

# Nanosized magnetite in low cost materials for remediation of water polluted with toxic metals, azo- and antraquinonic dyes

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**Abstract** Nanosized magnetite has emerged as an adsorbent of pollutants in water remediation. Nanoadsorbents include magnetic iron oxide and its modifiers/stabilizers, such as carbon, silica, clay, organic moieties (polymers, aminoacids, and fatty acids) and other inorganic oxides. This review is focused on the recent developments on the synthesis and use of magnetic nanoparticles and nanocomposites in the treatment of contaminated water. The emphasis is on the influence of the iron oxide modifiers on some properties of interest such as size, BET area, and magnetization. The characteristics of these nanomaterials are related to their ability to eliminate heavy metal ions and dyes from wastewater. Comparative analysis of the actual literature was performed aiming to present the magnetic material, its preparation methodology and performance in the elimination of the selected pollutants. Vast information has been properly summarized according to the materials, their properties and preferential affinity for selected contaminants. The mechanisms governing nanomaterial's formation as well as the interactions with heavy metals and dyes have been carefully analyzed and associated to their efficiency.

**Keywords** nanomagnetite, water remediation, toxic metals, dyes, supported magnetite

## 1 Introduction

Water pollution by heavy metals and dyes has become a serious problem because of their adverse effects on ecological systems and human health. Heavy metals such as Pb, Cr, Hg, As among others, demonstrated to be highly

carcinogenic and mutagenic at relatively low concentrations [1]. The presence of heavy metals in water has toxic effects to living organisms, when they find above their permissible concentrations. Their effects depend on the specific metal characteristics [2]. Cadmium occurs naturally in metal minerals together with zinc, lead and copper. Meanwhile, cadmium compounds are used as stabilizers in polyvinylchloride (PVC) products, color pigments, several alloys, in phosphate fertilizers and most commonly in rechargeable nickel-cadmium batteries. Cigarette smoking is a major source of cadmium exposure. Exposition to natural as well as anthropogenic sources of cadmium may be life-threatening. Arsenic is a widely distributed metalloid, occurring in rock soil, water and air. Inorganic arsenic compounds are normally present in groundwater that is used for drinking in several countries all over the world, whereas As-organic compounds are present principally in fish. Through fish consumption, they may affect human life provoking by illnesses.

Chromium is found in soils, rocks and living organisms. It is commonly used in industry for its anti-corrosive properties. Other applications include pigments, paints and leather tanning. Contact with chromium can result in severe health problems ranging from simple skin irritation to lung carcinoma. Lead is one of the most toxic heavy metals for human life. It is found in water and food. The long-term accumulation of  $Pb^{2+}$  in the human body may cause serious damage to the brain and central nervous system. It has become in a serious threat especially to children's health.

Mercury is other heavy metal considered as extremely hazard for human. It may cause kidney carcinoma, neurological damage, paralysis, chromosome's breakage and birth defects.

Dyes may be toxic to the aquatic life in effluent waters, being some of them mutagenic and carcinogenic. There are more than 100,000 types of dyes, which are used in

different industries including paper, plastic, leather, pharmaceutical, food, cosmetic and textile. These last industries produce a large amount of colored effluents, which are directly discharged into surface water without any previous treatment or with minor treatment. In addition, the by-products of some organic dyes degradation (such as synthetic azo-dyes) represent a potential environmental hazard. They contain aromatic amine compounds that are toxic to many organisms [3].

Due to the environmental hazards and health effects of heavy metals and dyes, drinking water and wastewater regulations have been toughened. So the development of efficient processes, able to produce effluents that fit with the law limit concentration values is urgently needed.

Diverse technologies have been developed for the removal of heavy metals and dyes from different sources of water [4]. Between them chemical precipitation, ion exchange and adsorption are the preferred because of their potential for scale up. Chemical precipitation involves the use of a precipitating agent that, under suitable pH conditions, induces the formation of an insoluble solid [5].

Ion-Exchange requires an ion – exchanger that is a solid capable of exchanging either cations or anions from the surrounding aqueous solution. These treatments require matrices for ion exchange that are usually synthetic polymeric resins [6].

Adsorption is a mass transfer process by which a substance is transferred from the liquid phase to the surface of a solid, and becomes bound by physical and/ or chemical interactions. A great variety of materials applies

as adsorbents of a great variety of pollutants. Commonly general functional groups and/or porous surface are required to ensure the efficiency of the procedure. In general, there are three main steps involved in pollutant sorption onto solid sorbent: (i) the transport of the pollutant from the bulk solution to the sorbent surface; (ii) adsorption on the sorbent’s particle surface; and (iii) transport within the sorbent particle. The use of adsorbents in the nanoscale strongly enhances the removal efficiency because of the high exposed surface able to interact with the adsorbate [7]. Magnetic nanoadsorbents appear as a very attractive kind of material because of their multiple properties such as high efficiency and rapid recovery due to high specific surface area, easy handling and low cost. Magnetic separation provides a suitable route for online separation. Briefly, particles with affinity to target species are mixed with the heterogeneous solution. Such particles tag the target species. External magnetic fields are then applied to separate the tagged particles from the solution. The magnetic material can be reutilized several times according to its chemical structure and its binding properties [8].

In the Table 1 the advantages and disadvantages of diverse remediation method are summarized .It is further worth noting the economical aspect related to each technique. Based on our own experience, fabrication cost of magnetic nanoparticles with a suitable coating (poly-saccharides, surfactants) is approximately US\$ 7.66 per gram of nanoparticles. Fees associated to other methodologies are highly variable as a function of raw materials, the

**Table 1** Different technologies applied to water remediation

remediation method	advantages	disadvantages	reference
chemical precipitation	relatively inexpensive equipment requirement, and convenient and safe operations	-large amount of chemicals to reduce metals to an acceptable level for discharge. -excessive sludge production that requires further treatment, -slow metal precipitation. -poor settling, the aggregation of metal precipitates.	[5]
ion exchange	used successfully at industrial scale for effluents remediation (mainly heavy metals).	-it does not work with concentrated metal solution as the matrix gets easily fouled by organics and other solids in the wastewater. -it is nonselective and is highly sensitive to the pH of the solution. -high costs when specific membranes are required.	[6]
adsorption with non- magnetic adsorbents	versatile, economically viable (depending on their source).	-technical applicability and cost-effectiveness. -limited reutilization and recycle. -production of extra residues. -generally dependent on the wastewater pH.	[7]
adsorption with nanomagnetic adsorbents	better intrinsic properties, such as chemical activity and fine grain size, as compared with the classic substances including normal scale good dispersion in solution, -very high specific surface area, -ability to be controlled and separated with an external magnetic field. -reutilization and regeneration by simple procedures.	scale up non evaluated	[9]

efficiency and reusability possibilities.

Environmental impact of discharged dyes into water is high because dyes are difficult to decolorize and up to 15% of total applied pigments are lost during the dyeing process. Several groups have reported novel magnetic carrier technology (MCT) because other adsorbents showed low adsorption capacities or separation problems. One of the first articles reporting the use of hyperbranched polymer (HP) modified-magnetic materials was published in 2010. Few reports were available in 2010, even when studies on the use of nanocomposites (with biopolymers, polymers, silica or other oxides) have been widely published during past seven years. New nanomaterials are becoming mimetic of enzymes [9], especially when used in the context of advanced oxidation processes (AOP) and with hydrogen peroxide as oxidant. A mimetic is a compound that has the same abilities that an enzyme but without the complexities of the protein.

In most cases, a substrate such as the dye 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulfonate (ABTS) or 3,5,3',5'-tetramethylbenzidine (TMB) was used to test the nanomaterials' peroxidase mimetic properties through the convenient colorimetric reaction in the presence of hydrogen peroxide. Applications included the hydrogen peroxide, glucose and DNA detection, aptasensors, immunoassays, immunostaining and pollutant removal, mainly phenolic and aniline derivatives and therefore including dyes. Surprisingly, Gu et al. recently discovered that both  $\text{Fe}_3\text{O}_4$  and  $\gamma\text{-Fe}_2\text{O}_3$  exhibited dual enzyme-mimetic properties (i.e., catalase and peroxidase mimics) [10]. Even more,  $\text{Fe}_2\text{O}_3$  demonstrated to have oxidase mimic properties and it has been applied for glucose detection.

The main dyes studied and reported in the open literature are depicted in Fig. 1 whereas Fig. 2 shows the basic structure of magnetite.

In general, when dyes are the concern, the main groups of reported nanosized materials used for remediation are

- bare pure magnetite or substituted magnetite as adsorbents,
- nanoparticle magnetite as nanozymes (used with hydrogen peroxide as mimetic of peroxidase),
- nanosized magnetite as Fenton-like systems with hydrogen peroxide,
- nanoparticled magnetite as part of composites with other compounds as an additive or major or minor components with oxides, suboxides, polymers and biopolymers and
- magnetite modified at the surface with different additives, such as surfactants

The field of nanosorbents has grown exponentially past ten years [11–13]. However, this review is focused on magnetite as adsorbent and as a catalytically active material.

The aim of this contribution is to present a brief view on nano-magnetite, surface functionalized nano-magnetite and magnetic nanocomposites, their methods of synthesis

and their behavior regarding to heavy metals ions and azo and anthraquinonic dyes adsorption from water. This manuscript includes the underlying mechanisms responsible for the adsorption, as well as the published studies on reusability.

## 2 Nano-magnetite

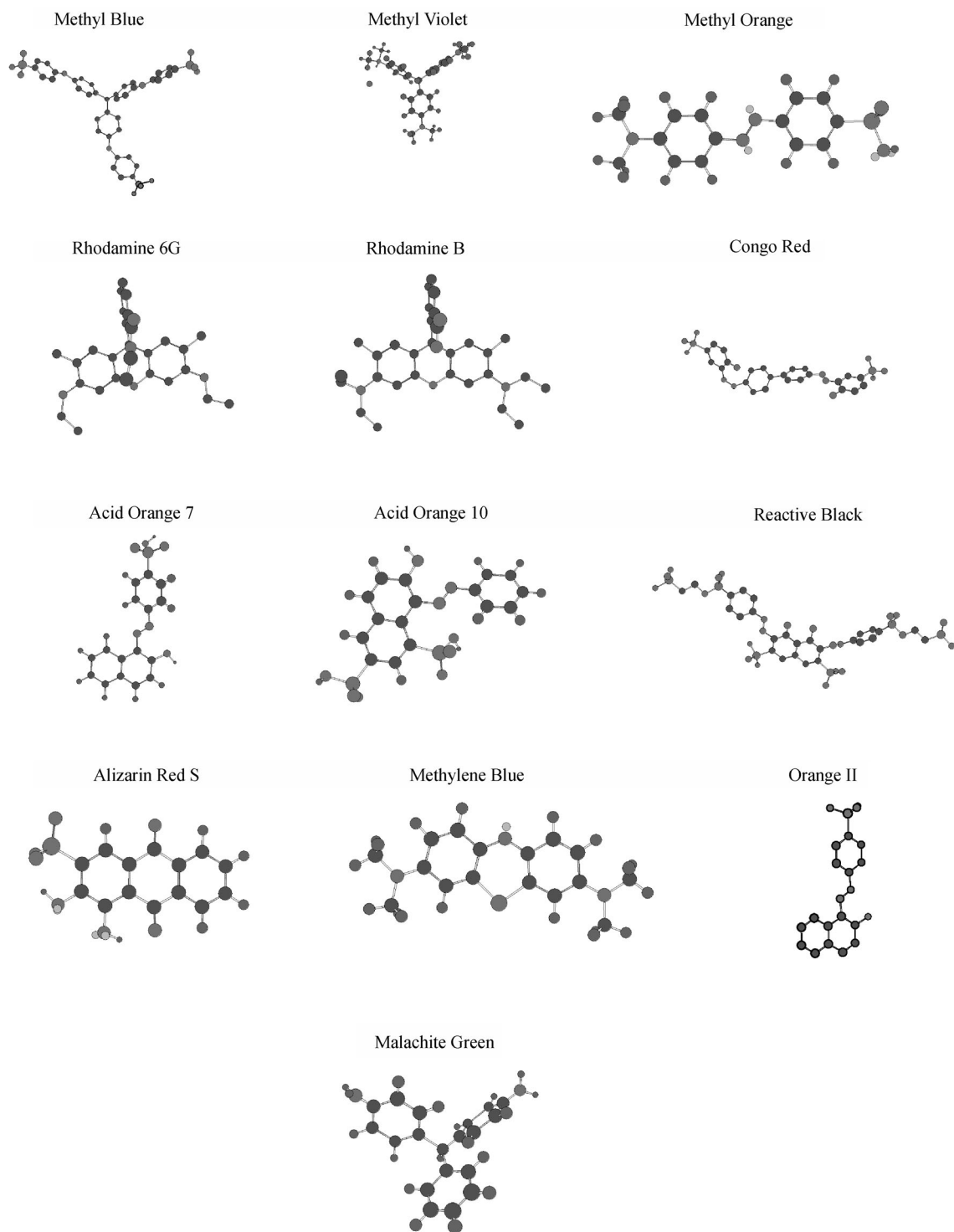
### 2.1 Synthesis and properties

Magnetite ( $\text{Fe}_3\text{O}_4$ ) and/or nano-magnetite have been of scientific and technological interest because of their unique magnetic properties.

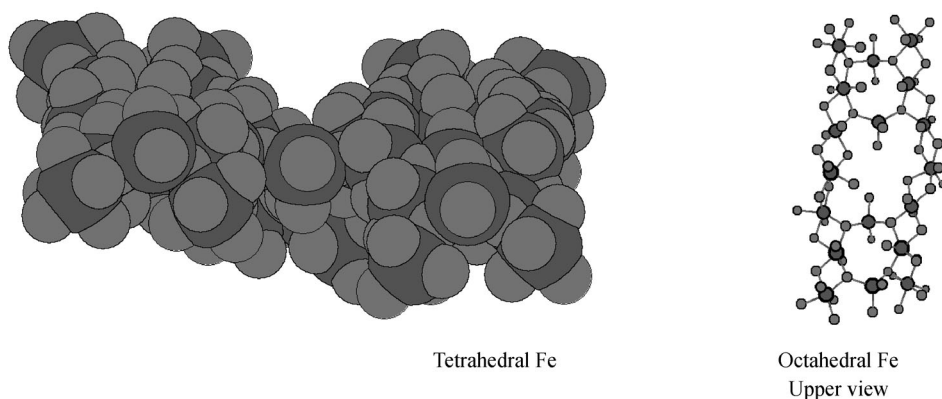
Magnetite has an inverse spinel structure in which the oxygen forms a cubic close-packed array; half of the  $\text{Fe}^{3+}$  cations occupy tetrahedral sites, while the other half and the  $\text{Fe}^{2+}$  cations occupy the octahedral sites. It is a ferrimagnet. Due to the superexchange oxygen-mediated coupling in the crystal lattice, iron ions have opposite magnetic moment directions. In magnetite, since the number of  $\text{Fe}^{3+}$  in each lattice site (tetrahedral and octahedral) is the same, the magnetic moments from  $\text{Fe}^{3+}$  cations cancel each other, and as a result, the total net magnetization is due to the  $\text{Fe}^{2+}$  cations only. The properties of these magnetic nanomaterials change dramatically from bulk to the nanometric size. As the size decreases, the magnetic material changes from a multi-domain structure to a single-domain structure, resulting in novel magnetic properties.

These magnetic nanoparticles exhibit amphoteric surface activity, easy dispersion ability and, due to their very small dimensions, a high surface-to-volume ratio, resulting in a high metal ion adsorption capacity. The physical and chemical properties of nano-magnetite are greatly affected by the method of synthesis. Thus, an efficient, economical, scalable and non-time consuming methodology to prepare magnetic nanoparticles is desired for practical applications and fundamental research. Several synthetic procedures have been reported in the literature along the past decades including chemical precipitation, thermal decomposition, sol-gel reactions, etc [11–14]. There are critical points to define the experimental conditions in order to achieve monodisperse magnetic particles with suitable size and stability in water.

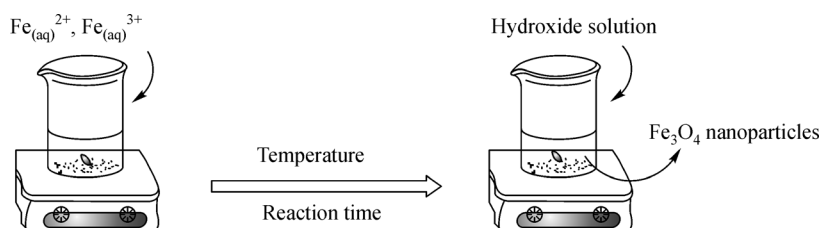
*Co-precipitation method:* This is the most common method for the preparation of magnetite from iron salts to obtain superparamagnetic particles of this iron oxide, without any stabilizing surfactant agents [15]. In brief, the magnetite nanoparticles are usually prepared by aging a stoichiometric mixture of ferric and ferrous salts (2:1  $\text{Fe}^{3+}/\text{Fe}^{2+}$ ) in aqueous medium. To reach complete precipitation, the pH should be between 8 and 13 in an inert environment. Scheme 1 shows a representation of co-precipitation method. As it is well known, the size and shape of magnetite nanoparticles can be tailored with the



**Fig. 1** Dyes analyzed in the manuscript. Sulfonic groups characterize anionic dyes whereas N=N, NH and NH<sub>2</sub> groups characterize cationic dyes



**Fig. 2** Local structure of magnetite



**Scheme 1** Representation of co-precipitation method

reaction conditions related to the process such as pH, ionic strength, temperature, nature of the salts (perchlorates, chlorides, sulfates and nitrates) and  $\text{Fe}^{3+}/\text{Fe}^{2+}$  concentration ratio. There is a very recent and complete research evaluating the impact of the main synthetic parameters on the properties of magnetic nanoparticles [16].

The particles obtained via co-precipitation have a broad size distribution; other alternative methods have been developed to produce nanoparticles with more uniform particle size distribution. Several attempts to obtain iron oxide nanoparticles of well-defined size have been carried out. This aspect will be discussed later in the section dedicated to the surface functionalization.

**Hydrothermal and high-temperature reactions:** Hydrothermal **synthesis** of  $\text{Fe}_3\text{O}_4$  nanoparticles have been reported in the literature [17]. The reactions are carried out in aqueous media in reactors or autoclaves at high pressure and temperature. Two main routes are feasible for the formation of ferrites: hydrolysis, oxidation or neutralization of mixed metal hydroxides. Ferrous salts are used in the first method. The reaction conditions, such as solvent, temperature, and reaction time, usually have important effects on the formation of magnetite particles.

**Sol-gel reactions:** The sol-gel process is a suitable wet route to the synthesis of magnetite nanoparticles [18]. This process is based on the hydroxylation and condensation of molecular precursors in solution, originating a “sol” of nanometric particles. Further condensation and inorganic polymerization lead to a three-dimensional metal oxide

network denominated wet gel. These reactions are performed at room temperature so further heat treatments are needed to acquire the final crystalline state. From the literature, it is clear that the properties of a gel are very dependent upon the structure created during the sol stage of the sol-gel process. The main parameters that influence the kinetics, growth reactions, hydrolysis, condensation reactions, and consequently, the structure and properties of the gel are solvent, temperature, concentration and nature of the precursors, pH, and agitation.

**Polyol Method:** Another interesting emerging method is the one-pot synthesis in polyol media [19]. The polyol process is a typical solvothermal method which can also be understood as a sol-gel method. It produces monodisperse superparamagnetic magnetite submicrospheres. The magnetic nanoparticles are prepared by using polyols (e.g. ethylene glycol (EG), diethylene glycol (DEG), triethylene glycol (TEG)) to reduce metal salts to metal non-aggregated particles. Polyols also serve as reducing agents as well as stabilizers to control particle growth and prevent interparticle aggregation. In this process, a precursor is suspended in a liquid polyol at certain temperature near the boiling point of the polyol. During the reaction, the metal precursor is dissolved in the diol, forming an intermediate. Then it is reduced to form metal nuclei which will then nucleate to originate metal particles. Submicrometer-sized particles may be synthesized by increasing the reaction temperature or inducing heterogeneous nucleation via foreign nuclei addition or forming in situ foreign nuclei. In

comparison to the aqueous method, this approach presents several advantages. First, the surface of the prepared magnetite nanoparticles is coated by hydrophilic polyol ligands in situ; therefore, the nanoparticles can be easily dispersed in aqueous media and other polar solvents. Second, the relatively higher reaction temperature of this method, in comparison with others, favors particles with higher crystallinity and therefore higher magnetization. Finally, the size distribution of the nanoparticles is far narrower than those particles produced by traditional chemical, wet methods.

The most important characteristics of the nanoparticles prepared by either of the methods above mentioned are basically its small size, superparamagnetism, high reactivity, large surface area and easy separation, among others. The solids are commonly characterized by different techniques. High-resolution transmission electron microscopy (HRTEM) gives access to the atomic arrangement. It may be used to study local microstructures and surface atomic arrangement of crystalline nanoparticles. XRD can be performed to obtain the crystalline structure of the nanoparticles. Dynamic light scattering (DLS) or quasi-elastic light scattering (QELS), gives information about the hydrodynamic radius of a corresponding sphere and the polydispersity of the colloidal solution. Magnetic properties may be determined using vibrating sample magnetometer (VSM) recording magnetization as a function of applied magnetic field. The surface area, also known as BET (Brunauer-Emmet-Teller) area, is one of the most important parameters regarding to these materials applications. It correlates with their adsorption capacity.

## 2.2 Applications as adsorbents of As, Pb, Hg, Cd and Cr

Recently, the use of magnetite nanoparticles has found extensive applications in several fields, among them wastewater purification [20]. As it was previously mentioned, the superparamagnetic properties make them attractive in separation. For this reason, in environmental applications, collecting the nanoparticles from large volumes of aqueous samples is rather easy. Several studies have been developed to adsorb heavy metals onto magnetic nanoparticles [4,21].

In particular, this review's section is devoted to the adsorption of As, Pb, Hg, Cd and Cr heavy metal by nanomagnetite. These toxic metals ions were selected due to their environmental impact regarding to the human health.

**Cadmium.** Shen et al. evaluated the adsorption efficiency of  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Cr}^{6+}$  onto magnetite nanoparticles synthesized by co-precipitation and polyol processes. Nanoparticles of 6–8 nm were obtained by co-precipitation and nanoparticles of 18–35 nm were obtained by the polyol method. The maximum adsorption capability was 7.45 mg Cd/g for nanoparticles of 35 nm (polyol-synthesized  $\text{Fe}_3\text{O}_4$ ). The authors obtained an increase to

34.9 mg Cd/g adsorption when the aqueous sample was treated with magnetite nanoparticles prepared by co-precipitation (size = 8 nm). Regeneration studies were also carried out. The results demonstrated that nanoparticles synthesized by co-precipitation could be effectively recovered for the re-adsorption of the metal ions. The removal efficiency was 72% up to five cycles [22]. In another work hollow magnetic  $\text{Fe}_3\text{O}_4/\alpha\text{-FeOOH}$  microspheres were synthesized and evaluated regarding to their adsorption capacity for cadmium ions [23]. The microspheres showed a diameter about 6–7  $\mu\text{m}$ , resulting from the self-assembly of nanosheets. The width of nanosheets were about 200–300 nm. The maximum Cd adsorption capacity was 164.5 mg/g. The authors elucidated a possible adsorption mechanism from FTIR data arising from characterization of the adsorbent before and after adsorption. They attributed the uptake to an ion-exchange mechanism among heavy metal ions and the hydroxyl groups on the surface of the adsorbents. All the assays in this work were performed without controlling the pH of the medium.

**Arsenic.** Many papers demonstrated that magnetic nanoparticles have high affinity for arsenic ions. Mayo et al. [24] synthesized  $\text{Fe}_3\text{O}_4$  nanoparticles of about 12 nm and tested them in terms of their ability to bind  $\text{As}^{+3}$  and  $\text{As}^{+5}$ . Their performance was compared with the obtained using  $\text{Fe}_3\text{O}_4$  commercial nanoparticles. The commercial magnetic nanoparticles presented sizes between 20 and 300 nm. They were more polydisperse and showed higher aggregation than the non-commercial magnetite. The authors demonstrated that the adsorption efficiency, in this case, was strongly influenced by the particle size. If the particle size decreased from 300 to 12 nm, the adsorption capacities, for both  $\text{As}^{3+}$  and  $\text{As}^{5+}$  increased nearly 200 times. Moreover,  $\text{Fe}_3\text{O}_4$  nanoparticles of about 17 nm were synthesized for Luther et al. [25] and used as adsorbents for As removal. These studies evaluated the effect of pH and the presence of interferences such as phosphates, sulfates and carbonates in the adsorption medium. The best pH range for arsenic removal (with both species) was from 6 to 10. The adsorption of arsenic ions on the magnetite nanoparticles in presence of  $\text{SO}_4^{2-}$  decreases around 50%. Meanwhile,  $\text{PO}_4^{3-}$  demonstrated to have a small effect on the adsorption of  $\text{As}^{3+}$  and  $\text{As}^{5+}$  onto  $\text{Fe}_3\text{O}_4$  nanoparticles. In the case of  $\text{CO}_3^{2-}$ , studies showed a decrease of about 10%–15% of the adsorbed arsenic ions amount even with high concentrations of the anion.

Liang-Shu Zhong et al. synthesized a 3D flowerlike iron oxide nanostructures ( $\alpha\text{-Fe}_2\text{O}_3$ ,  $\gamma\text{-Fe}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$ ). These materials were used as adsorbents in wastewater treatment for arsenic and chromium removal. The removal capacity was 4.65 mg/g for  $\text{As}^{5+}$  and 4.38 mg/g for  $\text{Cr}^{6+}$ . The mechanism for the removal was proposed by the authors to involve surface complexation and ion-exchange among the iron oxide surface and the toxic ions in the aqueous

solution [26]. Martina Kilianová et al. [27] synthesized ultrafine iron oxide nanoparticles (4 nm) by co-precipitation. The nanoparticles interacted magnetically to each other forming a kind of mesoporous structure with high surface area and enhanced adsorption capability for arsenic ions. The maximum adsorption was 45 mg of  $\text{As}^{5+}$ /g and the optimal pH region from 5 to 7.6. In this pH range arsenates were completely removed within 10 min of treatment.

**Chromium.** Adsorption with magnetite nanoparticles has been used as a method to remove Cr ions from aqueous environment [28].

Magnetite nanoparticles of roughly 30 nm were used to remove chromium from synthetic wastewater adjusting the pH to approximately 6. These authors also investigated the effect of the amount of magnetite nanoparticles, adsorption time, magnet rotation speed and temperature on Cr adsorption. They concluded that a higher amount of nanoparticles was correlated to higher Cr removal percentage. The adsorption equilibrium was achieved after 45 min. They obtained a removal efficiency of 99% for chromium [28].

A recent and interesting study evaluated the adsorption capacity of  $\text{Fe}_3\text{O}_4$  nanoparticles synthesized by co-precipitation with and without nitrogen gas as inert atmosphere (NCM and CM; respectively) [29]. The authors obtained 42.37% and 25.91% decrease of  $[\text{Cr}^{3+}]$  with NCM and CM, respectively. The higher adsorption capacity of NCM over CM was assigned to the higher surface area and larger Fe content in the synthesized NCM associated to the shapes and size of magnetic nanoparticles. NCM showed more active sites for adsorption. Both magnetic nanoparticles had an average size of 15 nm. NCM exhibited a series of hexagon chains with a space among the nanoparticles. This disposition increased the steric stabilization favoring monodispersing. As a difference, CM tended to agglomerate into clusters. BET surface areas were 125.8 and 107.6  $\text{m}^2/\text{g}$  for NCM and CM, respectively. The mechanism involved first the adsorption of  $\text{Cr}^{3+}$  onto magnetite, followed by a partial substitution of  $\text{Fe}^{3+}$  for  $\text{Cr}^{3+}$  through ion-exchanges.

Synthetic nano-magnetite particles were prepared under open vessel conditions and microwave-aged assisted hydrothermal conditions. These nanoparticles were used for  $\text{Cr}^{3+}$  and  $\text{Cr}^{6+}$  removals in batch experiences [30]. The size of the nanomaterials was approximately 27 nm for the open vessel synthesis and 25 nm for the microwave-assisted  $\text{Fe}_3\text{O}_4$  nanoparticles. The small differences in the sizes grain indicated that the aging conditions had little effect on the average size of the nano-magnetite materials. The authors found  $1.705 \pm 0.01$ , and  $0.555 \pm 2.2$  mg/g for  $\text{Cr}^{6+}$  and  $\text{Cr}^{3+}$ , respectively. Meanwhile, the binding of the  $\text{Cr}^{+3}$  was  $0.555 \pm 10.5$  mg/g to the microwave-assisted synthesized nanomaterials and  $1.20 \pm 0.04$  mg/g of  $\text{Cr}^{+6}$ .

Shen et al. [22] synthesized three different  $\text{Fe}_3\text{O}_4$  nanoparticles by co-precipitation, combining a surface

polyethylene glycol (PEG) decorating process and a polyol process. The three kinds of nanoparticles had an average particle size of 8, 12 and 35 nm for co-precipitation, PEG surface decorated nanoparticles and polyol process, respectively. These magnetic nanoparticles were applied for wastewater treatment, contaminated with different metal ions, such as  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Cr}^{6+}$ . Competitive adsorption was the mechanism in this case. The authors demonstrated that the separation of metal ions could be effectively achieved by changing the pH in the wastewater from 4 to 11. The adsorption percentage of  $\text{Cr}^{6+}$  was 97.6 at an optimum pH of 4 and using nanoparticles of 8 nm. In a recent study, Linnikov et al. [31] synthesized magnetite by different methods and used it as  $\text{Cr}^{6+}$  adsorbent. The methodology employed for the synthesis was (1) gas-phase synthesis, (2) chemical precipitation from aqueous solution, and (3) laser atomization. The structure was orthorhombic, tetragonal and cubic for the three magnetite nanoparticles prepared by (1), (2) and (3) respectively. Besides, the BET areas were 44.3, 21.9 and 68.8  $\text{m}^2/\text{g}$  for each kind of nanoparticles. All the  $\text{Fe}_3\text{O}_4$  presented diameters ranging from 16 to 54 nm. The authors evaluated the effect of temperature on  $\text{Cr}^{+6}$  adsorption efficiency. They observed that a rise in temperature sharply increased the efficiency of the adsorption process. They further noted that magnetite nanoparticles formed large aggregates (micron sizes) in aqueous solutions and this process influenced the adsorption behavior. The proposed mechanism for  $\text{Cr}^{+6}$  adsorption was irreversible chemisorption.

**Lead.** The adsorption of  $\text{Pb}^{2+}$  onto magnetite nanoparticles was analyzed by Nassar [32]. The adsorption performance of commercial  $\text{Fe}_3\text{O}_4$  was studied by the removal of  $\text{Pb}^{2+}$  in batch experiences. This study explored the effects of contact time, initial concentration of  $\text{Pb}^{2+}$ , temperature, pH and coexisting ions on the amount of adsorbed  $\text{Pb}^{+2}$ . The nanoparticles displayed an average size of 20–30 nm and BET surface area of 43  $\text{m}^2/\text{g}$ . The adsorption process was fast, and equilibrium was achieved within 30 min with a maximum adsorption capacity of 36 mg/g. The optimal pH value for  $\text{Pb}^{2+}$  adsorption was around 5.5. Furthermore, the authors found that the addition of  $\text{Ca}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ , and  $\text{Cd}^{2+}$  had not remarkable influence on  $\text{Pb}^{2+}$  removal efficiency. Desorption and regeneration studies concluded that magnetite nanoadsorbents could be used up to 5 cycles repeatedly, without impacting the adsorption capacity.

Giraldo et al. examined  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Mn}^{2+}$  removal using  $\text{Fe}_3\text{O}_4$  nanoparticles and found that the adsorption capacity depended on the metal ion electro-negativity. The synthesized magnetite nanoparticles were 8 nm in diameter. The maximum adsorption capacity was 0.180 mmol/g for  $\text{Pb}^{2+}$ , 0.170 mmol/g for  $\text{Cu}^{2+}$ , 0.160 mmol/g for  $\text{Zn}^{2+}$  and 0.140 mmol/g for  $\text{Mn}^{2+}$ . The authors also observed that the adsorption capacity was strongly dependent on solution pH and temperature. A

possible adsorption mechanism was proposed considering electrostatic attraction between metal ions and nanoparticles, influenced by the hydrated ionic radius of the metal cations [14].

Magnetite nanoparticles clusters with nanoparticle sizes between 6.8 to 31.2 nm at fixed cluster diameter of 120 nm were synthesized by a novel synthetic method of growth—dissolution—regrowth mechanism [33]. The magnetic nanoparticles demonstrated to be effective adsorbent materials for  $\text{Pb}^{2+}$ . The maximum lead adsorption was 177.5 to 36 mg/g depending on the grain size of the magnetic nanoparticles.

**Mercury.** Few studies have been reported on the adsorption of mercury ions on magnetite. The only found manuscript was devoted to the interaction between  $\text{Hg}^{2+}$  and magnetite in deoxygenated water [34]. The magnetite with a surface area of  $10.4 \text{ m}^2/\text{g}$  was synthesized by conventional co-precipitation method. The authors investigated the reduction of  $\text{Hg}^{2+}$  by magnetite through reaction of the magnetic particles with mercury ions in deoxygenated water, using  $^{203}\text{Hg}(0)$ . The reduction of mercury ions was followed by radioactivity measurements. The reduction of  $\text{Hg}^{2+}$  by magnetite was completed in 2h. The influence of the surface area on reduction rates of mercury was also evaluated. The results showed that the rate of reduction increased with increasing magnetite surface area from  $0.5$  to  $2 \text{ m}^2/\text{g}$  and kinetics assays were performed under acidic medium (pH 4.8–6.7). Mercury reduction was found to be strongly dependent on groundwater composition and reactive surface area.

From the analysis of the available literature, the adsorption capacity of nano-magnetite depended on the methodology employed for its preparation. The surface area and the size (two relevant properties in terms of the adsorption capability) were strongly affected by the synthetic procedure. Table 2 presents summarized data of characterization of magnetite nanoparticles synthesized using different methods and its performance as heavy metals adsorbents.

According to this revision; a feasible adsorption mechanism for toxic metal ions onto magnetic nanoparti-

cles may be proposed. Hydroxyls are the surface functional groups on the  $\text{Fe}_3\text{O}_4$  nanoparticles therefore they can participate in the reactions between the oxides and toxic heavy metals. The particularity of these hydroxyl groups ( $\text{OH}^-$ ) is that they are amphoteric and reactive. Depending on the solution pH, the surface oxide can act as acid or base and undergo protonation or deprotonation. Then, electrostatic interactions may take place among heavy metal ions and the surface oxides.

As a representative scheme, Figure 3 shows the two different routes for heavy metal adsorption with  $\text{Fe}_3\text{O}_4$  nanoparticles.

### 2.3 Applications in Azo and anthraquinonic Dyes Removal

Azo and anthraquinonic dyes are organic compounds responsible for the color of textile fabrics. Azo (around 70%) and anthraquinone (around 15%) compose the largest classes of dyes. The release of them into the environment causes serious problems. Adsorption is one of the most investigated techniques for dye removal [35]. Many manuscripts were found about magnetic composites and surface modified nano-magnetite for dyes removal.

Nanomagnetite has two roles if hydrogen peroxide and dyes are present: (i) dye and hydrogen peroxide adsorption; and (ii) catalyze the hydrogen peroxide oxidation. The applications of these materials will be discussed in the following sections.

#### 2.3.1 Nanomagnetite as dye adsorbent

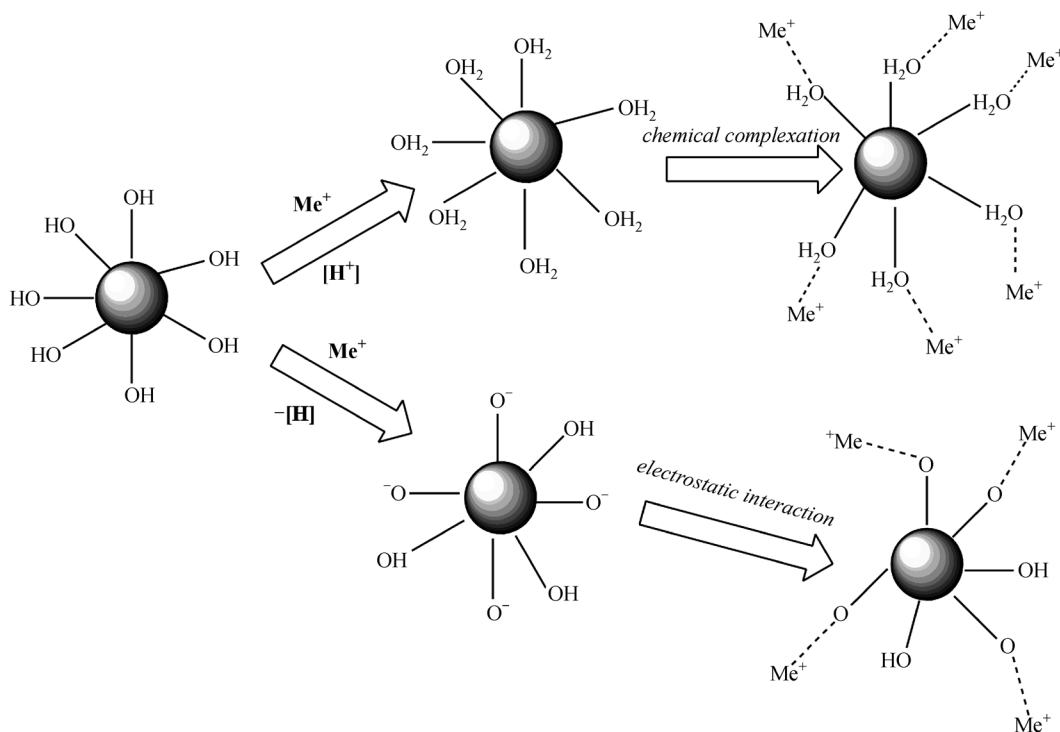
There are recent reviews that include the information on magnetite as adsorbent but also as magnetic composites (MC) and nanocomposites (MNC) [35].

Studies on adsorption of different dyes onto magnetite have explored several aspects such as influence of experimental conditions (pH, concentrations, temperature, time, and ionic force) and dye structure in the maximum uptake. Chaudhary et al. explored the applicability of the magnetite in cationic dye, anionic dye and an azo dye

**Table 2** Summarized characterization data of magnetite nanoparticles synthesized using different methods and its performance as heavy metals adsorbent

method of synthesis	BET area $(\text{m}^2 \cdot \text{g}^{-1})$	size/nm	heavy metal	max. adsorption capacity $(\text{mg} \cdot \text{g}^{-1})$	ref.
co-precipitation method	$1.9 \times 10^2$	6–8	Cd(II)	34.9	[21]
polyol process		18–35		7.4	
adaptation of co-precipitation	41.30	200–300	Cd(II)	164.5	[24]
co-precipitation	–	17	As(III)	5.7	[26]
			As(V)	4.8	
co-precipitation	100	4	As(V)	45	[28]
microwave assisted hydrothermal	–	27	Cr(III)	2.2	[31]
			Cr(VI)	1.7	
commercial magnetic nanoparticles	43	20–30	Pb(II)	36	[33]





**Fig. 3** Mechanism of heavy metal ion adsorption onto magnetite nanoparticles

removal in aqueous solution, desorption and recovering of dyes and reusability [36]. Different synthesis methods of magnetite, and diverse sizes and shapes have been explored in the field of environmental remediation. For example, ring-shaped hollow nanospheres and microspheres have been considered for pollutants removal [37].

Drawbacks like particle aggregation, surface deactivation, iron dissolution, contaminant release, stability, problems of magnetic solids recovering and potential nanoparticles toxic effects have to be considered [38].

With the source of iron salts as waste iron or tailings, Giri et al. prepared low cost magnetic nanoparticles (MNPs) able to adsorb methylene blue and Congo red with maximum monolayer adsorption capacities of 70.4 mg/g and 172.4 mg/g [39].

Liang-Shu Zhong et al. [26] synthesized nanosized  $\text{Fe}_3\text{O}_4$  that was used as adsorbent of Orange II. The magnetite nanoparticles could remove most of the Orange II present in the aqueous sample (100 mg/L of initial concentration) and demonstrated a removal capacity of 43.5 mg of azo-dye per g magnetite. The authors attributed the adsorption behavior to electrostatic interactions between the iron oxide surface and Orange II species in solution. Moreover, the magnetic adsorbent was regenerated by catalytic combustion at 300°C and the regenerated  $\text{Fe}_3\text{O}_4$  nanoparticles kept almost the same adsorption performance. It is possible to find combined studies of magnetite as adsorbent and as part of Fenton oxidation systems for azo-dyes removal [40].

Several problems have to be solved from reported results when using nanomagnetite as adsorbent:

a) Leaching of iron to aqueous solutions, specially  $\text{Fe}^{2+}$  at acidic pH, promoted or not through complexation, generally solved using adequate surfactants, additives or surface modifiers

b) Development of efficient methods of regeneration, through the increase of preparation stability and adsorption reversibility.

c) Surface activation to increase the adsorption capacity, through the improvement in the procedures to obtain nano sized magnetite with uniform and narrow size and shape distributions.

### 2.3.2 Nanomagnetite as part of Advanced Oxidation systems and Nanozymes

Magnetite has been used in the research of heterogeneous catalytic oxidation Fenton-like process [41].

In the surface-catalyzed mechanism, the interactions of  $\text{H}_2\text{O}_2$  with the iron oxide surface produced reactive radicals. These radicals attacked the pollutants in adsorbed or aqueous phases.

Minimum iron leaching, catalytic stability and multiple reuses without deactivation are key issues to make heterogeneous Fenton rentable, considering lowest environmental impact when dealing with toxic compounds [42].

Deng et al. [43] investigated the decolorization rate of Rhodamine B (RhB) solution in an iron oxide/ $\text{H}_2\text{O}_2$

system. At low H<sub>2</sub>O<sub>2</sub> concentration, the HO• radicals preferentially attacked the RhB whereas at high H<sub>2</sub>O<sub>2</sub> concentration, there was a competitive reaction between the substrate and hydrogen peroxide. Presence of Fe<sup>2+</sup> in the Fe-bearing minerals enhanced the production rate of HO• and the final efficiency of Rhodamine B elimination, at pH7. The material was reusable.

The advanced oxidation processes or AOP like H<sub>2</sub>O<sub>2</sub>/UV, O<sub>3</sub>/UV, and H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub>/UV use photolysis UV with H<sub>2</sub>O<sub>2</sub> and/or O<sub>3</sub> to produce OH radicals. Generally these processes are expensive and complex in practice to be applied to real scale systems because they involve the combination of different primary to tertiary treatment methods [44].

Yan et al. have recently discovered that magnetic nanoparticles Fe<sub>3</sub>O<sub>4</sub> (MNPs) presented an intrinsic activity similar to peroxidase [45]. These materials were called nanozymes. Nanozymes are the mimetic systems of catalase and peroxidase, being the metalloporphyrins like hematin biomimetic of enzymes. Figure 4 shows the periods when these systems appeared as attractive (bio) catalysts with hydrogen peroxide as oxidant.

In other researches, it was found that the catalytic activity of nanozymes was higher with smaller size particles [5,7].

Gao et al. [45] oxidized TMB (tetramethylbenzidine), DAB (di-azo-aminobenzene) and OPD (o-phenylenediamine) to give the same color variation as that of HR. However, long reaction times (6h) and high concentrations of nanoparticles were needed in the presence of high

concentrations of hydrogen peroxide to complete the degradation of the compounds. Only Fe<sup>2+</sup> was proposed as the responsible of the peroxidase-like activity of nanoparticles, but Prussian blue-modified γ-Fe<sub>2</sub>O<sub>3</sub> was prepared and demonstrated abilities to activate hydrogen peroxide [46]. There is competence of Fe<sup>2+</sup> with contaminants for electrons to produce reactive oxygen species (ROS), including O<sub>2</sub><sup>•-</sup>, H<sub>2</sub>O<sub>2</sub> and •OH radicals. Same authors found that the hydroxyl radicals may be generated at acidic conditions using MNPs. Superoxide was supposed to produce H<sub>2</sub>O<sub>2</sub> and •OH in contact with MNPs. O<sub>2</sub><sup>•-</sup> was predominant at alkaline conditions using MNPs. The authors proposed a two-step •OH formation mechanism: i-O<sub>2</sub><sup>•-</sup> produce hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) and ii-the formed H<sub>2</sub>O<sub>2</sub> reacts with dissolved Fe<sup>2+</sup> from MNPs generating •OH through Fenton reaction.

Interconversion of Fe<sup>2+</sup> and Fe<sup>3+</sup> at magnetite surface may be the key to the application of MNPs in Fenton heterogeneous systems for dyes removal [47].

From here and thereafter the modified magnetite will be analyzed as adsorbent and part of heterogeneous Fenton or Fenton-like systems.

It was demonstrated that increasing the high surface-area-to-volume ratio in magnetite, increases the active sites concentration for the reaction of toxic pollutants. Therefore, the mass required for treatment processes may be lower than in the case of using micron-sized particles. Furthermore, the removal capacity and reactivity of nanoparticles with nanometric sizes were higher than those with micrometric ones [22]. The smaller the

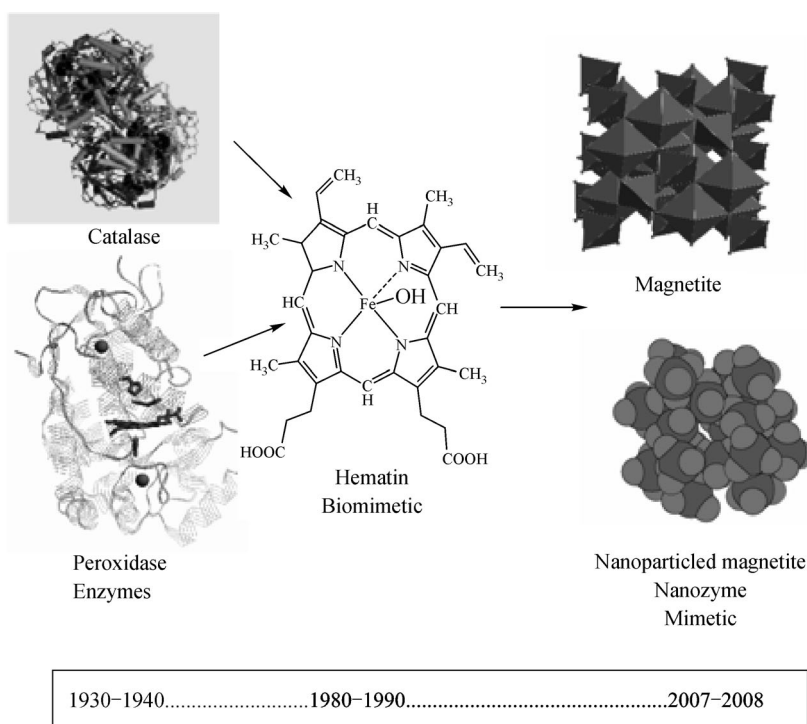


Fig. 4 Evolution from peroxidase and catalase enzymes to nanozymes last 80 years

particles, the higher their tendency to aggregate; and a reduction in the removal capacity is observed [48]. Thus, one of the most important challenges in different synthetic procedures of magnetite nanoparticles is the size control and aggregation. So the addition of chelating organic anions (carboxylate or  $\alpha$ -hydroxy carboxylate ions, such as citric, gluconic, or oleic acid), polymeric surface complexing agents or surfactants during the formation of magnetite could help to control the size; enhancing thus their adsorption performance. This aspect will be analyzed in the following sections.

### 3 Substituted nano-magnetite (Zn, Co, Mn, Ti o V)

The iron in the magnetite structure may be substituted isomorphically by other transition metals. Metals like Zn, Co, Ni and Cu occupy the sites meant for Fe. The catalytic capacity is the most enhanced characteristic [49]. It has been reported that elements from period four have increased the catalytic Fenton activity of magnetite structure with the exception of Ni, which demonstrated to have an inhibitory effect. Mechanisms of improvement were linked to oxygen vacancies at the surface, reduction of particle size and pore diameter and the increment of surface area [41].

Ferrites are complex iron oxides, which have ferromagnetic properties. Co-precipitation has the advantage of giving ferrites nanoparticles of better homogeneity [50]. Using this methodology, amorphous or poorly crystalline material may be converted to ferrite nano crystals by subsequent heating at elevated temperatures. Various common methods for ferrites preparation have disadvantages associated to forming impurity while grinding, poor compositional control and chemical inhomogeneity. These drawbacks may be overcome by the wet chemical synthesis via co-precipitation.

Among several possible metals, Mn, Co and Ni are the preferred to be incorporated to the magnetite structure. Costa et al. have explored the effect of Co, Mn and Ni in the magnetite structure, studying different concentrations of the substituent. In this case,  $\text{Fe}_3\text{O}_4$  was prepared from  $\text{FeCl}_3$ ,  $\text{NH}_4\text{OH}$  and  $\text{CH}_3\text{COONH}_4$  by co-precipitation of the precursor ferric hydroxyacetate followed by thermal treatment at  $430^\circ\text{C}$  using  $\text{N}_2$  atmosphere. The substituted magnetites  $\text{Fe}_{3-x}\text{Mn}_x\text{O}_4$ ,  $\text{Fe}_{3-x}\text{Co}_x\text{O}_4$  and  $\text{Fe}_{3-x}\text{Ni}_x\text{O}_4$  were prepared as described above with the addition of the nitrate salts of the metals Ni, Co and Mn [51]. These authors found different performance on the Fenton reaction depending on the kind of metal substituting Fe in magnetite structure.

According to the literature, the addition of Mn to  $\text{CoFe}_2\text{O}_4$  induces Co ions to migrate from octahedral to tetrahedral sites leading to structural changes and making it highly suitable to use in sensors, as catalyst and for treating

industrial wastes. An increased hysteresis is a drawback of these samples, which can be decreased by annealing the samples at high temperatures. Ahalya et al. prepared manganese ferrite ( $\text{MnFe}_2\text{O}_4$ ) and cobalt-doped manganese ferrite ( $\text{Mn}_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$ ,  $x = 0, 0.2, 0.4, 0.6$  and  $0.8$ ) at pH 11 and annealing temperature of  $900^\circ\text{C}$ . They reported particle sizes about 30–35 nm and determined that varying dopant concentrations strongly influenced the crystalline edges, surface morphology and magnetic properties of the samples [52].

Yang et al. reported a novel solvothermal process of making monodisperse non-stoichiometric M-ferrites porous spheres through reaction of  $\text{MCl}_2$  and  $\text{FeCl}_3$  in ethylene glycol solution with the introduction of dodecylamine. Porous spheres of Zn-ferrite, Ni-ferrite, Co-ferrite, Mn-ferrite and Mg-ferrite were prepared by varying the transition metal precursor. The as-synthesized ferrites were non-stoichiometric; whereas magnetic features of M-ferrites before and after calcination were directly correlated to chemical composition, morphology and size [53].

Other method to synthesize substituted magnetite is based on sol-gel – auto combustion. In brief, stoichiometric amounts of metal nitrates and citric acid (weighted as citric acid/metal ion mole ratio of 1:1) were dissolved separately in minimum amount of distilled water. All the individual solutions were mixed together and then the ammonia solution was slowly added to adjust the pH at 5–6. The resultant solution was kept on a hot plate magnetic stirrer at  $90^\circ\text{C}$  until gels were formed. After a few minutes, the gels self-ignited in an autocombustion until the whole citrate complex was consumed to yield nano-ferrite powders. The as-obtained ferrite powders were annealed at 400, 600, 800 and  $1000^\circ\text{C}$  for 2h [54].

#### 3.1 Applications as adsorbents of As, Pb, Hg, Cd and Cr

Different nanoscale ferrites have been tested for the removal of metals such as arsenic [55], chromium [56] and cadmium [57]. Liang et al. synthesized a series of Mn-substituted magnetites and investigated the effect of Mn substitution on the reactivity of magnetite regarding to the  $\text{Pb}^{2+}$  adsorption capability. They investigated the valence and local environment of both Fe and Mn in the spinel structure of magnetite by X-ray absorption fine structure (XAFS) spectroscopy. These authors determined that incorporation of Mn did not change the valence and local structure of Fe in the synthetic magnetite, if Mn valences were +2 and +3. The Mn distribution on the octahedral sites of magnetite surface increased with the increase in Mn content. The adsorbent ability increased from 26.40 to 36.27 mg/g when Mn was introduced in the iron oxide structure [58].

Tu et al. [57] prepared copper ferrites and used them for the removal of arsenate present in natural waters and real wastewaters. The adsorbents proposed by these authors reached an adsorption capacity of about 45.66 mg of As /g

of adsorbent performed the assay at room temperature and acidic pH.

Our group has used magnetic composites such as  $\text{CoFe}_2\text{O}_4$ ,  $\text{MnFe}_2\text{O}_4$  and chitosan to eliminate  $\text{Cr}^{6+}$  from aqueous solutions. Satisfactory levels of adsorption ranging between 45.1 and 39.2 mg/g were found using Co and Mn substituted magnetite, respectively [59].

A three-dimensional (3D) porous  $\text{NiFe}_2\text{O}_4$  adsorbent having significant magnetic properties was synthesized and employed in detoxification of  $\text{Pb}^{2+}$  contaminated aqueous solution. The adsorption rate was fast, reaching equilibrium in almost 60 min, whereas the adsorption capability was around 48.98 mg/g. In this case, involvement of hydroxyl groups in the adsorption mechanism was confirmed through FTIR analysis. It was hypothesized that the presence of pores in the magnetic adsorbent further enhanced the adsorption of  $\text{Pb}^{2+}$  [60].

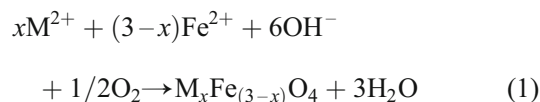
Adsorption works on the principle of ion-exchange between adsorbate (heavy metal ion) and adsorbent (ferrite), as it was previously described for the case of bare nanomagnetite as adsorbent. The large surface area, enhanced pore size, high pore volume and catalytic nature of nano materials made them suitable candidates for their use in adsorption. Mn ferrites have been useful to adsorb and remove toxic  $\text{Cr}^{6+}$  from aqueous systems. These authors informed that adsorption efficiency rises with an increasing quantity of adsorbent and it was higher for samples prepared at pH 11. The adsorption efficiency decreased with increasing annealing temperatures of the sample due to increased crystallite size, and made difficult the ion exchange. In addition, with increasing initial  $\text{Cr}^{6+}$  concentrations the adsorption decreased. The adsorbed metal may be desorbed from ferrite and the adsorbent further reused [61].

In general, the ability of the ferrites to act as efficient adsorbents was related to characteristics such as small size, large surface area, easy separation and large number of active sites for interaction with different contaminants. These properties were responsible for high adsorption capacities by increasing the surface area, free active valences, and surface energies of nanoparticles.

Other potential mechanism to ion interaction with ferrites was associated to the formation of complexes between adsorbate and adsorbent. In several cases, the adsorption process took place at pH conditions where both components (adsorbent and metal ion) exhibited similar surface charge; hence, electrostatic interactions were not favored.  $\text{Me}^{2+}$  was a Lewis acid while the functional surface hydroxyl group of ferrite had Lewis basic properties in deprotonated form to bind the  $\text{Me}^{2+}$  cation. Then, mono and binuclear inner-sphere complexes were formed. Inner-sphere complexes have coordinate-covalent bonding as the primary force and more stable than the outer-sphere complexes, where electrostatic bonding was the main bonding force [62].

Besides the simple adsorption procedure to the removal

of heavy metals from water sources, recent reports deal with the formation of magnetic ferrite in the contaminated media. The base of this treatment lies in the use of a  $\text{Fe}^{2+}$  salt that is added to an aqueous solution containing a pool of heavy metals (i.e, Cd, Cu, Pb, Cr, Zn, Ag, Hg, Ni, Sn and Mn.). The formation of magnetic ferrite was promoted by  $\text{M}^{2+}$  (an ion located in group 2 of Periodic table), according to the Equation 1:



Treating wastewater with high concentrations of heavy metals ions with ferrite involved the reaction of the Equation above by inserting heavy metal ions into the spinel structure formed from iron and oxygen. For yielding high quality ferrite and suppressing the formation of the other crystal phases, the pH needs to be controlled at 9–11 and reaction temperature over  $70^\circ\text{C}$ . A dosage of  $\text{Fe}^{2+}$  5–10 times higher than the required content in solution was needed to ensure satisfactory removal efficiency.

The advantage associated to this technique was the soft magnetism that allowed fast separation from the solution by using an external magnetic field. Time and cost were expected to be much less than those of traditional processes, such as sedimentation or filtration [63]. The disadvantages of these ferrites are related to their inefficiency against some heavy metals ions, such as Pb, Cd, and Cu, and the resultant sludge cannot pass the toxicity characteristic leaching procedure (TCLP) limits. Anyway, these drawbacks could be solved as a function of the experimental conditions for instance increasing the concentration of  $\text{Fe}^{2+}$ , adjusting the pH, etc. Figure 5 displays a schematic representation of ferrite method for the removal of heavy metals from aqueous solutions.

This methodology was highly recommended in cases where a complex mixture of heavy metals ions was present in the wastewater. Jie-Chung Lou et al. informed that most of the supernatants after conventional single-step ferrite process complied with the effluent standard of Environmental Protection Administration in Taiwan. However, the sludge did not satisfy the toxicity limits due to high Cd, Cu, and Pb ions concentrations. The performance of these ferrites in removing heavy metals ions from wastewater was subsequently investigated and the parameters were optimized in terms of temperature and pH. After this optimization, all heavy metal ions in supernatant and sludge could fulfil the contamination levels regulated by law. In addition, the sludge was examined by XRD. It forms a stable spinel structure, which could be effectively separated by external magnetic field [63].

### 3.2 Applications in Azo and anthraquinonic dyes removal

The use of bare magnetite as well as ferrite nanoparticles

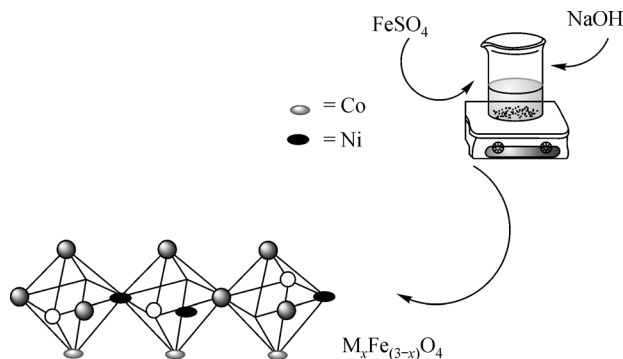


Fig. 5 Schematic representation of elimination of heavy metals ions by ferrite method

for dye remediation has been scarcely reported in the open literature, in comparison with heavy metal or other contaminants elimination.

Stoyanova et al. prepared nanosized cobalt and iron–cobalt spinel oxides – bulk and supported on MgO– and tested as catalysts for oxidative degradation of a textile monoazo-dye, (Acid Orange 7(AO7)), in aqueous solution using peroxymonosulfate as oxidant [64]. Nearly 100% AO7 removal was achieved within a short treatment time and with negligible Co and Fe leaching from the catalyst's particles during the degradation process.

Costa et al. reported that the introduction of Co and Mn into magnetite structure to form  $\text{Fe}_{3-x}\text{Co}_x\text{O}_4$  and  $\text{Fe}_{3-x}\text{Mn}_x\text{O}_4$  strongly promoted both the  $\text{H}_2\text{O}_2$  decomposition and the degradation of organic compounds in an aqueous medium [65].

Nguyen et al. presented a simple and efficient method for the preparation of magnetic  $\text{Fe}_2\text{MO}_4$  (M:Fe and Mn) and magnetic activated carbons by impregnating the activated carbon with simultaneous magnetic precursor and carbon modifying agent followed by calcinations [66].

The obtained magnetic adsorbents exhibited high surface areas and porosities and could be easily manipulated by an external magnetic field. The  $\text{Fe}_2\text{MnO}_4$ /carbon exhibited enhanced activity in Fenton oxidation of methyl orange compared with the  $\text{Fe}_3\text{O}_4$ /Carbon sample. It was found that 100% degradation and 59% Total organic content (TOC) removal of 50 mg/L Methyl Orange (MO) could be achieved by using  $\text{Fe}_2\text{MnO}_4$ /Carbon in 120 min of reaction. Stability of the catalyst was demonstrated in up to three consecutive experiments showing that the reaction is essentially heterogeneous.

The aim of the study of Benes et al. was to characterize catalytic effect of heterogeneous magnetically separable iron mixed oxides ( $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Mn}^{2+}$  ferrite and magnetite) on decolorization of synthetic dyes by hydrogen peroxide. The most effective catalyst  $\text{FeOFe}_2\text{O}_3$  (25 mg/mL with 100 mmol/L  $\text{H}_2\text{O}_2$ ) produced more than 90% decolorization of 50 mg/L Bromophenol Blue, Chicago Sky Blue, Evans Blue and Naphthol Blue Black within 24 h. The fastest decomposition proceeded during

the first hour of the reaction. All the catalysts also caused a significant decrease of the chemical oxygen demand (COD). The authors tested dyes as sulfoftaleins (Bromophenol Blue), azo dyes (Chicago Sky Blue, Evans Blue, Reactive Orange 16, Naphthol Blue Black), fluorescein derivatives (Eosin Yellowish), triphenylmethanes (Phenol Red), phthalocyanines (Cu Phthalocyanine) and anthraquinones. All azo dyes and triphenylmethane dyes were oxidised more easily than fluorescein type and sulfoftalein type dyes [12].

Cr-containing magnetites were applied in the heterogeneous Fenton degradation of cationic and anionic dyes. The Cr improved the catalytic activity of magnetite in heterogeneous Fenton reaction, varying the improvement with the substitution level. The tested dyes were MB (a cationic dye) and AOII (an anionic dye).  $\text{Cr}^{3+}$  occupied octahedral sites of magnetite. High conversions of dyes were found when the Cr substituted magnetite was added (from 40 to 90%)[67].

The preparation of superparamagnetic nanocomposites including Mn to be applied in dye degradation has been recently reported [68]. The mechanistic aspects are more and more studied especially in substituted magnetites, particularly with  $\text{V}^{3+}$ ,  $\text{Ti}^{4+}$  and  $\text{Cr}^{3+}$ .  $\text{V}^{3+}$  and  $\text{Cr}^{3+}$  participated in  $\text{Fe}^{2+}$  regeneration whereas  $\text{Ti}^{4+}$  increased the surface area and hydroxyl concentration at surface [69].

## 4 Nanosized magnetite with surface functionalization (surfactants, polyaminoacids and low-cost polymers)

### 4.1 Synthesis of functionalized nanosized magnetite

As it was demonstrated by data on previous sections, pure iron oxide nanoparticles and their metal alloys were effective adsorbents for heavy metals ions and dyes. However, their application was restricted because of some drawbacks associated to their low stability in aqueous media, among others. This problem affected the long-term performance and applicability of the separation process.

The most straightforward strategy to overcome these limitations was their modification with organic or inorganic moieties that stabilize them in suspension. Using this procedure, magnetic nanoparticles of the type core-shell structure may be obtained [70]. In general, the external coating plays a dual role: as stabilizer and functionalized surface; thus increasing the adsorption capacity and selectivity toward the target pollutants. Figure 6 displays the synthetic pathways of magnetic nanoparticles with additives.

Three types of interactions may be distinguished among magnetic nanoparticles: London—Van der Waals, mag-

netic forces and interactions of the electrical double layer. The preceding two attractive interactions among the particles must be counteracted by the later repulsive force to make them stable, for instance in a non-polar solvent. However, the repulsive force is very small. To get well-dispersed MNPs in a solvent, the nanoparticles must undergo surface modification to make them able to adsorb one layer of surfactant on the surface. Thus, the repulsive force from the stabilizer-coated particles can overcome the attractive forces between the particles.

The coating of magnetic nanoparticles may be achieved through two general approaches: ligand addition and

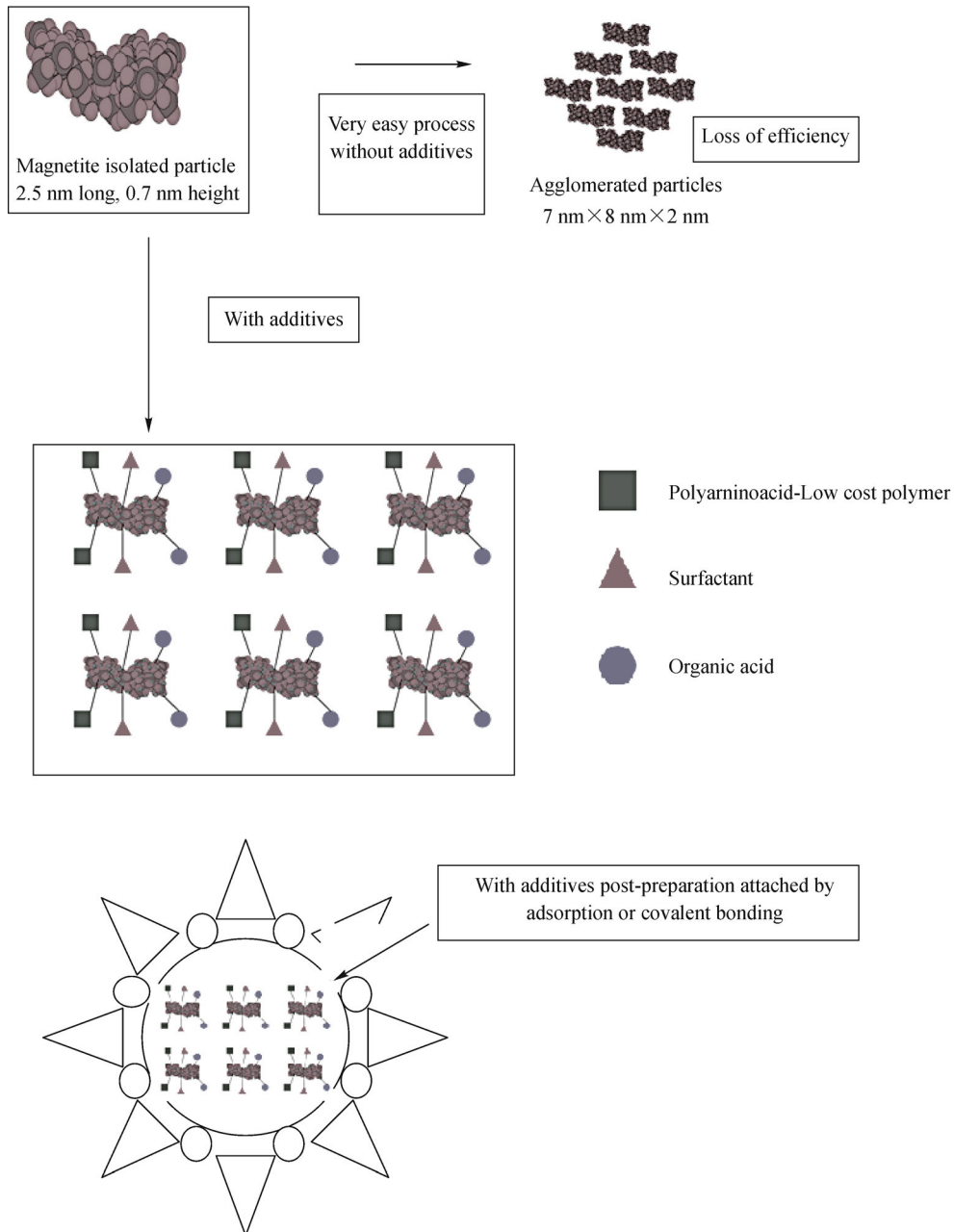


Fig. 6 Synthesis pathways of MNP with additives

ligand exchange [71]. Figure 7 depicts these two methodologies. In ligand addition, the stabilizing agents can physically adsorb on the magnetic nanoparticle surface because of various physico-chemical interactions, including electrostatic, hydrophobic, hydrogen bonding, etc. Besides physical adsorption, coating materials with abundant hydroxyl, carboxyl, and-amino groups can readily and steadily absorb on the surface of bare magnetite by coordinating with the iron atoms. Even for nanoparticles with pre-existing hydrophobic coating, newly added amphiphilic agents could also stick physically or chemically on the surface to complete phase transfer.

Among the vast amount of chemical compounds potentially useful for magnetite core stabilization, a general classification may be done considering surfactants, polymeric moieties and specific molecules/compounds strongly related to the nanosystems applications. Polymeric modifiers have been extensively reviewed in a previous work [16]. Hence, we will focus here on surfactants of different nature (i.e., ionic and organic such as Oleic Acid (OA) and Sodium Dodecyl Sulfate or DSD) with potential in environmental remediation and other novel modifiers such as polyaminoacids and short polyfunctional molecules like aminoacids and organic carboxylic acids. Biopolymeric coatings (i.e., chitosan, alginate, gum arabic) and other natural compounds (i.e., humic acid, cyclodextrins, and dextrans) or different small molecules (sugars) will not be considered.

From the available literature, long chain surfactants appear as classic and useful modifier agents and between them, OA has been undoubtedly the most broadly utilized [72]. The incorporation of OA responded to a dual purpose; first, it was used to give stability to nanoparticles

avoiding aggregation; and second to generate a hydrophobic surface able to interact with non-polar substrates; or to make the MNPs easy to disperse in non-polar solvents.

Colvin's group mentioned that by controlling the volume of the oleic acid, sizes between 8 to 28 nm of iron oxide nanoparticles may be synthesized [73]. In these examples, the oleic acid coordinated to the Fe atom forming iron oleate complexes. It was reported that this process could retard the nucleation of iron particle [70].

Ionic surfactants, such as sodium dodecyl sulfate (SDS) were also employed in order to obtain hydrophilic MNPs [15]. For instance, Sharifabadi et al. have synthesized NPs of  $\text{Fe}_3\text{O}_4$  via traditional co-precipitation method using SDS as stabilizer. The prepared NPs were characterized by XRD and TEM. These authors indicated that SDS modified NPs can be used as an efficient adsorbent material for adsorption of cationic dyes from aqueous solutions [74]. Besides co-precipitation, the water-in-oil microemulsion route has been employed to prepare nanosized magnetite NPs. The use of surfactants of different nature was evaluated regarding this methodology. According to this report, the presence of SDS in a microemulsion media induced the interaction between  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  and  $\text{SO}_4^-$  in the core of the reverse micelles. Hence, there was a competition between  $\text{SO}_4^-$  and  $\text{OH}^-$  reacting with iron ions. The effect of a head group charge can be rationalized in terms of the impact of the electrostatic interaction on the rate control of iron ions diffusion and of the reaction with the  $\text{OH}^-$  [74]. Figure 8 displays photographs of aqueous dispersions of MNPs modified with SDS obtained in our group in presence and absence of magnetic field.

In the case of aminoacids (AA) and polyaminoacids (pAA) they have lateral functional groups on their structure

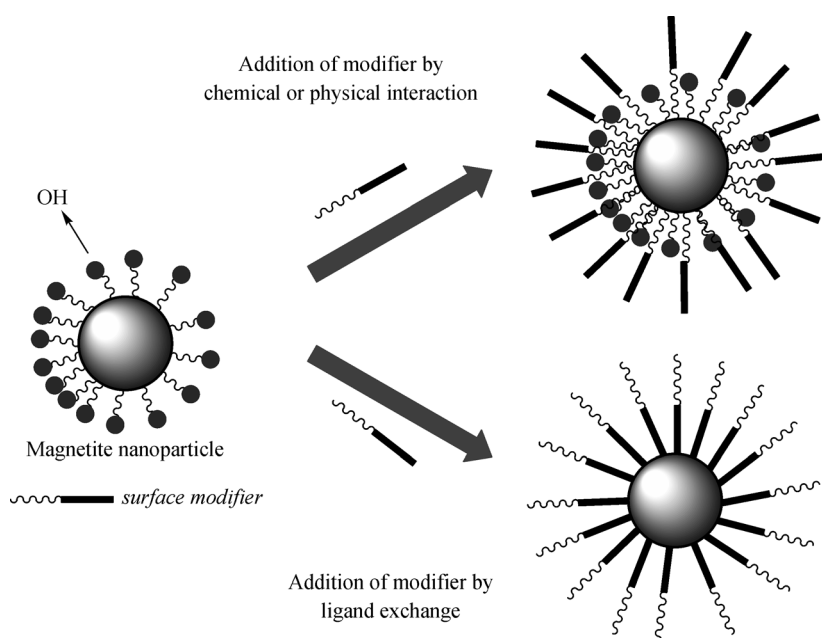


Fig. 7 The two mechanisms to surface modification of MNPs



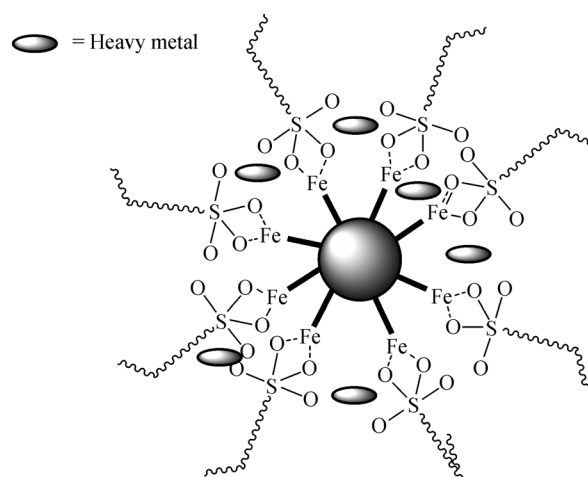
**Fig. 8** Photographs of aqueous dispersions of MNPs modified with SDS in presence and absence of magnetic field

including hydroxyl, carboxyl, amine, and aliphatic, carbonyl, and thiol, sulfur, oxygen and nitrogen. These groups enable these compounds to interact not only with the magnetite surface, but also with heavy metals ions, dyes as well as with a wide gamma of pollutants. For instance, cysteine with three functional groups have a certain binding affinity to metal ions especially Fe atoms, so it can be effectively conjugated into magnetite nanoparticles' surface. In a recent work, a stabilized ferrofluid based on magnetic nanoparticles (about 21.9 nm core diameters and 1.6 nm of coating) was synthesized via co-precipitation using cysteine as surfactant. They calculated the coating density and demonstrated that a high density coating was formed on the nanoparticles surface [75]. The incorporation of AA or polyAA to the magnetic core was performed in a posterior step on the previously synthesized magnetic nanocores [74]. Marinescu et al. reported a novel synthetic procedure to AA incorporation on magnetic NPs surface, involving only one step. They obtained magnetite by decomposition of polynuclear aminoacids complex compounds of  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$ , at pH = 11. In this work, the presence of AA was verified by several characterization techniques. These authors informed that synthesized nanoparticles seemed to be organized into a core shell system, where the inner-core was formed from unit cells of magnetite. A way to control the self-assembly and the physical properties of the synthesized nanoparticles consisted in the correlation with descriptors representing the aminoacid chemical structures. A relationship between the used aminoacids and the properties of magnetite NPS was found (magnetization, size, magnetite core diameter and the magnetite at each nanoparticle core) [76,77].

#### 4.2 Applications as adsorbents of As, Pb, Hg, Cd and Cr

The role of SDS in the efficiency of magnetic nanoparticles to adsorb heavy metals ions has not been well defined in available reports. Two general procedures were proposed:

i-using magnetite NPs previously stabilized/modified with SDS; ii-using bare magnetite NPs dispersion; incorporating SDS to the aqueous polluted solution. In this last case SDS was added to favor the interaction with the heavy metal ions. Figure 9 displays the interactions proposed for heavy metals cations with magnetite nanoparticles and SDS. Adeli et al. have synthesized SDS-coated  $\text{Fe}_3\text{O}_4$  NPs and used them for the adsorption of Cu, Ni and Zn. They demonstrated that in the absence of SDS coating, metal ions were hardly adsorbed. However, by increasing the amount of SDS, adsorption increased remarkably by the gradual formation of SDS aggregates on the surface of  $\text{Fe}_3\text{O}_4$  NPs. In this case, the surfactant was added to the magnetite NPs aqueous dispersion in the presence of heavy metals ions [78].



**Fig. 9** Interactions of heavy metals cations with magnetite nanoparticles and SDS

SDS-coated  $\text{Fe}_3\text{O}_4$ -NPs were prepared and applied for pre-concentration and determination of  $\text{Hg}^{2+}$  ions from water samples.  $\text{Hg}^{2+}$  was quantitatively extracted and an enhancement factor for the heavy metal extraction of 1230-fold was obtained comparing the use of NPs to conventional extraction techniques. The presence of surfactants on the surface of mineral oxides plays a key role in the elimination of Hg. According to the concentration of added surfactants, they can form various aggregates on the surface (hemimicelles, mixed hemimicelles, and admicelles). Based on the obtained results, increasing the amount of SDS up to 50 mg will cause an increase of the extraction recovery. This trend was observed after an equilibrium concentration where recovery remained constant [79].

A list of acid, silane, and diols has been shown to interact with the iron oxide surface. The ubiquitous nature of the carboxylate containing ligand made it the most useful anchor group for generating a wide range of magnetic nanoparticle adsorbents. In this context, aminoacids (AA) are particularly attractive because the additional



NH<sub>2</sub> groups enhance the possibilities for heavy metals ions (and other pollutants) interactions. The literature regarding to magnetic-AA nanosystems applied to water remediation is still limited, but the results are very promissory.

Poly  $\gamma$ -glutamic acid (PGA)-coated Fe<sub>3</sub>O<sub>4</sub> magnetic nanoparticles ( $\gamma$ -PGA/Fe<sub>3</sub>O<sub>4</sub> MNPs) were fabricated using the co-precipitation method.  $\gamma$ -PGA/Fe<sub>3</sub>O<sub>4</sub> MNPs (52.4 nm, 88.41 m<sup>2</sup>/g) had smaller particle size and larger specific surface area than Fe<sub>3</sub>O<sub>4</sub> MNPs (62.0 nm, 76.83 m<sup>2</sup>/g). The  $\gamma$ -PGA/Fe<sub>3</sub>O<sub>4</sub> MNPs removed over 99% of Cr<sup>3+</sup>, Cu<sup>2+</sup> and Pb<sup>2+</sup>, and over 77% of Ni<sup>2+</sup> in deionized water and it was more efficient than  $\gamma$ -PGA and Fe<sub>3</sub>O<sub>4</sub> MNPs. The authors attributed the difference to the large specific surface area of  $\gamma$ -PGA/Fe<sub>3</sub>O<sub>4</sub> MNPs [80].

Poly-L-cysteine (PLCysn) ( $n = 20$ ) was immobilized onto the surface of commercially available magnetic  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles, and was used as a selective heavy metal ion chelator. PLCysn functionalization was confirmed using FTIR and the quantitative Ellman's test. Metal ion binding capacities for As<sup>3+</sup>, Cd<sup>2+</sup>, Cu<sup>2+</sup>, Ni<sup>2+</sup>, Pb<sup>2+</sup> and Zn<sup>2+</sup> were determined at pH 7.0 and compared to adsorption capacities for unfunctionalized  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles. For all metal ion examined, binding capacities (mol metal/g support) were more than one order of magnitude higher than those obtained for PLCysn on traditional supports. For As<sup>3+</sup>, Cu<sup>2+</sup>, Ni<sup>2+</sup> and Zn<sup>2+</sup> the binding capacities were also higher than the metal adsorption capacities of the unfunctionalized particles. Metal uptake was determined to be fast (< 2.5 min) and metal recoveries higher than 50% were obtained for all of the metal ions except As<sup>3+</sup>.

The authors proposed that improved metal selectivity could be achieved by combinatorial peptide library screening or by using peptide fragments based on known metal binding proteins [81].

#### 4.3 Applications in azo and anthraquinonic dyes removal

Magnetic nanoparticles (MNPs) treated with 3-glycidioxypropyltrimethoxysilane (GPTMS) and lysine (Lys) (MNP-GPTMS-Lys) were prepared by Zhang et al. Magnetite modified with glycine adsorbed cationic and anionic dyes but capacity for the anionic was much lower than for cationic dye removal [82]. When Lysine was used, azure and methylene blue as cationic dyes were removed and the adsorption of anionic dyes also improved. Reuse by three times of MNP-GPTMS-Lys was very successful and no loss of efficiency was found for different dyes.

Magnetite nanoparticles covered with an anionic biopolymer poly(*c*-glutamic acid) (PGA-MNPs) were synthesized and characterized using methylene blue adsorption capability. Dye removal mechanism by PGA-MNPs was supposed to take place due to electrostatic interaction through exchange of protons from side-chain carboxyl groups on PGA-MNPs surface. Nanoparticles demonstrated to be superparamagnetic with average

diameter of near 12 nm and magnetization of 59.2 emu/g. The Langmuir adsorption capacity was near 79 mg/g at 301 K and pH 6.0 [83]. PGA coating did markedly improve the stability of MNPs in such a way that iron leaching decreased significantly.

The use of a cationic surfactant (cetyltrimethylammonium Bromide or CTAB) coating of magnetite applied in the removal of reactive Black 5 (RBBA), Reactive Red198 and Reactive Blue 21 demonstrated that CTAB affected the adsorption of the dyes [84]. A chemisorption mechanism described by a second order kinetic model was proposed [85].

## 5 Nanosized magnetite as part of composites with inorganic moieties (TiO<sub>2</sub>, SiO<sub>2</sub>) or supported magnetite on clay and carbon

As it was extensively commented along this manuscript, prevention of superparamagnetic nanoparticles from aggregation and leaching of iron to the solution is a great challenge among researchers working in this topic [86]. In this sense, magnetic composites have become an interesting alternative to this end. In this section, we will focus on magnetite as part of composites with other inorganic entities such as titanium and silicate oxides, clay, carbon, etc.

Magnetic carbon nanocomposites are defined as materials composed of magnetite embedded in a carbon matrix which morphology include activated carbon, fullerene (C<sub>60</sub>), carbon nanofibers, carbon nanotubes, expanded graphite, and graphene. Thus, the combination of carbon with magnetic nanoparticles to produce a magnetic composite provides new functional hybrid materials with the synergy of all the components. The resulting material presents great advantages for environmental remediation among others [86]. Figure 10 displayed a TEM micrographes of carbon-magnetite supported nanoparticles. The latter corresponds to carbon-magnetic composite synthe-

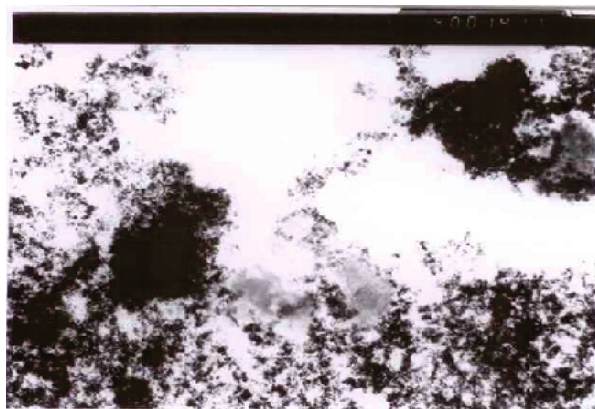


Fig. 10 TEM micrograph of a CNT/Fe<sub>3</sub>O<sub>4</sub>

tized in our group.

Clays are low-cost and available materials functioning as excellent cation exchangers, which were used to adsorb contaminants. Their adsorption capacity resulted from a relatively high surface area and a net negative charge on their structure, which attracted specially cations. On the other side, the presence of magnetite provided the advantage to the material be removed from the medium by a simple magnetic field [87].

Other widely investigated nano/composites were those formed by silica-coated magnetite or titanium oxide-magnetite composites. These hybrid materials have, as the other previously mentioned, the great advantage of combining functional surface and magnetism [88]. Silica-supported magnetite has attracted researchers' interest due to their large uniform nano-pore structures which lead potential application in adsorption, catalysis, etc.

Two strategies could be implemented for preparing composites containing superparamagnetic particles: (1) direct encapsulation of the magnetic nanoparticles within the non-magnetic matrix or (2) deposition of the magnetic nanoparticles at the surface of previously synthesized non-magnetic beads. The nanoparticles may be either adsorbed from colloidal solution or generated in situ using appropriate metal precursors [89,90]. Thus, the most employed methods to obtain magnetic composites were sol-gel, hydrothermal reaction [91], or by co-precipitating the iron salts onto the matrix [92]. For a schematic representation of these methods, see Fig. 11.

### 5.1 Applications of modified magnetites as adsorbents of As, Pb, Hg, Cd and Cr

The use of magnetic carbon and its nanocomposites to remove heavy metal ions from water has been reported [93,94]. Jingming Gong et al. [94] synthesized a novel hierarchically structured material composed by magnetite-

carbonaceous microspheres. In this study, the carbon precursor was chitosan, where the as-synthesized precursor of iron oxide-chitosan was transformed in magnetite-carbonaceous microspheres by calcination at elevated temperature. This procedure was called annealing. The magnetite-carbonaceous nanoparticles consisted of a magnetic core of 22 nm in diameter and a carbon shell of 12 nm in thickness and 206.6 m<sup>2</sup>/g BET area. This high value was attributed to the hierarchical structure of the magnetic-carbonaceous microspheres. The material was employed for the adsorption of Pb<sup>2+</sup> demonstrating a maximum adsorption capacity of about 126 mg/g.

Xiaoyao Guo et al. [95] synthesized graphene magnetic material (GO-Fe<sub>3</sub>O<sub>4</sub>) by hydrothermal method. The GO-Fe<sub>3</sub>O<sub>4</sub> demonstrated to be effective for the removal of heavy metals such as Cr<sup>6+</sup>, Pb<sup>2+</sup>, Hg<sup>2+</sup>, Cd<sup>2+</sup> and Ni<sup>2+</sup> from aqueous solution. The maximum adsorption values were about 17.29, 27.95, 23.03, 27.83 and 22.07 mg/g, for each metal, respectively.

Carbon nanotubes (CNT) were another chosen modifier of magnetic phase. A recent review summarized the use of magnetic-CNTs as sorbent materials in solid-phase extraction for the removal of different heavy metals ions such as Pb<sup>2+</sup>, Cd<sup>2+</sup>, As<sup>5+</sup>, Cr<sup>3+</sup>, Hg<sup>2+</sup>, As<sup>3+</sup>, etc [92]. Furthermore, Bavio et al. [96] synthesized oxidized multiwall carbon nanotubes (MWCNTs) with HNO<sub>3</sub>, KMnO<sub>4</sub>, HNO<sub>3</sub> and HSO<sub>4</sub>. Then, iron oxides were synthesized and supported on selected MWCNTs. The authors tested the performance of the material in arsenic removal. Variables such as pH, concentration of magnetite nanoparticles and contact time were analyzed for arsenic adsorption. The maximum adsorption capacity was about 40 mg As/g adsorbent.

A one-pot solid-phase route to synthesize magnetic iron oxide carbon nanotubes (MIO-CNTs) was recently reported [86]. This material presented a surface area of about 209.8 m<sup>2</sup>/g, good dispensability, desirable magnetic properties and promising aptitudes for As<sup>3+</sup> and As<sup>5+</sup>

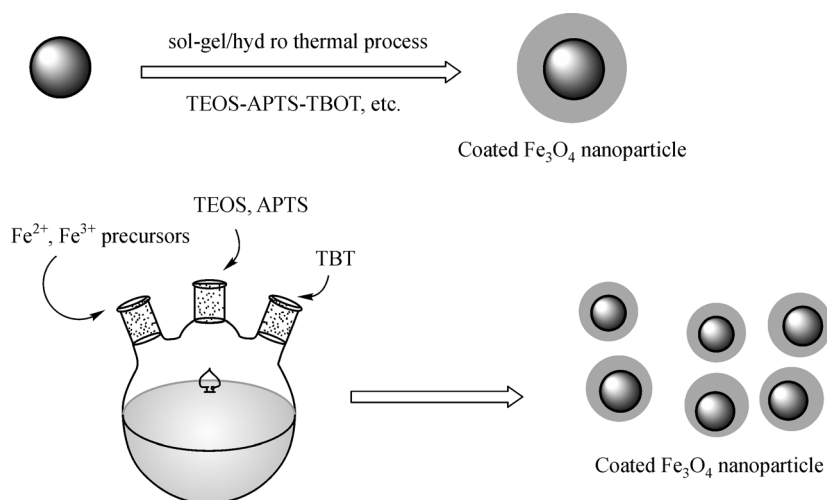


Fig. 11 Representation of sol-gel or hydrothermal reaction synthesis for magnetic composites

elimination. The maximum adsorption capacities were 47.4 and 24.1 mg/g, for  $\text{As}^{3+}$  and  $\text{As}^{5+}$ , respectively. Thiol-functionalized multiwall carbon nanotube/magnetite nanocomposites (CNTs/ $\text{Fe}_3\text{O}_4$ ) were synthesized by Cheng Zhang [93]. These materials presented an enhanced adsorption capacity because of the excellent affinity of thiol group for heavy metals. The adsorption properties of the CNTs/ $\text{Fe}_3\text{O}_4$  nanocomposite were tested for the removal Hg and Pb ions in aqueous medium. The maximum adsorption capacities were roughly 65.5 and 65.4 mg/g for  $\text{Hg}^{2+}$  and  $\text{Pb}^{2+}$ , respectively.

Other interesting magnetic composites employed for environmental remediation were those involving magnetic nanoparticles and mesoporous silica [97]. Penka I. Girginova et al. [98] used silica-coated magnetite to remove  $\text{Hg}^{2+}$  from water. The authors prepared the adsorbent material by first hydrolysis of  $\text{FeSO}_4$ , which was then modified with amorphous silica shells. These shells were also functionalized with organic moieties containing terminal dithiocarbamate groups. The surface area of the particles decreased from 13  $\text{m}^2/\text{g}$  ( $\text{Fe}_3\text{O}_4$ ) to 11  $\text{m}^2/\text{g}$  (silica-coated magnetite). The material displayed a high efficiency for  $\text{Hg}^{2+}$  uptakes from aqueous solutions, reaching about 74% removals.

Other magnetic silica mesoporous materials were synthesized demonstrating great capacity for Hg removal due to its high surface area [97]. The adsorbent material exhibited pore sizes of near 6.7 nm and surface area of 297  $\text{m}^2/\text{g}$ . These nanoadsorbents were able to eliminate almost 97% of  $\text{Hg}^{2+}$  after 7 h of treatment.

In Table 3, different magnetic nanocomposites based on carbon, graphenes, carbon nanotubes, silica- and  $\text{TiO}_2$ -magnetite nanocomposites are compared in terms of their properties and efficiency of heavy metals removal.

## 5.2 Applications in azo and anthraquinonic dyes removal

Tables 1 and 3 from the review of Sivashankar et al. summarized the adsorption capacity of magnetic composites for dyes [35]. Organosilane-functionalized magnetite achieved 241 mmol/g for Brilliant blue at pH 6.5 whereas monoamine modified magnetic silica had an adsorption capacity of 61 mg/g at pH 3 and 25°C for Acid orange 10.

Al Amrani et al. reported silica samples prepared through precipitation of silica in the presence and absence

of magnetite. The solids were treated with 3-aminopropyltriethoxysilane (APTS) and characterized using FT-IR, X-Ray Diffraction or XRD, Surface area (BET), pore volume and pore diameter measurements. The adsorption behavior of both silicas toward Acid Orange 10 in aqueous solutions was studied at different experimental conditions including different contact time, several pH and different initial concentrations. Regeneration of the dye-loaded silica was carried out using aqueous solution of pH 10. Desorption ratio of 98% was obtained over three adsorption/desorption cycles [99].

The adsorption capability of Nano crystalline  $\text{Fe}_{3-x}\text{La}_x\text{O}_4$  ( $x = 0, 0.01, 0.05, 0.10$ ) ferrite to remove cresol red (CR) from aqueous solution was evaluated by Zhao et al. Compared with undoped magnetite, the adsorption values were increased from 37.4 to 79.1 mg/g when tested using 30 mg/L of CR with 15 mg of solid in 50 ml of solution at 13°C. The experimental results proved that it is possible to increase the adsorption capacity of magnetite by doped  $\text{La}^{3+}$  ions. In this manuscript, substituted magnetite (107.64 mg/g) was compared with carbon nanotubes (450.5 mg/g) for CR adsorption [100].

Farrokhi et al. [101] reported the use of mixed oxides based on Zn and Fe. Zinc oxide was immobilized on magnetite nanoparticles by chemical method and it was used as an adsorbent to remove Reactive Black 5 (RB5) dye from aqueous solution. The removal of RB5 was studied as the function of adsorbent dosage, pH, initial RB5 concentration, hydrogen peroxide and ionic strength using salts. Adsorption of RB5 by  $\text{ZnO-Fe}_3\text{O}_4$  composite was maintained even after five successive cycles. The adsorption experiments were carried out in 1,000 ml Erlenmeyer flask with 30 mL of RB5 solution (from 10 to 200 mg/L at pH 7) and 2 g of  $\text{ZnO-Fe}_3\text{O}_4$ . The mixture was stirred at 150 r/min and at  $25 \pm 2^\circ\text{C}$ . Removal of RB5 was increased with increasing initial  $\text{H}_2\text{O}_2$  concentrations from 2 to 5 mmol/L. Removal of RB5 without  $\text{H}_2\text{O}_2$  increased from 68.2% at 2 min to near 87.6% at 120 min, and with 2 and 5 mmol/L of  $\text{H}_2\text{O}_2$  was increased from 74.6% to 100% and from 93.8% to 99% going from 2 to 120 min [102].

A sewage sludge derived porous carbon (SC) was used for the adsorption and degradation of 1-diazo-2-naphthol-4-sulfonic acid (1,2,4-Acid) with  $\text{H}_2\text{O}_2$ . The performance was compared to the one found for magnetic nanoparticles

**Table 3** Maximum adsorption of heavy metals using magnetic nanocomposites: graphene, carbon nanotubes, silica as a function of their properties

material in MNPs	BET area /( $\text{m}^2 \cdot \text{g}^{-1}$ )	size /nm	heavy metal	max. adsorption capacity/( $\text{mg} \cdot \text{g}^{-1}$ )	ref.
carbon	206.6	22	$\text{Pb}^{2+}$	126	[96]
graphene	62.43	38.57	Cr(VI), Pb(II), Hg(II), Cd(II) and Ni (II)	17.29, 27.95, 23.03, 27.83 and 22.07	[97]
carbon nanotubes	–	60	As(V)	39.93	[98]
carbon nanotubes			Hg(II) and Pb(II)	65.52 and 65.40	[95]
mesoporous silica	11	80	Hg(II)	13 $\mu\text{g}/\text{L}$	[100]

(MNPs). The 2 h treatment in SC/H<sub>2</sub>O<sub>2</sub> system rendered 94% of 1,2,4-Acid and 48.1% total carbon reduction, higher than the 46% and 24.3% obtained by using MNPs [103]. Besides malachite green (MG) and rhodamine B (RB) adsorption from aqueous solutions was studied by batch adsorption technique using Fe<sub>3</sub>O<sub>4</sub>/MWCNT. Near 94% MG and 98% RB removal were achieved in 80 min using 10 mg Fe<sub>3</sub>O<sub>4</sub>/MWCNT, at pH 6 and 298 K [104].

Zhang et al. reported the preparation of magnetic Fe<sub>3</sub>O<sub>4</sub>/C core-shell nanoparticles and their use for removal of organic dyes from aqueous solution through adsorption. Adsorption performances of the nanomaterial were tested with removal of methylene blue (MB) and cresol red (CR). The effects of pH, adsorption time and capacity of the nanocomposites were studied. The adsorption capacities for MB and CR were 44.4 mg/g and 11.2 mg/g, respectively [105]. Negative potential of the magnetic nanocomposites provides weak electrostatic interaction between the cationic dye and the nanomaterials. pH was crucial to adsorption and higher adsorption was found with MB at alkaline pHs.

Magnetic activated carbons exhibited high surface areas and porosities and can be easily manipulated by an external magnetic field. The Fe<sub>2</sub>MnO<sub>4</sub>/AC-H exhibited enhanced activity in Fenton oxidation of methyl orange versus the Fe<sub>3</sub>O<sub>4</sub>/AC-H sample. 100% degradation and 59% TOC removal of 50mg/L Methyl Orange was achieved by using Fe<sub>2</sub>MnO<sub>4</sub>/AC-H in 120 min of reaction [66]. Activated carbon/Fe<sub>3</sub>O<sub>4</sub> nanoparticle composites were obtained using a modified method with HNO<sub>3</sub>. The resulting nanocomposites had 1000 to 1300 m<sup>2</sup>/g of BET area. Their efficiency for methyl orange (MO) removal was from 175 to 250 mg/g. Fe<sub>3</sub>O<sub>4</sub> nanoparticles was located at the pores of activated carbon. These adsorbents could be regenerated using hydrogen peroxide and re-used several times. Iron leaching was very low at pH over 3 [106].

Recent reviews presented the complexity of the new applications using carbon nanotubes as the support for nanoparticles of magnetite [107]. The production of radicals is being researched actively [108].

There are several studies looking at the practical aspects of the application of nanoadsorbents and the problems to solve such as the optimization of the recovery of used nanoadsorbent, the regeneration process and the disposal of the regeneration solutions and the exhausted adsorbent [109]. The review of Garrido Ramírez et al. summarizes recent research on the use of clays and iron-oxide minerals in Fenton-like reaction and on nanocatalysts [110].

## 6 Conclusions

This review focused on the use of magnetite based nanomaterials for the elimination of heavy metals and selected dyes from different sources of water. Recent literature has been analyzed (more than 100 references,

most of them of 2012–2014) aiming to provide an integral view on the state of the art of this topic. Different magnetic materials, from raw nanomagnetite to magnetite combined with several compounds have been included. The role of the additives incorporated to the iron oxide was analyzed regarding to some properties of interest (size, area BET, magnetization) related to their ability and efficiency as pollutant adsorbents.

It is worth noting that novel modifiers were chosen to this revision such as aminoacids, graphene, carbon nanotubes, etc.

The methods of preparation were also described, and associated to the final characteristics of prepared magnetic materials.

Comparative analysis regarding to the performance of each nanomaterial to the elimination of each kind of contaminant was achieved, on the basis on the most actual published data.

This contribution provides a rapid guide to the researchers working in this topic to select the most convenient magnetic material, prepared following the most adequate method to achieve satisfactory results in the adsorption of dyes or heavy metals from aqueous samples.

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