University Journal of Research
ISSN (Online) 2455-1724

Doped Iron Oxide Nanoparticles for Wastewater Treatment

Shweta Patel[a], **Ajay Kumar Gupta**[b*]

[a]*Ganpat University- Mehsana Urban Institute of Sciences, Kherva, Gujarat, India*
[b]*Ganpat University- Research & Development, Kherva, Gujarat, India*

Abstract

Nanotechnology has developed to the point where it is currently possible to manufacture, characterise, and specifically adjust the functional feat ures of nanoparticles for waste-water treatment. Multiple novel nanomaterials have been introduced recently to improve the performance and adsorption capacities of eliminating pollutants from waste-water. Nanocomposites made from Iron oxide nanoparticles (IONPs) consist of maghemite (γ-Fe2O3) and/or magnetite (Fe3O4) particles having average size between 1 to 100 nm. They possess exceptional optical, physico-chemical properties. The potential for quick magnetic recovery, simple chemical modification, recyclability, solar sensitivity, nontoxicity, and robust design of magnetic oxide nanocomposites encourages their usage in wastewater treatment. Magnetic oxide nanocomposites offer significant promise as new and innovative wastewater remediators, with significant environmental and financial benefits. However, the nexus between the magnetic and adsorption properties of superparamagnetic nanocomposite materials is what makes them desirable for commercial use. This review article describes various synthesis routes for the preparation of nanoparticles having unique properties for their application in waste-water treatment.

Keywords: *Magnetic nanoparticles; Surface Functionalization; Wastewater treatment, Iron oxide, Desalination.*

INTRODUCTION:

Although water covers more than 70% of the earth's surface, most of it cannot be consumed by humans. Only 2.5% of the world's total freshwater supply is found in freshwater lakes, rivers, and subterranean aquifers. Fresh water is unfortunately not only incredibly limited, but also very unevenly distributed. According to a comparison of water supply and consumption made by the United Nation, by the middle of this century, around 2 and 7 billion people would experience water scarcity.

Increasing amount of toxic metals, dyes and other contaminants in water stream is a serious challenge globally. Contamination of heavy metals can generally occur from industrial waste, municipal waste, agricultural waste, rainfall, soil erosion etc. Chemical contaminants, organic and inorganic particles, poisons, dyes, biological pollutants, and other dangerous substances are all found in water pollution. Heavy metals that are known to be present in waste water including chromium (Cr), lead (Pb), mercury (Hg), arsenic (As), zinc (Zn), copper (Cu), cadmium (Cd), nickel (Ni), and the platinum group of elements [1]. After consumption of contaminated water leads to accumulation of these heavy metals in skin, kidney and liver cancer and has adverse effects in human health [2]. Heavy metals are non-biodegradable which cannot be degraded by natural ways and causes harmful effect on human health and environment when contaminant level goes beyond permissible level. Low concentration of heavy metals in water stream can also be extremely harmful for the human health and entire eco system [3]. Some examples of heavy metals and their toxic effects in human and environment are given in table 1.

---

*Corresponding Author
E-mail address: director.research@ganpatuniversity.ac.in

Heavy metal	Source	Hazardous effect in environment	Toxic effects in human health	Maximum Permissible Limit(mg/lit)
Arsenic	Antifungal wood preservatives, pigments, coal	Soil and water pollution	Lung cancer, Kidney damage	0.01
Lead	Paint, pesticide, emulsion	Soil and water pollution	Kidney damage, cardiovascular disease	0.01
Chromium	Chemical industry, cement, pigments	Soil and water pollution	Reproductive problems, Lung cancer, Nausea, allergies	0.05
Mercury	Combustion of fossil fuels and other industrial release	Soil and water pollution	Major damage in brain and kidneys, vision or hearing loss, memory loss	0.006
Nickel	Chemical industry, forest fires	Soil and water pollution	Allergy, cardiovascular and kidney diseases	0.1
Cadmium	Welding, smelting	Soil and water pollution	Kidney damage	0.003
Copper	Electrical and metal manufacturing	Soil and water pollution	Gastrointestinal illness, abdominal and muscle pain, kidney failure	2

Table: 1 Toxic effects of Heavy metals in environment and human health

UNIQUE PROPERTIES OF NANOPARTICLES:

Nanocomposites made from Iron oxide nanoparticles (IONPs) consist of maghemite (γ-Fe2O3) and/or magnetite (Fe3O4) particles having average size between 1 to 100 nm. They possess exceptional optical, physical and chemical properties. Recent research examines the potential for valorisation of ferrous waste by-products from the metallurgical industry. It focuses on sources, types of ferrous compounds, circular economy methods for conversion into value-added products used in environmental remediation, and potential harmful effects on the environment and human health [4]. Their unique properties exist because of their high surface area and small size which is almost close to that of the atomic scale. To provide IONPs their unique characteristics for various types of industrial applications, the surfaces of IONPs can be changed with organic or inorganic materials, such as polymers, proteins, silica, metals, etc. [5]. These particles also have magnetic properties and due to this they have high potential in biomedical and other industrial applications. However, the magnetic properties of IONPs are affected by synthesis methods, iron salt ratios, chemical structure and composition etc. Other molecules of interest, such as medicines, proteins, toxins, dyes, etc., can bind to these IONPs. Due to their targeting ability, these IONPs can be generated in alternating magnetic fields for use in hyperthermia or can be directed to an organ, tissue, or tumour using an external magnetic field. Hence, The IONPs can be utilised for a broad range of other biomedical applications, including cellular therapy, medication delivery, tissue healing, magnetic resonance imaging (MRI), and more [6-7].

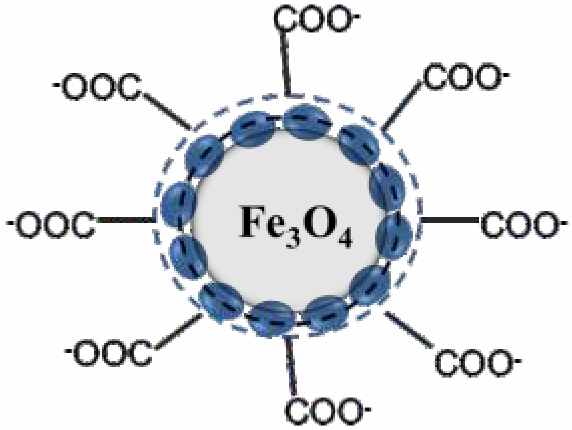

Figure 1: Negatively charged iron oxide nanoparticles

However, the IONPs sometimes suffer from poor superparamagnetism, high ferrimagnetism, reduced coercivity (Hc) and relative remnant magnetization (Mr/Ms), which makes them difficult to target them magnetically resulting in poor outcomes in disease management. To enhance the magnetic values of IONPs, there have been several attempts by doping of these particles with other metal ions such as copper, nickel, cobalt etc. The dopant behaviour of IONPs has been investigated by several researchers. Doping can have a significant improvement on the magnetic properties of the resulting nanoparticles because of the complex nature of the ferrimagnetism of magnetite [7].

Doping of IONPs with cobalt metal ions can be done to synthesize cobalt ferrite (CoFe2O4) nanoparticles with extremely high coercivity (Hc) and Ms/Mr values (Figure-2) [8]. By doping materials with various cobalt concentrations and stabilising them with a layer of citric acid, the magnetic characteristics can be changed. The average size of the pure iron oxide particles was 8 nm, while the cobalt ferrite showed an increase to 12 nm. However, it was discovered that citric acid stabilisation increased the particles' hydrodynamic diameter to about 100 nm (Figure 1). It was also reported by the authors that by substituting more than 10% of the total Fe atoms by Cobalt, a significant linear increase in Hc and Mr/Ms was obtained. Mössbauer spectroscopy further revealed the presence of Fe3+ predominantly in every sample. Instead of the more pronounced octahedral site-preference of bulk CoFe2O4, relative spectral regions of Mössbauer sub-spectra indicated a mostly random distribution of Co2+ ions. Studies on cell viability demonstrated that the Co-doped iron oxide nanoparticles are not more toxic than those that are made of pure iron oxide. Also the heating efficiency in cobalt doped IONPs were found to enhance to such a level that makes them suitable for magnetic hyperthermia and other biomedical applications [4]. In another study, Intra- and inter particle magnetism of cobalt-doped iron-oxide nanoparticles were examined by developing stable suspensions of CoxFe3-xO4 nanoparticles. It was demonstrated that by doping of 7%, 10%, and 12% cobalt into the IONPs gives similar superparamagnetic blocking temperatures, coercivities, and functional anisotropies, which indicates a significant impact of cobalt inclusion. The ferritin shell offered a continuous inter particle separation between systems, preventing exchange interactions from changing the local, atomic magnetism among nanoparticles, allowing for a clear comparison exposing the nature of the inter particle interactions. (i.e., nanoparticles from metal-to-metal interaction). According to the experiments, interconnections significantly affected the dynamical freezing of the magnetizations of the cobalt-doped nanoparticles (such as time-dependent magnetism), suggesting longer-range correlations among nanoparticles with Co doping [9].

The potential applications of pure and doped iron oxide and hydroxide nanoparticles, which can be prepared in various phases and composites to meet the specific requirements of different applications such as Mössbauer spectroscopy is an efficient technique to investigate the local structure and distribution of cations in these nanoparticles. The review focuses on the local structure transformation, spin dynamics, dipole-dipole interactions, and diffusion of iron oxide nanoparticles, based on the findings obtained using Mössbauer spectroscopy [10]. The porous structure, high porosity, and large surface area of electrospun nanofibers make them promising materials for waste-water applications. Some reviews discuss the properties of these nanofibers and how they can be modified to enhance their suitability for specific wastewater treatment and oil/water separation processes [11]. Kerroum et al prepared the zinc doped IONPs to comprehend the effect of different concentrations of zinc doping on the magnetic, structural and hyperthermia properties of the particles. This study, which used EDX data, demonstrated that the Zn and Fe are uniformly distributed across the entire volume of the IONPs for all the zinc substituted ferrites. The saturation magnetization values (Ms) increased with the amount of zinc doping up to x ~ 0.3, while for higher zinc doping (x ~ 0.5), the Ms decreased. The preference of Zn2+ ions to occupy the tetrahedral (A) sites was thought to be the cause of the increase in Ms, causing the Fe3+ ions to relocate to the octahedral (B) sites and displace the divalent Fe2+ ions [12]. Further evidence was shown by the results, which showed that Zn doping considerably enhances the magnetic and hyperthermia properties of IONPs. The effects of various hydrophilic nanomaterials, including mineral nanomaterials, metals oxide, two-dimensional transition, metal-organic framework, covalent organic frameworks and carbon-based nanomaterials are discussed. The influence of these nanoparticles on the surface and structural changes in the membrane, as well as the performance efficiency and antifouling resistance, are thoroughly examined [13].The intentional development of bimodal MRI and CT contrast agents based on nanocomplexes is illustrated by zinc doped ferrite nanoparticles with improved values of maximal saturation magnetization. Further boosting the effectiveness of magnetic hyperthermia was suggested by the authors using chain-like pre-aligned IONPs and those with high magnitude magnetic fields. The impact of Cu doping on iron oxide nanoparticles' relaxometric characteristics has been investigated. Cu core-doped IONPs (Cu-NP) were synthesized in a 10 min. one-pot synthesis at clinically applicable magnetic fields with the highest longitudinal relaxivity value ever recorded. With the help of targeted molecular imaging and angiography, this new nanomaterial proved that it is suitable for usage in vivo and can improve tumour diagnostics in animal models [14].

Apart from biomedical applications, large surface area of IONPs can be utilized to extract a range of ions from aqueous solutions. For example, Manganese doped IONPs were evaluated for the extraction of radionuclides from aqueous solutions such as ground water, human urine, river water and seawater [15]. Due to the photocatalytic efficiency of Copper (II), Iron (II), and Iron (III) Oxides and their Composite NPs, these materials can be utilized as heterogeneous Fenton catalysts for the removal of potentially harmful pollutants from wastewater as well as advantageous catalysts for the elimination of toxic organic dyes from textile waste-water [16]. For waste water treatment, the iron oxide nanoparticles with following purpose are most suitable.

1. Small size(500 nm)
2. High surface area
3. High magnetization value
4. Doping with other metal ions
5. Easy separation
6. Appropriate surface charge

SYNTHESIS OF NANOMATERIALS (DIFFERENT ROUTES OF SYNTHESIS)

Researchers have identified a number of techniques for producing magnetic iron oxides (MIONs), and some chosen works are given in Table 2. A comparison of the several ways to manufacture iron oxide nanoparticles revealed that 90% of nanoparticles are made by chemical processes, 8% through physical processes, and 2% through biological processes [16].

Table 2: Various methods for synthesis and contamination removal

Sr. No.	Functional Nanomaterials	Size	Synthesis method	Unique Properties	Effective removal	Ref.
1.	Superparamagnetic Fe_3O_4 / TiO_2 nanoparticles	50 nm	Co-precipitation	High Saturation magnetization, High surface area	As(V), As(III)	[17]
2.	Multi-walled carbon nanotube designed with Fe_3O_4 nanoparticles		Co-precipitation	Maximum adsorption capacity	Cu(II)	[18]
3.	EDTA modified Fe_3O_4 / Sawdust Carbon nanocomposites	10-20 nm	Biogenic green synthesis and co-precipitation	Small size, Surface derivatization	Methylene Blue and Brilliant Green	[19]
4.	Gelatin-conjugated hematite (α-Fe_2O_3) nanoparticles	4-6 nm	Co-precipitation	Small size, Maximum adsorption capacity	Lead	[20]
5.	Magnesium ferrite ($MgFe_2O_4$) nanoparticles		Sol-gel method	High adsorption capacity	Cr(VI)	[21]
6.	Fe_3O_4 functionalized multilayer graphene oxide		Co-precipitation	Photocatalytic degradation	Textile pollutants	[22]
7.	Magnetic $CoFe_2O_4/SiO_2/TiO_2$ nanoparticles	350 nm	Co-precipitation	Photocatalytic degradation	Degradation of 2,4-dinitrotoluene (2,4-DNT)	[23]
8.	Fe_3O_4 Nanoparticles	190 nm	Hydrothermal method	Maximum adsorption capacity	Hg(II)	[24]
9.	Clinoptilolite/starch/$CoFe_2O_4$ magnetic nanocomposite	50 nm	Co-precipitation	High surface area, Maximum adsorption capacity	Methylene blue, methyl violet, crystal violet (Cationic dyes)	[25]
10.	Carbon / Fe_3O_4 magnetic composites		Co-precipitation	Surface modification, Adsorption	Methylene blue	[26]
11.	Magnetic $MnFe_2O_4$ nanoparticles	5.1 nm	Co-precipitation	High saturation magnetization	Phosphate	[27]
12.	Polymer-brush functionalized magnetic nanoparticles	~ 80 nm	Thermal hydrolysis	Surface modification, Adsorption	Mercury	[28]

Sr. No.	Functional Nanomaterials	Size	Synthesis method	Unique Properties	Effective removal	Ref.
13.	Fe_3O_4 / cyclodextrin polymer nanocomposites	50 nm	Co-precipitation	Surface modification, Adsorption	Pb^{2+}, Cd^{2+}, Ni^{2+}	[29]
14.	Polypyrrole / Fe_3O_4 magnetic nanocomposite	10 nm	Co-precipitation	Surface modification, Adsorption	Fluoride	[30]
15.	α-Fe/ Fe_3O_4 nanocomposite		Hydrothermal method	Adsorption	Congo red dye	[31]
16.	Glycine-functionalized γ-Fe_2O_3 nanoparticles		Co-precipitation	Surface modification, Adsorption	Copper	[32]
17.	Thiol-functionalised silica-coated Fe_3O_4 nanoparticles	Pore 2.1 nm	Co-precipitation	Small size, Adsorption	Mercury	[33]
18.	Chitosan functionalised magnetic nanoparticles		Co-precipitation	Surface modification, Adsorption	Pb^{2+}	[34]
19.	Maghemite nanoparticles(45 nm)	45 nm	Co-precipitation	Adsorption	Congo red	[35]
20.	Polymer-modified magnetic nanoparticles	15-20 nm	Co-precipitation	Surface modification, Adsorption	Cd^{2+}, Zn^{2+}, Pb^{2+}, Cu^{2+}	[1]
21.	Surface modified magnetic Fe_3O_4 nanoparticles	20 nm	Sol-gel method	Surface modification, Adsorption	Uranyl ions	[36]
22.	Fe_3O_4 nanoparticles		Co-precipitation	Adsorption	3-methylindole	[37]
23.	Maghemite nanoparticles	~10 nm	Sol-gel method	Small size, Magnetic catalyst, Stability	Cr(VI)	[38]
24.	Humic acid coated magnetite nanoparticles	7-12 nm	Co-precipitation	Small size, Surface modification, Adsorption	Phosphate	[39]
25.	$La(OH)_3$/ Fe_3O_4 nanocomposites	150-250 nm	Co-precipitation & Hydrothermal method	Adsorption	Phosphate	[40]

Co-precipitation of metal oxides from a solution containing a base in an inert environment is a widely recognized and scalable technique among all identified ways of synthesis. The IONPs were synthesized and characterized, and the amount of degradation was evaluated using chemical oxygen demand (COD) determination. The results showed that the combination of UV light and IONPs was more effective in removing COD from synthetic petroleum wastewater than either treatment alone, with the photocatalytic degradation being 1.3-2.0 times faster, and following a pseudo-first-order kinetic model with rate constants ranging from 0.0133 to 0.0269 min−1. Therefore, the study concluded that the use of UV light in the presence of IONPs is a favorable and effective method for removing organic pollutants from petroleum refinery wastewater [41].

Fe_3O_4 /TiO_2 was synthesised to form a magnetically separable nanomaterial by simple co-precipitation method with varying Fe_3O_4 /TiO_2 percent. Fe_3O_4/TiO_2 nanoparticles have a surface area of up to 94.9 m^2/g. The pH of solution, duration of the reaction, the initial concentration, and the concentration of the adsorbent has all been studied as the main factors that affect adsorption efficiency [17]. EDTA modified magnetic sawdust carbon nanocomposites were synthesized using a green biogenic reduction and precipitation method having adsorption capacity of EDTA@Fe_3O_4/SC for MB and BG dyes was 227.3 mg/g and 285.7 mg/g, respectively [19]. Gelatin-conjugated hematite nanoparticles (HT NPs) synthesized by solid-state phase transformation in the presence of phosphate exhibit a significant Pb removal performance, with a high adsorption capacity of 169.49 mg/g [20].

Fe_3O_4 nanoclusters, prepared via hydrothermal method were designed with an organic molecule linker (dihydrolipoic acid, DHLA) to remove hazardous Hg(II) ions selectively [24]. Results of adsorption experiments showed that the synthesized magnetic nanocomposite clinoptilolite (CLT)/Starch/$CoFe_2O_4$ adsorbent has an excellent ability to adsorb cationic dyes such as methylene blue dye (MBD), methyl violet dye (MVD), and crystal violet dye (CVD) from water media after several consecutive cycles [25]. High crystallinity and strong magnetism (i.e. 26.27 emu/g) of $MnFe_2O_4$ were achieved at low temperatures having average particle size 5.1 nm [27].

The Hg^{2+} ion removal performance and efficiency of poly(2-aminoethyl methacrylate dithiocarbamate (MNPs-polyAEMA·DTC) were compared with its monolayer analogue, which was developed from the straight transformation of amino groups of (3-aminopropyl) triethoxysilane (APTES)-functionalized MNPs (MNPs-APTES) to DTC functional groups (MNPs-DTC) [28].

APPLICATION IN WASTEWATER TREATMENT:

Nanotechnology has developed to the point where it is currently possible to manufacture, characterise, and specifically adjust the functional features of nanoparticles for waste water treatment. For improving the effectiveness and adsorption capabilities of removing pollutants from wastewater, a variety of innovative nanomaterial adsorbents have been developed in recent years (Figure-3). Water scarcity is a major issue on a global scale. Local demand has surpassed conventional resources in many regions of the world. More efficient water use, lower distribution losses, and increased use of recycled water can all assist to reduce this issue, but desalination of seawater or brackish water is necessary if there is still a shortage. the methods of desalination currently in usage (such as evaporation and reverse osmosis system etc.) require extensive use of energy in terms of electric power or steam. The following categories provide a general classification of water desalination processes [38,39,44]:

(1) Thermal energy:

a) Evaporation e.g. thermal vapor compression, multi-effect distillation, solar distillation etc.

b) Crystallization e.g. freezing, hydrate formation and membrane distillation etc.

(2) Mechanical energy:

a) Evaporation e.g. Mechanical Vapor Compression (MVC)

b) Filtrations e.g. Reverse Osmosis (RO) and Forward Osmosis (FO) etc.

(3) Electric energy i.e. selective filtration e.g. Electrodialysis (ED)

(4) Chemical energy i.e. exchange e.g. Ionic Exchange (IE)

Most of these technologies have their own limitations, costly and difficult to apply in industrial waste-water stream. Nanotechnologies could be used in the water industry for waste water treatment, desalination, monitoring, and purification. This, in principle, prevents future water shortages to a significant extent. However, it is still a long way away from becoming a reality to believe that nanotechnology's "magic" will resolve every water issue. Desalination applications are still in the R&D stage due to these technologies' poor availability and high cost. None of them have yet achieved industrial scales. Employing techniques including membrane separation, chemical precipitation, electrolysis, adsorption, ion exchange and evaporation are some of the most effective ways to treat these effluents. Adsorption, which is extremely selective and beneficial for the removal of trace metal ions, is the most often used conventional method for the removal of contaminants [45]. Recently, smart adsorbent materials with higher porosity and surface area have been developed by the ball milling technology, which shortens the adsorption process and improves adsorption effectiveness [46]. Due to their cost-effectiveness and complexity of preparation, these adsorbents are only used in a limited number of applications.

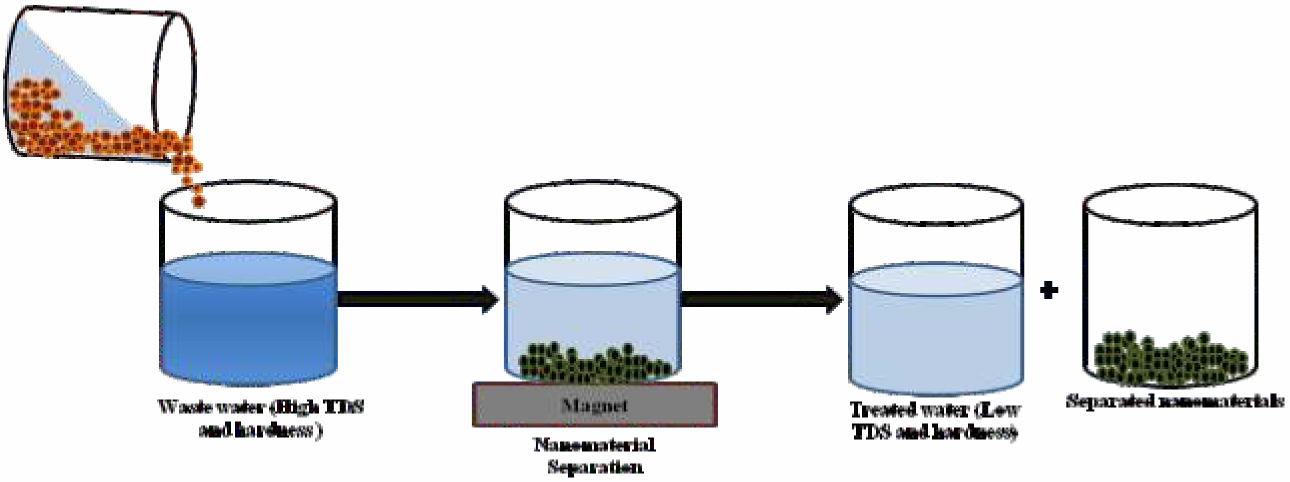

Figure 3: Application of Iron oxide nanoparticles in waste-water

The effectiveness and adsorption characteristics of removing pollutants from wastewater have been improved by the development of numerous innovative nanomaterial adsorbents. The dopant behaviour of IONPs has been explored by many researchers. Several academics have revealed on recent efforts to design intelligent magnetic oxide nanocomposites for wastewater treatment. However, the nexus between the magnetic and adsorption properties of superparamagnetic nanocomposite materials is what makes them desirable for commercial use. The potential for simple magnetic recovery, facile chemical modification, flexibility, solar responsiveness, nontoxicity, and versatility of magnetic oxide nanocomposites encourages their usage in wastewater treatment [47].

The maximum photo-electrochemical activity was found in the arrays of nanorod (Co_3O_4/TiO_2) that were synthesized in acid solution. Due to the heterojunction between Co_3O_4 and TiO_2, the Co_3O_4 exhibited a more exceptional photo-electrochemical performance in methylene blue and hydroquinone degradation [48]. The significant adsorption capacity of 175.43 mg/g was successfully accomplished at a temperature of 40 °C under optimum conditions. Due to their magnetic nature, magnetic magnesium ferrite ($MgFe_2O_4$) nanoparticles are simply recovered from the aqueous solution, making them economical and even after seven consecutive adsorption-desorption cycles, they still maintained an efficiency loss of less than 20% for the removal of Cr(VI) ions [21]. In less than 5 seconds, the magnetic separation process of the Fe_3O_4/reduced graphene oxide (Fe_3O_4/RGO) nanocomposites removed Cr(VI) with a 99.9% removal efficiency. Most importantly, after 10 cycles, the Cr(VI) adsorption rate can still remain as high as 98.13% and the single recycle quality of the nanocomposites can continue to be over 80% [49]. α-Fe_2O_3/ZnSe nanocomposite photocatalysts, was made under friendly conditions with the exception of some intricate post-treatment for the dye abatement procedure [50]. The photocatalytic degradation of 2,4-DNT was investigated using $CoFe_2O_4/SiO_2/TiO_2$ nanoparticles and studied on the effects of various experimental variables, including 2,4-DNT initiator concentration, pH value, and catalyst dosages on degradation efficiency [23].

CONCLUSION AND FUTURE PERSPECTIVES:

For the elimination of contaminants from wastewater, ground water, and surface water, magnetic nanoparticles, a rapidly expanding field with recently discovered and investigated methods, are of significant interest. Because the surface atoms on such tiny particles behave more like individual atoms, Magnetic nanoparticles can play a crucial role in the development of more efficient green catalysts. Magnetic nanoparticles with large surface area, strong magnetization, and ease of separation make them good candidates for wastewater application. Iron oxide nanoparticles in waste water treatment particularly in desalination applications i.e. reduction in TDS of the effluent have been either used as an electrolyte media or as a filtration system to achieve the desalination of the waste water. The nanomaterials made of iron oxides have shown excellent surface properties and efficiencies in both individual and composite forms. Ongoing research is focused on addressing more complicated issues related to water purification, and nanocomposites are showing promise in the removal of pollutants from water. Further developments in nanomaterial properties are expected to enhance their effectiveness in water separation and purification. Also, recent trends in additive manufacturing of advanced nanomaterials can offer opportunities for engineering of tailor-made materials for removal of specific pollutants. This would require additional analysis of how the nanoparticles and the intended contaminants interact with each other. Chemical or physical modification of these materials could further improve their effectiveness in water purification processes.

A significant number of new nanocatalyst are needed to be developed to eliminate variety of water pollutants that can be effectively eliminated by this photocatalytic method, including pathogens, viruses, and dangerous contaminants like pesticides, phenols, and azo dyes. Use of nanotechnologies in water recycling and purification presents a theoretically and potentially promising solution that may help in preventing future water shortages. Future research should focus on developing a low site area, high-efficiency, large-scale nanoparticles assisted treatment process for commercial use.

REFERENCES:

- F. Ge, M. M. Li, H. Ye, and B. X. Zhao, “Effective removal of heavy metal ions Cd^{2+}, Zn^{2+}, Pb^{2+}, Cu^{2+} from aqueous solution by polymer-modified magnetic nanoparticles,” J. Hazard. Mater., vol. 211–212, pp. 366–372, 2012, doi: 10.1016/j.jhazmat.2011.12.013.
- M. Hua, S. Zhang, B. Pan, W. Zhang, L. Lv, and Q. Zhang, “Heavy metal removal from water/wastewater by nanosized metal oxides: A review,” J. Hazard. Mater., vol. 211–212, pp. 317–331, 2012, doi: 10.1016/j.jhazmat.2011.10.016.
- V. Masindi and K. L. Muedi, “Environmental Contamination by Heavy Metals,” Heavy Met., 2018, doi: 10.5772/intechopen.76082.
- E. Matei, “Ferrous Industrial Wastes—Valuable Resources for Water and Wastewater Decontamination,” Int. J. Environ. Res. Public Health, vol. 19, no. 21, 2022, doi: 10.3390/ijerph192113951.
- A. K. Gupta, R. R. Naregalkar, V. D. Vaidya, and M. Gupta, “Recent advances on surface engineering of magnetic iron oxide nanoparticles and their biomedical

applications," Nanomedicine, vol. 2, no. 1, pp. 23–39, 2007, doi: 10.2217/17435889.2.1.23.

- A. K. Gupta and M. Gupta, "Synthesis and surface engineering of iron oxide nanoparticles for biomedical applications," Biomaterials, vol. 26, no. 18, pp. 3995–4021, 2005, doi: 10.1016/j.biomaterials.2004.10.012.
- L. Wu, B. Shen, and S. Sun, "Synthesis and assembly of barium-doped iron oxide nanoparticles and nanomagnets," Nanoscale, vol. 7, no. 39, pp. 16165–16169, 2015, doi: 10.1039/c5nr05291b.
- S. Dutz, N. Buske, J. Landers, C. Gräfe, H. Wende, and J. H. Clement, "Biocompatible magnetic fluids of co-doped iron oxide nanoparticles with tunable magnetic properties," Nanomaterials, vol. 10, no. 6, 2020, doi: 10.3390/nano10061019.
- E. Skoropata, "Intra- and interparticle magnetism of cobalt-doped iron-oxide nanoparticles encapsulated in a synthetic ferritin cage," Phys. Rev. B - Condens. Matter Mater. Phys., vol. 90, no. 17, 2014, doi: 10.1103/PhysRevB.90.174424.
- B. Wareppam, E. Kuzmann, V. K. Garg, and L. H. Singh, "Mössbauer spectroscopic investigations on iron oxides and modified nanostructures: A review," J. Mater. Res., vol. 38, no. 4, pp. 937–957, 2022, doi: 10.1557/s43578-022-00665-4.
- A. A. Nayl, "Review of the Recent Advances in Electrospun Nanofibers Applications in Water Purification," Polymers (Basel)., vol. 14, no. 8, 2022, doi: 10.3390/polym14081594.
- M. A. A. Kerroum, "Quantitative analysis of the specific absorption rate dependence on the magnetic field strength in $ZnxFe_3-xO_4$ nanoparticles," Int. J. Mol. Sci., vol. 21, no. 20, pp. 1–24, 2020, doi: 10.3390/ijms21207775.
- R. M. Al-Maliki et al., "Classification of Nanomaterials and the Effect of Graphene Oxide (GO) and Recently Developed Nanoparticles on the Ultrafiltration Membrane and Their Applications: A Review," Membranes (Basel)., vol. 12, no. 11, 2022, doi: 10.3390/membranes12111043.
- I. Fernández-Barahona, "Cu-Doped Extremely Small Iron Oxide Nanoparticles with Large Longitudinal Relaxivity: One-Pot Synthesis and in Vivo Targeted Molecular Imaging," ACS Omega, vol. 4, no. 2, pp. 2719–2727, 2019, doi: 10.1021/acsomega.8b03004.
- M. J. O'Hara, J. C. Carter, C. L. Warner, M. G. Warner, and R. S. Addleman, "Magnetic iron oxide and manganese-doped iron oxide nanoparticles for the collection of alpha-emitting radionuclides from aqueous solutions," RSC Adv., vol. 6, no. 107, pp. 105239–105251, 2016, doi: 10.1039/c6ra22262e.
- M. Zia, A. R. Phull, and J. S. Ali, "Challenges of Iron Oxide Nanoparticles," Powder Technol., vol. 7, no. 6, pp. 49–67, 2016, http://dx.doi.org/10.2147/NSA.S99986.
- F. Beduk, "Superparamagnetic nanomaterial Fe_3O_4-TiO_2 for the removal of As(V) and As(III) from aqueous solutions," Environ. Technol. (United Kingdom), vol. 37, no. 14, pp. 1790–1801, 2016, doi: 10.1080/09593330.2015.1132777.
- N. Temnuch, A. Suwattanamala, S. Inpaeng, and K. Tedsree, "Magnetite nanoparticles decorated on multi-walled carbon nanotubes for removal of Cu^{2+} from aqueous solution," Environ. Technol. (United Kingdom), vol. 42, no. 23, pp. 3572–3580, 2021, doi: 10.1080/09593330.2020.1740328.
- N. Kataria and V. K. Garg, Application of EDTA modified Fe_3O_4/sawdust carbon nanocomposites to ameliorate methylene blue and brilliant green dye laden water, vol. 172. Elsevier Inc., 2019.
- H. J. Kim, J. M. Lee, J. H. Choi, D. H. Kim, G. S. Han, and H. S. Jung, "Synthesis and adsorption properties of gelatin-conjugated hematite (α-Fe_2O_3) nanoparticles for lead removal from wastewater," J. Hazard. Mater., vol. 416, no. February, p. 125696, 2021, doi: 10.1016/j.jhazmat.2021.125696.
- B. Verma and C. Balomajumder, "Magnetic magnesium ferrite–doped multi-walled carbon nanotubes: an advanced treatment of chromium-containing wastewater," Environ. Sci. Pollut. Res., vol. 27, no. 12, pp. 13844–13854, 2020, doi: 10.1007/s11356-020-07988-x.
- M. P. da Silva, Z. S. B. de Souza, J. V. F. L. Cavalcanti, T. J. M. Fraga, M. A. da Motta Sobrinho, and M. G. Ghislandi, "Adsorptive and photocatalytic activity of Fe_3O_4-functionalized multilayer graphene oxide in the treatment of industrial textile wastewater," Environ. Sci. Pollut. Res., vol. 28, no. 19, pp. 23684–23698, 2021, doi: 10.1007/s11356-020-10926-6.
- S. Sepahvand, M. Bahrami, and N. Fallah, "Photocatalytic degradation of 2,4-DNT in simulated wastewater by magnetic $CoFe_2O_4/SiO_2/TiO_2$ nanoparticles," Environ Sci Pollut Res., vol.29, pp. 6479–6490, 2021, https://doi.org/10.1007/s11356-021-13690-3.
- S. Venkateswarlu, M. Yoon, and M. J. Kim, "An environmentally benign synthesis of Fe_3O_4 nanoparticles to Fe_3O_4 nanoclusters: Rapid separation and removal of Hg(II) from an aqueous medium," Chemosphere, vol. 286, no. P2, p. 131673, 2022, doi: 10.1016/j.chemosphere.2021.131673.
- R. Foroutan, S. J. Peighambardoust, S. Hemmati, H. Khatooni, and B. Ramavandi, "Preparation of clinoptilolite/starch/$CoFe_2O_4$ magnetic nanocomposite powder and its elimination properties for cationic dyes from water and wastewater," Int. J. Biol. Macromol., vol. 189, pp. 432–442, 2021, doi: 10.1016/j.ijbiomac.

2021.08.144.

- M. Lu, G. H. Xia, and X. D. Zhao, “Surface modification of porous suspended ceramsite used for water treatment by activated carbon/Fe_3O_4 magnetic composites,” Environ. Technol., vol. 34, no. 15, pp. 2301–2307, 2013, doi: 10.1080/09593330.2013.765925.
- S. Xia, X. Xu, C. Xu, H. Wang, X. Zhang, and G. Liu, “Preparation, characterization, and phosphate removal and recovery of magnetic $MnFe_2O_4$ nano-particles as adsorbents,” Environ. Technol., vol. 37, no. 7, pp. 795–804, 2016, doi: 10.1080/09593330.2015.1085099.
- A. Farrukh, “Design of polymer-brush-grafted magnetic nanoparticles for highly efficient water remediation,” ACS Appl. Mater. Interfaces, vol. 5, no. 9, pp. 3784–3793, 2013, doi: 10.1021/am400427n.
- A. Z. M. Badruddoza, Z. B. Z. Shawon, W. J. D. Tay, K. Hidajat, and M. S. Uddin, “Fe_3O_4/cyclodextrin polymer nanocomposites for selective heavy metals removal from industrial wastewater,” Carbohydr. Polym., vol. 91, no. 1, pp. 322–332, 2013, doi: 10.1016/j.carbpol.2012.08.030.
- M. Bhaumik, T. Y. Leswifi, A. Maity, V. V. Srinivasu, and M. S. Onyango, “Removal of fluoride from aqueous solution by polypyrrole/ Fe_3O_4 magnetic nanocomposite,” J. Hazard. Mater., vol. 186, no. 1, pp. 150–159, 2011, doi: 10.1016/j.jhazmat.2010.10.098.
- L. Wang, J. Li, Z. Wang, L. Zhao, and Q. Jiang, “Low-temperature hydrothermal synthesis of α-Fe/ Fe_3O_4 nanocomposite for fast Congo red removal,” Dalt. Trans., vol. 42, no. 7, pp. 2572–2579, 2013, doi: 10.1039/c2dt32245e.
- N. C. Feitoza, “Fabrication of glycine-functionalized maghemite nanoparticles for magnetic removal of copper from wastewater,” J. Hazard. Mater., vol. 264, pp. 153–160, 2014, doi: 10.1016/j.jhazmat.2013.11.022.
- O. Hakami, Y. Zhang, and C. J. Banks, “Thiol-functionalised mesoporous silica-coated magnetite nanoparticles for high efficiency removal and recovery of Hg from water,” Water Res., vol. 46, no. 12, pp. 3913–3922, 2012, doi: 10.1016/j.watres.2012.04.032.
- F. C. Christopher, S. Anbalagan, P. S. Kumar, S. R. Pannerselvam, and V. K. Vaidyanathan, “Surface adsorption of poisonous Pb(II) ions from water using chitosan functionalised magnetic nanoparticles,” IET Nanobiotechnology, vol. 11, no. 4, pp. 433–442, 2017, doi: 10.1049/iet-nbt.2016.0166.
- A. Afkhami and R. Moosavi, “Adsorptive removal of Congo red, a carcinogenic textile dye, from aqueous solutions by maghemite nanoparticles,” J. Hazard. Mater., vol. 174, no. 1–3, pp. 398–403, 2010, doi: 10.1016/j.jhazmat.2009.09.066.
- S. Sadeghi, H. Azhdari, H. Arabi, and A. Z. Moghaddam, “Surface modified magnetic Fe_3O_4 nanoparticles as a selective sorbent for solid phase extraction of uranyl ions from water samples,” J. Hazard. Mater., vol. 215–216, pp. 208–216, 2012, doi: 10.1016/j.jhazmat.2012.02.054.
- S. Ben Hammouda, N. Adhoum, and L. Monser, “Synthesis of magnetic alginate beads based on Fe_3O_4 nanoparticles for the removal of 3-methylindole from aqueous solution using Fenton process,” J. Hazard. Mater., vol. 294, pp. 128–136, 2015, doi: 10.1016/j.jhazmat.2015.03.068.
- J. Hu, G. Chen, and I. M. C. Lo, “Removal and recovery of Cr(VI) from wastewater by maghemite nanoparticles,” Water Res., vol. 39, no. 18, pp. 4528–4536, 2005, doi: 10.1016/j.watres.2005.05.051.
- M. Rashid, N. T. Price, M. Á. Gracia Pinilla, and K. E. O'Shea, “Effective removal of phosphate from aqueous solution using humic acid coated magnetite nanoparticles,” Water Res., vol. 123, pp. 353–360, 2017, doi: 10.1016/j.watres.2017.06.085.
- B. Wu, L. Fang, J. D. Fortner, X. Guan, and I. M. C. Lo, “Highly efficient and selective phosphate removal from wastewater by magnetically recoverable $La(OH)_3$/ Fe_3O_4 nanocomposites,” Water Res., vol. 126, pp. 179–188, 2017, doi: 10.1016/j.watres.2017.09.034.
- C. O. Akintayo, O. H. Aremu, W. N. Igboama, S. M. Nelana, and O. S. Ayanda, “Performance evaluation of ultra-violet light and iron oxide nanoparticles for the treatment of synthetic petroleum wastewater: Kinetics of cod removal,” Materials (Basel)., vol. 14, no. 17, 2021, doi: 10.3390/ma14175012.
- A. Subramani and J. G. Jacangelo, “Emerging desalination technologies for water treatment: A critical review,” Water Res., vol. 75, pp. 164–187, 2015, doi: 10.1016/j.watres.2015.02.032.
- A. Panagopoulos, “Water-energy nexus: desalination technologies and renewable energy sources,” Environ. Sci. Pollut. Res., vol. 28, no. 17, pp. 21009–21022, 2021, doi: 10.1007/s11356-021-13332-8.
- S. Y. Pan, A. Z. Haddad, A. Kumar, and S. W. Wang, “Brackish water desalination using reverse osmosis and capacitive deionization at the water-energy nexus,” Water Res., vol. 183, p. 116064, 2020, doi: 10.1016/j.watres.2020.116064.
- S. M. Anush and B. Vishalakshi, “Modified chitosan gel incorporated with magnetic nanoparticle for removal of Cu(II) and Cr(VI) from aqueous solution,” Int. J. Biol. Macromol., vol. 133, no. 1(i), pp. 1051–1062, 2019, doi: 10.1016/j.ijbiomac.2019.04.179.
- R. Li, “Removing tetracycline and Hg(II) with ball-milled magnetic nanobiochar and its potential on polluted irrigation water reclamation,” J. Hazard. Mater., vol. 384, no. June, 2020, doi: 10.1016/j.jhazmat.2019.121095.
- E. C. Nnadozie and P. A. Ajibade, “Multifunctional

magnetic oxide nanoparticle (MNP) core-shell: Review of synthesis, structural studies and application for wastewater treatment," Molecules, vol. 25, no. 18, 2020, doi: 10.3390/molecules25184110.

- Y. Du, "Trace amounts of co3o4 nano-particles modified tio2 nanorod arrays for boosted photoelectrocatalytic removal of organic pollutants in water," Nanomaterials, vol. 11, no. 1, pp. 1–13, 2021, doi: 10.3390/nano11010214.
- X. Zhang, "Magnetic graphene-based nanocomposites as highly efficient absorbents for Cr(VI) removal from wastewater," Environ. Sci. Pollut. Res., vol. 28, no. 12, pp. 14671–14680, 2021, doi: 10.1007/s11356-020-11634-x.
- R. Khurram, Z. Wang, and M. F. Ehsan, "α-Fe_2O_3-based nanocomposites: synthesis, characterization, and photocatalytic response towards wastewater treatment," Environ. Sci. Pollut. Res., vol. 28, no. 14, pp. 17697–17711, 2021, doi: 10.1007/s11356-020-11778-w.

● ● ● ●