Chapter 6

Spinel Ferrite Based Nanomaterials for Water Remediation Application

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Abstract

The decreasing levels of consumable water on earth have been a serious issue and this issue makes the researchers and scientists develop new technologies for the purification of polluted water. Several reports have been carried on wastewater remediation by utilizing spinel ferrite-based nanoparticles and their composites. The spinel ferrites-based nanoparticles utilized for wastewater treatment was cost effective, chemically stable, easily retrieved and reusable. The present work addresses the various fabrication techniques for the preparation of spinel ferrite-based nanoparticles and their utilization for the removal of organic and inorganic pollutants through the adsorption paths.

Keywords

Spinel Ferrites, Fabrication Techniques, Adsorption Mechanism, Organic and Inorganic Pollutants, Wastewater Remediation

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1. Introduction

Water is present in abundant concentration on earth, but the main issue is that only 1% of the water is consumable. From the last decades, consumable water was utilized tremendously for the household works, consumption, industrial work and for many other works which, therefore, makes the level of consumable water decreasing according to the day-to-day life requirements [1]. Moreover, the increasing industrial establishment and population growth will be responsible for the shortage of consumable water on earth. There were various pollutants as organic, inorganic, radiological, and biological, present in water getting from natural resources and thus, making it very difficult to take water for consumption [2,3]. These pollutants are toxic in nature and are dangerous for the human and other living life. Around 80 percent of the diseases are caused in human beings due to polluted water consumption and moreover, 3.5 million people die every year due to water borne diseases. The requirement for clean water increases day by day in the world and for doing this, a number of technologies such as photocatalytic degradation, adsorption, bacterial degradation etc. were taken into practice [4,5]. Out of all these techniques, adsorption and photocatalytic degradation is considered as one of the

important approaches for wastewater remediation [6,7]. The adsorption technique is very effective in eliminating pollutants by transferring the polluting reagents from standard media to alternative media in relation to destroy it.

In modern times, spinel ferrites have attracted various researchers and authors from all over the world due to its superior properties such as large surface to volume ratio [8], superparamagnetic nature, high chemical stability [9], high adsorption abilities and moreover, is considered as one of the best photocatalysts for the degradation of pollutants. Based on magnetism, spinel ferrites of chemical formula, MFe_2O_4 where M represents divalent metal ion, are categorized into normal spinel, inverse spinel, and mixed spinel ferrite [10]. A greater attention has been given to the category of spinel ferrite due to its excellent applications such as magnetic storage devices, biomedical, water remediation and many more. The A-A, B-B and A-B exchange interactions were present in the structure of spinel ferrites where A-B interaction was stronger than the B-B interaction and thus, magnetism in spinel ferrites can be observed due to the exchange interactions between the various cations present at the interstitial sites i.e. A-site (tetrahedral site) and B-site (octahedral site) [11,12]. The magnetic property in the spinel ferrites shows its dependence towards the distribution of cations at the interstitial sites and therefore, substitution of dopant ions at the octahedral sites will be responsible for the weakening of A-B exchange interactions [13,14]. Under the cation distribution, in case of normal spinel ferrites, divalent metal ions are distributed among the A-site whereas, ferric ions prefer to occupy the B-site. In inverse spinel ferrites, divalent metal ions occupied the B-site but under mixed spinel ferrites, both the divalent and ferric ions try to occupy the A-site and B-site, respectively. For the water remediation application, spinel ferrite based magnetic nanoparticles were turn out to be very essential for the elimination of pollutants with the utilization of adsorption and photocatalytic degradation technologies [15–19] and these has been extensively utilized in industries to eliminate organic pollutants, dyes, and toxic metallic elements [20–23]. Spinel ferrites are easily retrieved from the resultant mixture and therefore, retrieved material was further utilized for number of reuse cycles [24]. The aim of this book chapter was to address the spinel ferrites and their fabrication approaches. Moreover, to provide a detailed study of spinel ferrites for water remediation application incorporating adsorption.

2. Approaches for the fabrication of Spinel ferrites

There are various approaches for the fabrication of spinel ferrite-based nanoparticles such as sol-gel, auto-combustion, co-precipitation, citrate precursor, solid state reaction and many more [25–27]. To synthesized high quality magnetic nanoparticles, appropriate fabrication technique was taken into practice. The microstructural, optical, magnetic and

adsorption properties of spinel ferrites can be improved using incorporation of metal ions at the interstitial sites- Tetrahedral site (A-site) and Octahedral site (B-site). Therefore, the proper selection of fabrication technique will be responsible for deciding the properties of final product [28]. The various approaches for the preparation of nanoparticles were discussed as:

2.1 Solid state reaction technique

The solid-state reaction approach was utilized for the fabrication of spinel ferrite based magnetic nanoparticles by taking two starting solid chemical precursors. For the synthesis, a stoichiometric amount of the starting precursors of AR graded was taken for ball milling around 10 to 12 hours. The chemical reagents are interspersed with distilled water by wet blending in a mortar pestle [29] and then, it was calcinated in a muffle furnace at specified temperature for specified hours. The ball milling of calcinated powder was again taken into practice and most of the times, surfactants were utilized for the reduction of particle size of magnetic nanoparticles. The fabricated magnetic nanoparticles were again pressed into pellets using a hydraulic press and then, these pellets were sintered in a muffle furnace at 1000 °C to 1500 °C for 5-7 hours, respectively. Therefore, the final fabricated nanoparticles were ready for analyzing their properties.

2.2 Sol-gel auto-combustion technique

The sol-gel auto-combustion technique belongs to a category of wet chemical approach utilized to fabricate solid nanoparticles. The metals-based magnetic nanoparticles can be prepared by using technique in which the starting precursors were the metal nitrates and citric acid and here, citric acid acts as a fuel. For the fabrication of nanoparticles, firstly stoichiometric amounts of starting precursors were taken in distilled water and stirred on magnetic stirrer with a hot plate until both the aqueous solutions become clear. Mixed both the aqueous solutions and set their pH~7 by adding few drops of ammonia solution [30]. For the making of gel, add stoichiometric amount of gel precursor called ethylene glycol. Fused out the gel at 100 °C to 150 °C on magnetic stirrer with hot plate to undergo auto-combustion until a loose black material will be obtained [14,31]. The final residue was grinded using mortar pestle to get fine nanoparticles and then, it was calcinated in a muffle furnace at 800 to 1000 °C for 4 to 5 hours. Therefore, the final nanomaterials were ready for their characterization to analyze its various properties. A number of spinel ferrite based nanomaterials have been fabricated with the usage of sol-gel auto-combustion technique [32,33]. Using a hydraulic press, the fabricated powder was pressed in the form of pellets and sintered in a muffle furnace at a specified

temperature for some hours, respectively. The Schematic chart of sol-gel auto-combustion technique were provided in Fig. 1.

2.3 Co-precipitation technique

The co-precipitation technique is one of the effective and appropriate techniques for the fabrication of magnetic nanoparticles which incorporates metal chlorides as the starting precursors. Firstly, the stoichiometric weights of metal chlorides are mixed with distilled water and the solution is stirred for 2 hours on a magnetic stirrer. Add few drops of $\text{NH}_4(\text{OH})_2$ solution to set the pH of the given solution and stir it continuously. After stirring, the precipitates start inside the solution at the bottom of the beaker and then, these precipitates are separated out by centrifugation, respectively. The precipitates were washed many times for the removal of extra impurities with the utilization of distilled water. The schematic chart of co-precipitation fabrication approach was provided in Fig. 2.

Figure 1: Schematic representation of sol-gel auto-combustion fabrication technique.

Figure 2: Schematic representation of co-precipitation fabrication technique.

2.4 Citrate precursor technique

The citrate precursor technique is cost effective and a less time consumption fabrication technique which incorporates metal nitrates and citric acid as the starting precursors and it also controls the homogeneity of the fabricated nanoparticles. The stoichiometric amounts of starting precursors were mixed with distilled water. The solution was heated at a temperature of 50-80 °C on magnetic stirrer with hot plate for two hours until a solid residue is obtained and then, this solid residue is crushed into fine powder. The grinded fine powder was calcinated at a temperature of 700-900 °C for five hours, respectively. Therefore, the final nanoparticles were obtained. The Schematic representation of citrate precursor fabrication technique was provided in Fig. 3.

Figure 3: Schematic representation of citrate precursor fabrication technique.

2.5 Hydrothermal technique

The hydrothermal fabrication technique is one of the productive and low temperature approaches to produce high crystallinity and less agglomerated nanoparticles. The whole process was taken out in an autoclave (Teflon lined) at a temperature of 100-170 900 °C. Under this technique, the in a Teflon lined autoclave in which starting precursors were the metal chlorides which were mixed one by one with distilled water and stirred on a magnetic stirrer with hot plate at room temperature [34]. To the stirring solution, KNO₃ or NaOH solution were added and then, pH of the final solution was balanced by adding few drops of ammonia solution. The formed residue was washed several times for the removal of chloride concentration still present in the final product and moreover, washing with ethyl alcohol was also carried out for the prevention of agglomeration [35]. The final residue was then annealed in a Teflon lined autoclave at a temperature of 100-200 °C, respectively. Many times, surfactants were taken into practice for controlling the growth, size, and nucleation of fabricated nanoparticles. The chart of hydrothermal synthesis technique was provided in Fig. 4.

Figure 4: Schematic representation of hydrothermal fabrication technique.

3. Spinel ferrites nanoparticles and composites used for wastewater remediation

The comprehensive applications of spinel ferrites nanoparticles and their composites in wastewater remediation have been clearly demonstrated in research. Their use as adsorbent, photocatalyst, sensor and membrane modification etc. Organic dyes, heavy metal ions, pesticides, antibiotics and a large range of aromatic compounds are the most dangerous substances found in wastewater [36]. Natural water unsafe for consumption and even harmful to marine species due to the prevalence of these toxins in water. A variety of methods have been implemented for the remediation of wastewater, with differing degrees of effectiveness. A few of these methods include adsorption strategies focused on filtration, ion exchange, coagulation, anaerobic therapy, aerogels, hydrogels, and non-magnetic metal oxides [37,38]. For the elimination of pollutants from water, these remediation options may be used; but several issues impede their use, such as inadequate pollutant removal, adsorbent recovery complexity, absence of cost-effectiveness of the process, and in some situations the waste sludge is voluminous and requires careful design and a significant amount of disposal space is needed [5,39]. Owing to the above drawbacks, existing adsorbents used in the treatment of wastewater are not suitable. Therefore, we need an adsorbent that is cheap, reliable, reusable and easily retrieved [40,41]. Accordingly, the most suitable materials are spinel ferrites nanoparticles and their composites that can offer alternatives to waste water treatment. Because of their exceptional chemical and physical properties, which allow them to extract a wide variety of pollutants and easily retrieved and reusable. Compared to their bulk counterparts, spinel ferrites nanoparticles and their composites have many benefits, especially in terms of greater adsorption efficiency, cost-effectiveness and pollutants removal capacity [42]. In addition, ease retrieved and ability to reuse retrieved adsorbents for many reuse cycles without losing their adsorption efficiency compared to other non-magnetic nanoparticles-based adsorbents make spinel ferrites nanoparticles and their composites one of the popular materials and recently have been utilized broadly for the remediation of wastewater. According to the literature, spinel ferrites nanoparticles are favored for wastewater remediation due to its huge surface area and large number of active sites for contact with pollutants present in the aqueous solution [43,44]. Moreover, spinel ferrites nanoparticles have superparamagnetic properties that arises from their nanoparticle size, allowing them to be easily removed by external magnetic fields from the aqueous solution. The spinel ferrites nanoparticles might be used directly or as a central material by covering them with sufficient functional groups for the handling of wastewater. For instance, by surface functionalization using an appropriate functional group like amines, trimethoxy silane and phosphoric acid etc. the properties of spinel ferrites nanoparticles are enhanced significantly [45]. By introducing polymers to

nanoparticles, such functional groups could be added during the preparation of nanoparticles. Besides the stabilization of spinel ferrites nanoparticles, these functional groups enhance the selectivity in aqueous solution by hyper-branching, ionic or electrostatic interactions. Many isotherms as well as kinetic models are utilized to verify the adsorption potential of various spinel ferrites nanoparticles and their composites [46]. Mainly most frequently utilized models for isotherm are Langmuir and Freundlich isotherm models and for kinetics pseudo first and pseudo second order kinetic models. The adsorption isotherm models help to determine the maximum adsorption capacity of the adsorbent and also explain the interaction between the adsorbent and adsorbate. While the kinetic models help to determine the adsorption rate and behavior of adsorption [47,48].

4. Adsorption pathways

Adsorption process is largely regulated by certain type of interaction between the adsorbent and adsorbate, precisely the surface charge and hydroxyl groups playing a major role in adsorption. The most feasible methods of physicochemical interaction includes ion-exchange, weak forces including van der Waals forces, hydrogen bonding, dipole–dipole and π - π interactions, these are capable of eliminating various contaminants from wastewater by adsorption [49,50]. Furthermore, chemisorption due to the chemical interactions is feasible when there is successful sharing of electrons between the adsorbate and adsorbent and physisorption occurs when there is weak attractive forces between the pollutant and adsorbent's surface as shown in the Fig. 5 [51].

Different mechanisms rely on the form of adsorption and type of contaminant available. There are toxins found in wastewater and the spinel ferrite nanoparticles/spinel ferrite nanoparticle composites are being used to handle wastewater treatment [52]. For more illustration, the ion-exchange process for Pb (II) adsorption on $\text{Co}_{0.6}\text{Fe}_{2.4}\text{O}_4$ was found to be a significant adsorption mechanism. In this work, when $\text{pH} < 7$, the adsorption process is mainly based on ion exchange mechanism and outer-sphere surface complexes, whereas for $\text{pH} > 7$, inner-sphere surface complexes are observed [53]. An alternative study showed that adsorption through the method of ion-exchange and electrostatic attraction were the key adsorption mechanisms for copper ion adsorption on the surface of EDTA functionalized silica-coated Fe_3O_4 [54]. Results from the adsorption analysis on many spinel ferrite nanoparticles indicate electrostatic activity and ion-exchange as the key adsorption mechanism for cationic dyes, because surfactant groups are present on these nanoparticles [55,56]. One way to imagine this is to think about extracting MB and Congo red together in the presence of MnFe_2O_4 nanoparticles. During this phase, the

hydrogen bond association between the dye and the hydroxyl groups found in MnFe_2O_4 was discovered to be an important adsorption mechanism [57].

Figure 5: Shows general adsorption mechanism with its basic types.

Similarly, the predominant adsorption mechanism of arsenate on $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles during the removal of arsenate from treated water was found to be inner-sphere complex formation [58]. Because of the various influences on the adsorption mechanism, the nature of the contaminant and the adsorbent such as functional groups, pore structure, oxidation state, and surface charge all significantly affect the outcome.

5. Factors affecting the adsorption ability of spinel ferrite nanoparticles

Multiple factors such as synthesis methods, types and particle size of the adsorbent, dosages, pH value of wastewater, initial concentration of contaminants, temperature, and charge and size of adsorbate all influence the adsorption capacity of spinel ferrite nanoparticles and their corresponding composites. The aforementioned factors (Fig. 6) have already been well studied in regards to adsorption and removal of contaminants [30, 46].

Figure 6: Shows different factors affecting the adsorption ability of spinel ferrite nanoparticles.

5.1 Particle size

Generally, adsorption is related to particle size of nanoparticles, referred to as the nanoscale effect. Larger particle size generally correlates with higher adsorption capacity due to increased surface area- to - volume ratio [60].

5.2 pH value

The pH of the solution determines the volume of content that can be adsorbed, since the surface charge of the spinel ferrite nanoparticles and spinel ferrite nanoparticle composites is influenced by the pH of the solution. For example, spinel ferrite nanoparticles have a greater positive charge at a lower pH and a greater negative charge at a higher pH. This statement supports anion adsorption at lower pH and cation adsorption at higher pH [61]. For example, the best adsorption of Mo(VI) 33.4 mg g⁻¹ on γ -Fe₂O₃ nanoparticles between pH 4 and 6. The removal efficacy of CuFe₂O₄ for Mo(VI) declined as the pH was raised, with a maximum removal competence at pH 2.75, but almost no removal of Mo(VI) was observed at pH >10. This is related to the growth in attraction between MoO₄²⁻ and positively charged spinel ferrite nanoparticle at declining pH [62]. Related to this, the effect of pH, initial metal concentration, and adsorbent dosage on the removal of Cu(II) were extensively analyzed. As the pH grew from 2.0 to 5.3, the elimination of Cu(II) on Fe₃O₄ NPs improved from 0.73 to 99.1 percent. At a pH of 5.3, the removal decreased up to 66% due to initial solution concentration enhancement, although adsorbent dose from 0.1 to 1 g improved the removal from 41.65% to 97.05% [63].

5.3 Temperature

Under the conditions used in the experiment, adsorption capacities of spinel ferrite nanoparticles mainly influence temperature. Depending on the form of favored chemical reaction, increasing or decreasing temperature determines the accessible free adsorption site. In endothermic reactions with the increase in temperature, adsorption capability increases; as exothermic reactions increase in temperature, adsorption capacity decreases. Pb(II) sorption on $\text{Co}_{0.6}\text{Fe}_{2.4}\text{O}_4$ which was synthesized by a thermal decomposition technique and was found to be endothermic and spontaneous in nature [53,64].

5.4 Calcination temperature

The ability of adsorption is based on the calcination temperature of spinel ferrite nanoparticles. As a result, the calcination temperature and the amount of time used for calcination both affect the size and pore size of nanoparticles, which influences both the surface area and pore size of nanoparticles. In this work process included impregnation and calcination at three separate temperatures with cotton as a template, during which the resulting hollow fibre NiFe_2O_4 nanoparticles were used for CR removal. The calcination temperature was increased, but only the highest pore volume was achieved for NiFe_2O_4 synthesized at 600°C . Thus, NiFe_2O_4 synthesized at 600 degrees Celsius had higher adsorption capacity of CR (89.85 mg g^{-1}) [65]. In order to produce a good technology for complete removal of each targeted contaminant from wastewater, it is absolutely essential to understand the impacts of each parameter.

6. Organic pollutants removal

Spinel ferrites nanoparticles and their composites have demonstrated good adsorption capacity for organic pollutants that are released into the atmosphere from different sources. The organic pollutants are adsorbed on the spinel ferrites nanoparticles and their composites by chemisorption or physisorption [66]. In this section, a brief overview of the current literature dealing with the elimination of organic pollutants present in wastewater.

Naik et al. synthesized the cobalt doped manganese ferrite by combustion method [67]. The structure of prepared sample was confirmed with the help of different characterization techniques. The particle size distribution the prepared samples were confirmed by TEM (Transmission Electron Microscope) analysis and range is 15-30 nm. The variation of magnetic moment and magnetization was analyzed with the help of VSM (Vibrating Sample Magnetometer). At a room temperature antifungal activity of the prepared samples was examined against *Rhizopus* fungi. Additionally, prepared ferrites

were examined for adsorption of methylene blue dye and maximum removal percentage was reported 92.06 % for $\text{Mn}_{0.8}\text{Co}_{0.2}\text{Fe}_2\text{O}_4$.

In another study, spinel cobalt ferrite was synthesized successfully through hydrothermal technique [68]. The prepared ferrite was functionalized with the help of humic acid and epichlorohydrin. The prepared ferrite adsorbent was utilized for removal of triarylmethane dyes such as malachite green dye, methyl violet 2B, and basic fuchsin. The maximum removal capacity for malachite green dye, methyl violet 2B, and basic fuchsin were 48.74, 62.62 and 96.49 $\mu\text{mol/g}$ by functionalized spinel cobalt ferrite. And the different adsorption parameters were optimized like effect of pH, dye concentration, ionic strength, temperature, and contact time. The experimental data well fitted for pseudo-second order kinetic model and Langmuir isotherm model. The thermodynamic experiments have shown that the processes of adsorption are spontaneous-endothermic. Moreover, the functionalized cobalt ferrite was examined for ten reuse cycles and findings demonstrated that no significant change after ten reuse cycles.

Yavari et al. synthesized the CoFe_2O_4 ferrite nanoparticles and prepared ferrite nanoparticles successfully functionalized by amine groups [69]. The prepared amine group functionalized cobalt ferrite nanoparticle was utilized for removal of acid blue 92, direct green 6 and direct red 80. The maximum reported adsorption capacity for acid blue 92, direct green 6 and direct red 80 were 625, 384.6 and 333.3 mg/g respectively. The different adsorption parameters were optimized such as effect of pH and dose, initial dye concentration and contact time at 25°C . The three different isotherm models such as Langmuir, Freundlich and Tempkin isotherm models were examined and findings show that experimental data best fit for Langmuir isotherm model. Similarly, the three different kinetics models such as pseudo first-order, pseudo second-order and intraparticle diffusion models were examined and findings show that experimental data best fit for pseudo second order kinetic model.

Tatarchuk et al. synthesized the TiO_2 on CoFe_2O_4 nanocomposite by the Pechini sol gel technique with the help of chelating agents (citric acid and ethylene glycol) [70]. The prepared sample was utilized for the adsorption of dichromate anions and congo red dye. The reported highest removal percentage for dichromate anions and congo red dye were 83% and 61% respectively. The three different isotherm models such as Langmuir, Freundlich and Dubin-Radushkevich isotherm models were examined and analysis demonstrated that experimental data best fit for Langmuir isotherm model. In another study, Wu et al., synthesized the cobalt ferrite modified with rare earth metals (Ho^{3+} , Tb^{3+} , Sm^{3+} , Pr^{3+}) through hydrothermal technique in the absence of surfactant and template [71]. The prepared cobalt ferrite modified with rare earth metals nanoparticles utilized for the adsorption of Congo red dye. The findings are demonstrated that after

doping of rare earth metals adsorption capacity of the ferrite samples increased dramatically. The reported maximum adsorption potential for Congo red dye was 158.0 mg/g and 178.6 mg/g by $\text{CoFe}_{1.9}\text{Ho}_{0.1}\text{O}_4$ and $\text{CoFe}_{1.9}\text{Sm}_{0.1}\text{O}_4$ respectively. The experimental data best fit for pseudo second order kinetics model and Langmuir isotherm model.

Afkhami et al., synthesized the maghemite nanoparticles modified by sodium dodecyl sulfate and prepared sample utilized for the adsorption of cationic dyes such as janus green b, thionine and brilliant cresyl blue from aqueous solution [72]. The reported highest removal capacity for janus green b, thionine and brilliant cresyl blue dyes were 172.4, 166.7 and 200.0 mg/g respectively. In another study, maghemite nanoparticles coated with sodium dodecyl sulfate synthesized by Shahri and Niazi, and maghemite nanoparticles were prepared by co-precipitation technique [73]. The different adsorption parameters were optimized for adsorption of acridine orange dye from aqueous solution. The reported optimized conditions were 30.0 mg/L dye concentration, 0.8 g/L adsorbent dose, pH of dye solution = 5.1 and adsorption time = 43 min. Under the optimized conditions highest adsorption capacity was 285.82mg/g. The Langmuir and Freundlich isotherm models were analyzed and the experiment data best fit for Langmuir isotherm model.

Jiang et al. synthesized nickel ferrite / activated carbon composite prepared by hydrothermal technique [74]. The prepared sample was utilized for the adsorption of methyl orange azo dye and the highest adsorption capacity was reported 182.82 mg/g at 29.85°C. The experimental best fit for Langmuir isotherm model and pseudo second order kinetics model. And thermodynamic analysis examined that methyl orange azo dye adsorption on nickel ferrite / activated carbon composite was endothermic and spontaneous process. Moreover, the summary of organic pollutants removal from wastewater by spinel ferrites nanoparticles and their composites are mentioned in Table 1. As seen in Table 1, the spinel ferrites nanoparticles and their composites are most significant adsorbent for the removal of organic pollutants from aqueous solution.

Table 1: The spinel ferrites nanoparticles and their composites are used for organic pollutants removal from aqueous solution with their adsorption capacity.

Sr. No.	Adsorbent name	Organic Pollutants	Adsorption capacity	Reference
1.	Mn _{0.8} Co _{0.2} Fe ₂ O ₄	Methylene blue dye	92.06 %	[67]
2.	Epichlorohydrin-crosslinked humic acid with spinel cobalt ferrite	Malachite green dye, Methyl violet 2B, and Basic fuchsin	22.59, 24.67 and 31.25 mg/g	[68]
3.	Spinel cobalt ferrite/humic acid	Malachite green dye, Methyl violet 2B, and Basic fuchsin	17.30, 18.85 and 21.42 mg/g	[68]
4.	Spinel cobalt ferrite	Malachite green dye, Methyl violet 2B, and Basic fuchsin	2.00, 2.68 and 3.16 mg/g	[68]
5.	Amine group functionalized cobalt ferrite nanoparticle	Acid blue 92, Direct green 6 and Direct red 80	625, 384.6 and 333.3 mg/g	[69]
6.	TiO ₂ on CoFe ₂ O ₄ nanocomposite	dichromate anions and congo red dye	83% and 61%	[70]
7.	Maghemite nanoparticles coated with sodium dodecyl sulfate	Janus green b, Thionine and Brilliant cresyl blue dyes	172.4, 166.7 and 200.0 mg/g	[72]

8.	Maghemite nanoparticles coated with sodium dodecyl sulfate	Acridine orange dye	285.82 mg/g	[73]
9.	Nickel ferrite/ activated carbon composite	Methyl orange azo dye	182.82 mg/g	[74]
10.	MgFe ₂ O ₄ nanoparticle	Basic fuchsin	1.23 mg/g	[75]
11.	CoFe _{1.9} Sm _{0.1} O ₄	Congo red dye	178.6 mg/g	[71]
12.	CoFe _{1.9} Ho _{0.1} O ₄	Congo red dye	158.0 mg/g	[71]
13.	CuFe ₂ O ₄ /drumstick pod biomass composite	Malachite green	952.4 mg/g	[76]

7. Organic pollutants removal

Spinel ferrites nanoparticles and their composites are both economically and technologically very significant in wastewater treatment for the elimination of inorganic pollutants, as they have many advantages such as enhanced adsorption ability, relatively low cost of production, and ease of regeneration and separation. The polluted water is remediated with spinel ferrites nanoparticles and their composites, contaminants could be easily adsorbed to nanoparticles or composites and then separated from a matrix using an external magnetic field. The pure spinel ferrites nanoparticles, ferrites nanoparticles modified with metal oxide or any other appropriate organic functional groups are widely used for water remediation [46]. For example, Asadi et al. synthesized CoFe₂O₄ and MnFe₂O₄ spinel ferrites nanoparticles prepared by co-precipitation method [77]. The prepared ferrites nanoparticles were utilized for removal of Zn (II) ions from wastewater. The reported magnetization for CoFe₂O₄ and MnFe₂O₄ spinel ferrites nanoparticles were 37.54 and 61.39 emu/g, respectively. The different adsorption parameters were optimized for adsorption of Zn (II) ions from aqueous solution. Under optimized 6 pH the reported maximum adsorption capacity for CoFe₂O₄ and MnFe₂O₄ spinel ferrites nanoparticles were 384.6 and 454.5 mg/g respectively. The experimental data best fit for Langmuir isotherm model and pseudo second order kinetics model. From the thermodynamics analysis concluded that Zn (II) ions adsorption was spontaneous and exothermic process. Moreover, the prepared samples were also investigated for adsorption-desorption cycles.

In another study, Tavares et al., synthesized the magnetic nano adsorbent (CoFe_2O_4 , MnFe_2O_4 and Fe_3O_4). The prepared magnetic nano adsorbent utilized for the removal of As (V) ions [78]. Tu et al. synthesized CuFe_2O_4 ferrite nanoparticles and prepared ferrites nanoparticles was utilized for the adsorption of As(V) ions [79]. The removal of arsenic (V) by this recycled CuFe_2O_4 ferrite nanoparticles exhibited an L-shaped nonlinear isotherm, indicating restricted binding sites on the CuFe_2O_4 ferrite surface. The highest arsenic (V) adsorption potential of the CuFe_2O_4 ferrite nanoparticle at pH 3.7 was 45.66 mg/g and adsorption capacity reduced with pH due to improved electrostatic repulsion between arsenic (V) and CuFe_2O_4 ferrite surface. The findings indicate that the recycled CuFe_2O_4 ferrite nanoparticle without surface alteration is an efficient adsorbent for the adsorption of arsenic (V) from aqueous solution.

Because of high toxicity to human and marine environments, the elimination of lead from the wastewater system has drawn substantial public attention. For example, Sreekala et al. synthesized the CuFe_2O_4 ferrite nanoparticles through a green technique and its utilized for Pb (II) ions adsorption [80]. The green technique means cost effective, non-toxic and environmentally sustainable procedure utilizing plant extracts. In this research work author used *Simarouba glauca* leaf extract as a capping and reducing agent. According to the batch adsorption analysis prepared CuFe_2O_4 ferrite nanoparticle demonstrated that excellent adsorption capacity for Pb (II) ions from wastewater. The reported maximum adsorption percentage was 80%. In another study, Khan et al., synthesized the CuFe_2O_4 composite with drumstick pod biomass by co-precipitation method [76]. And prepared composite utilized for lead ions adsorption from aqueous solution. Different adsorption parameters were optimized for Pb (II) ions adsorption and under optimized conditions reported maximum adsorption capacity was 921.1 mg/g. The adsorption experimental data was best fit for Langmuir isotherm models. In another study, Putri et al., synthesized the natural iron sand based $\text{Mg}_{1-x}\text{Ni}_x\text{Fe}_2\text{O}_4$ ferrite nanoparticles with the help of co-precipitation technique [81]. The prepared nano ferrites used for the removal of Pb and Cu ions from aqueous solution. Under the optimized conditions maximum removal capacity was achieved 190.5 mg/g. Furthermore, the summary of inorganic pollutants removal from wastewater by spinel ferrites nanoparticles and their composites are mentioned in Table 2. As seen in Table 2, the spinel ferrites nanoparticles and their composites are most significant adsorbent for the removal of inorganic pollutants from aqueous solution.

Table 2: The spinel ferrites nanoparticles and their composites are used for inorganic pollutants removal from aqueous solution with their adsorption capacity.

Sr. No.	Adsorbent name	Inorganic Pollutants	Adsorption capacity	Reference
1.	CoFe ₂ O ₄	Zn (II)	384.6 mg/g	[77]
2.	MnFe ₂ O ₄	Zn (II)	454.5 mg/g	[77]
3.	CoFe ₂ O ₄ , MnFe ₂ O ₄ and Fe ₃ O ₄	As (V)	-	[78]
4.	CuFe ₂ O ₄	As (V)	45.66 mg/g	[79]
5.	CuFe ₂ O ₄	Pb (II)	80%	[80]
6.	CuFe ₂ O ₄ /drumstick pod biomass composite	Pb (II)	921.1 mg/g	[76]
7.	Mg _{1-x} Ni _x Fe ₂ O ₄	Pb and Cu ions	190.5 mg/g	[81]
8.	Rice Straw/ CoFe ₂ O ₄ nanocomposite	Fe and Mn	84.25%, 92.45%	[82]
9.	Rice Straw/ CoFe ₂ O ₄ nanocomposite	Cu, Cd, Zn, Ni and Pb	100%	[82]
10.	γ-Fe ₂ O ₃	Cu(II), Zn(II) and Pb(II)	111.11, 84.95 and 71.42 mg g ⁻¹	[83]

8. Future prospects

The spinel ferrite-based nanoparticles for wastewater remediation needs high quality control for the elimination of pollutants and nanoparticles from the polluted water after remediation i.e., firstly to reduce the cost of nanoparticles by their recovery and reuse after being utilized, and second to overcome the health impact. The application of spinel ferrite-based nanoparticles in fresh water and wastewater remediation was limited and it was one of the biggest gap or issue that has been observed. For wastewater remediation, simulated wastewater was taken for the experiment where cations and anions were present in co-exist situation and practically, simulated wastewater does not consider as real wastewater. Therefore, increasing level of contaminants in the wastewater will be responsible for the increase of active sites in the structure of spinel ferrite-based nanoparticles. This will result in the elimination of anions and cations from the wastewater on the phenomenon of preferential discharge. Thus, the proceeding tests were not effective in the overall elimination of cations and anions from the stimulated wastewater as it does not belong to a real-life issue. So, it was very important to do a systematic way of including all the constituents which were present in the real-life environmental specimens. Moreover, a few studies have been addressed on the effect of

spinel ferrite-based nanoparticles on the human health and environment habitat, so, it was very crucial to study their detailed toxicity impact.

Conclusion

Spinel ferrite-based nanoparticles have multifunctional applications in the research areas of magnetic storage devices, recording media, switching devices, high frequency devices, wastewater remediation. Therefore, these ferrites have been tremendously utilized for the elimination of organic as well as inorganic pollutants from polluted water via adsorption. The nanoparticles were highly reactive in nature as a matter of toxicity concern so, it was very important to analyze their toxic behaviour before commercial use or for application concern. Moreover, new technologies were taken into consideration for the fabrication of spinel ferrite-based nanoparticles in regards with environmental and safety research concern. A deep research on the real wastewater remediation have been carried out in which different types of pollutants have been present. The spinel ferrites have excellent capabilities such as high adsorption and disinfection ability in regards with pollutants. Thus, the improvement of remediation technology by utilizing spinel ferrite-based nanoparticles not only lightens the present society issue of poor-quality water but also changes the predictable reagents being utilized for wastewater remediation with better quality amenities and running of safe water quality under sustainable conditions.

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