




Magnetite immobilized metal nanoparticles in the treatment and removal of pollutants from wastewater: a review

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ABSTRACT

The increase in population and industrial activities has resulted in harmful pollutants in our water sources that cause a concern for our future health and environmental well-being. These pollutants include pharmaceuticals, nitroarenes, synthetic dyes, oil and heavy metals that can be toxic, carcinogenic and lead to multiple organ failure. Conventional methods used to remove these toxins are of high cost, poor recyclability and low efficiency. Therefore, it is important to find suitable methods to purify industrial and household wastewater. Nanoparticles possess useful characteristics such as high surface-to-volume ratio, high optical absorption coefficient and tunable band edges for optimized catalytic capability. Magnetite NPs in specific have proven great efficiency in the removal and degradation of such pollutants as it is affordable, recyclable and easy to remove in the presence of an external magnetic field. Surface functionalization of these magnetic NPs is seen as an excellent bridge between homogeneous and heterogeneous catalysis. A metal catalyst immobilized on the surface of these magnetic nanoparticles (MNPs) affords customization and optimization of their properties for targeted applications. This study briefly discusses the synthesis of the magnetic core and different immobilization methods used to secure a metal catalyst onto its surface. This is followed by a detailed discussion where these metal catalysts immobilized on MNPs are used to improve its absorption and degradation capabilities in wastewater treatment.

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Introduction

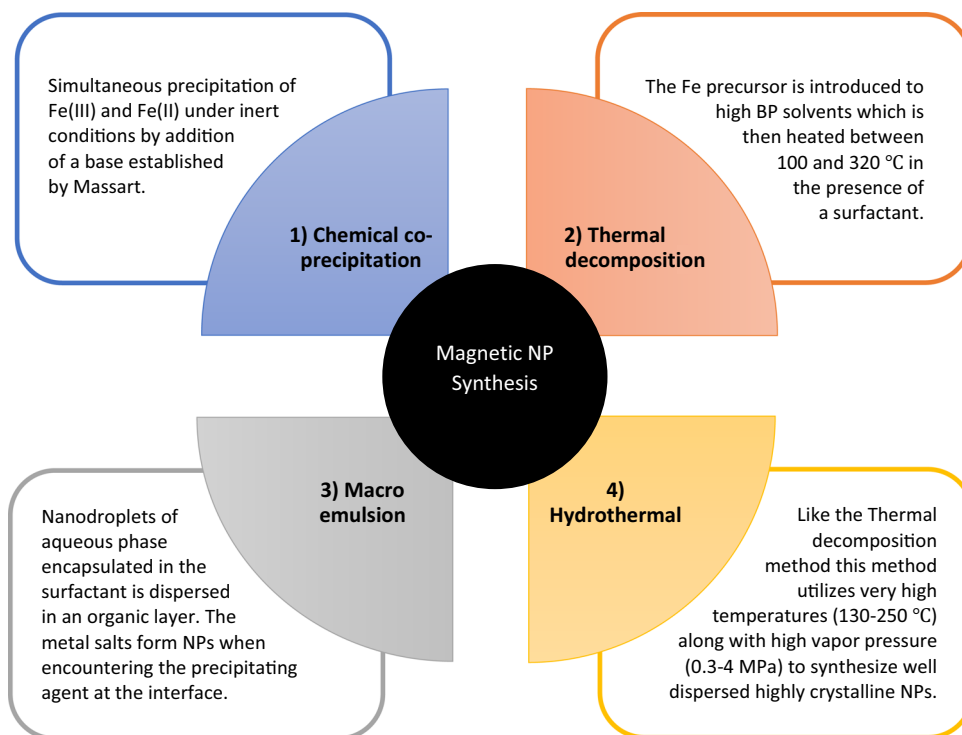
Water contamination has been a persistent global issue as it has been the root for many health and environmental problems that trouble our food security. The drastic increase in the world population along with the increased need for food and industrial production has contributed to this problem. These toxins include heavy metals, radionuclides, oil, natural organic matter, pharmaceuticals, dyes, nitrogen and phosphorous compounds, which can accumulate in nature and cause severe health and environmental damage. [1–4] These toxins are conventionally removed via biological methods using various microorganisms, physiochemical methods such as coagulation, electro-coagulation, chemical precipitation, irradiation and ion exchange or physical methods such as filtration, sedimentation and skimming. These methods are ineffective, slow and result in high chemical waste that is difficult to manage. [5, 6] Nanotechnology has proven to be one of the greatest advancements in this fields as nanoparticles (NPs) have high absorbing capability and good catalytic capability due to a large surface-to-volume ratio increasing the contact area available for catalysis to occur. NPs have attracted a lot of attention due to their unique behavior, shapes and electron movement on its surface. [7, 8] The particle is defined as ranging between 1 and 100 nm in size allowing for a large surface-to-volume ratio resulting in many active sites available for catalysis to occur. [9] As the particle consist of multiple atoms clustered together it enables electron movement on its surface as well as multiple sites of catalysis on its surface. The possible manipulation of the shape, composition, monodispersity, microstructure and surface coatings allows for alterations in the catalytic ability and absorption capacity of the nanoparticle. This leads to improved recyclability along with increased selectivity, activity and stability. [10] In addition, NPs can also consist of more than one metal through relatively easy synthesis methods. Bimetallic NPs are unique as they utilize some characteristics of both the individual metals present as well as new characteristics due to the interaction of the two metals with one another. [11] These characteristics are unique electronic, optical and magnetic properties that improve the overall stability and catalytic efficiency of the NPs. [12] When preparing NPs researchers aim to synthesize monodispersed NPs. As monometallic NPs

frequently lack in control over size, stability, activity and selectivity, bimetallic NPs have thus received great interest to improve these factors. [13]

Magnetite is a combination of Fe(II) and Fe(III) salts that undergone co-precipitation under basic conditions and has unique superparamagnetic characteristics and absorption capabilities. [14] It is one of the oxides abundantly present in iron ores and as iron is the most abundant transition metal, the use of this metal in catalysis allows for a more affordable and sustainable alternative to traditional catalysts. [15] Magnetite has been widely utilized for the removal of toxins from different water sources including monometallic iron NPs and bimetallic iron alloys or core shell NPs. [16–18] The use of magnetite not only allows for absorption and removal of these toxins but can also be modified as recyclable heterogeneous catalyst to convert the toxins to other value-added products. In addition to its magnetic characteristic magnetite is preferred as a catalyst support due to its size and shape control as well as its non-toxic properties and being classified as being relatively inert. [19] Multiple synthetic approaches have been reported for the preparation of MNPs including chemical, physical and biological approaches. Chemical synthesis is, however, preferred as it allows for better control over the shape and size of the NPs. [20–23] The most popular chemical synthesis methods used include co-precipitation, thermal decomposition, microemulsion and hydrothermal methods as seen in Fig. 1 [24–27]; however, other methods such as vapor deposition, spray pyrolysis, laser pyrolysis, sol-gel, polyol and no-thermal plasma methods have also been reported. [28–32] From these methods chemical co-precipitation is the most favored as it is seen as simple, inexpensive and does not require toxic solvents or harsh reaction conditions. [33] This method, however, lacks in control over shape and particle size [34] in which cases thermal decomposition or hydrothermal methods can be utilized. [25, 35] The macroemulsion method of synthesis is, however, not preferred as it delivers low yields, requires a lot of solvent and is complicated to execute. [36–38]

Although superparamagnetic iron oxide nanoparticles (SPIONs) are greatly reported in the removal and treatment of various water pollutants, they often lack in activity compared to other metal NPs. [16–18] Various immobilization methods enable the active metals to be anchored onto the surface of the magnetic NP. This allows researchers to easily bridge the

Figure 1 Most popular chemical synthesis methods of SPIONs. [24, 26, 34, 35].



gap between homogeneous and heterogeneous catalysis as the surface catalyst can be carefully tailored for its intended application. The use of SPIONs as a core and immobilization of active metals on the surface allows for the benefits associated with magnetite while optimizing reactivity. The use of these NPs as supports can also help to improve the stability and recyclability of previously unstable NPs. [39] The benefits of this design method thus allow for more active, stable and easily recyclable catalysts and absorbents to remove hazardous materials. Here we review the synthesis of nano-metal catalysts immobilized on magnetite as a support, and their efficiency in the treatment of common water pollutants.

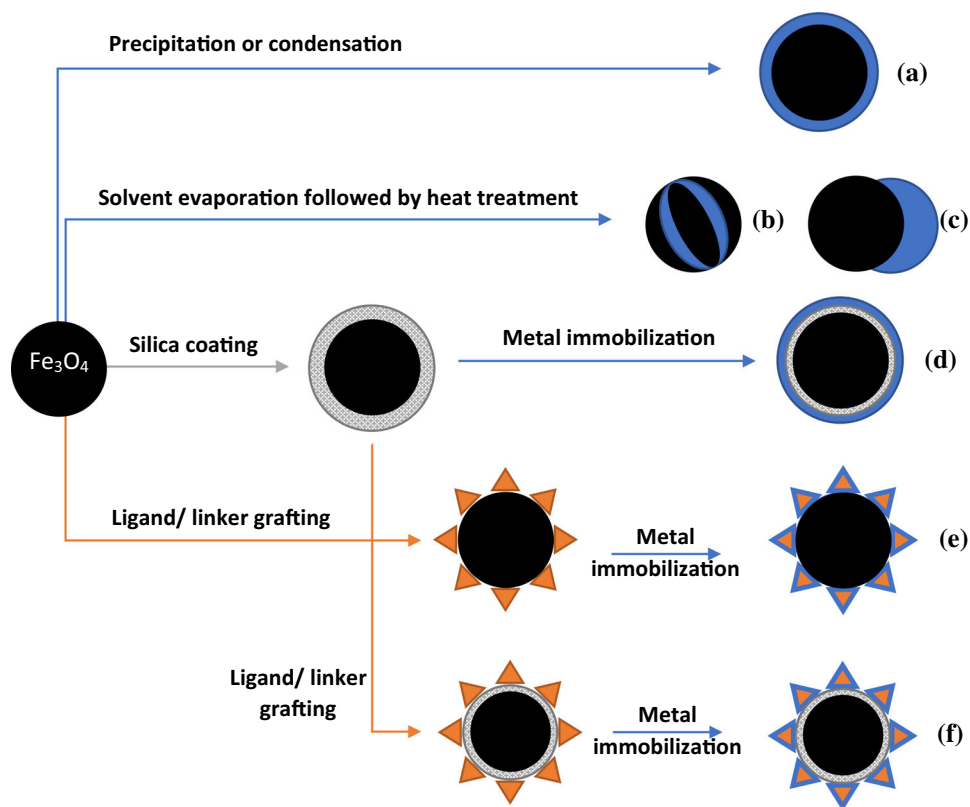
Methods to support catalysts on magnetite

There are multiple methods of successfully immobilizing metal NPs onto the SPION surface. The choice of method is able to tailor its stability, morphology and electron movement and should thus be considered as an important aspect when designing a catalyst or absorbent. This article focused on impregnation, co-precipitation, dumbbell composites, coating, grafting and coating-grafting methods as depicted in Fig. 2.

(a) *Impregnation* is the most popular method of introducing a metal catalyst onto the magnetic surface. This method is the easiest and least expensive method where the metal catalyst is simply precipitated or condensed directly onto the surface of the magnetic support. This method, however, lacks in a stabilizer and often leads to poor reproducibility of shape and size achieved. This resulted in more complicated methods being studied to introduce some control. [40]

(b) *Co-precipitation* method mixes the active metal and supports to enable nucleation and growth of the combined solid precursor of the active metal and support. The method incorporates solvent evaporation followed by heat treatment which result in different metal oxide domains on the magnetic surface that can be substituted with a transition metal of choice. The one-step process allows for very high active metal loadings while still maintaining a small particle size. This method is often preferred for producing catalysts with very high loadings. Nucleation is very sensitive for fluctuations in the reaction conditions which can lead to inhomogeneous growth patterns or the precipitation of different phases. New techniques such as continuous consecutive precipitation and spray-drying have thus been developed to overcome this hurdle. [41, 127]

Figure 2 Methods of supporting metal catalysts on the surface of magnetite a impregnation, b dumbbell, c co-precipitation, d coating, e grafting and f coating-grafting. [40–45].



(c) *Dumbbell composites* are defined as two different functional NPs in intimate contact with one another. The interfacial interaction originates from electron transfer across the interface of these different NPs. The unique structure is commonly obtained by sequential growth of a second NPs on an allocated specific area on the magnetic center obtained by solvent evaporation followed by heat treatment. This method is also similar to the impregnation method but relies heavily on the promotion of heterogeneous nucleation while suppressing the homogeneous nucleation from occurring. This is achieved by utilizing an optimum seed-to-precursor ratio and careful control of the heating profile to maintain the precursor concentration below the homogeneous nucleation threshold throughout the synthesis process. This method requires more intense control than the previous two discussed, but the unique structure has shown great promise for specified applications. [42, 128]

(d) *Coating* is one of the most common methods employed to avoid problems associated with naked magnetite. The core is coated and stabilized by an appropriate substance followed by precipitation of the metal catalyst on its surface. Silica is one of the

most popular oxides reported in the coating process of magnetite as it is environmentally safe, affordable and abundantly available. This is usually achieved by the sol-gel method which is followed by a second layer containing an active metal. This method is advantageous as the addition of a stabilizer results in much more robust catalysts. This stabilizer does, however, increase the size substantially which in turn results in lower surface area-to-volume ratios thus decreasing the activity of the MNP. [43]

(e) *Grafting*, other than silica, tailored ligands can also be used as a linker between the magnetic center to an active metal center. This method aims to protect the magnetic center from oxidation and increases its stability. These ligands can be carefully selected to tailor the electron movement, selectivity and activity of the MNP. It does, however, increase the cost associated with these MNPs generated. [44]

(f) *Coating-grafting*, combining the first two named methods both silica and a tailored ligand is utilized to bound the selected metal catalyst to the magnetic surface. The ligand commonly used in this process contains a triethoxysilane group capable of binding to both the silica surface and the preferred metal catalyst. Not only does this protect the magnetite center

but also allow for additional control over specific metal anchor points. This method is not commonly used as it is complex, expensive and generates very large particle sizes. [45]

Applications of catalysts immobilized on magnetite in wastewater treatment

Organic pollutant removal

Pharmaceutical degradation

Pharmaceuticals are a common pollutant that enters our wastewater sources through household disposal. This causes concern to human health as prolonged exposure can result in behavioral changes, inhibition of cell proliferation and damage to reproduction system. [46] It is also an environmental risk as these drugs can disturb natural ecosystems by killing crucial microorganism or promote the existence of drug resistant organisms. [47] Common pharmaceutical pollutants include ibuprofen (IBP), phenol, norfloxacin (NFX), acetaminophen (APAP), carbamazepine (CBZ) and pantoprazole. These chemicals are not removed by conventional wastewater treatment; thus, studies have focused on the use of absorbents or photocatalysts as a possible way of removal or degrading these pollutants.

Photo-catalytical decomposition is a green method utilizing light energy to activate the catalyst in degrading of the pollutant. Bi_2WO_6 stabilized on the magnetic core via a thin carbon interlayer has been reported for the photocatalytic decomposition of phenol assisted by H_2O_2 . Fe_3O_4 synthesized via the solvothermal method was coated with a thin carbon layer which enabled the growth of Bi_2WO_6 nanoplates on its surface. The NPs were extremely large with a diameter ranging between 500 and 600 nm. Evaluating the catalyst in phenol degradation in the presence of H_2O_2 and UV irradiation shows 100% decomposition within 240 min. [54] Fe_3O_4 coated with Bi_2WO_6 via hydrothermal methods was also evaluated in the photocatalytic degradation of IBP using solar light and H_2O_2 . These NPs are much smaller with an average diameter of 84 nm with Bi_2WO_6 distributed across the surface of the magnetite. The study showed that the degradation is inactive in dark conditions and improved in the presence of H_2O_2 . These results indicated that the

active species in the $\text{Fe}_3\text{O}_4/\text{Bi}_2\text{WO}_6$ nanocatalyst is the photogenerated holes present in the Bi_2WO_6 , degrading 82% IBP within 120 min. This catalyst is of interest as it utilized sky light rather than UV irradiation proving that it can be used in open natural environments rather than UV plants. This study also indicated that the catalyst is recyclable with no significant loss in activity over three consecutive runs. However, this activity was dramatically lowered during the fourth and fifth run with no explanation given by the authors. [55]

Additionally, $\text{Fe}_3\text{O}_4/\text{Bi}_2\text{WO}_6$ has been immobilized on graphene sand by in situ wet impregnation methods for the photocatalytic removal of antibiotics from wastewater. The $\text{Fe}_3\text{O}_4/\text{Bi}_2\text{WO}_6/\text{GSC}$ of 70 nm in size was evaluated in the photo-catalytical degradation of OTC and AMP under solar light. This catalyst exhibited the synergistic effect of its metal center and graphene surrounding to optimize catalysis by absorption of the antibiotic onto its surface followed by degradation to CO_2 , H_2O and NO_3^- ions. The catalyst showed improved activity compared to $\text{Fe}_3\text{O}_4/\text{Bi}_2\text{WO}_6$ along with easy separation and reuse of up to ten times without significant loss in activity. [56] A more recent study by Karbasi et al. proves the presence of FeO_x intra-gap states on $\text{Fe}_3\text{O}_4/\text{Bi}_2\text{WO}_6$ materials which enhances the degradation of pharmaceuticals under light by decreasing the internal band gap on Bi_2WO_6 . This study synthesized Fe_3O_4 via co-precipitation and Bi_2WO_6 immobilized onto its surface via hydrothermal synthesis to give flower-like magnetic catalysts, of different $\text{Fe}_3\text{O}_4:\text{Bi}_2\text{WO}_6$ ratios, between 20 and 40 nm. The optimum ratio decreased the internal band gap of Bi_2WO_6 by 0.3 eV. This catalyst was evaluated under low intensity light where it proved efficient in the removal of NFX within 1 h and was able to degrade 97% NFX within 210 min. The catalyst was also deemed stable over at least 5 consecutive cycles. The photogenerated holes present on the surface of the Bi_2WO_6 is still its main active site responsible for high photodegrading toward NFX. [57]

Iron-based MNPs have been widely reported as efficient catalysts for Fenton degradation of tetracycline (TC). Various modifications have thus been explored in improving its removal and degrading efficiency. These include the use of AC [129], cellulose [130] and graphite-like carbon nitride [131] among others. The excellent Fenton activity and recyclability achieved by these iron NPs lead to the

addition different metal catalysts onto its surface. This includes mesoporous bimetallic Fe/Co synthesized using the nanocasting strategy using KIT-6 mesoporous molecular sieves as a hard template to generate particles of 10 nm i.d. with 4 nm pores. These NPs showed good performance for degrading TC achieving a removal rate of 86% after 3 h. [132] $\text{Fe}_3\text{O}_4/\text{CuO}/\text{C}$ was also investigated as visible light driven heterogeneous catalyst for TC degradation. These magnetic CuO composites were synthesized by a two-step process of bio-templating followed by hydrothermal processes. The characterization showed that the bio-template's porous, corn stalk morphology was retained when loaded with a substantial amount of CuO and Fe_3O_4 NPs. The magnetic composite was highly efficient in TC degradation within 60 min across a wide pH range. [133] Simple and fast synthesis of magnetic polydopamine (PDA) Au-Fenton catalyst was reported by Zhai et. al. through the UV irradiation method at 365 nm. The $\text{Fe}_3\text{O}_4\text{PDA}/\text{Au}$ catalyst reached a TC removal efficiency of 93% after 5 h. The removal efficiency further increased to 97% when the catalyst was recycled while no substantial metal leaching was observed. [134]

Reduction of nitroarenes

An increase of nitro aromatic waste is another side effect of our growing industrial and agricultural activities. These compounds are used in the production of insecticides, synthetic dyes and herbicides. [58] Nitro pollutants are a severe risk to our environment and health due to their toxic and carcinogenic nature. [59, 60] Studies have thus focused on

several catalytic degradation methods of removing these pollutants such as electrochemical methods [61], photo-catalytical degradation [62] and reduction of the nitro group to an amino group. [63] Catalytic reduction has the additional advantage of forming aminophenol products which is less toxic and can be utilized in preparation of drugs, photo developing agents, fuels and wood, and leather staining. [64, 65] The use of MNPs in the catalytic reduction of nitroarenes has gain a fair amount of attention over recent years, as they allow for easy removal and recycling of the catalyst and the results summarized in Table 1.

Synthesis and the catalytic capability of flower-like magnetite have been reported by Datta et al. The flower-like morphology was achieved by precipitation of iron chloride in the presence of oxalic acid to form iron oxalate which was dried and thermally treated in air followed by more intense thermal treatment under H_2 . These nanoflowers could reduce a variety of nitroarenes in the presence of hydrazine hydrate with good yields of up to 98%. This is said to be due to its unique structure allowing for high surface area. The catalyst also proved excellent recyclability of up to 10 runs without loss in activity. [66] Some of these catalysts utilize expensive metals on the surface of the magnetic core to achieve high catalytic capability associated with these metals while benefitting from the affordability and recyclability of the magnetic core to decrease the overall production cost of the catalyst. One of these catalysts include $\text{Fe}_3\text{O}_4@\text{NC}@\text{Pt}$ reported by Qiao et al. as successful in the selective reduction of various nitroarenes. These catalysts were synthesized by carbonization of glucose on the Fe_3O_4 microsphere surface under

Table 1 Comparison of magnetic catalysts used in 4-NP reduction from literature

Catalyst	Reducing agent	Temperature (°C)	Time	Yield %	Selectivity %	References
Flower-like magnetite	Hydrazine hydrate	90	15 min	99	96	[66]
$\text{Fe}_3\text{O}_4@\text{NC}@\text{Pt}$	Hydrazine hydrate	70	4 h	99	100	[67]
$\text{Rh}@\text{Fe}_3\text{O}_4$	THDB	60	5 min	> 99	100	[70]
$\text{Pd}@\gamma\text{-Fe}_2\text{O}_3$	Pressurized H_2	10	240 min	> 99	74	[68]
		20	80 min	> 99	97	[68]
		30	80 min	> 99	97	[68]
$\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{polysalophen-Pd(II)}$	NaBH_4	80	90 min	76	96	[69]
$\text{Fe}_3\text{O}_4@\text{CS-AgNi}$	NaBH_4	20	1 h	100	100	[72]
CuFe_2O_4	NaBH_4	Reflux of $\text{H}_2\text{O}/\text{EtOH}$	1 min	91		[73]

hydrothermal conditions. The carbon layer was subsequently doped with ethylenediamine whereafter the Pt was precipitated onto its surface. The catalyst was then utilized in the reduction of 23 different nitroarenes in the presence of hydrazine hydrate showing good catalytic activity, chemical selectivity to a wide range of substrates. The catalyst also proved great recyclability in 10 consecutive runs without loss in activity. [67]

Pd has also shown promise in reduction of nitroarenes when immobilized on magnetite. Hajdu et al. reported a new technique of maghemite synthesis by utilizing sonochemical treatment of Fe(II) in polyethylene glycol followed by combustion to give MNPs of 22 nm. The Pd was then reduced within the hot spots of the iron NPs by acoustic cavitation resulting in catalytically active Pd sites on the maghemite surface. The catalyst was evaluated for nitrobenzene reduction at 273 K, 293 K and 303 K achieving conversion of > 99% at each temperature. High selectivity's of 96.7% and 97% were achieved at 293 K and 303 K, respectively, while it drastically lowered to 73.8% for 283 K. The lowered selectivity was ascribed to the intermediate nitrobenzene not being transformed to aniline. The catalyst was easily removed from the reaction mixture but showed a drastic decrease in the conversion during recyclability studies dropping from 93% in run 2 to 36% achieved during run 4. The author ascribed this drastic drop to the lack of a catalyst regeneration step between consecutive runs. [68] Other magnetic Pd catalysts include $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{polyalophen-Pd(II)}$ which incorporated the Pd(II) complex onto the magnetite surface to achieve 76% conversion of 4-nitrophenol (4-NP) with 96% selectivity for 4-aminophenol (4-AP). The magnetic Pd-complex was also investigated for the reduction of other nitro benzenes such as nitrobenzene, 1,3-dinitrobenzene and 4-methyl-1-nitrobenzene that achieved yields of 96%, 98% and 90%, respectively. [69]

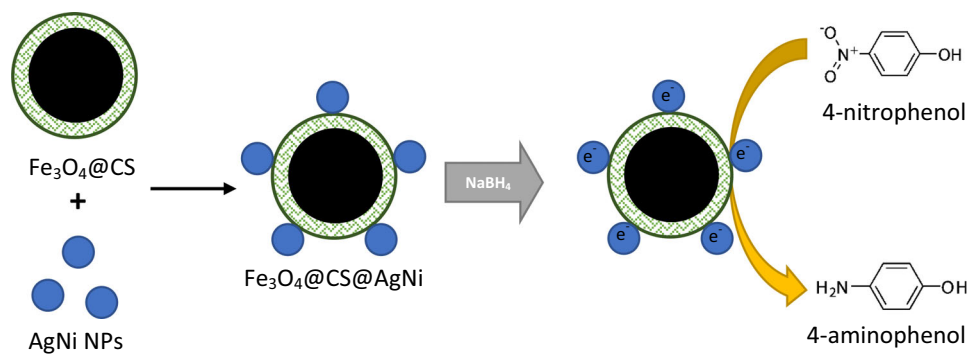
Shaikh et al. reported the use of simple impregnation method to immobilize Rh on magnetite as reusable catalyst in nitroarene reduction. The catalyst proves very efficient in the reduction of a range of nitroarenes in the presence of tetrahydroxydiboron (THDB) and was able to convert > 99% 4-NP–4-AP within only 5 min with 100% selectivity. This study was the first report of THDB used as a hydrogen source during nitroarene reduction. This catalyst was

also determined stable as it was easily removed after conversion and reused up to 5 consecutive runs without loss in activity. ICP-OES analysis showed that no Rh leaching occurred while TEM proved no surface deformation or aggregation occurred during consecutive runs. The sub-nanoregion Rh nanoparticles deposited on magnetite used in the presence of THDB thus exhibit the unbeatable results for the reduction of 4-NP. [70]

Chen et al. reported single step prepared Ag/ Fe_3O_4 NPs as a simple but facile synthesis consisting of spontaneous oxidation–reduction/co-precipitation. This one-pot reaction resulted in Ag MNPs of approximately 20 nm. The morphology and composition of these Ag MNPs could be adjusted by tailoring the reaction conditions which in turn affected the catalyst efficacy. These NPs were tested as catalysts in 4-NP reduction in the presence of NaBH_4 and could easily be retrieved after conversion was achieved. The reduction reaction was altered by changing the pH, temperature, reaction time, and catalyst loading. The catalyst proves to achieve high conversion at room temperature with a rate constant of 0.0196 s^{-1} . The catalyst could easily be recycled making it ideal for industrial use. The catalyst also showed promise in reduction of several other nitroarenes [71]. Ag has also been utilized in bimetallic NPs anchored on core shell magnetite/chitosan (CS) supports and the synthesis shown in Fig. 3. The $\text{Fe}_3\text{O}_4@\text{CS-AgNi}$ catalyst was evaluated for the reduction of various nitroarenes in the presence of NaBH_4 and showed 100% conversion of 4-NP achieving 100% selectivity. Its reusability was investigated in the reduction of nitro benzene and showed no significant loss in activity for up to 7 runs. [72]

The incorporation of more affordable Ni catalysts allows for further decrease in the production cost. Thus, a range of transition metals has been utilized on the surface of the MNPs in the attempt to produce efficient, affordable and recyclable catalysts for conversion of this pollutant. Zeynizadeh et al. reported the use of $\text{NiFe}_2\text{O}_4@\text{Cu}$ catalyst for the reduction of nitroarenes to arylamines. The NiFe_2O_4 core was synthesized by co-precipitation of Ni and Fe(II) under basic conditions. This core was then coated by reducing the Cu ions onto its surface resulting in NPs ranging between 10 and 40 nm. The catalyst was then evaluated for the reduction of a variety of 22

Figure 3 Synthesis of $\text{Fe}_3\text{O}_4@\text{Chitosan}(\text{Cs})@\text{AgNi}$ NPs and its application in 4-NP reduction to 4-AP in the presence of NaBH_4 . [72].



nitroarenes in the presence of NaBH_4 . They prove to achieve high yields of up to 91% within 1 min under mild conditions and easily separated by a magnet. This catalyst was reused for 7 consecutive runs without much loss in activity. The catalyst is promising as it is easy to synthesize, proved efficient, stable over multiple runs and easy to separate and recycle. [73] Cu has also been incorporated into the Fe NP structure through facile hydrothermal synthesis described by Feng et al. These NPs had an average diameter of 160 nm. The catalyst was tested for the reduction of both 4-NP and monitored only by UV–Vis where it proved significant decrease in the 4-NP and formation of the 4-AP within 40 s of introducing the catalyst. [74] Further kinetic studies determined the reduction rate constant as $1.2 \times 10^{-1} \text{ s}^{-1}$ which is impressive when compared to other nanocatalysts such as $1.1 \times 10^{-2} \text{ s}^{-1}$ achieved by more expensive Au- Fe_3O_4 dumbbell-like catalyst. [75]

Dye degradation

Dyes commonly used in the textile industry such as methylene blue (MB), methylene orange (MO) and Rhodamine B (RhB) are a big threat to our environment and health as they can be toxic with some having mutagenic and carcinogenic health impacts. These dyes are generally hard to remove due to their chemical and biological stability. [76] Fe_3O_4 nanoparticles synthesized by various methods have proven successful in degradation of organic compounds such as RhB [77], Orange G (OG) [78] and Basic Violet [79]. Although these NPs show great promise in these reactions, more research has been done to improve the catalyst by modification with organic supports and immobilization of other metal catalysts onto its surface. Organic supports include laboratory-synthesized carbon and silica supports as

well as recycled materials retrieved from everyday waste. The synthesized supports include well-known carbon and silica supports such as activated carbon (AC) [80], montmorillonite (MMT) [81], mesoporous carbon [82] and mesoporous silica [83] which can all function as additional stabilizers and absorbents on the Fe_3O_4 surface. Other modification methods include addition of metal catalysts onto the surface of the MNPs that may induce charge separation and crystal defects which in time increases the electron movement or extend recombination rates. [84]

The use of MNPs modified with other metal oxides in the degradation of these dyes have been well reported. Oxides such as CuO, ZnO, NiO, and TiO_2 are highly porous, able to absorb light and have unique electronic structures. [85–88] Combining these metal oxides with Fe_3O_4 allows for easy separation and recycling of the catalyst from natural water sources. Atla et al. prove that ZnO-coated MNPs can be utilized in degradation of MB toxins in wastewater. The paper focused on three different core–shell $\text{Fe}_3\text{O}_4/\text{ZnO}$ NPs: $\text{Fe}_3\text{O}_4/\text{ZnO}$, $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{ZnO}$ and $\text{Fe}_3\text{O}_4/\text{SiO}_2\text{-APTES}/\text{ZnO}$ successfully synthesized by co-precipitation and solvothermal methods. The photodegradation of MB was done under sunlight irradiation and showed a drastic increase in the photoactivity of the silica containing NPs due to the synergistic effect of the silica adsorption and the ZnO catalyzing the MB. $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{ZnO}$ was able to achieve 100% degradation of MB within 60 min. The three catalysts were recycled up to four times and showed no significant decrease in the activity, indicating that the catalyst is stable and efficient in magnetic separable catalysis. [89]

Highly stable $\text{Fe}_3\text{O}_4/\text{Ni}$ NPs were synthesized via a green biosynthesis method utilizing extracts of *Euphorbia maculata* aerial parts as a cheap environmentally safe and rapid alternative to chemical

methods. These NPs were relatively small at 30 nm and consist of alcohol stabilizing groups on the surface. The photocatalytic activity of various dye pollutants were tested such as Congo red (CR), MB and RhB under UV irradiation. These NPs achieved good activity with maximum dye removal of 89% CR within 60 min. The magnetic Ni NPs did, however, show lower activity than the CuO NPs synthesized in the same manner. They did, however, show excellent recyclability up to four runs with no significant loss in activity indicating that the NPs have excellent photocatalytic stability. [90]

Yolk shell $\text{Fe}_3\text{O}_4/\text{void}/\text{CdS}$ NPs were successfully synthesized via a one pot coating-etching process with $\text{Fe}_3\text{O}_4/\text{SiO}_2$ as a core and utilized in the photo-Fenton degradation of MB in the presence of H_2O_2 . This process coats the $\text{Fe}_3\text{O}_4/\text{SiO}_2$ NPs with a CdS shell while simultaneously etching away the inner SiO_2 shell to achieve a void between the Fe_3O_4 core and the CdS shell. These Yolk shell NPs were monodispersed with a total size of 200 nm and shell thickness of 15 nm. The catalyst showed good activity toward degradation of the MB under UV irradiation. The study proved that the unique structure along with the synergistic effect between the Fe_3O_4 and CdS greatly enhanced the activity of these NPs. This catalyst was also compared to the $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{CdS}$ NPs which showed much lower decomposing rates which indicated that the SiO_2 layer somehow isolates electron movement between the CdS shell and the Fe_3O_4 core. This article also reported the use of the TiO_2 and CeO_2 analogues which achieved similar efficiency. Generalizing that the yolk-shaped $\text{Fe}_3\text{O}_4/\text{void}/\text{semiconductor}$ NPs are a great alternative to designing robust photo-Fenton catalysts. Although this article mentioned the beneficial and easy removal of the MNPs, there was no report of recycling studies being performed. [91]

TiO_2 has received a lot of attention in the photocatalytic degradation of pollutants due to its long-term stability against photo- and chemical corrosion, strong oxidizing capability, biological and chemical inertness while being cost effective. [92–94] The first report of such a catalyst utilizes the sol-gel method to coat both colloidal and nanomagnetite with TiO_2 . This study used a sucrose solution and monitored the CO_2 formation as a model reaction to determine the rate of mineralization. The synthesized $\text{Fe}_3\text{O}_4/\text{TiO}_2$ NPs showed lowered activity compared to single-phase TiO_2 due to unfavored heterojunction between

the TiO_2 and magnetite. The catalyst also suffered from a degree of photo dissolution indicating decreased stability and making it unfit for such applications. [95] Similar catalysts have also been reported for the degradation of RhB. The study focused on $\text{Fe}_3\text{O}_4/\text{TiO}_2$ NPs prepared via a poly(styrene-acrylic acid) (PSA) template method by first synthesizing the monodispersed PSA spheres whereafter the Fe(III) ions were introduced and reduced into these spheres followed by absorption of TBOT onto the shell of the composite. The PSA core was then dissolved and removed by THF. The $\text{Fe}_3\text{O}_4/\text{Ti}(\text{OH})_x$ was finally converted to $\text{Fe}_3\text{O}_4/\text{TiO}_2$ via the solvothermal method. This method resulted in hollow spherical structure of 400 nm with an $\text{Fe}_3\text{O}_4/\text{TiO}_2$ shell of 50 nm wall thickness. These composites exhibited good photocatalytic degradation of RhB under UV irradiation. [96]

As Cu is an inexpensive and environmentally safe metal well known for its catalytic efficiency, multiple reports have focused on its application in water treatment. $\text{Fe}_3\text{O}_4/\text{C}/\text{Cu}_2\text{O}$ bean-like core-shell NPs have been successfully synthesized and tested in the degradation of various dyes. The synthesis utilizes the self-assembly approach as it is low cost and environmentally friendly resulting in NPs of 420 nm and a shell thickness of 5–10 nm with the carbon acting as a linker between the Fe and Cu layers. The catalyst shows powerful activity for photocatalysis of RhB, MO, and Alizarin red (AR) under visible light irradiation compared to commercially available Cu_2O NPs achieving near 100% decomposition of MO in 180 min. [97] Other studies reported $\text{Fe}_3\text{O}_4/\text{Cu}_2\text{O}$ NPs synthesized at different $\text{Fe}_3\text{O}_4:\text{Cu}_2\text{O}$ ratios and found the best catalyst to be a 6:4 ratio which achieved a 90% degradation of MO after 90 min irradiation time. [98] As both these NPs are relatively large with small available reaction area, $\text{Fe}_3\text{O}_4/\text{Cu}_2\text{O}/\text{Cu}$ porous NPs are seen as the superior system. The study utilized Fe_3O_4 NPs stabilized by L-cysteine and coated it with Cu using thermal decomposition methods. This method resulted in nanosheets that accumulated together to form a pinecone-like structure with average diameter of 100 nm. This unique structure allows for a porous structure that is able of improving the electrochemical and physiochemical properties of the catalyst. This porous structure allowed for improved photocatalytic degradation of MO of 96% within only 20 min irradiation time while obtaining the excellent

recyclability of up to 5 cycles. [99] Zhao et al. took the Cu MNPs further by introducing Ag as an additional metal present on the surface. The article reported $\text{CuFe}_2\text{O}_4/\text{AgBr}$ NPs of different $\text{CuFe}_3\text{O}_4:\text{AgBr}$ ratios synthesized by facile sol-gel and hydrothermal methods. The introduction of the AgBr to the NPs in this study increased the photocatalytic capability by increasing the NPs efficiency in charge transport. This NPs were tested in the degradation of both MO and tetracycline hydrochloride (TC) over 160 min achieving 91.1% and 89.1% degradation, respectively. [100] All these Cu NPs were tested and proven effective in the recycling test due to their magnetic character.

Recent reports of various Au-coated SPION NPs have acknowledged further advancement in the field of wastewater treatment as they prove efficient in both the reduction of MB in the presence of NaBH_4 as well as the efficient absorption and removal thereof in the absence of a reducing agent as seen in Fig. 4.

This study investigated 18 different Au/ Fe_3O_4 nanosystems consisting of different phosphine stabilizers, Au loading and reducing agents employed. 1,3,5-triaza-7-phosphaadamantane (PTA) and triphenylphosphine (PPh_3) were employed as stabilizers and prove sufficient in the long-term degradation of MB, up to 6 months, while the unmodified catalyst was active in reduction of MB but quickly returned to its original oxidized form with removal of the catalyst. The study also states that using sodium citrate as a reducing agent rather than NaBH_4 drastically promotes the catalyst's reducing capability. [101] Although the reduction of these toxic dyes in wastewater is important, it does not solve the long-

term problem faced with concern to dye pollution as the degraded form can still accumulate and oxidize back to MB in the presence of O_2 over time. [96] With further investigation, the ideal solution was achieved by this study as it enables absorption and magnetic retrieval of this dye from water source achieving maximum absorption of up to 95%. This is of great environmental and economic interest as it allows for both the efficient removal of the toxin but also the decrease in reducing agents and solvents required for degradation of these compound and allows for the possibility in dye recycling. [101]

Organic pollutant absorption

As discussed in Sect. "Dye degradation," organic pollutants can result in great health risks in humans and nature as they are not easily removed with traditional water treatment methods and can accumulate over time. These compounds include polycyclic aromatic hydrocarbons (PAHs), pharmaceuticals, pesticides, industrial used dyes and commercially used oil. [39, 102] Magnetite has a high surface-to-volume ratio, strong absorption capability and fast kinetics and allows for easy magnetic separation making it ideal for removal of unwanted organic matter. [48] Furthermore, these nanoparticles can easily be regenerated with minimum secondary waste. [103–105] The surface of MNPs has thus been extensively modified with absorbent material such as graphene [103], AC [106], polymers [107] silica [108] and micelles [109] in the pursuit to successfully improve SPIONs absorption capability while maintaining its magnetic capability and recyclability.

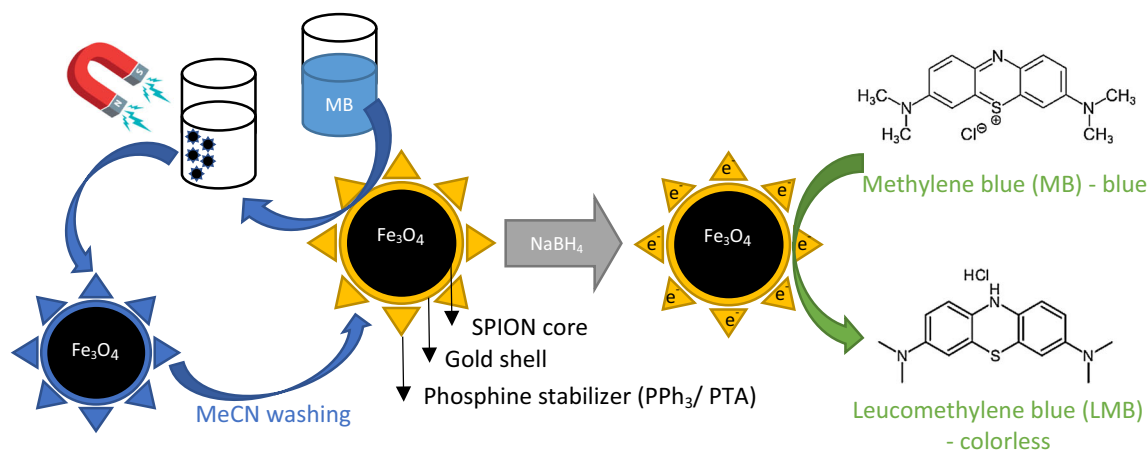


Figure 4 Use of gold-coated SPIONs in both reduction and extraction of MB. [101].

Moringa oleifera Lam. seed husks (MOM) Fe₃O₄ showed absorption of 94% of various pharmaceuticals within 720 min. [49] Fe₃O₄@AC has been utilized in absorption of > 99% of pharmaceuticals within 6 min and reusable up to 5 runs without any loss in activity. [50] Silica based MNPs has also been reported by Peralta et al. as it absorbed 80% of pharmaceuticals within 200 min. [51] Coating magnetite with red mud also showed great promise for removal of a range of antibiotics such as erythromycin (ERY), sulfamethoxazole (SMX) ciproflaxin (CIPRO), clarithromycin (CLAR), oxytetracycline (OXY) and doxycycline (DOXY). [52] The use of additional metal catalysts on the surface of these SPIONs for absorption of such pollutants is very limited to date but proves to be a promising field of research. The results of these absorption studies are summarized in Table 2.

Caravaca et al. reported on the use of Fe₃O₄@Ag in the absorption of amoxilin (AMX) from wastewater. This study presented a simple novel procedure achieving 100% adsorption of AMX within 5 min. This adsorbent is thus advantageous as it is much faster and easily removable compared to previous adsorbents studied. The MNPs proved sufficient and stable for a wide range of pHs and could successfully be regenerated at a pH of 1 and reused 3 times with no significant loss in its absorption capability. The catalyst was also deemed sufficient at low concentrations making it suitable in the removal of these trace pollutants from natural water sources. [53]

The small (16–27 nm) easy to synthesize Au-coated SPIONs reported by Lukhele et al. are thus a great alternative adsorbent to investigate as they allow for much larger surface-to-volume ratio. These NPs can also be altered and used as catalyst in degrading of the dye when needed and prove to be recyclable up to 5 consecutive runs with negligible loss in absorption capability. This is of great environmental and economic interest as it allows for both the efficient removal of the toxin but also the decrease in reducing agents and solvents required for degradation of these compound. [101]

Other metal catalysts utilized as toxic dye adsorbents on a magnetic surface include MgO. The core-shell Fe/MgO NPs were synthesized via a facile precipitation-calcination method. The iron NPs were prepared by aqueous-phase reduction using Fe(III) and KBH₄. This was followed by coating with TEOS and subsequent addition and reduction of the Mg(II) ions onto its surface to give the MgO shell. These NPs were then calcinated at 400 °C and resulted in core shell NPs with a core diameter of 55 nm and shell thickness of 12 nm. These NPs were tested in the adsorption of MO from wastewater. These NPs prove to be extremely efficient in MO adsorption with a maximum adsorption capacity of 6948 mg/g. The Fe₃O₄@SiO₂@MgO NPs also resulted in some mineralization of the MO. The magnetic MgO NPs further prove the capability of adsorbing Pb and MO simultaneously with the Pd further promoting the MO adsorption. [110] These magnetic MgO NPs thus

Table 2 Comparison of MNPs used in the absorption and removal of organic water pollutants

Adsorbent	Immobilization method	NP Size (shell thickness)	Sorption capacity (mg/g)/sorption efficiency (%)*				References
			MB	MO	AMX	Diesel oil	
Fe ₃ O ₄ /Au@P P = PPh ₃ or PTA	Impregnation	16–27 nm	(95%)*				[61]
Fe ₃ O ₄ @SiO ₂ @MgO	Coating	55 nm + (12 nm)	6948				[110]
Fe ₃ O ₄ @Ag	Impregnation	12 nm	(100%)*				[53]
Fe ₃ O ₄ @Cu@PS & Fe ₃ O ₄ @Ni@PS	Impregnation → in situ polymerization	15–20 nm	6400				[39]
Fe ₃ O ₄ @PS	Hydrothermal → emulsion polymerization	200–300 nm	3000				[105]

*Sorption efficiency was reported in % and shown in brackets

show great promise to remove these pollutants from environmental sources.

Other pollutants investigated include oil spills that have often caused great environmental damage. For this study the authors bridged the gap between polymer catalysis and synthesis of polymer stabilized nanoparticles by introducing metals capable of polymerization on the SPION surface. [39] As polymers have been widely used in both the stabilization and an absorbent on the SPIONs surface, this is of great interest in decreasing the production cost associated with polymer-coated NPs. Cu- and Ni-coated SPIONs were thus successfully synthesized by precipitation methods yielding relatively small NPs of 15–20 nm. Using these NPs as catalyst in coordination polymerization reaction of styrene in the presence of modified methylaluminoxane (MMAO) resulted in the desired magnetic polymer capable of oil absorption from the water surface (Fig. 5). As this study focused on a variety of Ni- and Cu-coated SPIONs as catalysts it yielded a diverse group of absorbents that differ in polymer chain length, metals involved, polymer density on the surface and metal-to-polymer ratios to find the optimum combination for this application. These magnetic polymers could be successfully applied to the simulated oil spills and prove sufficient in the selective absorption of oil from

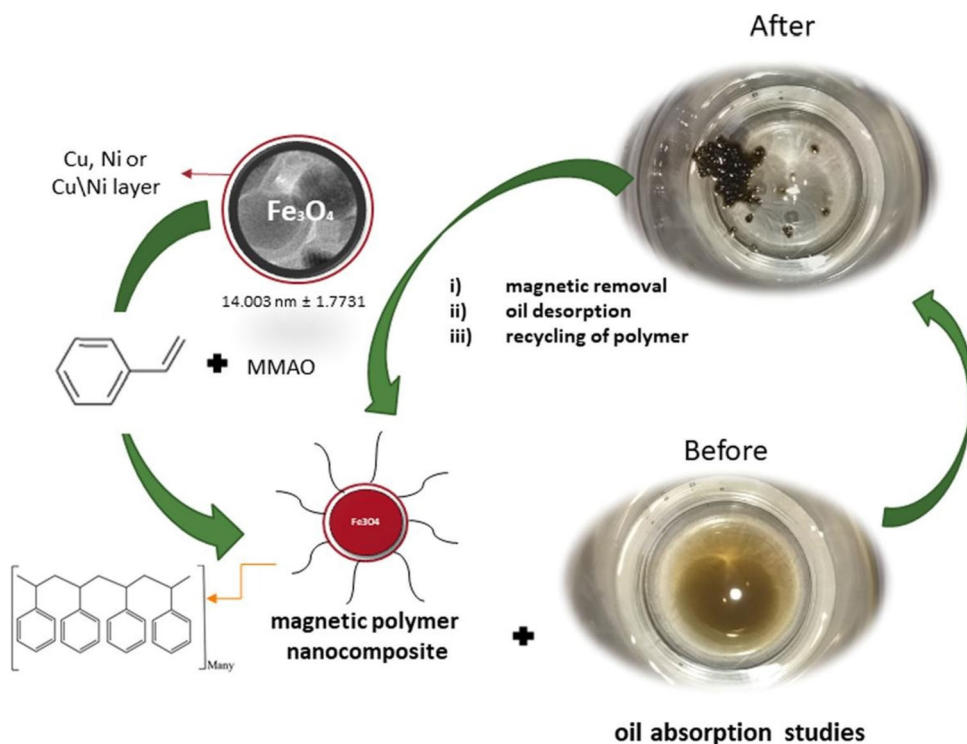
water sources with sorption capacities (SC) of up to 6.4 its own mass. This shows a large improvement compared to the $\text{Fe}_3\text{O}_4/\text{PS}$ previously reported to reach a maximum SC of 3. [111] The improved SC was ascribed to the absorbents smaller size resulting in a higher surface-to-volume ratio as well as the short polymer chain length obtained during catalysis which allowed for maximum oil penetration. These absorbents could successfully be isolated from the absorbed oil by ethanol washing and used up to 5 consecutive runs with slight decrease in its absorption capability. [39]

Inorganic pollutant removal

Toxic element absorption

Other pollutants that are a great threat for our health and food security include heavy metals that are released through metallurgy, mining, chemical plants, metal refineries, agriculture and household wastewater. These polluting metals include Pb, Hg, Mo, Cr, Zn, As, Se, etc., which can be a severe health threat as it can lead to kidney failure, central nervous damage, cancer and lung problems among others. [112, 113] Magnetite has received attention in separation of these toxic metals due to their ease of

Figure 5 Ni- and Cu-impregnated Fe_3O_4 used to synthesize magnetic polymers via coordination polymerization, which in turn allows for the successful removal of diesel oil from the water surface. Reprinted from Ref. [39] with permission from Elsevier.



separation and recyclability. Some core–shell magnetic materials evaluated include the iron/iron oxide NPs encapsulated in organic materials such as polyethyleneimine [114], polyrhodanine [115], oleate [116], polyethylene glycol [117], chitosan [118] and humic acid [119]. Porous materials have also been utilized in the coating of MNPs. Fe₃O₄/GO [120], Fe₃O₄/carbon nanotubes (CNTs) [121] and Fe₃O₄/carboxylic multi-walled CNTs [122] are some of the magnetic porous structures that have proven efficient in trapping these hazardous metals. Although the use of MNPs for the removal of hazardous metals has received a lot of attention and show great promise in capture and absorption of metal contaminants, little research has been done on the incorporation of additional metal catalyst on the magnetic surface to try and improve its capability of absorption. The results of these absorption studies are shown in Table 3.

One of the approaches published incorporates the use of MnO into the structure of magnetite to improve its absorption efficiency. The first of which is coating the magnetite with amorphous MnO₂ via a facile hydrothermal method. This resulted in a 3D flower-like structure being observed. The TEM results showed aggregation of the small NPs with an average size of 60 nm while DLS measurements indicated an average overall size of 218 nm due to the aggregation observed. The Fe₃O₄/MnO₂ NPs were evaluated in the absorption and removal of Cu(II), Pb(II), Zn(II) and Cd(II) where it proved to be relatively fast and efficient. The efficiency was, however, drastically lowered by hydrochemical conditions

such as low pH, the presence of Ca(II) ions and increased ionic strength. Cd(II) absorption was further investigated and showed a maximum absorption capacity of 53.2 mg/g and very good recyclability of up to 5 runs with little loss in the activity but did, however, show some structural damage that occurred by these processes. [123] Another approach reported by Kumar et al. utilized Fe₃O₄/Mn and GO-coated Fe₃O₄/Mn in the absorption and removal of Pb(II), As(III) and As(V). These NPs were synthesized by co-precipitation techniques, and the average particle size calculated from XRD as 11 nm and 6 nm, respectively. The latter are situated on the surface of graphene flakes. The Fe₃O₄/Mn generated proved to be much better in absorption of these heavy metals compared to the core–shell structures due to its stabilized small size. The Fe₃O₄/Mn/GO composites had even better absorption capabilities achieving 673, 146 and 207 mg/g for Pb(II), As (III) and As(V), respectively. [93] These NPs were additionally compared to various commercial absorbents including different compositions of GO, EDTA, and chitosan hybrids as well as naked magnetite and Fe–Mn composites which prove superior with only few layered GO being more efficient achieving capacities of up to 842 at RT. [110] The Fe₃O₄/Mn/GO composites were, however, able to benefit from the magnetic capability of the NPs for easy removal and excellent recyclability, even after 5 runs. [124]

The Ni-incorporated version of these flower-shaped Fe₃O₄/MnO₂ NPs was reported by Xiang et al. The Ni/Fe₃O₄ NP were synthesized via co-precipitation methods in the presence of PVP. This

Table 3 Comparison of MNPs used in the absorption and removal of inorganic water pollutants

Absorbent	Immobilization method	NP size (shell thickness)	Sorption capacity (mg/g)/sorption efficiency (%)*					References
			Pb(II)	Cu(II)	Cd(II)	Zn(II)	As(III)/ (V)	
Fe ₃ O ₄ @SiO ₂ @MgO	Coating	55 nm + (12 nm)	1477					[110]
Fe ₃ O ₄ @MnO	Impregnation	60 nm	(95%)*	(95%)*	53	(80%)*		[123]
					(95%)*			
Fe ₃ O ₄ @Mn	Co-precipitation	11 nm	488				97/ 136	[93]
Fe ₃ O ₄ @Mn@GO	Co-precipitation	6 nm	673				146/ 207	[93]
Few layered GO			842					[110]
NiFe ₃ O ₄ /MnO ₂	Co-precipitation → grafting	400–500 nm	86					[125]
			(80%)*					

*Sorption efficiency was reported in % and shown in brackets

PVP could then function as grafting sites for immobilization of MnO_2 on the magnetic surface to successfully synthesize flower-like $\text{NiFe}_3\text{O}_4/\text{MnO}_2$ NPs of 70–100 nm in size. These NPs further cluster to microspheres with an average diameter of 400–500 nm. These NPs proved to successfully remove Pb(II) from water sources at a maximum adsorption capacity of 86 mg/g. This study also proves sufficient removal of Pb(II) in the presence of Mg(II), Cu(II), and Zn(II). [125]

The core-shell Fe/MgO NPs discussed in Sect. “Reduction of nitroarenes” also showed further promise in Pb adsorption with a very high maximum adsorption capacity of 1477 mg/g. [110] This is slightly lower than the non-magnetic flower-like MgO NPs reported by [126] as 1980 mg/g but does, however, benefit from the magnetic characteristics of the magnetic core by ease of removal. The paper does, however, report the formation of Fe/MgO-Pb composites. This is promising as these Pb incorporated composites can improve adsorption capacity of MO but decreases its reusability in Pb adsorption.

Conclusions

With an increase of harmful organic and inorganic pollutants in our water sources, various methods of water purification have been investigated. NPs, specifically the use of MNPs, have been one of the greatest advancements in this field as it allows for easy separation, quick absorption and/or catalytic degradation of the pollutants. Surface modification of SPIONs has been greatly studied to improve its absorption capability through addition of various ligands. This is, however, not sufficient and resulted in research to shift to the addition of other metal catalysts onto its surface. This has led to excellent progress in wastewater treatment as the additional metal can be carefully selected for its respective application.

Studies have focused on new and intuitive immobilization methods to produce robust absorbents and catalysts that can be successfully recycled. Many of the immobilization methods reported prove great advancements in the stabilization of the NPs through use of various ligands and/or surfactants to inhibit agglomeration from occurring. The use of ligands and surfactants also allows for better electron transfer in the catalytic or absorption capability. The metal

catalyst on the surface allows for increased activity while still utilizing the magnetic advantages of the magnetic core. Many of the NPs reviewed within this article are, however, large limiting its surface-to-volume ratio. Future synthesis should thus focus on producing smaller NPs to increase the NP contact area.

The successful immobilization of metal catalysts on the surface of SPIONs has resulted in a diverse set of NPs which showed very good activity in the degradation of organic pollutants such as pharmaceuticals, nitroarenes and synthetic dyes. Pharmaceuticals easily undergone photo-catalytic degradation by various $\text{Bi}_2\text{WO}_6/\text{SPION}$ composites, but little studies were done in testing of other metal catalysts in this application. Reduction of nitroarenes were, however, well reported on as it used a diverse range of metal catalysts on the SPION surface; however, the focus was toward expensive metals while singular reports showed great promise for the use of more affordable metals. Dye degradation by these magnetic catalysts was well reported on and showed significant improvement in the catalytic activity and recyclability of these magnetic catalysts.

As many of these pollutants are still harmful in their degraded form or capable of returning to their original toxic form the ideal will be to completely remove them from wastewater. MNPs with carefully selected metal catalysts on its surface can coordinate and remove the toxin along with the absorbent. This has resulted in a new field of possibilities that has potential to overwhelm the wastewater treatment sector. This has the advantage of reducing the chemicals used in these treatment processes while benefiting from a reusable and easy separable absorbent. In both the catalytic degradation and absorption studies reported for wastewater treatment the authors lack the use of natural water samples consisting of extremely low pollutant concentrations and a mixture of other compounds and minerals. There have also been very little reports of the possible toxic effects these NPs might have when introduced to our water sources.

In conclusion, metal catalysts immobilized on SPIONs have open many possibilities as a non-invasive wastewater treatment solution. The excellent results achieved by these NPs show great promise for the MNPs to be incorporated in water treatment facilities as they are easy to recover and reuse. The risk of using these NPs should, however, first be

thoroughly studied in their possible toxicity effects to determine whether it will be suitable outside of a well-monitored laboratory setting.

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Declarations

Conflict of interest There are no conflicts to declare.

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