetite usually is sensitive to oxidation by air, for environmental applications results much better to work with maghemite that will preserve its properties throughout the processes [72]. Magnetite is transformed to maghemite by heating up to 250°C or by acid treatment with nitrate/nitric acid. The main problem using this synthesis method is that the IONPs obtained, usually present a wide particle size distribution and poor crystallinity since they are prepared at temperatures below 100°C.

3.1.2 Thermal decomposition

This synthesis technique is based on the decomposition of organometallic precursors of Fe in high boiling point organic solvents in the absence of oxygen and the presence of massive amount of surfactants. It is possible to finely tune the size and shape of the IONPs just by controlling the boiling temperature of the solvent, the reactivity and concentration of the iron precursor, and the surfactants (typically fatty acids) chain lengths. The high reaction temperature used in thermal decomposition (>300°C), creates IONPs with narrow size distributions and excellent crystallinity in a range size between 5 and 100 nm [74, 75]. Due to the presence of organic surfactants (oleic acid, oleylamine...), the raw product has hydrophobic character and forms stable dispersions in many organic solvents like hexane, cyclohexane and toluene. However, these particles cannot be dispersed in water, being necessary a second step, like a ligand exchange reaction or the coating with an amphiphilic polymer, to transfer the synthesized IONPs to aqueous medium [76].

3.1.3 Polyol method

The polyol synthesis method was specifically designed for the development of nanostructured materials. Polyols are a family of solvents whose characteristics and properties (boiling temperature, viscosity, polarity) depends mainly on the length and alcohol substitution of methylene chains. They take advantage of the boiling temperatures of multivalent alcohols in their liquid phase to fix the temperature of reaction. It is interesting to highlight that the boiling temperature increases with the number of –OH moieties, the same with the molecular weight, viscosity and polarity [77, 78]. The main advantage of the use of polyols is that they provide reaction temperatures like the ones obtained in organic media, but the obtained IONPs are hydrophilic and can be dispersed in water like the ones produced in aqueous media.

Due to the diversity of polyols, it is possible to control the reaction temperature, just by selecting one with the interested boiling point. These temperatures can range between 200 and 320°C. Besides, glycol chains of the polyols can be used to control the particle sizes. **Figure 5** shows the TEM images of different IONPs with their size distribution obtained by Hachani *et al.* [79] where they proved that the length of the polyol chain is strictly related to the size of the obtained particles. They confirmed by thermal gravimetric analyses that each polyol was attached to the surface supporting the crucial role of the solvent on the growth of the IONPs. Moreover, thanks to the high polarity of the polyols, many common metallic salts are soluble and can be used as precursors for the synthesis of magnetite or other cobalt or zinc ferrites [80].

This well-known synthesis method was firstly described in 1989 by Fievet *et al.* when they synthesized metal powders of gold, copper, cobalt and lead in the micrometer range [81]. In that seminal work, they carried out reactions in a polyol-based media from the ionic form of each oxide, hydroxide or salt. In general, they

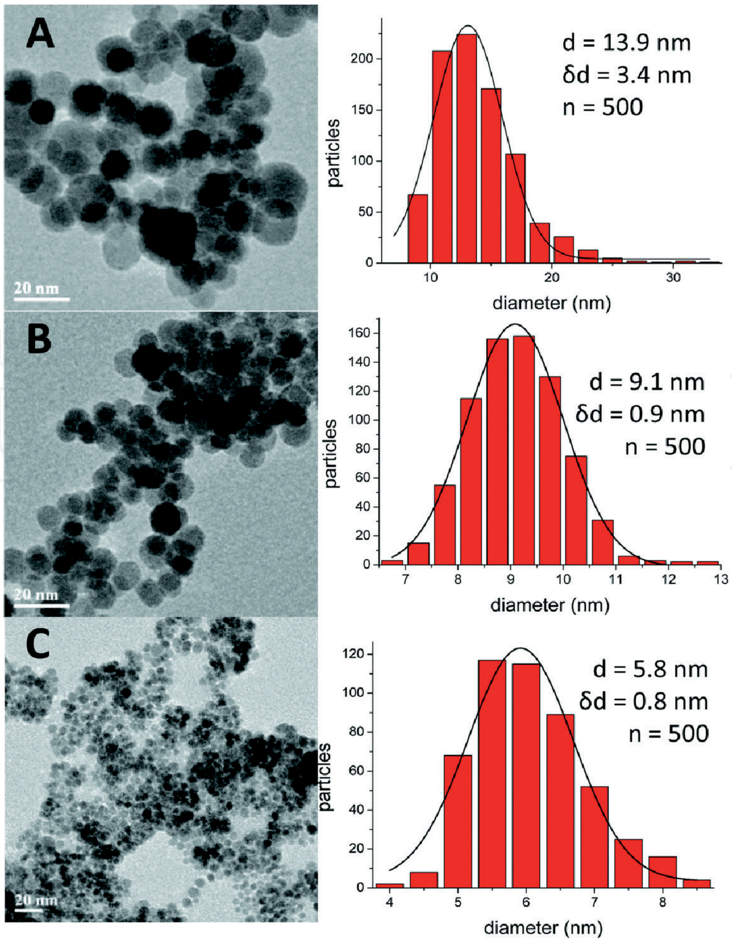

Figure 5.
Iron oxide nanoparticles synthesized with different polyols: (A) Tetraethylene glycol, (B) triethylene glycol and (C) diethylene glycol [79] - Published by The Royal Society of Chemistry.

demonstrated that polyols can act simultaneously as solvents, reducing agents and in certain cases as protective agents. Moreover, surfactant abilities of polyols are usually considered weak due to their relatively low molecular weighted molecules, thus they can be easily removed and exchanged by specific functional groups depending on the IONPs application [81].

An interesting approach to synthesize single (5–15 nm) and multicore (20–300 nm) IONPs and other metal ferrites is to combine the polyol method with a microwave assisted heating or with high pressure autoclaves. The microwave assisted polyol method is a versatile technique with improved yields, shorter residence times and highly reproducibility. The polyol molecules are able to adsorb microwave radiation due to their high polarity, with dielectric constants ranging from 20 to 45 [80, 82]. On the other hand, the polyol synthesis performed in a high pressure autoclave can decrease reaction times in a well-sealed environment and control of the size and the aggregation of the particles by controlling the synthesis parameters [83].

3.2 Colloidal stabilization

Magnetic attraction between nanoparticles compromise the colloidal stability of the suspension inducing agglomeration or even large precipitates [72, 84]. Depending on the application, the lack of colloidal stability may reduce the efficiency of the material. Therefore, it is necessary to develop compatible coatings that increase either the electrostatic or the steric repulsion between IONPs. Usually, IONPs are coated with polymers, surfactant agents, ligands, or inorganic materials like noble metals, oxides or silica that can prevent the dissolution of the particle, stabilize them at the working pH or introduce functional groups for the attachment of specific molecules. For environmental applications, tuning the nanoparticle surface, either in aqueous media by using small molecules or inorganic coating, or in organic media using surfactants, has been shown to improve its adsorption and catalytic capacities.

3.2.1 Small molecules

The modification of the nanoparticle surface with small molecules having a carboxylic or phosphate group with high coordination capacity to the iron atoms assures long term colloidal stability. The variety of molecules used is immense, some of the most commonly used are phosphonates, dimercaptosuccinic acid (DMSA), 11-mercaptoundecanoic acid or citric acid, small molecules with charged functional groups that provide excellent electrostatic stability.

If the IONPs were synthesized in aqueous media, the coating molecules can be introduced directly in the reaction media or preferably in a second step after the synthesis of the nanoparticles. In the case of IONPs obtained by the thermal decomposition method, it is possible to introduce functional groups by ligand exchange during the water transference. For example, in the coating with DMSA, one of the carboxylic groups of this molecule would replace the one at the surface of the IONPs with oleic acid, and the other carboxylic groups will remain facing outwards providing high negative surface charge in a wide pH range and a carboxylic functional group for further functionalization depending on the application [85].

3.2.2 Engineered silica coating

Coatings with silica (SiO_2) have now become a promising and important pathway for the development of coated magnetic colloids for different applications due to its biocompatibility, stability, easy conjugation with different functional groups that offer high selectivity and specificity [72]. Most of the SiO_2 coating strategies for magnetic colloids result in core-shell structures with an ionic positive charge that activate the surface and avoids aggregation (isoelectric point = 2–3). This diamagnetic coating reduces the magnetization per gram of material, but also increase the colloidal stability avoiding aggregation issues that results inconvenient for many applications [86].

The coating routes to obtain IONPs@SiO_2 can be divided into three categories: pre-synthesized silica matrices, in-situ fabrication of core-shell structures, and silica coating in already synthesized nanoparticles. This last one been the most common technique, where Stöber method is the easiest pathway to obtain homogeneous particles by hydrolysis and polycondensation of tetraethyl orthosilicate under alkaline conditions with temperatures above 60 °C [86]. SiO_2 layer over the IONPs can also be growth by a sol–gel process, where the silica shell is limited by a water-in-oil reverse microemulsion [87]. With these processes it is possible to control the shell thickness and to design a matrix with enhanced properties for specific applications.

It is also possible to design a high surface area Fe_3O_4@SiO_2 nanostructures where mesopores can be potentiated by porogenic agents that allow its in-situ formation through the SiO_2 shell. In this approach, nanoparticles are first coated by reverse microemulsion to add a first protective silica layer and the porogenic-doped shell is added by the Stöber method in a secondary step [58]. A schematic pathway for these kind of approach is showed in **Figure 6** were it is also pointed out how the porosity of silica engineered structures can be incremented by creating a hollow structure with hydrothermal or etching methods [88]. This example shows how the multitude of designing parameters of this kind of grafting molecules convert the Fe_3O_4@SiO_2 nanocomposites in a versatile material for environmental processes.

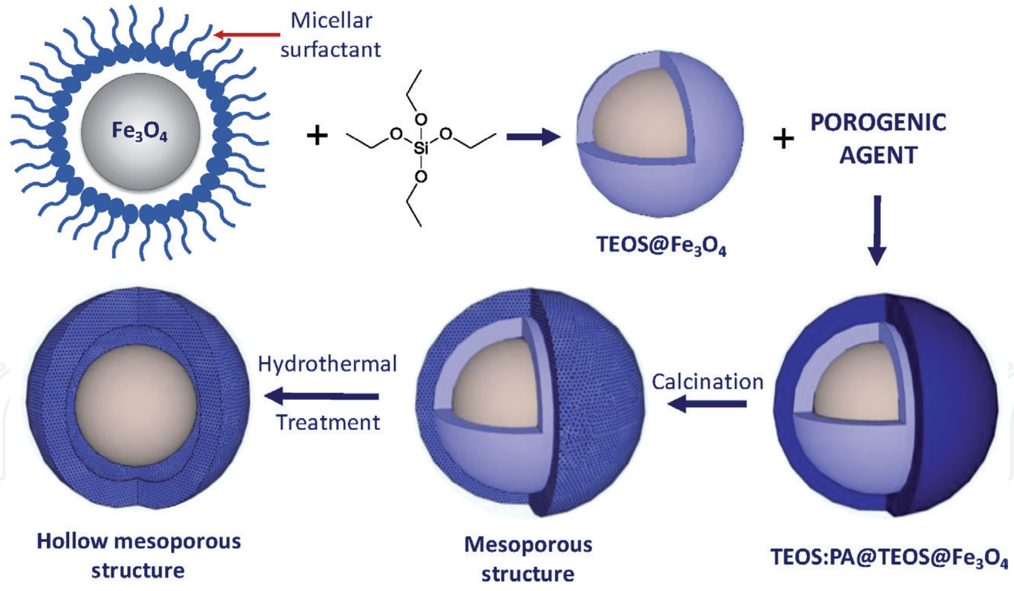

Figure 6.
Grafting iron oxide nanoparticles with engineered silica structures.

3.2.3 Organic coatings

Since many alternative energies processes are performed with oils or organic solvents, it is also important to develop IONPs soluble in organic media. Just as hydrophobic particles can undergo a ligand exchange to be redispersed in water, hydrophilic ones can be coated with molecules that allow their dispersion in organic media. For example, an interesting way to increase the stability in organic solvents is to add, in an additional step after the synthesis of the nanoparticles, a surfactant with a hydrophobic end. This step consists in the mixture of the surfactant on the IONPs aqueous suspension at ~80 °C and is frequently used for ferrofluids preparation. Oleic acid is one the most common compounds used for these purposes as it is a fatty acid formed by a terminal carboxylic acid group (–COOH) and a long hydrophobic alkyl chain. The resulting particles are quite stable in many organic solvents like hexane, toluene, cyclohexane, etc. [84].

For biodiesel production some studies have shown that iron oxides catalysts modified with polymers presented higher efficiencies [89]. Calcining organic compounds over nanoparticles surfaces can lead to a high surface area material with carbonaceous residues for enhanced adsorption and catalytic properties.

4. Promising magnetic features

The unique magnetic features of the iron oxide colloids represent one of the most exploitable characteristics of these materials for developing novel applications in the environmental area. In this section, we will review the physical principles of the superparamagnetic behavior observed in magnetic particles at the nanoscale and how it can be used in water remediation and biofuel generation.

At the macroscale, the magnetic materials minimize their magnetic energy breaking the alignment of their atomic moments into regions of coherent magnetization known as magnetic domains. The size of these domains depends on the anisotropy and saturation magnetization of the material. When the size of the solid is reduced to the size of a single magnetic domain, all the atomic magnetic moments of the material are oriented in the same direction and rotate coherently with the applied field (macrospin approximation). If we continue decreasing their size, we observe the characteristic magnetic response of small magnetic nanoparticles known as superparamagnetism. For magnetite nanoparticles smaller than 50 nm, the thermal fluctuations observed at room temperature are able to disorder the moments, cancelling the global magnetization of the sample. Consequently, in the absence of a magnetic field, the superparamagnetic nanoparticles present no remanent magnetization, avoiding the instability problems related to magnetic aggregation. However, when a magnetic field is applied, for example by approaching a magnet, the nanoparticles recover their magnetism with a high susceptibility and will be dragged towards the magnet proximity [90, 91].

Interestingly, when the superparamagnetic nanoparticles are subjected to an alternating magnetic field, they are able to absorb the magnetic energy and dissipate it as heat. The applied AMF forces the inversion of the spins of the atoms in a hysteretic process. During this process of magnetization reversal, the AMF energy will be transformed into heat increasing the temperature of the close environment of the nanoparticles. The way in which IONPs dissipate energy depends on the relaxation process and it is a function of the particle size, magnetic anisotropy and the viscosity of the media. The two principal relaxation mechanisms reported are Brown and Néel [92].

In the first mechanism, Brownian relaxation, the magnetic moment rotates with the particle within the medium, thus it is only observed when the particles are dispersed in a liquid medium. In this case, the time required to reverse moments by this mechanism (τ_B) depends on the hydrodynamic volume (V_h), the viscosity of the solvent where the particles are located (η) and the absolute temperature (T), as shown by the following expression, Eq. (2) where k_B is Boltzmann's constant [93]:

$$\tau_B = \frac{3V_h \eta}{k_B T} \tag{2}$$

On the other hand, the Néel mechanism describes the relaxation of the magnetic moment within the particle crystal axis. This mechanism is always present, and it is the only one that intervenes in the relaxation of magnetic moments when the particles are in compacted powder or in a frozen liquid where they cannot physically rotate. The expression for the relaxation time (τ_N) of the magnetic moments by Néel mechanism is as follows in Eq. (3):

$$\tau_N = \tau_0 e^{K_{eff} V_{MAG} / k_B T} \tag{3}$$

where, T is the temperature, V_{MAG} the magnetic volume of the particle, K_{eff} the energy by unit of volume needed to reverse the magnetic moment orientation (effective anisotropy) and τ_0 the inverse value of the Larmor frequency [94].

When the particles are small (<~20 nm), we can consider that $\tau_N < < \tau_B$ and the relaxation of the magnetic moment takes place by Néel relaxation. On the other hand, for larger nanoparticles in which the magnetic moment is blocked in the direction of the easy axis of magnetization within the particle, it is satisfied that $\tau_B < < \tau_N$, and the main relaxation mechanism is the Brownian rotation. The superparamagnetic IONPs that are usually employed in environmental applications are in an intermediate range in which both relaxation mechanisms might be present [94].

This superparamagnetic behavior is beneficial for wastewater treatment and catalysis in two aspects. On one hand, IONPs can be dispersed in the absence of a magnetic field without problems of magnetic aggregation and later be separated with a magnet once they have achieved their purpose like adsorbed a specific pollutant on their surface. On the other hand, they can be selectively heated under an AMF using moderate field conditions, which can rise reaction yields and shorten residence times.

4.1 Boosting environmental processes

Apart of the fact that IONPs can be efficiently recovered with an external magnetic field, facilitating its regeneration and reuse, environmental processes like the presented in previous sections can also be enhanced by taking advantage of the magnetic heating power of IONPs in the presence of AMF. In the case of adsorption with IONPs, Rivera *et al.* presented the improvement of the adsorption capacity of chromium under an AMF [95]. Here, they showed much higher adsorption yields for IONP systems heated up with AMF than with common thermal heating even though both systems were set at the same global temperature. The heat generated by the IONPs is dissipated in their surface what generates local temperature much greater than those measured in the reaction media, giving rise to better adsorption yields. Furthermore, in a more recent work they used the same principle to improve the reaction yields of the methylene blue degradation in the presence of IONPs and AMF [96].

The advanced oxidation processes have also been benefited by the use of IONPs, although the influence of the AMF has not been deeply studied yet. **Figure** 7 shows the reaction mechanism that these particles can undertake in combination with hydrogen peroxide using the potential of IONPs as in situ nanoheaters. There are just a few references on this matter, where typical studies only focus in the increasing degradation yields with the increasing temperatures in common thermal reactors but they do not take advantage of the IONPs selective heating. Among the limited references on the subject, Munoz *et al.* were also able to prove that the catalytic wet peroxide oxidation of antibiotic sulfamethoxazole presented rates significantly faster with an AMF than in a typical CWPO system [97].

Recently, magnetic colloids have been used as catalysts to enhance biomass hydrodeoxygenation reaction with magnetic induction heating, proving that this heating can provide a better environment for the reaction to take place in [98]. Furthermore, the potential heating of these catalysts have only been analyzed in a few environmental reaction mechanisms. One of them is the CO_2 methanation presented by Rivas-Murias *et al.* where they achieved conversions >95% using a cobalt ferrite catalyst under a 93 kHz and 53 mT AMF with a SAR value of 270 W/g [99].

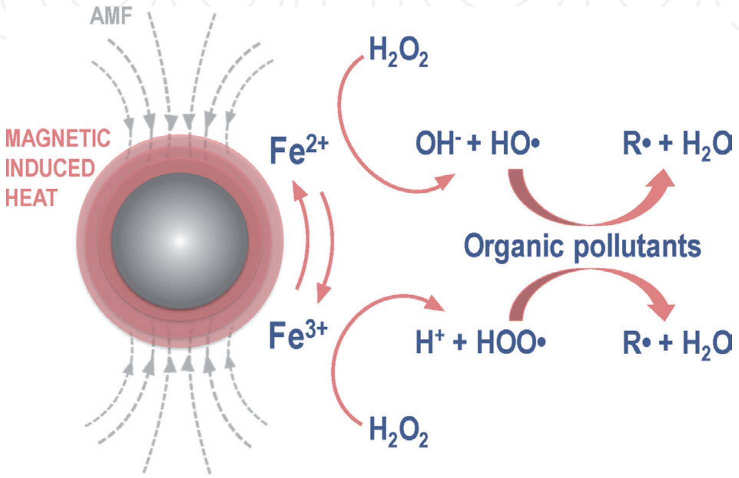

Figure 7.
An environmental catalytic process: Advanced oxidation of organic pollutants using iron oxide nanoparticles under an alternating magnetic field (AMF). (R: degradation products).

Our research group has recently tested the potential of IONPs as AOPs catalyst and local heating source on the decontamination of landfill leachate and complex textiles wastewater. The mineralization efficiency of the AOP of industrial wastewater was increased by magnetic induction heating of the nanocatalyst resulting in much quicker degradations in the presence of AMF compared to conventional heating. In general, magnetic induction-driven processes are a promising alternative for the improvement of well-known chemical reactions and real wastewaters remediation techniques.

5. Conclusion

This chapter shows the wide range of possible applications of magnetic iron oxide colloids in the field of environmental applications. It probes how iron oxide nanoparticles are excellent platforms to overcome many of the current technological challenges of this area. The chapter reviews the most recent references on water treatment and alternative fuels production in which iron oxide colloids has been used as treatment agents or catalysts. We have covered the areas of adsorption, advanced oxidation processes, hydrocarbon synthesis, biofuels and catalytic cracking of long chain hydrocarbons. Using iron oxide colloids has been proved to be a promising alternative for these processes and recent works in the field have shown an excellent performance of this material.

However, in order to obtain a competitive material, it is important to control parameters such as the particle size, coating and stability of the magnetic colloids. The analysis made here provides details of the most common synthesis and colloidal stabilization methods to create magnetic iron oxide colloids for this application.

The prospection of using iron oxide colloids tends to take advantage of the presence of Fe atoms at the surface working as catalysts for the degradation of contaminants through Fenton reactions, and their magnetic properties, not only for magnetic separation but also for the possibility of heating under an alternating magnetic field, enhancing catalytic and remediation processes.

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Conflict of interest

"The authors declare no conflict of interest."

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