Chapter 7

Application of Magnetic Nano Particles and their Composites as Adsorbents for Waste Water Treatment: A Brief Review

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Abstract

The present review highlights the different types of nano ferrites and their surface modified composites as an alternative adsorbent in waste water treatment. In this review, the recent progresses and potential applications of SFNPs/SFNCs for the removal of organic and inorganic contaminants through adsorption routes are critically reviewed. There are number of water purification techniques but the adsorption is one of the simplest, effective and economical method for wastewater purification. Adsorption isotherm models, kinetic models, thermodynamic parameters and adsorption mechanism have also been discussed. The present article lists different type of adsorbents and reviews state-of-the-art of the removal of different pollutants from water. The efforts have been made to discuss the sources of contamination and toxicities of pollutants. The possible techniques of recovery and reuse, toxicity, research gaps and the future perspective of SFNPs are also discussed in brief. Based on this review, it is possible to conclude that SFNPs and their derivative composites have unlimited capacity in addressing array of problems encountered in water and wastewater treatment. The present study highlights the future areas of research for waste water treatment.

Keywords

Spinel Ferrite, Spinel Ferrite Composites, Wastewater, Adsorbents, Dyes, Regeneration

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1. Introduction

Spinel Ferrites Nanoparticles have interesting aspects in magnetic properties when accompanied with other functional properties like catalytic activities. It is also important to mention here that the magnetic properties of spinel ferrite nanoparticles are strongly dependent on the particle size and shape up to some extent. These are also called as universal and multifunctional due to their excellence magnetic properties, simple chemical composition, and wide applications in several areas which include water and wastewater treatment, biomedical, catalyst and electronic device.

The structural equation of spinel ferrite is MFe_2O_4 , where M is a divalent metal ion. For the last few decades, many researchers studied the physical properties of ferrites substituting M with Ni^{2+} , Zn^{2+} , Mg^{2+} , Cu^{2+} , Mn^{2+} , etc.[1,2,3,4]. Spinel ferrites are competitive crystalline materials due to their excellent magnetic properties together with the electrical properties. The magnetic and dielectric properties of ferrites play a crucial role in choosing their applications. Ferrites show an almost semiconducting behaviour that is greatly affected by doping. Magnetic properties of spinel ferrites are sensitive to

the type of cations and their distribution amongst the two interstitial sites of the spinel lattice; the tetrahedral and the octahedral sites [5], Changes in the cation distribution between the two interstitial sites alter the spin moment algebraic sum which strongly affects the magnetic and electric properties.

Magnetic properties are due to the super exchange interaction between cations located in tetrahedral and octahedral coordinated sites throughout the surrounding oxygen anions [6]. The doping process at any interstitial site not only impacts the total magnetic moment but also it may control the particle growth and consequently the material properties [7-9], In the formula MFe_2O_4 , depending on the position of M(II) and Fe(III) site preference, three possible spinel ferrite structures are known, namely normal, inverse and mixed. In a normal spinel structure of ferrite, M (II) located at tetrahedral sites while Fe (III) at octahedral sites. In an inverse spinel structure of ferrite, Fe (III) equally distributed at both sites while M(II) occupy only at octahedral sites. In a mixed spinel structure of ferrite, both ions randomly occupy the tetrahedral and octahedral sites. $ZnFe_2O_4$ is an example of normal spinel ferrite, Fe_3O_4 and $NiFe_2O_4$ are common examples for inverse spinel ferrite while $MnFe_2O_4$ is a good example for mixed spinel ferrite.

Scientific advancement and industrialization have been both beneficial and problematic for the environment and to human populations. Problems associated with drinkable water are particularly notable. The vast advancement in the field of science and technology for making life easy and comfortable, many electronic and consumer products have become essential part of household and office as daily routine. The uncontrollable growth in human population and excessive usage of these products contaminated all the natural resources e.g. water, soil and air essential to sustain life on earth. Now, water pollution is a global problem and concentration of toxic pollutants in the water bodies are well above the designated limits established by world health organization (WHO) and environmental protection agency (EPA). Water quality has become an eminent issue as ground water level has enormously gone down and its contamination by natural contaminants like fluoride and arsenic, man-made chemical pollutants such as dyes, pesticides and insecticides and biological contaminants is rising at an alarming rate due to outburst of population, irrigation and industrialization.

The inconsistency in awareness, socio-economic development, education, poverty, practices and rituals of people in villages has further worsen the problem. This has resulted in the enormous health burden of poor water quality, as ground water is the decentralized source of potable water to about 85% of the rural population in India. It is estimated that annually, around 37.7 million Indians are affected by waterborne diseases; around 1.5 million children are estimated to die of diarrhoea alone. That is why, the government of India has categorized this as one of the major National Missions of India.

And even though a depletion of groundwater resources has been recorded throughout the world, there is an increasing demand for clean water to support human populations, industries, and living organisms [10-12]. For all these reasons, water is no longer considered a free resource. In several developing and developed countries, individuals are paying for clean water and furthermore, some governments have imposed water tariffs [13]. The most significant water problems include: (i) groundwater depletion, (ii) contamination of fresh water resources (rivers, lakes, wells and ponds), and (iii) a high demand for fresh water (due to a rapid increase in population and urbanization) [14, 15] [16]. Polluted water significantly affects the health of the communities, aquatic ecosystems, the sustainability of the natural environment, and the economic and social welfare of society. For example, it has been reported that inadequate water supplies, in terms of both quantity and quality, coupled with poor sanitation globally account for the death of approximately 30 000 people per day. Of these cases, 80% occur in rural areas with the highest percentage occurring among infants[17].

There are other types of contaminations such as heavy metals occurring as trace metals in aqueous systems but their level of contamination is increasing from different activities such as geological, mining, agricultural, acidic rain and industrial waste in aqueous environment. No doubt, there are certain metals like Manganese (Mn), Iron (Fe), Cobalt (Co), Copper (Cu), Vanadium(V) and Zinc (Zn) which are essentials to human body in trace amount called as essential metals. Heavy metals such as arsenic, lead, antimony, mercury, selenium, chromium etc. are very harmful and toxic in nature even in micro level range. Among different heavy metals, Lead (Pb) is the poisonous metal which is widely used in industries dealing in the production of lead acid batteries, solder, alloys, ammunition, refinery and plumbing [18]. The allowed limit set by world health organization(WHO) for lead in drinking water is 0.01 mg/l [19]. The increased concentration of lead in water leads to many serious diseases like inhibition of haemoglobin, kidney damage, loss of memory and reproductive effects in human being [20]. Therefore, removal of Pb (II) ions from contaminated water is necessary for sustainability of environment.

The need for clean, safe and utmost quality water is increasing day by day throughout the world and it ultimately resulted into the need of new and cost-effective methods for water purification. A satisfactory solution to these problems is the recovery of clean and fresh water from contaminated one. In this regard, different approaches to develop highly efficient water purification methods have been undertaken [21-32]. The removal of such toxic elements and compounds which are present in low concentrations is a difficult and challenging task. Various remediation technologies have been developed for the removal of pollutants including toxic heavy metals, dyes, pesticides, fertilizers, organic acids, and

halogen attend and phenolic compounds, among others. Techniques such as precipitation, incineration, flocculation, coagulation, ion exchange, reverse osmosis, membrane filtration, electrochemistry, photo electrochemistry, advanced oxidation processes, and biological methods have demonstrated different degrees of remediation efficiency [33]. There were certain drawbacks of the methods like low removal efficiency, high production of sewage sludge, non-cost-and-energy efficiency, generation of toxic by-products, as well as the addition of more potentially toxic chemicals into the environment. Among all these methods, adsorption technique has been the most effective, simplest, economical, less time consuming, environmental friendly and offers high performance also. This method is widely used to remove different types of metal ions from the tainted aqueous system at industrial level [34, 35]. In this process, different types of natural as well as synthetic adsorbents such as clay, mineral oxides, rice husk, fly ash, meso porous materials, nano materials etc. have been reported to remove pollutants from water. The most common adsorbents for removal of different pollutants from aqueous solution are discussed briefly [36].

Researchers from various fields, including environmental, chemical, biotechnological and material science, have come together to develop novel adsorbents to solve wastewater treatment problems [37-47]. Published reports describe the development of a range of adsorbents including: carbon-based three-dimensional architectures [48], three-dimensional graphene-based macrostructures (3D GBM)[49] , magnetic chitosan composites (MCCs) [43], ordered meso-porous materials [50], inorganic nano-adsorbents [51], nano adsorbents [52], agricultural biomasses [53], graphene nano-sheets [54], metal-organic frameworks [55], sludge-derived activated carbons [56], bio sorbents [56, 57], tailored zeolites [58] and bio-derived materials [59]. Activated carbon (AC) is one of the most successful well developed adsorbent materials known for years, and is, still playing a very important role in commercial applications.

But the AC is inappropriate for inorganic pollutant removal because of its non-polar surface and also has low adsorption affinity for low molecular weight polar organic pollutants [60] which further limit its applications. The effectiveness of various adsorbents for the removal of impurities from the aqueous systems have been discussed and Chitosan is found to be most important materials in adsorption applications. Amino and hydroxyl groups present in the molecules contribute to many possible adsorption interactions between chitosan and pollutants (dyes, metals, ions, phenols, pharmaceuticals/drugs, pesticides, herbicides, etc.)[61] [62].

Adsorption is a surface phenomenon and it involves the attachment of dissolved impurity on the surface of the adsorbent. An ideal adsorbent should have (i) high performance, (ii) rapid adsorption, (iii) cost-efficient, (iv) environmentally non-toxic, (v) reusability, and

(vi) ease of separation for commercial application. The promising new generation adsorbent materials developed so far are magnetic nano-adsorbents that have these features of high surface area, tunable morphology, ease of separation after sorption, and high efficiency [63, 64].

2. Nano Materials as Adsorbent

Due to their extraordinary physico-chemical properties, the nano-materials have gained much attention in the past two decades in water purification. Among different nano materials, nano ferrites and their composites are showing high potential in waste water purification due to their extra magnetic character which makes their separation easier after treatment. Spinel ferrite magnetic materials are emerging composite metal oxides for removal of aqueous pollutants from the contaminated water due to their size, shape and high surface area [65].

These excellent features of spinel ferrites might give long-lasting and excellent performance in water treatment [66], and aggregation related problems were overcome [67]. Additionally, spinel ferrites and their composites can be prepared in the form of different structure and shapes as per the utilization in various systems, including hierarchical [68], hollow spheres [69] [70], three-dimensional (3D) porous [71], [72] hollow fibres [73], beads [74], and rods [75]. Materials with high porosity and morphology typically exhibit high adsorption properties for a variety of pollutants.

There is vast literature available on spinel ferrites but in the recent years, these spinel ferrites and their composites have gained attraction because of their potential utilization in environmental applications, primarily for the removal of toxic pollutants from water. The reason behind the development of nano composites for purification is their increased affinity, and capacity for selectivity of different pollutants from aqueous system, and particularly due to the following reasons [76-82].

1. Removal of inorganic/organic pollutants at low concentration.
2. High adsorption of hazardous pollutants.
3. Reduction in the toxicity of different pollutants by altering their oxidation state.
4. Providing modifiable reactive surface.
5. Facile removal of adsorbed pollutants from the surface of nano materials.
6. Cost effectiveness and reusability.

The present review work is a combine approach to discuss detailed study of various surface modification methods with their general mechanism and features; applications of

different ferrites and their surface modified composites as adsorbent for treatment of organic and inorganic pollutants from waste water; discussion on regeneration of different ferrites and their composites by using various desorption agents and representing the advantages and disadvantages of such types of materials. The past few years has documented a substantial growth in the publication of numerous review articles on different ferrites with focus on synthesis, physical and chemical properties and their applications. In this review, the emphasis has been laid onto the various pros and cons of several synthetic pathways for creating different types of nano ferrite, need for surface modification with general adsorption mechanism for the treatment of organic and inorganic pollutants from water, and their regeneration.

3. Different Synthesis Techniques of SFNP

For the purification of wastewater, which is contaminated with various harmful particles, should be removed efficiently by using various adsorbents. From literature review, it is very well known that spinel ferrite nanoparticle (SFNP) or spinel magnetic particles (SMP) are preferred for wastewater treatment because of its high surface to volume ratio and provide high area to interact with contaminated particles [83, 84]. Most of SFNP shows magnetic behaviour and therefore with the help of external magnetic field, aqueous solution contamination can be removed. Different SFNP synthesised by different synthesis techniques shows different adsorption capacities for the contamination. Even same material synthesised by different techniques shows different adsorption capacity for the same ions as shown in Table 1.

SFNP can be used directly and indirectly for the removal of pollutants from the waste water. Indirectly means coating the SFNP with desirable functional group and SFNP as core material. As core is magnetic these can be used as magnetic separator and coating of such functional group which improve the surface properties, such as phosphoric acid, amine group, trimethoxy silica etc.

Adsorption capacity of various SFNP or SFNC mostly calculated by isothermal equations and pseudo first and second order kinetic equations given by Longmuir and Freundlich models [65, 86, 92] . Adsorption capacity greatly influenced by the distribution of cations that is position of cation is tetrahedral or octahedral sites, because chemical properties of material depend upon the position of cation sites.

Table 1: Data showing variation in adsorption capacity with the method of preparation of different spinel ferrite particles.

Ferrite	Method of preparation	Absorptive removal	Removable capacity(mg/g)	pH value	References
GO-MnFe ₂ O ₄	One-pot hydrothermal	Pb ²⁺	621.11	6	[85]
GO-MnFe ₂ O ₄ nanohybrids	Coprecipitation	As ³⁺	146		[86]
MnFe ₂ O ₄ nanoparticles		As ⁵⁺	207		
		Pb ²⁺	673		
		As ³⁺	97		
		As ⁵⁺	136		
		Pb ²⁺	448		
MnFe ₂ O ₄ -graphene composite	Solvothermal	Pb ²⁺	100	5	[87]
		Cd ²⁺	76.90	7	
MnFe ₂ O ₄	Sol-gel	Cr ⁴⁺	175.43	2	[88]
Co Fe ₂ O ₄	Hydrothermal	CR	244.5	7	[89]
NiFe ₂ O ₄ /ZnO	Hydrothermal	CR	221.73	13	[90]
Fe ₃ O ₄ /GO	impregnation	Black 5 dye	164	3	[91]
Fe ₃ O ₄ /GO	Coprecipitation	Black 5 dye	188	3	[91]

Mechanism of the process and factors that effects the adsorption process such as, when surface to volume ratio increases in the nano scale then hydroxyl group is very effective in controlling adsorption [93] . Mostly ion-exchange, inner outer complex, weak interactions hydrogen bond and Π - Π interactions etc. are responsible for contamination removal, which is listed below in Table 2.

Table 2: Data contained ferrite nanoparticles showing mechanism for removal of pollutants.

Particle name	Removal ion	Mechanism	Reference
MnFe ₂ O ₄	MB	Hydrogen bound interaction	[94]
γ- Fe ₂ O ₃	Arsenate	Inner sphere-complex formation	[95]
NiFe ₂ O ₄	Cr(VI)	Physisorption	[96]

The removal capacity of SFNP and its composites also depends upon the synthesis techniques used, as listed in Table 1. Same spinal ferrites nanoparticles synthesised by different techniques gives different removal capacity for same ions from the aqueous solution [65, 97-99]. Generally, with the decrease in size the removal capacity increases, called nanoscale effect [100, 101] pH also plays significant role in adsorption process as in low pH aqueous solution surface of SFNP is positively charged i.e anions, whereas if pH is high, surface is negatively charged which means it is cation.

Table 3: Data showing removal capacity of ferrites for contamination in specific pH value.

Ferrite	Contamination ion	Removal capacity (mg/g)	pH	References
γFe ₃ O ₄	Mo (VI)	33.4	4-6	[101]
Cu Fe ₂ O ₄	Mo(VI)	30.58	2.75	[102]
Cu Fe ₂ O ₄ -rGO	Pb ²⁺	299.9	5.3	[103]
	Hg ²⁺	157.9	4.6	
MnFe ₂ O ₄	As ³⁺	93.8	3	[104]
	As ⁵⁺	94.4	7	
CoFe ₂ O ₄	As ³⁺	100.3	3	[104]
	As ⁵	73.8	7	
Fe ₃ O ₄	As ³⁺	49.8	3	[104]
	As ⁵	44.1	7	
Co _{0.1} Al _{0.03} Fe _{0.1} γO _{0.4} .	MB	~12	3	[105]
		~37	5	
		~81	9	
		~98	11	

4. Types of contamination

The waste water is contaminated by various regions. The contamination in water may be Organic or Inorganic.

4.1 Organic Contaminations

Organic contamination is due to industrial waste which can be effectively removed by the nanoparticles from the literature survey it is found that SFNP is good in this. Organic contamination mostly included dyes, pesticides and pharmaceuticals [106, 107]. All these contaminations are discussed in detail as below:

Dyes: Dyes has complex ring shaped or planar structure with Π - bond in resonance. Therefore, dyes are stable and not easily removed from waste water. When various dyes are discharged from industries it pollutes the water which causes various harmful effect to the environment as well as human life[98] [103, 104]. From literature review, MFe_2O_4 SFNP are effective in removal of harmful contaminations from wastewater and these SFNP are easily removed due to its magnetic properties as well as can be used several times without decrease in capacity of removal of contaminated ions. This is listed in Table 4.

SFNP which are generally used for removal of dyes from waste water are Fe_3O_4 NP, γ - Fe_3O_3 and MFe_2O_4 where $M = Mg, Mn, Co, Ni, Zn$ etc. some of them are discussed below along with their removal capacity which is listed in Table 4.

In Fe_3O_4 NP and NCs, the surface functionalization increases due to its small size, therefore externally useful in removal of dyes from waste water. Some composites of Fe_3O_4 NP are listed below along with removal capacity of dyes from the waste water [86, 108]. From literature review it is noticed that the removal capacity of SFNP is increased when used in composites of SFNP. For example, when Fe_3O_4 NP coated with Humic Acid (HA) absorption capacity for methylene blue increase three times and shows stability in range 3–11 for pH value. When graphene is incorporated with SFNP there is increase in properties such as recovery and removal capacity [91, 109, 110].

Table 4: Data showing removal capacity of various dyes using ferrites with pH and temperature.

Ferrite	Contamination	Removal capacity (mg/g)	pH	Temperature In °C	References
Chitosan-glutamic-Fe ₃ O ₄ @SiO ₂	MB, CV, CLY	180.1, 375.4, 217.3	7	25	[111]
Chitosan-Fe ₃ O ₄ @SiO ₂	MB, CV, CLY	28.8, 78.8, 17.6	7	25	[111]
HA- Fe ₃ O ₄	MB	93.1	8.4	25	[108]
Fe ₃ O ₄ /GO	Black 5 dye	164	3	25	[91]
Fe ₃ O ₄ /SiO ₂ - GO	MB	97	7	25	[109]
Fe ₃ O ₄ /SiO ₂ - GO	MB	102.6	7	45	[109]
Fe ₃ O ₄ /SiO ₂ - GO	MB	111.1	7	60	[109]
GO-Fe ₃ O ₄ hybrid composites	MB, NR	162.2, 171.3	3-7	N/A	[112]
CoFe ₂ O ₄ @SiO ₂ -NH ₂	Cu ²⁺ , Cd ²⁺ , Mn ²⁺	170.829, 144.948, 110.803	4-6.5	35	[113]
P25-CoFe ₂ O ₄ -PANI	MO, TB, BBR	~172, ~160, ~135	N/A	60	[114]
AC- NiFe ₂ O ₄	MO	182.8	4.4-8.4	30	[115]
NiFe ₂ O ₄	RB5 dye		1	25	[116]
ZnFe ₂ O ₄	AR88	111.1	7	30	[117]

Note : Methyl Orange (MO), Trypan Blue (TB), Brilliant Blue R (BBR), Acid Red 88 (AR88), crystal violet (CV).

γ - Fe₃O₃ is also used largely for removal of organic dyes from biomedical and industrial areas. γ - Fe₃O₃ (Maghemite) coated with dodecyl sulphate improved its adsorption capacity. It removes 285.8 mg/g of acridine orange at room temperature with pH 5.1 [118]. Also, with pH 6 at room temperature the capacity of γ - Fe₃O₃ to remove cationic

dyes thionine and Janus green b brilliant crystal blue from the wastewater with removal capacity 166.7, 172.4 and 200.0 mg/g. γ - Fe_3O_3 is also non-toxic as well as has good adsorption capacity. When γ - Fe_3O_3 is made composite with SiO_2 then removal capacity for methyl blue increases to 116.09 mg/g by physical adsorption mechanism [119].

Some water pollutants such as direct red (DR), direct green red 6 (DGR6), and acid blue 92 (AB92) dyes can be removed using CoFe_2O_4 nanoparticles effectively, when functional group amine is attached with CoFe_2O_4 its removal efficiency increases which is shown in the table 4[120]. Whereas CoFe_2O_4 composite made with titania- CoFe_2O_4 polyaniline, it is concluded anionic dyes are removed effectively than cationic dyes because anionic dyes contribute to electrostatic attractions with positively charged part of polyaniline [114]. Adsorption capacity of this for MO, TB, BBR dyes is given in Table 4. When NiFe_2O_4 NPs are used for wastewater treatment then it shows good photocatalytic properties as well as removal capacity for dyes [71, 90, 121-126].

When NiFe_2O_4 made composite activated carbon (AC) then removal capacity for methyl orange dye improved to 182.8 mg/g at 30°C [115]. For photocatalytic degradation of contamination and antimicrobial, ZnFe_2O_4 NPs are used [127-129]. Also, when ZnFe_2O_4 prepared by microwave assisted hydrothermal method then acid red 88 dye is effectively removed from wastewater [117]. But with the increase of temperature from 20 to 80 °C adsorption equilibrium decreases. For acid red dyes absorbed by ZnFe_2O_4 at 30°C with pH 7 is equal to 111.1 mg/g.

Pharmaceuticals are also a major contamination in water [130, 131]. And many of these pharmaceuticals are not removed by generally used wastewater treatment plants, so easily found in surface water or in small amount in ground water, which causes harmful effect on health of humans as well as animals [131-137]. Number of treatments are available in literature, but application of spinel ferrite nanoparticles and nano-composites shows effective removal of pharmaceuticals from polluted water [130, 138]. But using other treatment some of species of lower molecular mass were generated which may be more harmful than of parent pollutant. From the literature review, treatment for pharmaceuticals and personal care products are effectively done by γ - Fe_2O_4 coated with zeolite which shows 95% of adsorption for the pollutants in wastewater.

Pesticides are used frequently in agriculture these days to enhance their production and to cure various harmful problems in agriculture like insects, fungus and weeds [137]. But these pesticides improve production but on the other side these are also toxic and contaminate the ground water by some amount. Firstly, used pesticides for controlling number of diseases such as malaria and typhus are organochlorine but this is banned by various countries since 1970. Organochlorine is stable and easily available in various

ground and surface water resources [138]. These days farmer used mostly organo phosphorus insecticides and triazine herbicides. These pesticides are high in toxicity and high resistance to degradation. Atrazine pesticides easily distribute into environment therefore have low concentration in water, but even in low concentration these are harmful for humans. SFNPs used effectively for removal of pesticides from contaminated water such as Fe_3O_4 NCs.

4.2 Inorganic contamination

Inorganic contamination also plays vital role in water pollution, it occurs naturally or may be caused by human being as their activities in areas such as mining, industries or agriculture. Most commonly occurring inorganic contaminations are caused by the presence of As, Cd, Cr, Pb, Hg, and Se. SFNP /SFNC shows the significant efficiency in the removal of contamination of water because these shows good adsorption capacity and easy to synthesize and can be separated easily due to its magnetic properties as well as cost effective [139, 140]. For waste water treatment, Fe_3O_4 when synthesized with Co – precipitation method, the contaminations in water such as nickel, copper, cadmium and chromium are removed effectively with pH 4 at temperature 20 °C for 24 hours[141]. Different SFNP or SFNC with different methods have different adsorption capacities whether they may have same surface area. These all contaminations are briefly explained below.

Water polluted by arsenic is highly toxic i.e. 50% more than arsenate, become the causes of cancer. It is easily mixed in environment [92] . Number of metal oxides was used for its removal but after removal, recovery of metal oxides was difficult. This problem is effectively overcome by the use of SFNP/SFNC because of their magnetic properties. With the help of external magnetic field, they are easily recovered and reused. CuFe_2O_4 shows good removal capacity for As^{5+} (45.7mg/g) at pH 3.7 but this adsorption decreases with the increasing value of pH due to electrostatic repulsion between AsO_4^{3-} and adsorbent surface [42, 142] MnFe_2O_4 shows effective removal of As^{3+} [143] .

Other pollutant cadmium is harmful when it is present more than recommended limit. It can become the cause of lung cancer, blood pressure, kidney failure etc.[144] Cd^{2+} is effectively removed by the use of SFNP such as CuFe_2O_4 when used at temperature 45 °C with pH 6[145].. However, when Cd^{2+} is removed by using Fe_3O_4 coated with citric acid, its removal capacity become temperature dependent i.e., decrease with decrease in temperature and vice versa. All the water pollutants are toxic as well as harmful for living organisms. Similarly, Chromium (Cr^{6+}) is harmful for humans and animals, also carcinogenic as well as causing health problems if present more than 0.05mg/L in domestic usable water, according to WHO [146] .These are treated efficiently by

MnFe₂O₄ and after removing chromium ions, these ferrite nanoparticles are retrieved using magnetic field which is provided externally [143]. The removal capacity of Chromium from industrial waste by MnFe₂O₄ is 89.16 but when used in the form of composite of γ -Fe₂O₃ with graphene and cellulose synthesized its removal capacity improved and gives exothermic reaction [147, 148]. CoFe₂O₄ also shows effective removal of Cr⁶⁺. But studies revealed that MnFe₂O₄ gives maximum & CoFe₂O₄ gives minimum removal of Cr⁶⁺ ions due to its large surface area whereas its recovery after reaction is minimum as compared with other SFNP used for chromium removal. Lead is harmful for living organism and causes various diseases, when used above a recommended limit i.e., 0.05 mg/L [97, 146] [149]. It is effectively used in batteries due to its high efficiency but also very toxic and not easy to dispose it off, therefore, banned by many countries. SFNP and its composites shows effective removal of Pb from wastewater, such as by CoFe₂O₄(NH₂) and MWCNTS–MnFe₂O₄(NH₂) comprise chitosan based SFNP shows high removal capacity of Pb at pH 6 is 370.6 mg/g due to high active sites present on chitosan [150].

Mercury is very toxic for human and aquatic life as it has very strong binding energy. Due to this property, it binds strongly with haemoglobin and proteins which restrict the proper functioning of these. This is strongly toxic which causes hindrance in kidney functioning, chest pain etc. SFNP such as γ -Fe₂O₃ coated with polyrhodanine shows Langmuir adsorption capacity for Hg²⁺ is 179 mg/g. It is also described best from pseudo second order reaction for adsorption of mercury by chemical reaction [151].

Selenium: Selenite (SeO₃²⁻) and Selenate (SeO₄²⁻) are two forms of selenium that exist in oxidation state Se⁴⁺ and Se⁶⁺ in inorganic solvent. These are more toxic than the organic solvent, if its value in drinking water is more than subscribed value that is 40 μ g/L [152] [153]. Various polymers, composites and oxides are used for the removal of selenium from wastewater but recovery of these adsorbents was difficult. Therefore, SFNP are used for the removal of selenium which gives effective results for removal as well as easily recovered due to its magnetic properties. CoFe₂O₄ shows highest removal capacity for Se⁴⁺ and Se⁶⁺ whereas MnFe₂O₄ gives least removal capacity. γ -Fe₂O₃ also gives significant removal capacity for selenium ions.

5. Adsorption Mechanism

Different adsorbates adsorb on different adsorbents in different ways. Physicochemical interactions of the adsorbate-adsorbent play a key role in an efficient adsorption system; thus, it is essential to understand the adsorption mechanism.

Surfactant coating is a well-known method that protects nano ferrites from oxidation, degradation and enhances their stability by changing structure, particle size, magnetic, electrical and adsorption properties. The process involves either a single layer or double layer formation on the surface of nano ferrites. The surface modification of spinel ferrites and their composites can be easily explained on the basis of electrostatic interaction between surfactant molecules and nano ferrite particles. There are various types of electrostatic interactions like as (i) π - π interaction, (ii) electrostatic interaction, (iii) ion exchange interaction, (iv) hydrogen bonding, (v) surface complex formation etc. exist between the surfactant molecules and nano ferrite particles. The generation of such electrostatic interaction stabilizes the colloidal nano particles and increases their stability with surfactant molecules with modification in their properties [154-156].

Surfactant coating on the surface of ferrites and their interaction toward different pollutants plays important role in adsorption system. The surfactant modified ferrite composite contains different types of functional groups depending on the nature of surfactant and act as active sites for adsorption of different inorganic and organic pollutants in the aqueous solution [79] and Carlos *et al*[157] reviewed different types of surfactants used for remodelling iron oxide surface and understand their utility as adsorbent for removal of heavy metal ions from water. The drastic increase in adsorption behaviour of surfactant modified iron was recorded compared to iron oxide. The studies reveal that different types of surfactant coated ferrites have ability to remove numerous types of inorganic and organic pollutants from the waste water[158].

Sorption mechanism of dyes has also been thoroughly described in terms of electrostatic attractions and hydrogen bonding [159]. At a lower pH the surface of ZnFe_2O_4 has a net positive charge, and anionic acid red 88 (AR88) adsorption was favourable [114]. With increasing pH, the surface becomes negatively charged and, lower sorption was observed, presumably due to an electrostatic repulsion between the anionic dye and the negatively charged ZnFe_2O_4 . When methyl blue and CR are adsorbed to MnFe_2O_4 , hydrogen bond interactions are the major mechanisms attracting dye and hydroxyl groups [94]. Fluorescence spectroscopy was used to further understand the synergetic effect of the interaction between methyl blue and CR. The factors that influence the adsorption performance of SFs and SFCs include (i) cation distribution in SFs, (ii) surface charge, (iii) annealing temperature, and (iv) material used to modify or functionalize SFs.

Adsorption behaviour of metal and their oxide doped nano ferrites can be well explained using ion exchange mechanism. As the dopant concentration increases in nano ferrite sample, it directly affects the crystalline structure and size of nano particles. The difference is due to variation in atomic size of dopant (metal or their oxide particles) ions

with the parent metal ions. The variation in atomic size between the parent metal ions and substituted dopant ions in crystal lattice surface directly affect the inter planner spacing, lattice constant between two crystal lattice and increase the concentration of free electrons in the crystal lattice. These variations in crystal lattice structure increase the active site on the doped surface, which involves change in adsorption behaviour of doped nano ferrites. The presence of free electron in crystal lattice surface helps to reduce the high oxidation state of pollutant to lower state, which in turn become less stable and easily adsorb on surface of doped surface nano ferrites. Table 2 shows the different mechanism used for contamination removal in various ferrites.

6. Desorption, Regeneration of Nano Ferrites and their Composites

The removal of the pollutants from aqueous solution using adsorbents is an important step, but desorption of the loaded pollutant from the adsorbent, to recover the adsorbent and to discard the pollutant is also important [160]. As the disposal of pollutant-loaded adsorbent may become a secondary pollution problem. The importance of regeneration in adsorption with respect to economic and environmental factors with highlights on regeneration procedures like thermal, electrical, ultrasonic and chemical methods has been discussed by Kulkarni et al.[161]. It depends upon the selection of desorption agent and operating factors such as temperature, pH and concentration. In particularly, the pH value is a critical parameter that influences the efficiency of desorption of different pollutants from adsorbent surface [161, 162]. Aqueous solutions of strong bases and strong acids are commonly used desorption agents to remove inorganic/organic pollutants from the adsorbent surface.

The following is a list of eluents and processes that have been chosen most often to desorb pollutant from SFs and their composite adsorbents:

- (i) Acids (HCl, HNO₃, H₃PO₄)
- (ii) Bases (NaOH, NaHCO₃)
- (iii) Organic solvents (ethanol, methanol, and acetone)
- (iv) Chelating agents (EDTA and thiourea)
- (v) Thermal regeneration

It is a Challenging task to retrieve these nanoparticles from liquid medium effectively because of their extremely small size. Magnetic Separation can be used to get spinel ferrite-based nanoparticles from the liquid medium. Magnetic field separation is superior to traditional centrifugation and filtration processes because it is more economical, selective and rapid.

7. Future Aspects

The potable water scarcity existing in many parts of the world and the necessity for water treatment confirm the need for efficient adsorbents. Magnetic nanoparticles and their composites with tailored size, composition, magnetic characteristics and structure are currently used for treating polluted water.

Although Fe_3O_4 has traditionally been used for water treatment applications, spinel ferrites like MFe_2O_4 ($\text{M}=\text{Mn, Cu, Co, Ni, Zn, Mg, Ca}$ etc.) are becoming more widely used. More selective, efficient, inexpensive, reusable and eco-friendly adsorbents should be developed and experiments be conducted with real industrial effluents. Researches are required to have a comparative study of different adsorbents for the removal of different contaminants from water considering the feasibility, effectiveness and cost under similar conditions.

Despite the strong capacity of SFNPs for removing varieties of toxic chemicals from wastewater, studies on the impact of SFNPs on human health and their environmental behaviour and ecological risk as well as the effects of SFNPs ending up as pollutants in the environment, are scant and are not fully addressed. Therefore, an in depth toxicity study is required.

Different type of adsorbents with greater stability (resistance to pH changes and concentrations of chemicals present in contaminated water) and the capacity for the simultaneous removal of multiple contaminants, such as toxic metal ions, organic dyes and bacterial pathogens should be developed. Despite various drawbacks and challenges that currently exist, a widespread and great progress in this area can be expected in the future.

Conclusions

Based on this review, it is possible to conclude that SFNPs/SFNCs have high adsorption and disinfection capacities toward various types of contaminants. It involves detailed discussion on tailored synthesis of different types of nano ferrites, the fine tuning of surface properties, and their application as adsorbents in wastewater treatment. The analysis reveals that the shape and size of different types of nano ferrites directly depend upon synthetic routes. Moreover, the characteristics of different types of nano ferrites are regulated by different factors such as precursor composition, pH of solution and annealing temperature.

Number of methods has been developed for purification of water but adsorption method has been found to be efficient and effective. Various types of adsorbents have been used

for removal of different pollutants from wastewater. In recent years the use of nanomaterials in water remediation has increased considerably. Adsorption efficiency is found to depend on the type of adsorbent, adsorbate, pH of solution, concentration of pollutant and temperature. Removal of pollutants has been discussed on the basis of different isotherm and kinetic models.

In addition, the use of SFNPs/SFNCs is an excellent option for water and wastewater treatment because wastewater can be reused, waste generation and environmental pollution is reduced, the treatment technology is simple and easy, and it is cost-effective. This is due to the dose requirement being low, easily recovered by an external magnetic field and used for several cycles.

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