Review Article

Functionalization of Magnetic Nano Particles: Synthesis, Characterization and Their Application in Water Purification

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Abstract: Contamination of fresh and marine sediments and water environments by oil spills, urban runoffs, industrial and domestic effluents is demonstrating to be of critical concern as the presence of contaminants affects aquatic organisms and can quickly disperse to large as highlighted by the recent Gulf oil spill disaster. Polycyclic aromatic hydrocarbons (PAHs), Poly chlorinated biphenyls (PCBs), dichlorodiphenyltrichloroethane (DDT) and heavy metals like mercury, lead and manganese are among the ubiquitous trace contaminants of marine and freshwater systems. Presence of these contaminants raise concerns as small quantities of the organic chemicals have been displayed to be carcinogenic to mammals and can pose a prohibition to both human health and the aquatic biota. Innovative operations for treating wastewater containing heavy metals often include technologies for reduction of toxicity. Nanotechnology has rampaged plethora of scientific and technological fields; environmental safety is no exception. One of the most promising and well developed environmental applications of nanotechnology has been in water remediation and treatment where different nanomaterials can help purify water meanwhile different mechanisms including adsorption of heavy metals and other pollutants, removal and inactivation of pathogens and diversion of toxic materials into less toxic compounds. Today nanoparticles, nanomembrane and nanopowder used for revelation and removal of chemical and biological substances include metals (e.g. Cadmium, copper, lead, mercury, nickel, zinc), nutrients (e.g. Phosphate, ammonia, nitrate and nitrite), cyanide, organics, algae (e.g. cyanobacterial toxins) viruses, bacteria, parasites and antibiotics. By tracing these technological advances to the physicochemical properties of nanomaterials, the present review outlines recent development in nanotechnology for wastewater treatment. The discussion covers candidate synthesis of magnetic nanomaterials (MNPs), properties and their mechanisms in water purification.

Keywords: Magnetic Nanoparticles, Wastewater Treatment, Heavy Metals, Thermal Decomposition, Hydrothermal, Sonochemical

1. Introduction

Nanoparticles are key focus of research for a wide elongated novel applications, not only because of their splendid properties, but also due to nano size compared with their bulk counterparts. Nanoparticles are intermediate between atomic and bulk level. At nano level, the properties greatly changed, as the size of the particles changed owing to their large surface to volume ratio. Because of their wide spread applications, a lot of research has been carried out for the synthesis of 1-dimensional (1D) nano structured (nanotubes [1-4], nanorods [5-7], nanobelts [8-10], nanorings [11-14], nanohelics [15, 16], nanowires [17, 18], nanofibres [18-20], nano sphere [21-24] nano flowers [24-27] and nano sheets [28, 29] like structures. Among these nanomaterials, magnetic nanoparticles (MNPs) are of keen interest to researchers owing to their praise worthy magnetic properties. Magnetic nanoparticles (MNPs) possess a wide range of applications, including magnetic fluids recording

[30], catalysis [31, 32], biotechnology/biomedicine [33], material sciences, photocatalysis [34], electrochemical and bioeletrochemical sensing [35], microwave absorption [36], magnetic resonance imaging [MRI] [37], medical diagnosis, data storage [38], environmental remediation [39] and, as an electrode, for supercapictors and lithium ion batteries (LIB) [40-41]. While talking of, various magnetic nano particles, magnetite (Fe_3O_4) has been used for a several wide number of applications due to its superparamagnetic properties but one property of being sensitive to oxidation and agglomeration, has lemmatized its use. The solution to this problem is, to protect the magnetic nanoparticles by various types of coatings. These shells not only protect the magnetic nano particles, but, also provide a new platform for further functionalization that enhances the properties of the magnetic nano particles. Nowadays, a lot of novel binary and ternary magnetic nano composites have been synthesized with various core shell structure including grapheme [42], carbon nanotube [43, 44], conducting polymer [45], metal oxide and other inorganic materials as coating on magnetic nanoparticles [46]. Bing and co-workers have synthesized Fe_3O_4 /Polyaniline hybrid microspheres for microwave absorption [35]. They used MNPs are commonly composed of magnetic elements, such as iron, nickel, cobalt and their oxides like magnetite (Fe_3O_4), magnetite (gama- Fe_2O_3), cobalt ferrite ($FeCoO_4$), chromium dioxide (CrO_4) [47]. Magnetic nanoparticles display the phenomenon of superparamagnetism, not keeping magnetized after the action of magnetic field, offering the advantage of reducing risk of particle aggregation. First, they have sizes that place them at dimensions comparable to those of a virus (20 ± 500 nm), a protein (5 ± 500 nm) or a gene (2 nm wide and 10 ± 100 nm long) [48]. Due to the discharge of large amounts of metal-contaminated wastewater, industries bearing heavy metals, such as Cd, Cr, Cu, Ni, As, Pb, and Zn, are the most hazardous among the chemical-intensive industries. Because of their high solubility in the aquatic environments, heavy metals can be absorbed by living organisms. Once they enter the food chain, large concentrations of heavy metals may accumulate in the human body. If the metals are ingested beyond the permitted concentration, they can cause serious health disorders [49]. Moreover, heavy metals cause serious health effects, including reduced growth and development, cancer, organ damage, nervous system damage, and in extreme cases, death. Exposure to some metals, such as mercury and lead, may also cause development of autoimmunity, in which a person's immune system attacks its own cells. This can lead to joint diseases such as rheumatoid arthritis, and diseases of the kidneys, circulatory system, nervous system, and damaging of the fetal brain. At higher doses, heavy metals can cause irreversible brain damage. Children may receive higher doses of metals from food than adults, since they consume more food for their body weight than adults. Wastewater

regulations were established to minimize human and environmental exposure to hazardous chemicals. Therefore, it is necessary to treat metal contaminated wastewater prior to its discharge to the environment.

Treatment of wastewater- which is contaminated by metal ions, radionuclides, organic and inorganic compounds, pathogenic bacteria and viruses- is essential for a healthy human life. Due to extended droughts, population growth and, very recently, the more stringent health-based regulations, this rush is even intensified through increasing demands for clean water. Water purification may be among the most developed environmental applications of nanomaterials. Innovations in the development of novel technologies to desalinate water are among the most exciting and promising pursuits. Water treatment usually involves adsorption and/or photocatalysis of contaminants and their reduction by nanoparticles (NPs) and bioremediation. Remediation is the process of pollutant transformation from toxic to less toxic in water and soil as shown in Fig. 1.

Water purification may be among the most developed environmental applications of nanomaterials. Innovations in the development of novel technologies to desalinate water are among the most exciting and promising pursuits. Water treatment usually involves adsorption and/or photocatalysis of contaminants and their reduction by nanoparticles (NPs) and bioremediation. Remediation is the process of pollutant transformation from toxic to less toxic in water and soil. Water quality can be greatly enhanced using nanosorbents, nanocatalysts and bioactive NPs. Besides, nanostructured catalytic membranes and NP-enhanced filtration are interesting nanotechnology-derived products. Novel water-purification strategies such as dendrimer-enhanced ultrafiltration are always welcome; nanomaterials are very promising in this regard. For instance, nanoporous activated carbon fibers with an average pore size of 1.16 nm have been shown to absorb benzene, toluene, xylene and ethylbenzene [50]. Moreover, some nanomaterials possess intrinsic antibacterial properties [51]. One of the most interesting features of nanomaterials (most especially NPs) is that their surface area is larger than bulk materials. Functionalization of nanomaterials with numerous chemical groups may be an additional advantage which contributes to the target-specificity of these materials [52 – 53]. Classical water treatment techniques including reverse osmosis, distillation, bio-sand, coagulation-flocculation and filtration are not capable of removing all heavy metal ions. Therefore, the need is felt for more robust methods and membranes to be used in water purification. Nanomaterials can be utilized to treat inorganic polluted water, dye wastewater, papermaking wastewater, pesticide wastewater and oily wastewater. In the simplest way, sorbents remove pollutants from contaminated water and are thus widely used as separation media. Furthermore, some nanomaterials possess excellent reductive capabilities and can hence be used to render toxic

pollutants less toxic. One perfect example is zero-valent iron which has been extensively employed for in situ or aboveground chemical reduction of organic pollutants in contaminated water. The extra advantage of zero-valent iron is that upon environmental application, it does not produce intermediate by-products which are usually observed when commercial Fe powders are used [54].
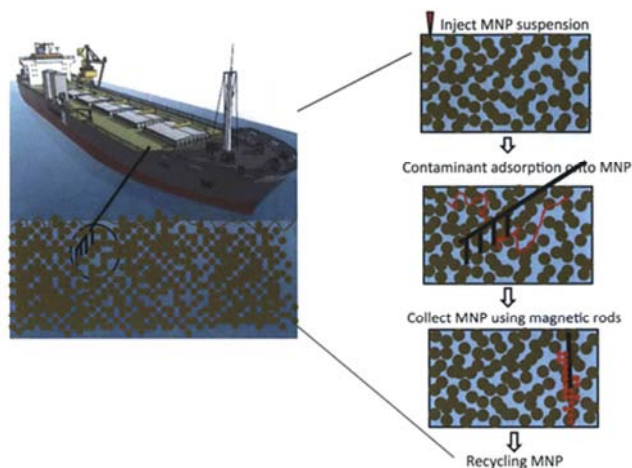

Fig. 1. *Schematic showing how to use magnetic nanoparticles (MNPs) in remediating.*

1.1. Magnetic Properties

Materials are classified by their response to an externally applied magnetic field. Descriptions of orientations of the magnetic moments in a material help to identify different forms of magnetism observed in nature. Five basic types of magnetism can be described: diamagnetism, paramagnetism, ferromagnetism, antiferromagnetism and ferrimagnetism. In the presence of an externally applied magnetic field the atomic current loops created by the orbital motion of electrons respond to oppose the applied field. All materials display this type of weak repulsion to a magnetic field known as diamagnetism. However, diamagnetism is very weak and therefore any other form of magnetic behavior that a material may possess usually overpowers the effects of the current loops. In terms of the electronic configuration of materials diamagnetism is observed in materials with filled electronic subshells where the magnetic moments are paired and overall cancel each other. Diamagnetic materials have a negative susceptibility ($\chi < 0$) and weakly repel an applied magnetic field (*e.g.*, quartz SiO). The effects of these atomic current loops are overcome if the material displays a net magnetic moment or has a long-range ordering of its magnetic moments [55]. All other types of magnetic behaviors are observed in materials that are at least partially attributed to unpaired electrons in their atomic shells, often in the 3d or 4f shells of each atom. Materials whose atomic magnetic moments are uncoupled display paramagnetism, thus paramagnetic materials have moments with no long-range order and there is a small positive magnetic susceptibility ($\chi \approx 0$);

e.g., pyrite [55]. Materials that possess ferromagnetism have aligned atomic magnetic moments of equal magnitude and their crystalline structures allows for direct coupling interactions between the moments, which may strongly enhance the flux density (e.g., Fe, Ni and Co). Furthermore, the aligned moments in ferromagnetic materials can confer a spontaneous magnetization in the absence of an applied magnetic field. Materials that retain permanent magnetization in the absence of an applied field are known as hard magnets. Materials having atomic magnetic moments of equal magnitude that are arranged in an antiparallel fashion display antiferromagnetism (e.g., troilite FeS). The exchange interaction couples the moments in such a way that they are antiparallel therefore leaving a zero net magnetization [56]. Above the Neel temperature (T_N) thermal energy is sufficient to cause the equal and oppositely aligned atomic moments to randomly fluctuate leading to a disappearance of their long range order. In this state the materials exhibits paramagnetic behavior. Ferrimagnetism is a property exhibited by materials whose atoms or ions tend to assume an ordered but non-parallel arrangement in zero applied field below a certain characteristic temperature known as the Neel temperature (e.g., Fe_3O_4) and Fe_3S_4). In the usual case, within a magnetic domain, a substantial net magnetization results from the antiparallel alignment of neighboring non-equivalent sublattices. The macroscopic behavior is similar to ferromagnetism. Above the Neel temperature, the substance becomes paramagnetic.

1.2. Superparamagnetism Phenomenon

Domains, which are groups of spins all pointing in the same direction and acting cooperatively are separated by domain walls, which have a characteristic width and energy associated with their formation and existence. The motion of domain walls is a primary means of reversing magnetization. Experimental investigation of the dependence of coercivity on particle size showed a behavior similar to that schematically illustrated in Fig. 2 [23, 57]. Size reduction in magnetic materials (multi-domain materials) resulting in the formation of single domain particles also gives rise to the phenomenon of superparamagnetism. Briefly, Superparamagnetism occurs when thermal fluctuations or an applied field can easily move the magnetic moments of the nanoparticle away from the easy axis, the preferred crystallographic axes for the magnetic moment to point along. Each particle behaves like a paramagnetic atom, but with a giant magnetic moment, as there is still a well-defined magnetic order in each nanoparticle [60, 61]. Superparamagnetic materials are intrinsically nonmagnetic but can be readily magnetized in the presence of an external magnetic field. The critical radius r_c for different particles differ based on shape, temperature and crystalline magnetoanisotropy [62, 63].
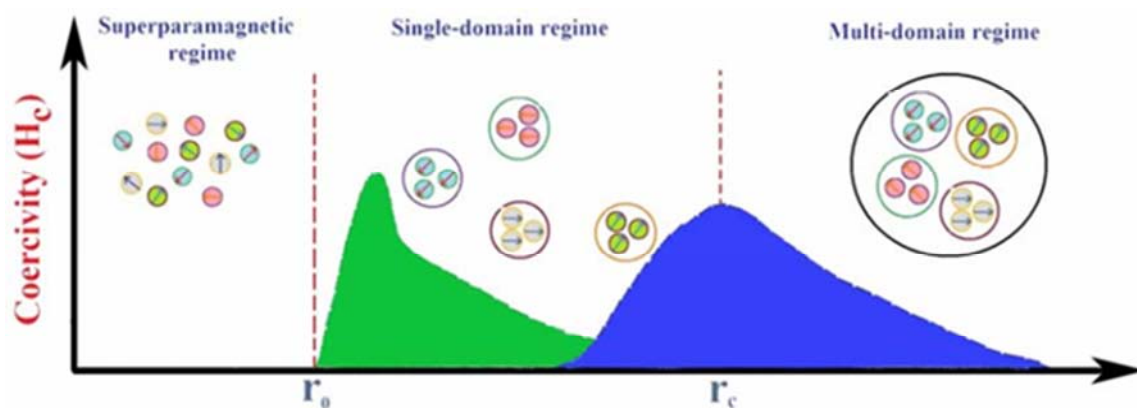
Fig. 2. *The dependence of coercivity on particle size [57].*

2. Preparation of Magnetic Nanoparticles

2.1. Preparation from Solution

Several chemical methods that are being used for the synthesis of magnetic nanostructures comprise of co-precipitation, thermal decomposition, microemulsion and hydrothermal methods. Thermal decomposition and hydrothermal approaches provide better results (both in terms of size and morphology) in comparison with other synthetic routes [64, 65]. Chemical sythesis involved the precipitation of nano particles from the solution. To achieve the monodisperse particles, the precipitation should comply with the LaMer and Dinegar model of homogeneous precipitation. According to this model, during precipitation from the solution at certain stage of super saturation, there occur a burst of nucleation that gradually grows in size by diffusion of solutes from the solution towards the nuclei until the monodisperse final size particle are obtained. The mechanism LaMer and Dinegar model is shown in Fig. 3.
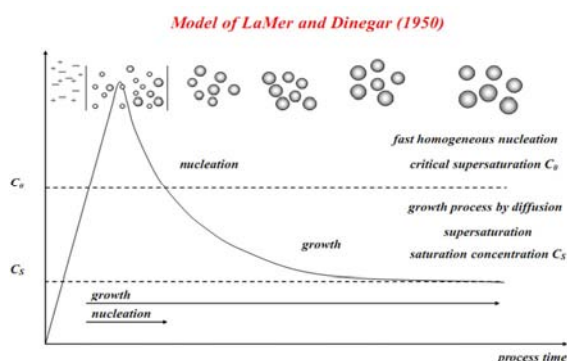

Fig. 3. *LaMer and Dinegar model of homogeneous precipitation.*

2.2. Thermal Decomposition

This method of synthesis involves the chemical decomposition of the substance at elevated temperature. During this method the breaking of the chemical bond takes place. This method of synthesis for magnetic nanostructures mostly use organometallic compounds such as acetylacetonates in organic solvents (benzyl ether, Ethylenediamine and carbonyls) with surfactants such as oleic acid, oleylamine, polyvinyl pyrrolidone (PVP), cetyltrimethyl ammonium bromide (CTAB) and hexadecylamine. In this method the composition of various precursors that are involved in the reaction determine the final size and morphology of the magnetic nanostructures. *Peng et al.* used the thermal decomposition approach for controlled synthesis (in term of size and shape) of magnetic oxide [66]. Using this methods nanocrystals with very narrow-sized distribution (4–45 nm) could be synthesized along with the excellent control of morphology (spherical particles, cubes) (cf. Figs. 4, 5).
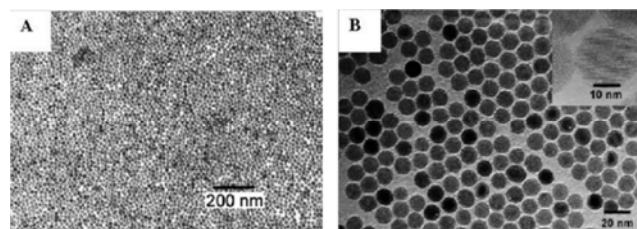

Fig. 4. *Maghemite nanoparticles prepared by thermal decomposition of Iron precursors: (a) FeCup3 (b) Fe(CO)5, where Cup: Nnitrosophenylhydroxylamine [67].*
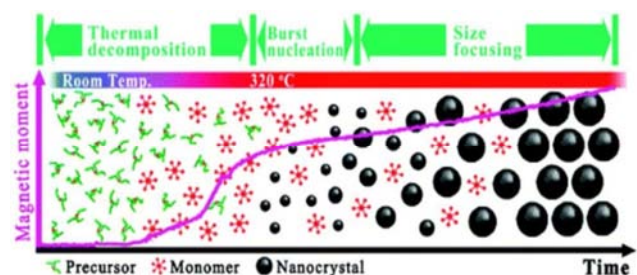

Fig. 5. *Effect of reaction temperature and reaction time on size, morphology and magnetic properties of MNPs.*

When thermal decomposition method is used, iron oxide nano particles with excellent control of size, morphology and good crystallinity have been resultantly fabricated by Alivisatos and co-workers [67]. The preparation of magnetic

nanoparticles for applications in biomedicine have fabricated maghemite nanocrystals with size of 3-9 nm by thermal decomposition of FeCup3 at 250 - 300°C. Recently, *Sun and Zeng et al.* [68] have demonstrated the fabrication of monodisperse magnetite nanoparticles with size ranges of 2-20nm by decomposition of iron (III) acetyl acetone at 260°C in the presence of benzyl ether, oleic acid and oleyl amine. In a more recent study, Nogues and co-workers have synthesized highly mono disperse cubic and spherical maghemite (Fe_2O_3) nanocrystals by using thermal decomposition method [69] as shown in Fig. 6.

The technique of thermal decomposition was not only used for synthesis of metal oxide magnetic nanocrystals but metal magnetic nanoparticles of 3d transition metals (Co, Ni, Fe) were also synthesized through introducing a reducing agent into a hot solution of metal precursor and surfactant [70]. With the precise control of temperature and the ratio of metal precursor to surfactant the magnetic nano particles with control size and shape have been synthesized.
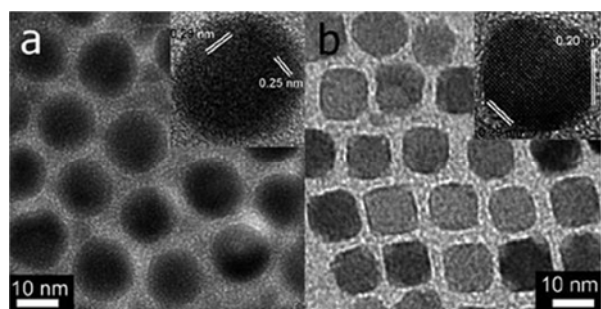

Fig. 6. *High resolution TEM images showing the mono disperse (a) nanosphere and (b) nanocubes achieved by thermal decomposition method.*

2.3. Hydrothermal Synthesis

Hydrothermal, also called solvothermal, is a syntheses method for preparation of MNPs and ultrafine powders in literature [23, 31, 71-77]. These reactions are performed in an aqueous media in reactors or autoclaves where the pressure can be higher than 2000 psi and temperatures higher than 200°C. Another important chemical synthesis technique that involves the use of liquid–solid–solution (LSS) reaction and gives excellent control over the size and shape of the magnetic nano particles is the hydrothermal synthesis. This method involves the synthesis of magnetic nano particles from high boiling point aqueous solution at high vapor pressure. It is a unique approach for the fabrication of metal, metal oxide [76, 77], rare earth transition metal magnetic nanocrystals [78], semi-conducting [79], dielectric, rare-earth fluorescent and polymeric [80]. This synthetic technique involved the fabrication of magnetic metallic nanocrystals at different reactions conditions. The reaction strategy is based upon the phase separation which occurs at the interface of solid–liquid–solution phases present in the reaction. For example the fabrication of monodisperse (6, 10 and 12 nm) Fe nanocrystals have been demonstrated by Sun *et al* and coworker [81]. *Wuwei* and co-worker have synthesized oblique and truncated nano cubes of α-Fe by one step facile hydrothermal method. This group studied the effect of volume ratio of oleylamine and acetylacetone for the fabrication of α-Fe_2O_3 with two different morphologies as shown in Fig. 7. The synthesize magnetic nano particles were used for photocatalytic degradation of organic dye and it was observed that truncated nano cubes possess much higher photocatalytic degradation activity as compared to oblique nano cubes [82].
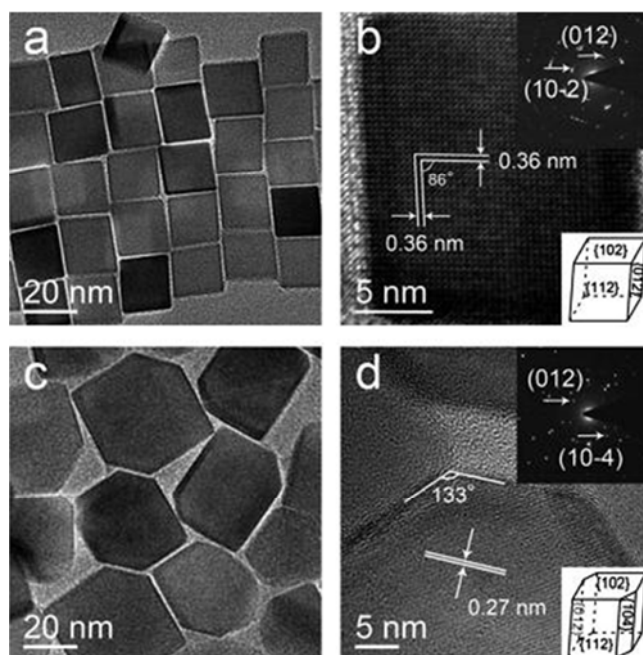

Fig. 7. *(a) TEM image of oblique nanocubes, (b) HRTEM image, FFT pattern and geometrical model of oblique nanocubes, (c) TEM image of truncated nanocubes, and (d) HRTEM image, FFT pattern and geometrical model of truncated nanocubes Reprinted from Ref [82].*

The mechanism of formation of the α-Fe$_2$O$_3$ nanoparticles with oblique and truncated morphology is given in Fig. 8. It was observed that the main cause of formation of two different morphologies is the presence of oleic acid. The presence of oleic acid led to the formation of oblique nano cubes whereas, truncated nano cubes are formed in the absence of oleic acid.
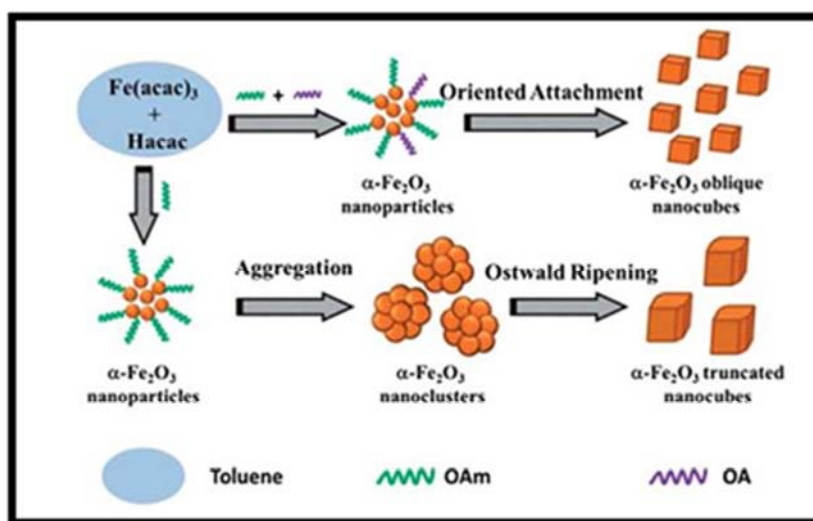

Fig. 8. *Mechanism of formation of oblique and truncated nano cubes.*

2.4. Microwave Assisted Synthesis

Microwave assisted method is a chemical method that use microwave radiation for heating materials containing electrical charges for instance polar molecule in the solvent or charge ion in the solid. As compared to the other heating methods microwave assisted solution fabrication methods have got more focus of research because of rapid processing, high reaction rate, reduce reaction time and high yield of product. Wang reported the synthesis of cubical spinal M^{II}Fe$_2$O$_4$ (M = Co, Mn, Ni) high crystalline structure in a short time of just 10 min by exposure the precursors to microwave radiation [83] shown in Fig. 9. They have also used the microwave radiations for the synthesis of magnetite (Fe$_3$O$_4$) and hematite (α Fe$_2$O$_3$).They have used FeCl$_3$, polyethylene glycol and N$_2$H$_4$.H$_2$O as precursors and found that the amount of N$_2$H$_4$.H$_2$O has a key role in controlling the final phase of Fe [84].
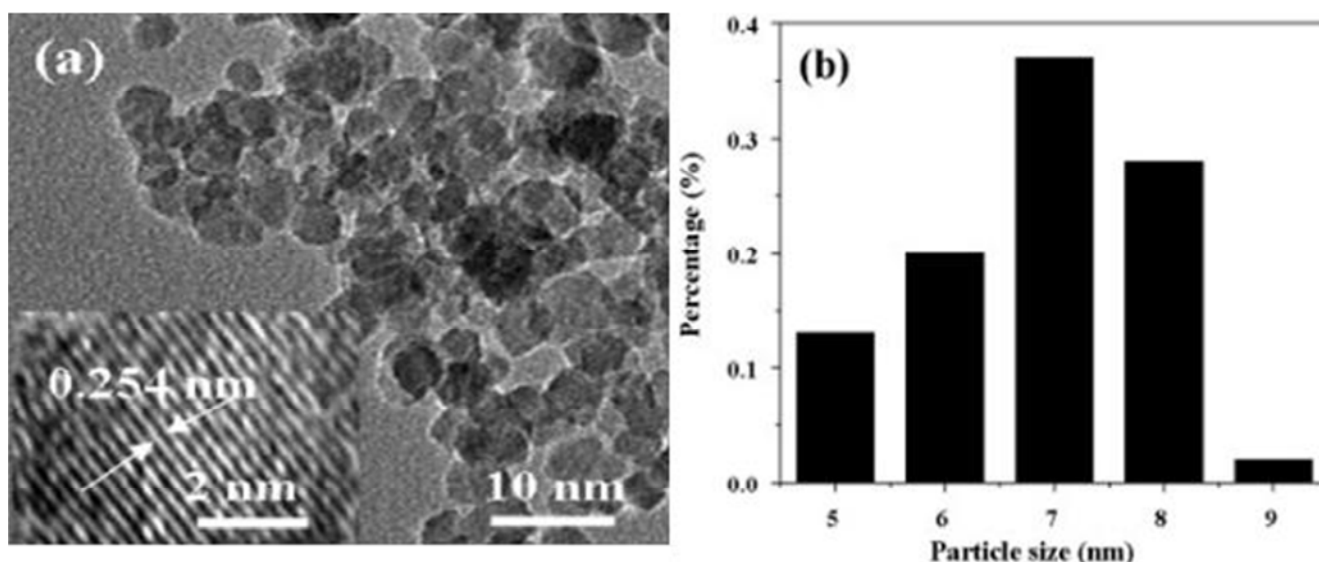

Fig. 9. *(a) TEM image of the MnFe$_2$O$_4$ and (b) the histogram showing particle size.*

2.5. Sonochemical Synthesis

As a competitive alternative to other time-consuming preparation techniques, the sonochemical method has been extensively used to generate novel materials with unusual properties. The physiochemical effects of ultrasound arise from acoustic cavitation, which comes from the formation, growth and implosive collapsing of bubbles in the liquid. The

implosive collapsing of the bubbles generate a localized hot spot through adiabatic compression or shock wave formation within the gas phase of the collapsing bubble. The conditions formed in these hotspots have been experimentally determined, with transient temperatures of 5000 K, pressures of 1800 atm and cooling rates beyond 10^{10} K s. These extreme conditions were beneficial to forming the new phase and have a shear effect for agglomeration, which is necessary to prepare the high monodispersive nanoparticles [85]. Kim *et al.* [86] synthesized Fe_3O_4 NPs by the use of sonochemical and co-precipitation methods. The crystallinity and magnetic properties of the obtained products by the use of the two methods were compared and obtained results showed that those of Fe_3O_4 NPs from the sonochemical method had a higher crystallinity and saturation magnetization than those obtained from the co-precipitation method.

3. Application of Magnetic Nanoparticles in Water Purification

Today most of the countries are facing drinking water problems and conditions are very severe especially in developing countries. The world is facing formidable challenges in meeting rising demands of clean water as the available supplies of freshwater are depleting due to (i) extended droughts, (ii) population growth, (iii) more stringent health based regulations and (iv) competing demands from a variety of users [87, 88, 89]. Clean water (i.e., water that is free of toxic chemicals and pathogens) is essential to human health. In countries such as India, 80% of the diseases are due to bacterial contamination of drinking water. The World Health Organization [90] recommended that any water intended for drinking should contain fecal and total coliform counts of 0, in any 100 mL sample. When either of these groups of bacteria is encountered in a sample, immediate investigative action should be taken. The removal or inactivation of pathogenic microorganisms is the last step in the treatment of wastewater [88]. The protection of water treatment systems against potential chemical and biological terrorist acts is also becoming a critical issue in water resources planning [89, 90] (cf. Fig. 10).

Research is underway to use advance nanotechnology in water purification for safe drinking. Nanotechnology, the deliberate manipulation of matter at size scales of less than 100 nm, holds the promise of creating new materials and devices which take advantage of unique phenomena realized at those length scales, because of their high reactivity due to the large surface to volume ratio [91]. Nanoparticles are expected to play a crucial role in water purification [92]. The environmental fate and toxicity of a material are critical issues in materials selection and design for water purification. No doubt that nanotechnology is better than other technique used in water treatment but today the knowledge about the environmental fate, transport and toxicity of nanomaterials [93] is still in infancy.
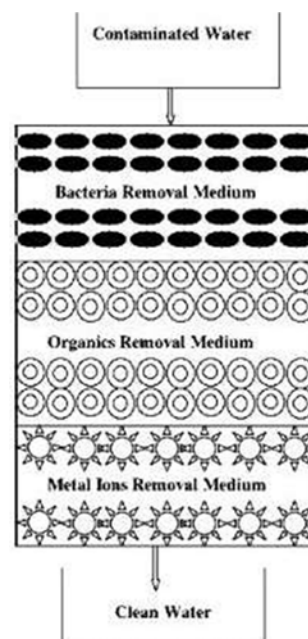

Fig. 10. *Schematic of a composite nanomaterial packed bed reactor for purification of water contaminated by mixtures of (i) metal ions, (ii) Organic solutes and (iii) bacteria.*

Advances in nanoscale science and engineering suggest that many of the current problems involving water quality could be resolved or greatly diminished by using nonabsorbent, nanocatalysts, bioactive nanoparticles, nanostructured catalytic membranes, submicron, nanopowder, nanotubes, magnetic nanoparticles, granules, flake, high surface area metal particle supramolecular assemblies with characteristic length scales of 9-10 nm including clusters, micromolecules, nanoparticles and colloids have a significant impact on water quality in natural environment [94]. Nanotechnology used for detection of pesticides [95] chemical and biological substances including metals e.g. (Cadmium, copper, lead, mercury nickel, zinc), Nutrients (e.g. Phosphate, ammonia, nitrate, nitrite), Cyanide Organics, Algae (e.g. Cyanobacterial toxins) Viruses, Bacteria, Parasites, antibiotics and Biological agents are used for terrorism. Innovations in the development of novel technologies to desalinate water are among the most exciting and seem to have promise [96]. Opportunities and challenges of using nanomaterials in the purification of surface water, groundwater and industrial wastewater streams is a matter of continuing concern. Misconceptions and One of the many impressions that people have about the future of nanotechnology is the expectation that nanoparticles can be used to kill harmful organisms, repair body tissue, in water quality improvement and to cure disease.

Recent applications of nanoparticulate silver have included open wound and burn treatment and preliminary studies have shown that a 20 ppm silver colloidal suspension (~30 nm diameter) in purified water has a 100% cure rate for malaria [97]. Titanium dioxide, especially as nanoparticulate anatase, is also an interesting antibacterial, with notable photocatalytic behavior. But ultrafine anatase has also been identified as cytotoxic and *in-vivo* studies have shown that it

can be severely toxic in the respiratory system [98, 99].

Nanocapsules and nanodevices may present new possibilities for drug delivery, gene therapy, medical diagnostics, antimicrobial activity etc. The effect of particle size on the adsorption of dissolved heavy metals to iron oxide and titanium dioxide nanoparticles is a matter laboratory-scale experiments. Iron oxide and titanium dioxide are good sorbents for metal contaminants. Spherical aggregates of nanoparticles that have a similar size and shape to the resin beads already used in water purification. ligands, fulvic acids, humic acids and their aggregates have a significant impact on contaminant mobility, reactivity and bioavailability. Nanoparticles can also be designed and synthesized to act as either separation or reaction media for pollutants. The high surface area to mass ratios of nanoparticles can greatly enhance the adsorption capacities of sorbent materials. Nanotechnology is a deliberate manipulation of matter at size scales of less than 100 nm holds the promise of creating new materials and devices which take advantage of unique phenomena realized at those length scales. In addition to having high specific surface areas, nanoparticles also have unique adsorption properties due to different distributions of reactive surface sites and disordered surface regions. Their extremely small feature size is of the same scale as the critical size for physical phenomena for example, the radius of the tip of a crack a material may be in the range 1-100 nm. The way a crack grows in a larger-scale, bulk material is likely to be different from crack propagation in a nanomaterial where crack and particle size are comparable.

Fundamental electronic, magnetic, optical, chemical and biological processes are also different at this level.

In the present section we will describe recent literature results related to the application of magnetite nanomaterials for the removal of heavy metals from water.

Yantasee et al. [100] prepared superparamagnetic iron oxide (Fe_3O_4) nanoparticles with a surface functionalization of dimercaptosuccinic acid (DMSA) and employed them as an effective sorbent material for toxic soft metals such as Hg(II), Ag(I), Pb(II), Cd(II), and Tl(I) ions which effectively bind to the DMSA ligands and for As(III) which binds to the iron oxide lattices. The nanoparticles could be separated from solution within a minute with a 1.2 T magnet. The authors compared the chemical affinity, capacity, kinetics, and stability of the magnetic nanoparticles to those of conventional resin based sorbents (GT-73), activated carbon, and nanoporous silica (SAMMS) of similar surface chemistries in river water, ground‐water, seawater, and human blood and plasma. DMSA Fe_{3O4} showed a capacity of 227 mg of Hg/g, a 30-fold larger value than that of GT-73.

Liu [101] developed humic acid (HA) coated Fe_3O_4 for removal of toxic Hg(II), Pb (II), Cu(II) from water. Fe_3O_4/ HA were prepared by co-precipitation procedure with cheap and environmentally friendly iron salts and HA. TOC and XPS analysis showed the as-prepared Fe3O4/ HA contains ~11% (w/w) of HA which are fractions abundant in O and N-based functional groups. TEM images and laser particle size analysis revealed the Fe_3O_4/HA (with ~10 nm Fe cores)

aggregated in aqueous suspensions to form aggregates with an average hydrodynamic size of ~140 nm (cf. Fig. 11). With a saturation magnetization of 79.6 emu/g, the Fe_3O_4/HA can be simply recovered from water with magnetic separations at low magnetic field gradients within a few Sorption of the heavy metals to Fe_3O_4/HA reached equilibrium in less than 15 min, and agreed well to the Langmuir adsorption model with maximum adsorption capacities from 46.3 to 97.7 mg/g. The Fe_3O_4/HA was stable in tap water, natural waters, and acidic/ basic solutions ranging from 0.1 M HCl to 2 M NaOH with low leaching of Fe (e3.7%) and HA (e5.3%). The Fe_3O_4/ HA was able to remove over 99% of Hg(II) and Pb(II) and over 95% of Cu(II) and Cd(II) in natural and tap water at optimized pH. Leaching back of the Fe_3O_4/HA sorbed heavy metals in water was found to be negligible (cf. Fig. 12).
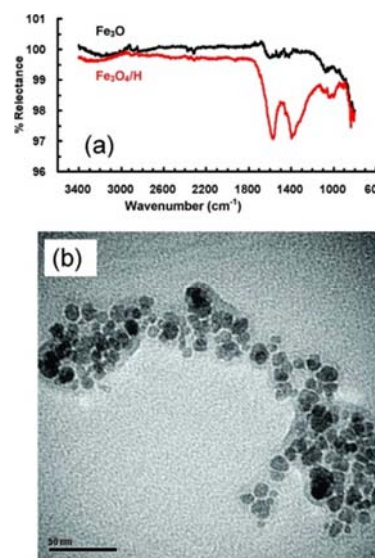

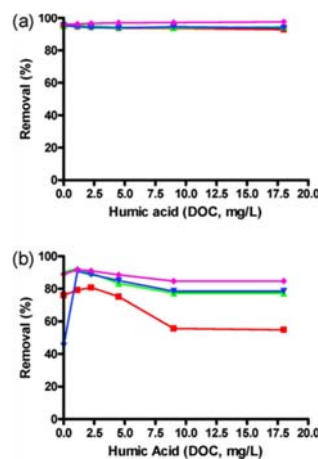**Fig. 11.** *IR Spectrum (a) and TEM Image (b) of the prepared Fe_3O_4/HA magnetic nanoparticle.s.*

Fig. 12. *Influence of humic acid in aqueous solutions on the removal of heavy metals by the as-prepared Fe_3O_4/ HA (a) and Fe_3O_4 (b). To 100 mL of aqueous solution containing 0.1 mg/L Hg(II), Pb(II), Cd(II), and Cu(II) (pH 6.0) was added 10 mg of Fe_3O_4//HA or Fe_3O_4.*

Wu et al. [102] showed that Fe_3O_4 can be used to disperse nano-Fe^0 and thus sustain Cr(VI) mitigation by nano-Fe^0. Fe^0 nanoparticles can attach to the surface of Fe by addition of large

Fe_3O_4-NPs into the reaction solution during the preparation of Fe^0 nanoparticles. The introduction of Fe_3O_4 prevents the aggregation of Fe^0 nanoparticles and keeps the high efficiency of the nanocomposite for Cr(VI) reduction. Their results suggest that higher proportions of Fe_3O_4 in the nanocomposite could increase the rate of Cr(VI) reduction, and the optimal ratio of Fe_3O_4:Fe^0 for Cr(VI) reduction was determined to be 40:1. The authors also showed that solution pHs significantly affect the rate of Cr(VI) reduction, with reactions occurring faster under acidic or neutral than basic conditions.

Yuwei [103] prepared magnetic chitosan nanoparticles by a simple one-step in situ co-precipitation method and characterized by means of X-ray diffraction (XRD), transmission electron microscope (TEM), Fourier Transform infrared spectroscopy (FTIR), vibrating sample magnetometer (VSM) and energy dispersive X-ray spectrometer (EDS) (cf. Figs. 13, 14). The sorption performance of the nanoparticles for removing Cu(II) from aqueous solution was investigated. The experimental results showed that the particles were super-paramagnetic, with the saturation magnetization of about 36 emu/g and the size was in the range of 8–40 nm. The EDS images confirmed the presence of Cu(II) on the surface of magnetic chitosan nanoparticles. The maximum sorption capacity was calculated to be 35.5 mg/g using the Langmuir isotherm model (cf. Fig. 15). The mechanism of Cu(II) sorption onto the magnetic chitosan nanoparticles was tentatively proposed.
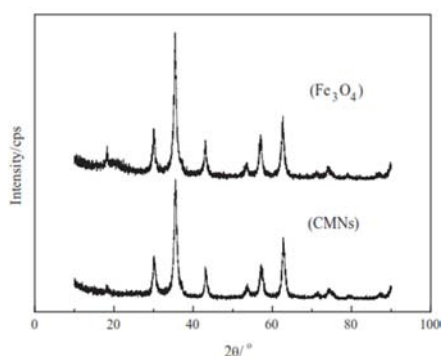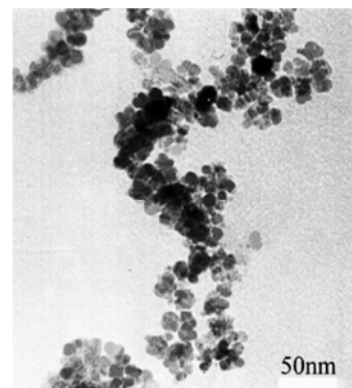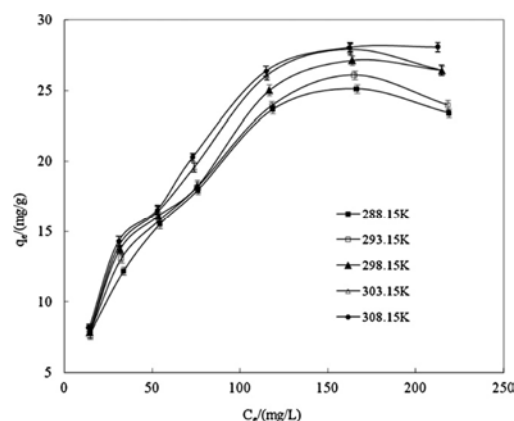

Fig. 14. TEM images of magnetic chitosan nanoparticles.

Fig. 15. Equilibrium adsorption isotherms for Cu(II)-magnetic nanoparticles system at different temperatures.

Fig. 13. XRD pattern of Fe_3O_4 and magnetic chitosan nanoparticles.

Ge [104] prepared and characterized novel Fe_3O_4 magnetic nanoparticles (MNPs) modified with 3-aminopropyltriethoxysilane (APS) and copolymers of acrylic acid (AA) and crotonic acid (CA). MNPs were characterized by transmission electron microscopy (cf. Fig. 16), X-ray diffraction, infra-red spectra and thermogravimetric analysis. The MNPs could efficiently remove the ions metal with high maximum adsorption capacity at pH above 5.5. The probable adsorption mechanism metal ions mainly interacted with the adsorbents by chelation between the ions and the carboxylate anion (cf. Fig. 17, 18).
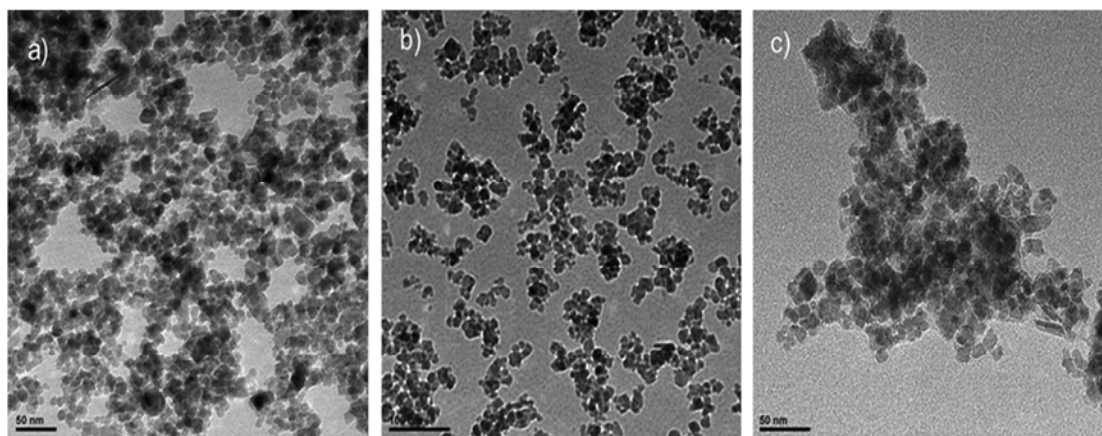

Fig. 16. Transmission electron microscope of magnetic nanoparticles (a) Fe_3O_4 (b) Fe_3O_4@APS, and (c) Fe_3O_4@APS@AA-co-CA.
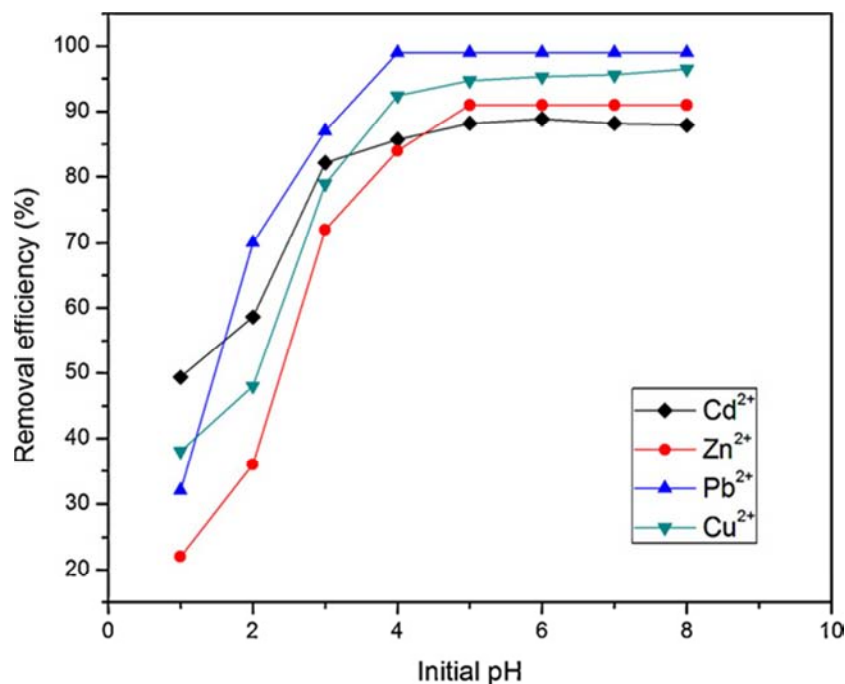
Fig. 17. *Effect of pH on the adsorption of metal ions; adsorbent: 0.05 g, concentration. of initial metal ions: 100 mg l−1, volume of metal ions solution: 50 ml, time: 2 h, at. 298 K.*
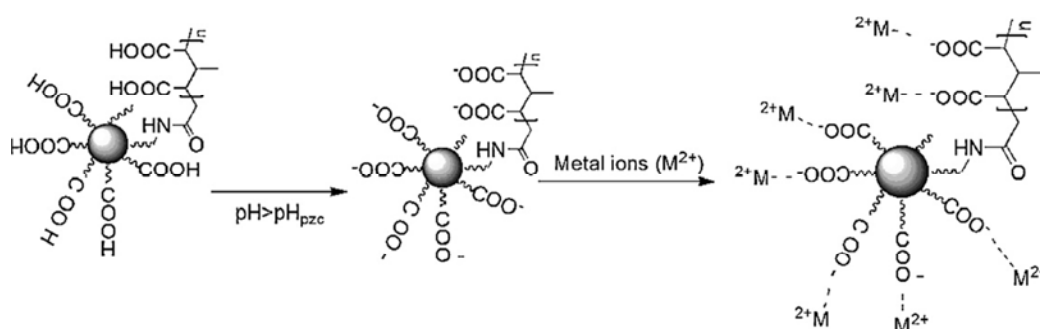

Fig. 18. *Schematic representations of possible mechanism for adsorption of metal ions by Fe₃O₄ @APS@AA-co-CA.*

Mahmoud [105] used combined sorption characteristics of a novel composite based on three sorbent–biosorbent systems. This was accomplished by surface modification of activated carbon with nano-Fe_3O_4 and loaded with baker's yeast (cf. Fig. 19). The sorbent–biosorbent materials were characterized by using SEM imaging (cf. Fig. 20) and FT-IR analysis. The magnetic solid phase extraction (MSPE) of Hg(II) from aqueous solutions was studied by measuring the metal sorption capacity and the maximum values were identified in the range of 250–800 µmol g^{-1}. The potential applications in removal of Hg(II) from different real matrices including water samples and saving lamb waste materials were also explored. The results of this study refer to the excellent percentage extraction values of mercury (II) (92.0±1.0–100.0 ±3.0%).
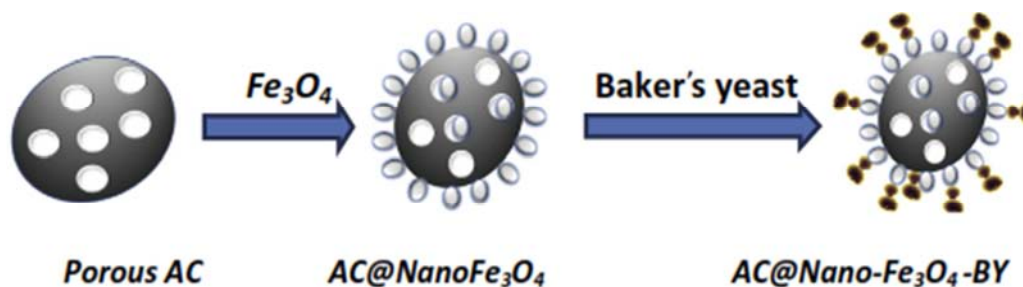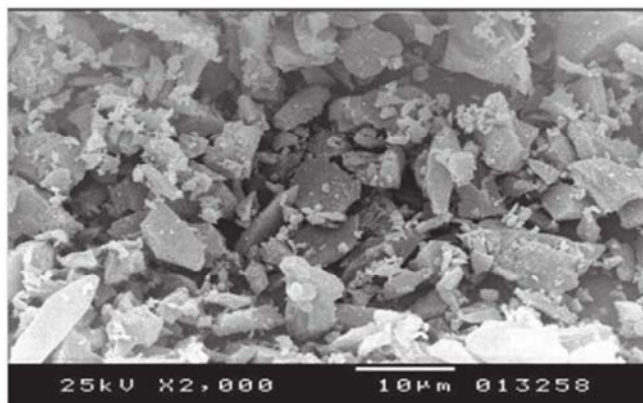

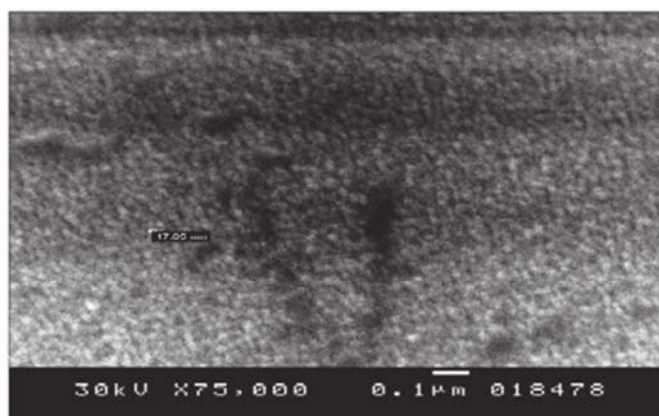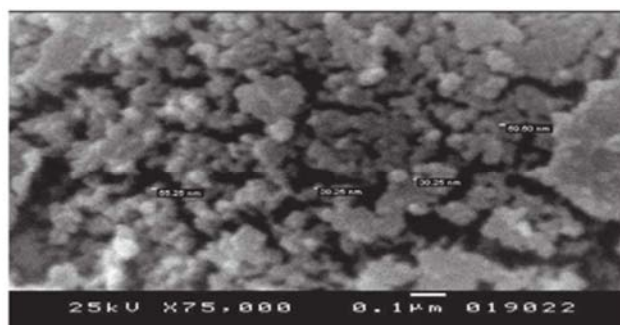**Fig. 19.** *Schematic diagram of various sorbents.*

(a) SEM image of AC

(b) SEM image of nano-Fe_3O_4

c) SEM image of AC@nano-Fe_3O_4

(d) SEM image of AC@nano- Fe_3O_4-

***Fig. 20.** SEM-images of sorbent–biosorbent systems(a-c).*

Aftabtalab [106] synthesized magnetite (Fe_3O_4) nanoparticles by sol-gel method for removing Cr(VI) from waste water. The synthesized magnetite nanoparticles were confirmed with X-ray diffraction, scanning electron microscopy, energy –dispersive analysis by X-ray spectrometer and vibrating sample magnetometer. The EDS results revealed synthetic magnetite nanoparticles have purity (cf. Fig. 21). The synthetic process is cost effective and eco-friendly because it is inexpensive and less toxic iron salt. Magnetite nanoparticles demonstrated high surface area to volume ratio which is associated to their ability for surface chemical modification. The results obtain from adsorption isotherms confirm magnetite nanoparticles have efficiency and high capacity for Cr(VI) and other pollution treatment from wastewater (cf. Fig. 22). The results obtain from adsorption isotherms shown magnetite nanoparticle have efficiency and high capacity for removal of hexavalent chromium at pH 8.2.
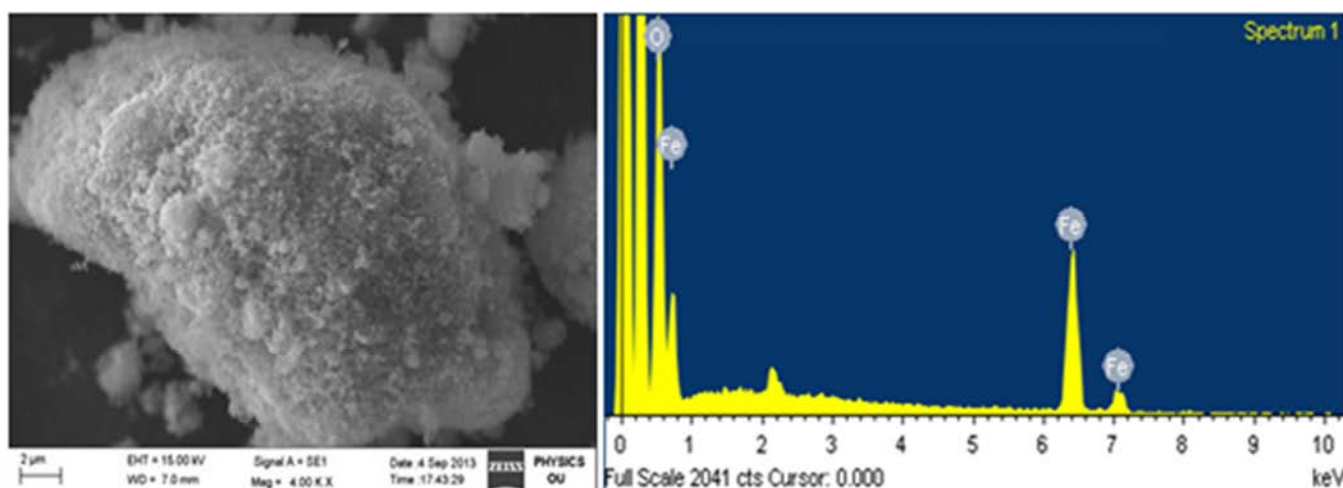

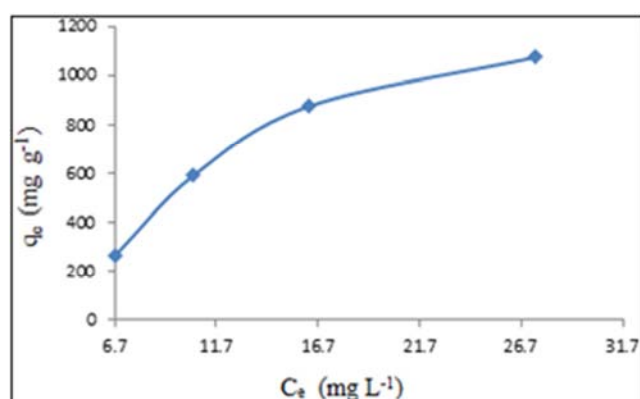**Fig. 21.** *SEM and EDS images of magnetite nanoparticles at 250°C.*

Fig. 22. *Plot of q_e vs. C_e for adsorption of Cr(VI) on to Fe_3O_4 nanoparticles at pH 8.2, 0.01 g Fe_3O_4.*

Xu et al. *[107]* introduced poly-allylamine-hydrochloride (PAAH) stabilization, magnetic nanoparticles (MNPs) to remove pathogenic bacteria by electrostatic interaction and magnet capture. High removal efficiency was achieved for four main pathogenic species, as *Escherichia*, *Acinetobacter*, *Pseudomonas* and *Bacillus*, and over 99.5% of the pathogens can be removed when the bacterial count was less than 105 CFU/mL. Related to various species, the MNPs have respective adhesion effects on bacterial cells, which are higher for *Acinetobacter* and *Pseudomonas*, due to the mechanisms of external cell structure and ion exchange capacity, but not the zeta potential of bacterial cell surface. With the practical application in real drinking water samples collected from reservoirs in Sheffield and Leeds, the results showed high bacteria removal efficiency (99.48%) and the total bacteria residual counts was as low as 78 CFU/mL, which met the drinking water standard of WHO (<100 CFU/mL). Further toxicity test indicated that no significant genotoxicity or cytoxicity existed in MNPs treated water, suggesting MNPs are biocompatible for safety issues in drinking water (cf. Fig. 23). As an effective, easy-operation and low cost technique, MNPs have bright future and great potential in practical drinking water treatment to remove pathogenic bacteria.
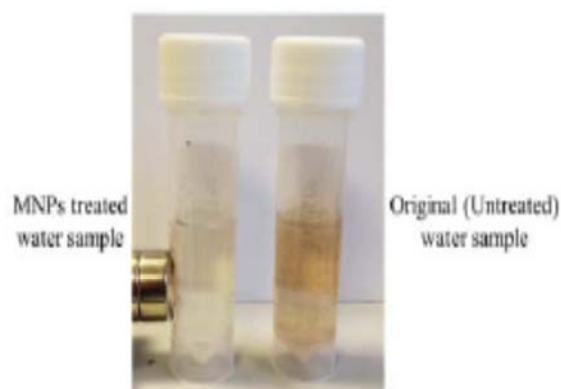

Fig. 23. *MNPs treated water sample before/after magnetic capture.*

Finally, we can show in the following table a comparison between some of different magnetic nanomaterials for water purification.

Table 1. *A comparison between using of different magnetic nanomaterials for water purification.*

No	Type of nanomaterials	Capacity	Purpose	Ref.
1	Fe_3O_4 + dimercaptosuccinic acid (as sorbent)	227 mg/g	Removal of toxic Hg(II), Ag(I), Pb(II), Cd(II), and Tl(I) metals	100
2	Fe_3O_4 + humic acid	46.3 to 97.7 mg/g	removal of toxic Hg(II), Pb(II), Cu	101
3	Fe_3O_4: Fe^0 nanoparticles		Cr(VI) reduction	102
4	Chitosan	35.5 mg/g	Removal of Cu(II) from aqueous solution	103
5	Fe_3O_4 + 3-aminopropyltriethoxysilane (APS) + copolymers of acrylic acid + crotonic acid	32.0 mg/g for Cd(II). 39.4 for Zn(II) 76.8 for Pb(II). 62.1 for Cu(II)	Removal of Cd(II), Zn(II), Pb(II), Cu(II)	104
6	Fe_3O_4 loaded with baker's yeast	250–800 $\mu mol\ g^{-1}$.	Removal of Hg(II) from different real matrices including water samples and saving lamb waste materials	105
7	Fe_3O_4	20-80 mgl^{-1}	Removal of Cr(VI) from waste water	106
8	poly-allylamine-hydrochloride	105 CFU/ml	Removal of pathogenic bacteria	107

Summary and Outlook

Clean water is essential to human health as it is including in pharmaceuticals and food. The world is facing formidable challenges in meeting rising demands of clean water as the available supplies of freshwater are decreasing due to (i) extended droughts, (ii) population growth, (iii) more stringent health-based regulations, and (iv) competing demands from a variety of users. Nanomaterials especially magnetic nanoparticles have a number of key physicochemical properties that make them particularly attractive as separation media for water purification. On a mass basis, they have much large surface areas than bulk particles. Moreover, magnetic nanoparticles can be functionalized with various chemical groups to increase their affinity toward a given compound. They can also serve as high capacity/ selectivity and recyclable ligands for toxic metal ions, radionuclides, organic and inorganic solutes/ anions in aqueous solutions. Magnetic nanoparticles also provide unprecedented opportunities to develop more efficient water-purification catalysts and redox active media due their large surface areas and their size and shape-dependent optical, electronic and catalytic properties. We envision that magnetic nanoparticles will become critical components of industrial and public water purification systems as more progress is made toward the synthesis of cost-effective and environmentally acceptable functional materials

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