



Spinel ferrite magnetic adsorbents: Alternative future materials for water purification?



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Abbreviations: AC, activated carbon; AC/CFO, activated carbon/cobalt ferrite; AC/NiFe₂O₄, activated carbon/NiFe₂O₄; ACFNP, amine functionalized cobalt ferrite nanoparticles; AF, acid fuchsin; AFM, atomic force microscopy; Ag-CoFe₂O₄-GO, Ag-CoFe₂O₄-graphene oxide; AO II, acid orange II; AO7, acid orange 7; APTS, (3-aminopropyl) triethoxysilane; AR, acid red; ARB, acid red B; AS-MNP, amino modified coated magnetic nanoparticles; ATR-FTIR, attenuated total reflection Fourier transform infrared spectroscopy; AY, alizarine yellow; BB-R, brilliant blue-R; BET, Brunauer-Emmett-Teller; BR, brilliant green; CCMNPs, chitosan-coated MnFe₂O₄ nanoparticles; Co-MPTS, MPTS-modified particles; Co-MNP, cobalt ferrite magnetic nanoparticles; CoFe₂O₄-FGS, CoFe₂O₄-functionalized graphene sheets; CoFe₂O₄-rGO, Cobalt ferrite-reduced graphene oxide nanocomposites; CoFe₂O₄/MgAl-LDH, Cobalt ferrite/Magnesium, Aluminium doped layered double hydroxides; CNTs, carbon nanotubes; CNTs-C, carboxylic carbon nanotubes; CNTs-N, amino carbon nanotubes; CR, congo red; CV, crystal violet; CTAB, cetyltrimethyl ammonium bromide; EBT, erichrome black-T; EDX, energy dispersive X-ray; EDTA, ethylenediaminetetraacetic acid; EXAFS, extended X-ray absorption fine structure; E-waste, electrical and electronic equipment waste; FANiFe₅₀, fly ash/NiFe₂O₄ composite (mass ratio 50:50); FMB, MnFe₂O₄ modified biochar; FR, fuchsin red; FTIR, Fourier transform infrared spectroscopy; GCF, CoFe₂O₄ with graphene nanocomposite; GNF, NiFe₂O₄ with graphene nanocomposite; GO, graphene oxide; GO-MFO, graphene oxide-MnFe₂O₄; GO-NH, graphene oxide-MnFe₂O₄ hybrid; GONF, graphene oxide based inverse spinel nickel ferrite; HDA-RGO-ZnFe₂O₄, ZnFe₂O₄ nanoparticles loaded on 1,6-hexanediamine-functionalized reduced graphene oxide; HGMS, high gradient magnetic separation; HRTEM, high resolution transmission electron microscopy; IC, indigo carmine; ICP-OES, inductively coupled plasma optical emission spectrometer; ICP-MS, inductively coupled plasma mass spectrometry; LDHs, layered double hydroxides; MCCs, magnetic chitosan composites; MCGO, magnetic chitosan/graphene oxide; MCGS, amino-functionalized magnetic composite of CoFe₂O₄-chitosan-graphene; MCNCs, magnetic MnFe₂O₄/chitosan nanocomposites; MB, methylene blue; MBC, magnetic biochar composite; MG, methyl green; MnFe₂O₄-G, graphene manganese ferrite; MnFe₂O₄/PW, biomagnetic composite; MNP, multi-walled carbon nanotubes coated with magnetic amino-modified CoFe₂O₄ nanoparticles; MNP-CTS, chitosan-functionalized MWCNT/CoFe₂O₄-NH₂ hybrid material; MNZnFe, magnetic zinc ferrite; Mo, molybdenum; MO, methyl orange; MSFs, magnetic spinel ferrites; MWCNTs, multi-walled carbon nanotubes; MWCNTs CoFe₂O₄, multi-walled carbon nanotubes decorated with CoFe₂O₄ nanoparticles; MnFe₂O₄ NCs, manganese ferrite mesoporous clusters; MPTS, (3-mercaptopropyl) trimethoxy silane; Ms, saturation magnetization; MV, methyl violet; n-MgFe₂O₄, nano-magnesso ferrite; NFBC, nano ferrite bentonite clay composite; NFO 600, NiFe₂O₄ 600 °C; NiFe₂O₄-CNTs, NiFe₂O₄-decorated multiwalled carbon nanotubes; NCs, nanocrystals; NPs, nanoparticles; nZVI, zero-valent iron; OTC, oxytetracycline; PAA/MnFe₂O₄, polyacrylic acid/manganese ferrite; PANI, polyaniline; PCB sludge, printed circuit board industrial sludge; PFO, Pseudo-first-order; PNA, three-dimensional porous NiFe₂O₄ adsorbent; PNCofe, porous nano-crystalline cobalt ferrite; PSO, Pseudo-second-order; PZC, point of zero charge; *q_e*, maximum adsorption capacity per mass (mg/g); *q_e'*, Maximum adsorption capacity per surface area (mg/m²); RB5, reactive blue 5; RE, rare earths; R-EPW, real electroplating wastewater; rGO, reduced graphene oxide; RhB, rhodamine B; RHC, rice husk/CoFe₂O₄ composite; SA, surface area; SD/MnFe₂O₄, sawdust/MnFe₂O₄; SDBS, sodium dodecyl benzene sulfonate; SDS, sodium dodecylsulfate; SEM, scanning electron microscopy; S-EPW, simulated-electroplating wastewater; SFs, spinel ferrites; SFCs, spinel ferrite composites; SFNPs, spinel ferrite nanoparticles; SFP, spinel ferrite powder; SPM60, sponge like porous MnFe₂O₄ (60 mL dosage of egg white); TBBPA, tetrabromobisphenol A; TC, tetracycline; TCLP, toxicity characteristic leaching procedure; TEM, transmission electron microscopy; TEOS, tetraethyl orthosilicate; TFCFMNP, thiol functionalized cobalt-ferrite magnetic nanoparticles; TG-DTA, thermogravimetry and differential thermal analysis; TY, titan yellow; US EPA, United States Environmental Protection Agency; VSM, vibrating sample magnetometer; XANES, X-ray absorption near-edge structure; XPS, X-ray photoelectron spectroscopy; XRD, X-ray diffraction; 3D Porous NiFe₂O₄, three dimensional porous NiFe₂O₄; 3D GBM, three-dimensional graphene-based macrostructures; 1:1.5 composite, CuFe₂O₄/activated carbon composite; γ-Fe₂O₃, maghemite; α-Fe₂O₃, hematite; Fe₃O₄, magnetite.

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ABSTRACT

Spinel ferrite (SF) magnetic materials are an important class of composite metal oxides containing ferric ions and having the general structural formula $M^{2+}Fe_2^{3+}O_4$ (where $M = Mg^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Fe^{2+}, Mn^{2+}$, etc.). SFs possess unique physicochemical properties including excellent magnetic characteristics, high specific surface area, surface active sites, high chemical stability, tunable shape and size, and the ease with which they can be modified or functionalized. As a result of their multifunctional properties, affordability, and magnetic separation capability, SF adsorbents are a top choice for water purification applications that require high adsorption efficiencies and rapid kinetics. In this review, we discuss adsorption performance and possible applications of SFs and their derivatives for treating a wide range of aqueous pollutants such as metal ions, dyes, and pharmaceuticals. Key parameters influencing the sorption performance such as particle size, shape, annealing temperature, functionalization, and metal ion doping have been comprehensively discussed. In addition, adsorbate–adsorbent interactions, desorption, regeneration, and utilization of spent adsorbent have also been summarized. The review also covered, how SFs are prepared from industrial waste using green synthetic routes and general remarks about toxicological effects.

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1. Introduction

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. Currently, there are droughts in both California and São Paulo, and there is lead contamination in some of the water in Flint, Michigan, all of which affect the availability of safe drinking water [1–9]. 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) [14–16]. A sustainable solution to these problems is the recycling or recovery of fresh water from tainted water. However, many lethal chemical compounds, such as metal ions, dyes, and pharmaceuticals, which originate from urban and industrial wastewater, can be present in drinking water, and may lead to human diseases and/or damage to the environment. For these reasons, a number of different approaches to developing highly efficient water purification methods have been undertaken [17–28]. Optimal water purification methods should be available at a low cost [16], so they are affordable to developing nations. Adsorption technology using a solid adsorbent meets these needs because it offers high performance, affordability, and an environmentally friendly application.

Researchers from various fields, including environmental, chemical, biotechnological and material science, have come together to develop novel adsorbents to solve wastewater treatment problems [29–38]. Published reports describe the development of a range of adsorbents including: carbon-based three-dimensional architectures [39], three-dimensional graphene-based macrostructures (3D GBM) [40], magnetic chitosan composites (MCCs) [41], ordered mesoporous materials [42], inorganic nano-adsorbents [43], nano-adsorbents [44], agricultural biomasses [45], graphene nanosheets [46], metal–organic frameworks [47], sludge-derived activated carbons [48], biosorbents [49], tailored zeolites, [50] and bio-derived materials [51]. Of all the adsorbents developed to date, activated carbon (AC), a material known for years, was one of the most successful, and is, still present in commercial applications. However, after extensive usage (AC becomes exhausted), pollutant loaded AC must be separated from the aqueous solution and regenerated, a process that typically involves filtration or centrifugation [52]. Problems arise when filters become blocked, or carbon is lost. Furthermore, AC has a non-polar surface making it inappropriate for inorganic contaminant removal, and it exhibits a low adsorption affinity for low molecular weight polar organic pollutants [53]. These shortcomings limit the prevalent applications of AC. On the other hand, many of the newly developed adsorbents are nanoparticles, meaning that removal from aqueous solutions after adsorption is difficult and the toxicity of nanoparticles is a concern [28,54,55]. An ideal adsorbent for commercial application should have following characteristics: (i) high performance, (ii) rapid adsorption, (iii) cost-efficient, (iv) environmentally non-toxic, (v) reusability, and (vi) ease of separation. When applied in a batch solution, the most difficult of these challenges has been an effective separation of the particles from aqueous solution. Recovery of the non-biodegradable sorbent after

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