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Review: Preparation, Properties, and Applications of Ferrites in Sustaining Environment

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Abstract: Recently, groundwater and drinking water have been severely contaminated by the amount of arsenic-containing wastewater discharged by industries over the past few decades, increasing the number of instances of arsenicosis on a daily basis. Spinel ferrite nanoparticles (SFNPs) and spinel ferrite nanocomposites (SFNCs) are promising candidates for efficiently removing arsenic from water and wastewater because of their unique physical and chemical properties. SFNPs and SFNCs have been studied extensively for their magnetic properties, which are contributed to by their structures and compositions. In addition, Ferrofluids have been found to have a novel ability to affect the chlorophyll ratio in some plants, indicating the high sensitivity of the LHC II system to ferrofluids. Very little but considerable work has been done by various researchers, which is useful in the sustainable growth of the environment. SFNPs and SFNCs have been found to be useful in arsenic and arsenate removal from groundwater and wastewater.

Keywords: magnetic nanoparticle; spinel ferrite; wastewater; sustaining environment.

1. Introduction

Industrial effluents discharged into water bodies cause water to become contaminated, which poses a major threat to human health, the environment, and natural ecosystems. Rapid industrialization, on the one hand, satisfies the needs of a growing population, but on the other, it causes water bodies to become contaminated. Because hazardous heavy metal ions are non-biodegradable and bio-accumulative, they cause serious problems when they contaminate water [1–3]. The primary sources of these heavy metal contaminants in aquatic systems include effluents from businesses like tanneries, mining operations, printing, textile dyeing, battery production, electroplating, printing, and pharmaceutical industries [4–6]. Heavy metals like arsenic, cadmium, chromium, mercury, and lead are frequently found in industrial effluents. They are very harmful to people and animals when present in concentrations above the allowable limit in water [7,8] (Figure 1).

Therefore, removing these heavy metal contaminants from water is urgently required. In addition, we cannot afford to squander the wastewater because of the growing issue of water scarcity [10,11], but we can disinfect it. This has led to a lot of interest in the development of several methods for removing contaminants from water, such as adsorption [12,13], coagulation [14], ion exchange [15], membrane filtration [16], electrochemical approach [17],

and chemical precipitation [18]. Figures 2 and 3 depict the Heavy Metal Removal Process from wastewater and different approaches to wastewater treatment, respectively.

Figure 1 Schematic diagram for heavy metal contaminant sources [9].

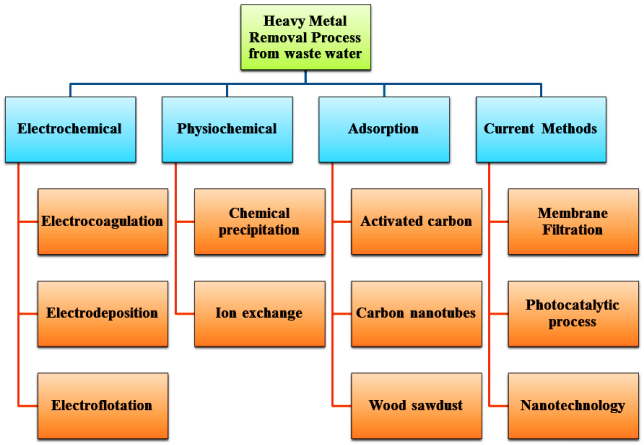

Figure 2. Heavy metal removal process from wastewater.

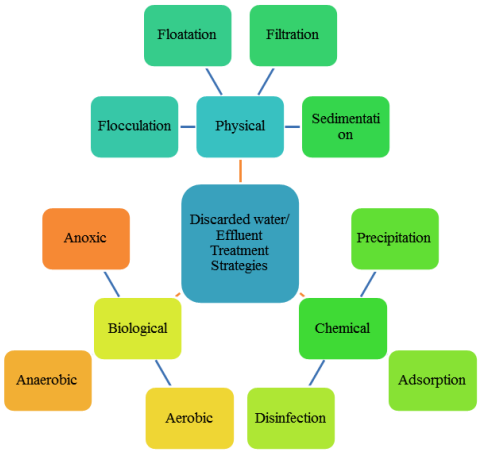

Figure 3. Different methods of wastewater treatment.

Among these heavy metal contaminants in aquatic systems, arsenate and arsenic are proving to be more toxic and affecting the groundwater and water bodies used for irrigation. Arsenic is a trace element toxic to the entire biota, and it has been sometimes implicated in accidents with human mortality or disease [19]. Depending on the redox conditions, arsenic occurs in nature as As(III) and As(V), and due to the relatively slow arsenic redox transformations, both oxidation states are often observed, with As(III) more toxic than As(V) [20-22]. Several spinel ferrite synthesis approaches and their applications are depicted in Table 1.

Table 1. The standard limit for selected heavy metals in drinking water is as follows (WHO, 2017).

Heavy metals contaminant	EPA maximum contamination level (mg/L)	WHO guideline value (mg/L)	Effects on human health
Lead	0.015	0.01	Damage to the fetal brain, diseases of the kidneys, circulatory system, and nervous system
Chromium	0.1	0.05	Headache, diarrhea, nausea, vomiting, carcinogenic
Cadmium	0.005	0.003	Kidney damage, renal disorder, human carcinogen
Copper	1.3	2	Liver damage, Wilson disease, insomnia
Arsenic	0.01	0.01	Skin manifestations, visceral cancers, vascular disease
Mercury	0.002	0.006	Rheumatoid arthritis and diseases of the kidneys, circulatory system, and nervous system
Nickel	--	0.07	Dermatitis, nausea, chronic asthma, coughing, human carcinogen
Zinc	5	3	Depression, lethargy, neurological signs and increased thirst

Spinel ferrite nanoparticles (SFNPs) and spinel ferrite nanocomposites (SFNCs) are magnetic oxides that contain iron oxide as the main constituent for exhibiting magnetism, irrespective of their crystal structure and composition. The naturally occurring ferrite is called magnetite. Magnetite has the chemical formula Fe_3O_4 or, more specifically, $Fe^{++}Fe_2^{+++}O_4$. The general composition of ferrites consists of iron oxides as their main component regardless of their crystal structure. On the basis of crystallography, ferrites are classified as cubical Spinels (S-type), cubical Garnets, Hexagonal Magnetoplumbite (M type), and other hexagonal ferrites such as W, Y, Z, X, and U etc. Several methods of synthesis of ferrite materials have been developed over the last fifty years. Recent advances in nanotechnology have made it possible to produce magnetic nanoparticles with much-improved properties. A lot of work has been done to study the magnetic properties of ferrites, which vary according to their composition and structure [23].

Tremendous utilization of these properties has been done in the field of engineering and technology. Researchers worldwide have done considerable work to utilize ferrites to remove arsenic and arsenate from groundwater and wastewater. Novel fabrication of ferrites for this use has been increased in recent years. Very few studies have been done to study the effect of ferrofluids on the chlorophyll ratio of some plants.

Various techniques are being used to remove these heavy metal pollutants from the water supply. Some of them are adsorption, precipitation, ion exchange, reverse osmosis, electrochemical treatments, membrane filtration, evaporation, flotation, oxidation, and biosorption [24]. Considerable work has been done to study the arsenic and arsenite removal efficiency of different classes of materials using the adsorption technique. Also, it is noticeable that magnetite materials and ferrites are of great interest in this field because they can be separated from contaminated water by using simple magnetic techniques, such as physical ones.

Photosynthesis may be considered a very popular concept despite the complex mechanisms underlying this tremendous conversion of energy, which is yet “reserved” for green plants (Fig. 4). Life scientists have identified the main photosynthesis mechanics, i.e., the light-harvesting complexes (LHC) I and II, where the solar energy absorbed by chlorophyll a is transferred step by step in the energy of the redox process controlled by enzyme complex chains. The roles of chlorophyll b and carotenes as the most important secondary pigments of

the LHC systems, able to sustain the photosynthesis energetic balance though they are not actively involved in the energetic conversion (in contrast with the chlorophyll a), have been much investigated [25]. Very little work has been done by selected researchers to investigate the effect of ferro-fluids on the chlorophyll levels and, thus, the LHC II system in some plant species.

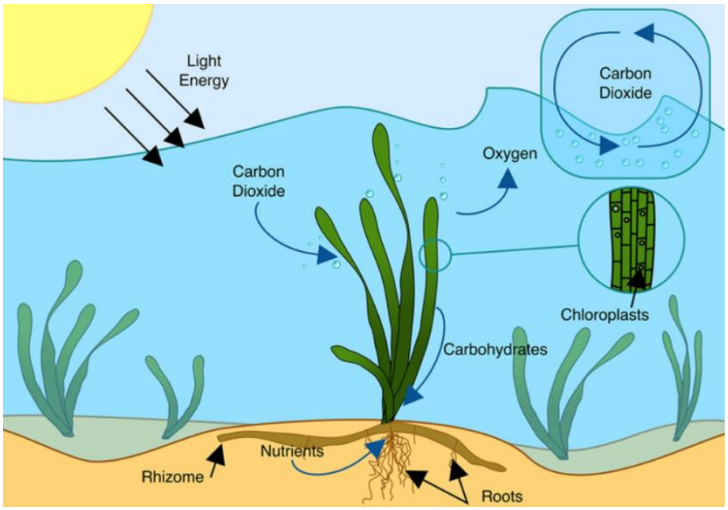

Figure 4. Photosynthesis electron transport chain [Photo Credit: https://www.scienceabc.com/].

2. Materials and Methods

Naturally occurring magnetite and synthetically prepared ferrites have been investigated for their arsenic and arsenate removal efficiency. Ferrites can be synthesized as per the required composition using any of the techniques available, such as standard ceramic techniques, Co-precipitation, Salt–melt method, ion exchange, sol-gel, citrate synthesis, hydrothermal synthesis, Glass crystallization, combustion method, and micro-emulsions methods [23]. Y. J Tu *et al*. reported a novel copper ferrite fabrication method using PCB sludge [26]. Table 2 depicts Various methods of spinel ferrite synthesis and their physical characteristics.

Table 2. Various methods of spinel ferrite synthesis and their physical characteristics.

Ferrite	Synthesis method	D_{XRD} (nm)	$D_{SEM/TEM}$ (nm)	Morphology	Applications	Ref.
Cobalt ferrite [$CoFe_2O_4$]	Auto-combustion	37–45	34–50	Agglomerate	–	[27]
	Solvothermal	–	100–200	Spherical	Absorbent	[28]
	Co-precipitation	37.5	50–90	Spherical	Catalyst for MCRs	[29]
	Sol-gel auto-combustion	17.16	11–15	Spherical	Supercapacitors	[30]
	Green chemistry/co-precipitation	13.2	9.72	Spherical	Drug delivery	[31]
Zinc ferrite [$ZnFe_2O_4$]	Combustion	22–32	–	Irregular flakes	Catalyst for MCRs	[32]
	Sol-gel	15	10–20	Nanotube	Photovoltaic	[33]
	Co-precipitation	16.8–27.3	75–250	Spherical	Light-absorbing layers	[34]
	Hydrothermal	8–10	–	–	Photocatalyst	[35]
	Solvothermal	–	20–2000	Spherical	Photocatalyst	[36]
Copper ferrite [$CuFe_2O_4$]	Sol-gel combustion	37.34	–	Sphere-shaped	Tartrazine degradation	[37]
	Hydrothermal	–	164.6	Spherical	Fluorescent sensor	[38]
	Solvothermal	54–62	20	Spherical	Pseudocapacitive	[39]
	Hydrothermal	–	20–40	Pseudo-spherical	Electrochemical detection	[40]
	Co-precipitation	39.61	20–60	Spherical	–	[41]
Nickel ferrite [$NiFe_2O_4$]	Hydrothermal	–	20–50	Hollow nano-spheres	Photoluminescence sensor	[42]

Ferrite	Synthesis method	D_{XRD} (nm)	$D_{SEM/TEM}$ (nm)	Morphology	Applications	Ref.
	Solvothermal	34.4	60-15	Octahedral crystals	Catalyst	[43]
	Co-precipitation	29	–	Spherical	Photocatalyst	[44]
	Hydrothermal	3.3–16.4	35–50	Nanorod	–	[45]
	Green chemistry/Sol-gel combustion	31	33–35	Spherical	Anticancer and antibiotic	[45,46]
Manganese ferrite [$MnFe_2O_4$]	Sol-gel pyrolysis	0.253	–	Irregular flakes	Absorbent	[47]
	Solvothermal	–	27–326	Hollow mesoporous	Drug delivery	[48]
	Citrate-gel auto combustion	6.9	–	Roughly spherical	Electrocatalyst	[49]
	Hydrothermal	–	42–510	Block nanotube	Photoelectrochemical	[50]
	Co-precipitation	33	33	Spherical	Catalyst for MCRs	[51]
Amide-based chemosensor	Green chemistry	--	--	--	Detection of toxic metal ions	[46]

The characterization of the ferrite adsorbents can be done by using techniques such as Transmission electron microscopy (TEM), Scanning electron Microscopy (SEM), Fourier Transform Infrared spectroscopy (FTIR), Powder X-ray diffraction (XRD) technique. The particle size and surface area can be studied using the BET surface analyzer technique [24]. Ferrite materials are studied for their arsenic adsorption capability by varying parameters such as pH, initial concentration of arsenic, and arsenate. The rate of adsorption, ability of desorption, performance under different pH values, and removal efficiency have also been studied by several authors in order to investigate the best ferrite for this application. Fig. 5 illustrates the methods of synthesis of magnetic nanoparticles.

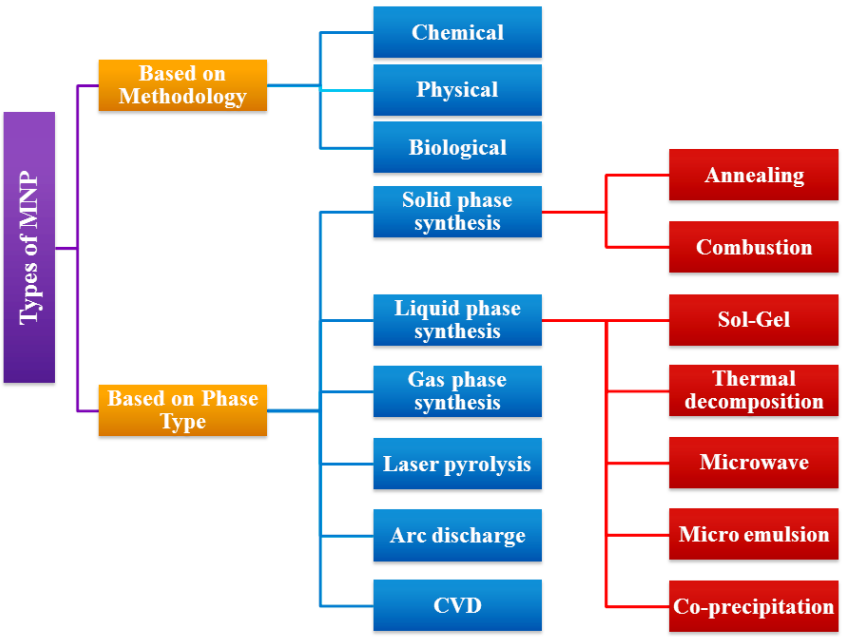

Figure 5. Methods of Synthesis of magnetic nanoparticles.

Magnetic fluids (MF) are stable colloidal suspensions composed of monodomain ferrite-based (MFe_2O_4) magnetic nanoparticles dispersed in organic or inorganic liquid carriers [52]. Conventional MF are organic-based colloidal suspensions stabilized by steric repulsions after coating the magnetic nanoparticles with surfactant agents. Ionic magnetic fluids (IMF) are water-based colloidal suspensions stabilized by Columbia repulsions after adding an electric surface charge density at the magnetic nanoparticles. The biocompatibility of many ferrofluids is under investigation [53]. However, there are many possibilities of applications of

biocompatible MF in biology and medical diagnosis and therapy, for instance, separation and purification of cells [54], MRI contrast agents [55], and magneto-thermo-cytolysis [56].

3. Results and Discussion

Among naturally occurring hematite, goethite, and magnetite materials, a faster rate of arsenic adsorption has been found to be in the case of magnetite, which decreased with increasing pH of solution [56]. Arsenate adsorption has been reported to depend on the adsorbent's iron content; the adsorption rate increases in the following order: goethite < hematite < magnetite < zero-valent iron. This clearly emphasizes the possibility of using magnetite materials for arsenate removal [57].

Yao Jen Tu et al. reported the X-ray Absorption Near Edge Structure (XANES), which was used to confirm arsenate removal from water using magnetic ferrite. The author showed that Fe_2O_3 synthesized using the hydrothermal method can effectively remove arsenate from water. Magnetic nano-ferrite synthesized by a hydrothermal method without surface modification appeared to be an effective adsorbent for As(V). The results show that this adsorbent has great potential for treating As-containing groundwater and can be recovered using an external magnetic field. The removal of As(V) using this material from alkaline waters and wastewaters may be significantly enhanced via pre-acidification of the waters [58].

Yao–Jen Tu et al. reported the synthesis of a spinal-structured magnetic nano adsorbent ($CuFe_2O_4$) using a novel process of leaching the P.C. B. sludge [58]. This adsorbent is cost-effective and has been tested thoroughly for arsenic adsorption. The copper ferrite nanoparticles were tested for As(V) adsorption at a pH ranging from 2.3 to 12.4. The amount of As (V) removed increased rapidly initially during the first sixty minutes. The arsenic (V) removal reached 100% within 300 minutes when pH was lower than 7. This shows a fast and complete removal of arsenic at lower pH. The adsorption rate was found to decrease with increasing pH, leading to incomplete removal. This pH dependence was apparently contributed to by the charge properties of both arsenic and copper ferrite [56-59]. The arsenic (V) adsorption isotherms were also studied at 27°C. The arsenic adsorption was highest at pH 2.3, decreased with increasing pH, and lowest at 12.4. During the adsorption of As(V), mainly at lower pH, there is a possibility of conversion of As(V) into As(III), which is more toxic and highly mobile in the environment. This possibility was ruled out by K edge XANES spectra analysis of As(V) adsorbed on the copper ferrite. It confirmed that As(V) was the predominant oxidation state of As adsorbed on copper ferrite, and no reduction of AS(V) to As(III) occurred in this case. An increase in copper ferrite dosage increases the adsorption rate at the same pH. In all concentrations of adsorbent dosage, the adsorption rate decreases with increasing pH. At a neutral pH of 7.1, 100% adsorption is possible with a 2 g per liter copper ferrite dosage [24]. Thus, magnetic ferrites have a vast possibility of industrial and small-scale contamination removal from water.

The influence of ferro-fluids in Opium poppy and Zea mays (maize) plant varieties has been reported in recent years. When petroleum ferro-fluid was applied to already germinated Opium seeds (VFG) and non-germinated seeds (VFnG), the results differed. When the already germinated Opium seeds were treated with 10 microliters per liter of ferrofluid and exposed to the north pole of a bar magnet, they developed plants with slightly increased chlorophyll a and b compared to pure water nonmagnetic control. The ferrofluid-treated, freshly germinated seed without magnetic field exposure showed better results. The values of chlorophyll a and b increased remarkably compared to the control for ferrofluid concentration, which corresponded

to 50 and 70 microliters per liter. The results are even better when the ferrofluid treatment is given to non-germinated seeds without external magnetic field exposure. A Remarkable increase in chlorophyll a and b contained in the plants whose seeds were treated with 50 and 70 microliter per liter was observed. The effect does not follow an even trend, which shows that the chlorophyll content can be stimulated and inhabited by changing the treatment concentration and applying external magnetic fields to treated variants. Thus, the chlorophyll ratio can be changed by using appropriate ferrofluid treatment on Opium seeds [25].

The ferrofluid treatment of Zea mays seeds also influenced the chlorophyll content; thus, the chlorophyll ratio in the young plants developed. Similar to the case in Opium seeds, it did not follow a simple increase or decrease trend; however, the chlorophyll ratio varied with treatment concentration. When 200 microliters per liter of concentrated ferrofluid was given the treatment of freshly germinated seeds of Zea mays, both the chlorophyll contained increased remarkably [60]. The results show that ferrofluid treatment can be a good way of increasing chlorophyll content in plants.

4. Conclusions

Ferrites can be very useful in serving as the adsorption agents in removing arsenic and arsenate from groundwater as well as wastewater, protecting public health and the environment. Plant chlorophyll can be regulated using ferrofluid treatment, and a vast area of research is opened in this field. This can be utilized to increase the growth of high oxygen generating non-fruit producing trees, such as Neem, without fearing contamination. Thus, ferrites can be utilized for protecting the environment.

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Conflicts of Interest

The authors declare no conflict of interest.

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