Iron Oxide Nanoparticles: Synthesis, Characterization and Applications

Rajkumar S. Sirsam*
UICT, NMU, Jalgaon
rajkumarsirsam@gmail.com

Sukanya Prakash Gadekar
UICT, NMU, Jalgaon
sukanyaprakash511@gmail.com

***Abstract*:- Iron oxide is a mineral compound which occurs in different forms like hematite, magnetite and maghemite. Fe-based nanoparticles act as new generation environmental remediation technologies, and provide cost-effective solutions to the most demanding environmental cleanup problems. The synthesis of magnetic iron oxide nanoparticles (IONPs) has been intensively developed not only for its fundamental scientific interest but also for its many technological applications, such as targeted drug delivery, magnetic resonance imaging (MRI), gas sensing, photocatalytic degradation of organic pollutant, etc. In this review, different methods like sol-gel, co-precipitation, micro-emulsion, thermal decomposition to prepare iron oxide nanoparticles have been described. Characterization of iron oxide nanoparticles is done by scanning electron microscopy(SEM), Transmission electron microscopy(TEM), X-ray powder diffraction(XRD), and Fourier transform infrared spectroscopy(FT-IR). Also various applications of iron oxide have been detailed in this article.**

***Keywords*:-** Iron Oxide Nanoparticles, Photodegradation, Co-precipitation, Magnetite, Gas sensing.

I. Introduction

Iron oxide is found in nature in different form. It exists in more than one crystal structure and each structure possess different structural and magnetic properties [1]. Chemistry, Physics, Materials Science, Chemical Engineering, Environmental Engineering and other related disciplines are majorly affected by iron oxide nanoparticles. Iron oxide Nanoparticles possess different electrical, optical and magnetic properties than their bulk counterparts [2]. Iron oxides like hematite (α-Fe_2O_3), magnetite (Fe_3O_4) and maghemite (γ-Fe_2O_3) are best suitable for nanoparticle synthesis due to their polymorphism property. These three iron oxides has unique biochemical, magnetic, catalytic, and other properties [3]. Hematite (α-Fe_2O_3), has the corundum structure, while magnetite (Fe_3O_4) and maghemite (γ-Fe_2O_3) have the cubic structure. Iron oxides has been studied extensively throughout the world in the last decade because it has applications in different fields like catalysts, gas sensors, high density magnetic recording media, printing ink, magnetic resonance imaging etc. Photocatalytic processes have potential application in conversion of solar energy into chemical energy and removal of heavy metals from waste water [4].

Magnetic iron oxide nanoparticles are have various advantages like they are physically and chemically stable, cheap to produce, , biocompatible, and environmentally safe [5].

Different types of Iron oxides are as follows:

1. Magnetite; Magnetite contains divalent and trivalent Fe ions. Its chemical formula is Fe_3O_4 or FeO·$Fe_2O_3$and has Black or grayish black colour. It has tetrahedral magnetic sub lattice and an octahedral sub lattice and has antiparallel. Magnetite is sensitive to oxidation as oxygen transforms magnetite to maghemite by oxidizing of Fe^{2+} ions [6].
2. Maghemite; Maghemite is formed by oxidation of magnetite. It Contains only trivalent Fe ions and has chemical formula γ-Fe_2O_3. Its a Brown color mineral. Maghemite is ferrimagnetic, too [6].
3. Hematite; Hematite is used as a starting material for the synthesis of magnetite (Fe_3O_4) and maghemite (γ-Fe_2O_3),

Hematite (α-Fe_2O_3) is widely used in catalysts, pigments and gas sensors due to its low cost and high resistance to corrosion.

II. Methods Of Synthesis

Iron oxide nanoparticles can be synthesized by following methods:

1. Physical Methods: Physical methods include gas-phase deposition, electron beam lithography, laser induced milling, powder ball milling, aerosol or vapour method such as spray & laser pyrolysis.
2. Biological Methods: Biological methods include Fungi mediated, bacteria mediated, protein mediated, algae mediated.
3. Chemical Method: Chemical methods include co-precipitation, micro emulsion, hydrothermal, thermal decomposition, electro-chemical deposition, sol-gel etc.

Every method gives nanoparticles of different properties like shape, average size, size distribution, crystallinity, magnetic properties, dispersibility, etc. The major factor to be looked upon during synthesis is controlling the nanoparticles characteristics, such as crystallinity, size and shape, polydispersity, porosity and morphology. The structural properties of iron oxide nanoparicles are greatly influenced by reaction parameters and this in turn have a critical influence on electrical, mechanical, optical and magnetic properties and thus determine its behaviour [1].

A. Co-precipitation:

Co-precipitation is the most conventional method for obtaining Fe_3O_4 or γ-Fe_2O_3. This method consists of mixing ferric and ferrous ions in a 1:2 molar ratio in highly basic solutions at room temperature or at elevated temperature [7]. The type of salts used (e.g. chlorides, sulfates, nitrates), the Fe^{2+}/Fe^{3+} ratio, the reaction temperature, the pH value and ionic strength of the media determines the size, shape, and composition of the magnetic nanoparticles. Spherical magnetite particles from 3 to 100nm can be obtained by this method. Magnetite particles can be subjected to deliberate oxidation to convert them into maghemite [8]. Hence, the synthesis of magnetite nanoparticles is done in anaerobic conditions to avoid the possible oxidation in air. The surfaces of so-produced iron oxide nanoparticles are rich in hydroxyl group [9].

B. Sol-gel:

Sol-gel synthesis method involve hydrolysis and condensation of metal alkoxides or alkoxide precursors. The result is dispersions of oxide particles in “sol”, which is then dried or gelled by removing the solvent or by chemical reaction [1]. Magnetic iron oxide nanoparticles possess high surface energies due to their large surface-to-volume ratio. Thus they tend to agglomerate and form clusters resulting in increased particle size. Inorder to prevent agglomeration the modification of surface nanoparticles is done by coating them with organic molecules, polymers, biomolecules or inorganic molecules, such as silica.

The solvent used in sol gel process is generally water. Basic catalysis enhances the formation of a colloidal gel, whereas acid catalysis gives a polymeric form of the gel [10]. Parameters that affect the structures and size of iron oxide nanoparticles are reaction rates, temperature, nature of precursors and pH.

C. Microemulsion:

Water-in-oil (w/o) microemulsion is prepared and this emulsion consists of nano sized water droplets dispersed in an oil phase. Emulsion is stabilized by surfactant molecules at the water/oil interface. The main advantage of the reverse micelle or emulsion technology is the diversity of nanoparticles that can be obtained. This variartion can be done by varying parameters like the nature and amount of surfactant and co-surfactant, the oil phase, or the reacting conditions [11-15]. Microemulsion and inverse micelles route can be employed for obtaining the shape- and size-controlled iron oxide nanoparticles.

Chin and Yaacob reported the synthesis of magnetic iron oxide NPs (less than 10 nm) via w/o microemulsion and compared it to the particles produced by Massart’s procedure [16].He found that particles produced by microemulsion technique were smaller in size and were higher in saturation magnetization [17].

D. Thermal Decomposition:

There is limited control over nucleation and growth by co-precipitation route. Thus, alternate synthesis method is needed to prepare high quality Fe3O4 nanoparticles [18].

The iron oxide nanoparticles produced by thermal decomposition method are usually well-controlled in size and shape. Nanoparticles are also well crystallized with a high saturation moment due to the high temperature [9].

The first report using thermal decomposition of iron oxide nanoparicle was made by Sun et al. in 2002 [19]. The method involved the thermal decomposition of iron oxide nanoparicle in the presence of surfactants, oleylamine and oleic acid.

Hyeon and co-workers [20] have also used a similar thermal decomposition approach for the preparation of monodisperse iron oxide nanoparticles.

Depending on the decomposition temperature and aging period particle sizes from 5–22 nm is obtained. Although the thermal decomposition method has many advantages for producing highly monodispersed particles with a narrow size distribution, it also has the big disadvantage that the resulting nanoparicless are generally only dissolved in nonpolar solvents.

III. Characterization Of IONPs

The most important part of experiments is characterization – it gives an opportunity to analyse results of experiments and to choose the next step to achieve expected results. Different parameters need different characterization techniques, an efficiency of analysis strongly depends on how suitable was the chosen characterization technique for certain parameter.

A. Scanning Electron Microscopy:

SEM is a type of versatile electron microscope that, due to its several characteristics, is commonly used to investigate the surface structure (polished or rough) or subsurface sample with relatively large dimensions. SEM image has a large depth of field and high resolution, which is easy to interpret and it provides a 3-D image As a result of the electron beam interaction with the sample surface, a series of radiation are emitted: (i) secondary electrons, which are emitted from the sample atoms with low energy (typically 50 eV or less); (ii) backscattered electrons (the reflection of images with topography contrast); (iii) X-ray detectors (used for chemical analysis). The radiation characteristics provide sample information such as topography of the surface, composition and crystallography [1].

B. Transmission Electron Microscopy:

TEM is a powerful tool in exploring a shape, crystallinity, mean size and size distribution of nanoparticles [6]. Nanoparticles were investigated with a JEOL 2100 FEG-TEM using 200 kV electron acceleration voltage, When electron gun emitted accelerated electrons collide with sample, two groups of interactions take place : elastic (electron is reflected with the same energy as before an interaction) and in elastic (initial energy is decreased – transmitted electrons, Auger electrons, secondary electrons, X-ray, etc). High energy of electrons provides low diffraction effect so resolution is high enough to explore crystallinity of nanoparticles. TEM detects the differences between initial and final energies of electrons transmitted through an ultrathin sample and constructs the image of the relief according to the density differencies. Nanoparticles sizes were measured (at least 50 measurements from different areas per 1 sample) and mean size with size distribution were calculated using the statistical software.

C. X-ray Diffraction:

XRD is a common characterization technique for metal nanoparticles, from which we can obtain the material composition, structure (three-dimensional coordinates of atoms, chemical bonding, molecular conformation and the electron density value, etc.) and the molecular interactions data from XRD analysis [21]. X-ray diffraction can be performed to obtain the crystalline structure of particles (angle position, width and intensity). The main details of crystallographic structures of iron oxides (hematite, magnetite, and maghemite) were established in 1915 by Bragg and Nishikawa. From the crystallographic structures, the crystallographic descriptions were established, such as orthorhombic, hexagonal, cubic, octahedral, tetrahedral, and the atomic coordinates of polymorphous iron oxides.

The average size of the synthesize were determined using Scherrer equation. The result of the calculation average grain size in nanometer. The breadth of the peak obtained by X-ray diffraction depends on the apparatus and crystallite size. For very small particle size (below 100nm) broadening from the apparatus is negligible and scherrer's formula permits calculation of the crystal size **$D= (K\ \lambda)/ (\beta \cos\theta)$**

Where:

D is the mean size of the ordered (crystalline) domains, which may be smaller or equal to the grain size;

K is a dimensionless **shape factor**, with a value close to unity. The shape factor has a typical value of about 0.9, but varies with the actual shape of the crystallite;

λ is the X-ray wavelength;

β is the line broadening at half the maximum intensity (FWHM), after subtracting the instrumental line broadening, in radians. This quantity is also sometimes denoted as $\Delta(2\theta)$;

θ is the Bragg angle (in degrees).

D. Fourier Transform Infrared (FTIR) spectrometry:

Fourier Transform Infrared (FTIR) spectrometry is a complex method of spectroscopy with the ability to identify materials and determine the quality of a sample. This method identifies materials by the "fingerprints" of molecules, as each FTIR spectrum is unique to the measured molecule [22]. Fourier transform infrared spectroscopy (FT-IR) has been used as a technique for the investigation of the characteristic functional groups of iron oxides and characterization of precursors from different synthesis methods. Hematite in its crystalline form contains no structural OH groups of water in 3400 cm–1, which is a characteristic of aqueous methods or characteristic of FT-IR technique, as a function of absorbed humidity (commonly based on potassium bromide – KBr) during the preparation of pellets FT-IR spectrum characteristics of maghemite showed peaks at 3740 and 3725 cm–1; both peaks can be attributed to singly coordinated OH and two strong bands at 3675 and 2640 cm–1, while magnetite (Fe_3O_4) shows spectrum broad peaks at 580 and 400 cm-1. The incoming infrared beam from a laser source passes through the beam splitter and changes into two separate identical beams. One beam reflects off a fixed mirror where the second beam reflects off a mirror that moves a few millimeters over time. The reflected beams rejoin at the beam splitter. The moving mirror allows continuous change of the reflecting beam such that it interferes with the other. This allows for the unique property in which the resulting beam contains every infrared frequency originating from the source [23]. The resulting beam then passes through the sample and is absorbed at different frequencies that correlate to the bonds within the molecule and the bonds' bending and stretching frequencies [22]. Since the plot involves measurements of absorbance at each frequency it is difficult to directly decode. Therefore a Fourier transform is performed manipulating the data such that it can easily be read and compared to other spectra for determination [23].

IV. Applications

A. As Gas Sensing Material:

The gas sensitivity (S) is defined as the ratio of the stationary electrical resistance of the sensor in air (R_{air}) to its resistance in the test gas (R_{gas}), that is, S) R_{air} / R_{gas} [32]. A number of studies have also been focused on iron oxide (Fe_2O_3), which, especially in the gamma, cubic phase, exhibits good sensing characteristics towards hydrocarbon gases, carbon monoxide and alcohol [24].

Fe2O3 is an n-type semiconductor, with the free carriers originating from oxygen vacancies. In the ambient environment, Fe2O3 nanocrystals are expected to adsorb both oxygen and moisture, in which moisture may be adsorbed as hydroxyl groups. The adsorbed O2- and OH- groups trap electrons from the conduction band of the Fe2O3 nanocrystals, inducing the formation of a depletion layer on the surface of the Fe2O3 nanocrystals. When exposed to test gases such as ethanol and acetic acid, gas molecules are chemi-adsorbed at the active sites on the surface of the Fe2O3 nanocrystals. These molecules will be oxidized by the adsorbed oxygen and lattice oxygen (O2-) of Fe 2O3 at the sensor working temperature (150 °C). During this oxidation process, electrons will transfer to the surface of the Fe2O3 nanocrystals to lower the number of trapped electrons, inducing a decrease in the resistance [31]. From the crystalline point of view, there are no interlayer spacings and tunnels through the crystal structure, revealing that increasing the surface area could then produce more activity sites for the gas sensors.

Kanai et al., 1992 showed that the sensitivity of iron oxide-based sensors can be enhanced by various doping schemes and a number of different dopants such as Pd , Sn, Ti, Zn etc have been used . While doping is an important factor for controlling the sensing characteristics, the sensor structure, and especially the thickness of its active layer, also has a great influence on the sensitivity. In fact, bulk and thick-film type sensors exhibit a relatively low sensitivity, which substantially improves when the same sensing material is used in a thin-film type sensor.

Kaushik et al.(2008,2009) fabricated a new glucose biosensor and a urea sensor based on iron oxide nanoparticles-chitosan nano composite . Wang and Tan (2007) have developed a novel amperometric glucose biosensor by immobilizing ferritin antibody on the surface of Fe3O4 nanoparticles. (Fe3O4NPs)/chitosan (Cs) composite film modified glassy carbon electrode(GCE) for determination of ferritin. A practical glucose biosensor was developed by Yang et al. (2009) by combining the intrinsic peroxidase-like activity of Fe3O4 nanoparticles and the anti-interference ability of the nafion film. The modified electrode could virtually eliminate the interference during the detection of glucose. Furthermore, Abolanle et al., (2010) successfully applied the biosensor to detect glucose in human serum sample. Recently iron oxide nano-particles have also been tested for sensing different toxic biological drug like dopamine.

B. Photo-Degradation Of Dyes & Heavy Metals:

Removal of dyes from wastewater is a major environmental problem because dyes are visible even at low concentration. The existence of highly colored waste is not only aesthetically disturbance, but it also impedes light penetration, thus up setting biological process within a stream, some dyes also being toxic or carcinogenic [39]. It is estimated that 10-50 % of the dye is lost in the effluent [40]. Therefore, the treatment of effluent containing such a dye is a interest due to its harmful impacts on receiving waters [41].

Various chemical and physical treatment techniques and processes have been used to remove the dye pollutants from contaminated water. The adsorption [42-44] and catalytic oxidation processes, especially heterogeneous photocatalysis [45, 46] are the most successful methods for removal of dye pollutants from water. Iron oxides include α-Fe2O3, γ-Fe2O3 and Fe3O4. Among these Iron oxides, α-Fe2O3 has the corundum structure, while the other two have the cubic structure [47, 48].

Most of the papers have been published demonstrating that magnetic Fe3O4 can be used for wastewater purification, such as to adsorb arsenite, arsenate, crom, cadmium, nickel [49, 50]. Fe3O4 also can be used to alkalinity and hardness removal, desalination, decolorisation of pulp mill effluent and removal of natural organic compounds [51]. After adsorption, Fe3O4 can be separated from the medium by a simple magnetic process. Thus, an efficient, economic, scalable and non toxic. Synthesis of Fe3O4 nanoparticles is highly preferred for potential application and fundamental research [52, 53].

The nanoparticles Fe_3O_4 is suitable to remove dye in the water by a simple magnetic separation process. K. K. Singh et al(2017), synthesized superparamagnetic Fe_3O_4 Nanoparticles coated with green tea polyphenols and demonstrated that they showed high adsorption capacity (7.25 mg/g) for removal of methylene blue (MB) dye in wastewater treatment. In addition, the particles could be easily separated from the liquid medium through magnetic separation and potentially reused in multiple cycles.

Poedji Loekitowati Hariani et al.(2013) showed that the optimum adsorption occurred at initial concentration of procion dye 100 mg L^{-1}, pH solution was 6, dosage of Fe_3O_4 0.8 g L^{-1} and contact time 30 minutes adsorption capacity was 30.503 mg g^{-1}. Akram Hosseinian et al.(2011) conducted the photocatalytic experiments for congo red (CR) and demonstrated that the mixture of α-Fe_2O_3 and Fe_3O_4 nanostructures were more efficient than α-Fe_2O_3 nanostructures.

C. As Catalyst:

Iron oxide-based materials have been found to be good candidates as cheap and efficient catalysts, especially in environmental catalysis [24]. Magnetic nanoparticles with core–shell structure may enable the development of a new type of catalyst. The shell consists of the catalytically active species, and the magnetic core can act as anchor to separate and recycle the catalyst. Iron oxide (usually mixed with other metal oxides) in particular, has been shown to be a very active (although unstable) catalyst for the oxygen evolution process as well as other related processes, such as water splitting, chlorine evolution, the oxidation of organic molecules, the oxygen reduction process and for the hydrogen peroxide decomposition. Even more important are iron oxide-based catalysts in non-electrochemical processes.

In a study on the catalytic efficiency of iron oxide (α-Fe_2O_3) nanoparticles in hydrogen peroxide decomposition results suggested that, besides the catalytic effect of the high surface area, there is a more complex factor – the surface quality of the catalyst driving their efficiency. In addition to the main effect of the sample’s crystallinity, other qualitative parameters such as the chemical composition and particle morphology of catalysts are important.

As a consequence, iron oxides hematite, magnetite and maghemite are extensively used in the catalysis of a number of reactions such as the synthesis of styrene, photocatalytic production of hydrogen and oxygen, removal of carbon monoxide, catalytic conversion of methane in aromatic compounds, thermal decomposition of ammonium perchlorate as well as in water treatment, catalytic decomposition of hydrogen peroxide, fuel cells and production of biodiesel [1].

Miyata et al. (1978) studied the catalytic activity of several iron oxides and oxide hydroxides of various particle sizes for the reduction of 4-nitrotoluene using hydrazine hydrate as reducing agent, and found β-FeOOH was the most effective catalyst. For oxidation/reduction and acid/base reactions, the most applied iron oxides as catalyst are magnetite and hematite. Such magnetic nanoparticles can be very useful to assist an effective separation of catalysts, nuclear waste, biochemical products, and cells [25-27].

The iron nanoparticles stabilized by 1,6-bis(diphenylphosphino) hexane or polyethylene glycol exhibit high activity for the cross coupling of aryl Grignard reagents with primary and secondary alkyl halides bearing b-hydrogenatoms. This catalyst has also proven to be effective in a tandem ring-closing/cross coupling reaction [28].

Magnetically separable mesoporous carbons constructed from mesocellular carbon and Fe/Fe_3O_4 core–shell ferromagnetic nanoparticles (approximately 30 nm in size) show good electron conductivity, large pore size, and large pore volume. After the immobilization of enzymes (glucose oxidase) these particles can be used as magnetically switchable bio-electrocatalytic systems [29]. Hyeon and co-workers have also tried to synthesize monodisperse magnetite nanocrystals and CdSe/ ZnS quantum dots both embedded in mesoporous silica spheres. These mesoporous silica spheres were applied to the uptake and controlled release of ibuprofen drugs. The release rate can be controlled by the surface properties of mesoporous silica spheres [30].

D. As a colouring and coating material:

The use of hematite and other iron oxides as natural red ceramic pigments has been practiced since prehistoric times. The iron oxides such as magnetite, hematite, maghemite and goethite are commonly used as pigments for black, red, brown and yellow colours respectively [24]. By reducing the particle size to nano range, transparent iron oxide pigments can be obtained. Manufacturing process of transparent iron oxide pigments depend on the control of physical and surface chemistry properties. Particle size is optimized to ensure that minimal light interference occurs thus maximizing transparency. According to Elizabeth(1992) in general particle size from 2 to 10 nm increases transparency 310 times when compared to the bulk form. Sreeram et al., 2006 found that transparent iron oxide pigments have good stability to temperature, the red can resist up to 300° C while the yellow, black, green and brown can withstand upto 160°C. These are strong absorbers of ultraviolet radiation and mostly used in automotive paints, wood finishes, construction paints, industrial coatings, plastic, nylon, rubber and print ink. The excellent weather fastness, UV absorption properties, high transparency and color strength makes trans-oxide to enrich the colors, increase color shades when combined with organic pigments and dyes.

E. Drug Delivery:

A very promising application of magnetic nanoparticles is in drug delivery as drug carriers, that is, so called “magnetic drug delivery” proposed in the 1970s by Widder et al. [33].

The concept of magnetic targeting is to inject magnetic nanoparticles to which drug molecules are attached, to guide these particles to a chosen site under the localized magnetic field gradients, hold them there until the therapy is complete, and then to remove them. The magnetic drug carriers have the potential to carry a large dose of drug to achieve high local concentration, and avoid toxicity and other adverse side effects arising from high drug doses in other parts of the organism.

Although considerable achievements have been reached in in-vivo applications, to date, actual clinical studies are still problematic. Many fundamental issues in magnetic drug delivery systems need to be solved, such as the size controlled synthesis and stability of magnetic nanoparticles, biocompatibility of the coating layers (polymer or silica), drug-particle binding and the physiological parameters [34-35].

Magnetic drug targeting employing nanoparticles as carriers is a promising cancer treatment avoiding the side effects of conventional chemotherapy. Iron oxide nanoparticles covered by starch derivatives with phosphate groups, which bound mitoxantrone have been used as chemotherapy. Alexiou et al. have shown that a strong magnetic field gradient at the tumor location induces accumulation of the nanoparticles [36].

Kohler et al. [37] have reported the development of a biostable methotrexate-immobilized iron oxide nanoparticle drug carrier that may potentially be used for real-time monitoring of drug delivery through magnetic resonance imaging. Methotrexate (MTX) was immobilized on the surface of the nanoparticle via a poly(ethylene glycol) self-assembled monolayer (PEG-SAM).

Gallo et al. [38] have shown that, after administration of magnetic microspheres containing oxantrazole, the brain contained 100-400 times higher oxantrazole levels than those obtained after the solution dosage form, indicating the successfulness of drug delivery via magnetic particles.

V. Conclusion

The present article briefly describes the characteristics of nano-sized metallic iron oxides, methods of synthesis, main techniques of characterization and also their application in gas sensing, photocatalytic degradation of dyes, drug delivery and others. The magnetic nano-crystals are receiving much attention as these are now emerging in biomedical applications with new possibilities. Surface functionalization and modification of magnetic nanoparticles remain area of research in this field.

The main challenge in synthesis of iron oxide nanoparticles is absolute control over the shape and size distribution of nanoparticles by changing different conditions during its synthesis.

Acknowledgment

We are greatly acknowledged to University Institute of chemical technology, North Maharashtra University, Jalgaon (M.S., India) for their support and research facilities.

References

1. Campos EA, Stocker-Pinto DVBS, Oliveira JIS, Mattos EC, Dutra RCL, Synthesis, Characterization and Applications of Iron Oxide Nanoparticles – a Short Review, J. Aerosp. Technol. Manag., São José dos Campos, Vol.7, No 3, pp. 267-276, Jul.-Sep., 2015.
2. Akram Hosseinian, Hourieh Rezaei, Ali Reza Mahjoub, Preparation of Nanosized Iron Oxide and their Photocatalytic Properties for Congo Red, World Academy of Science, Engineering and Technology International Journal of Chemical and Molecular Engineering Vol:5, No:4, 2011.
3. W Wuet al; Recent progress on magnetic iron oxide nanoparticles: synthesis, surface functional strategies and biomedical applications; Sci. Technol. Adv. Mater. 16 (2015) 023501 (43pp).
4. Radwa M. Ashour, Ahmed F. Abdel-Magied, Ahmed A. Abdel-khalek,O. S. Helaly; Preparation and Characterization of Magnetic Iron Oxide Nanoparticles
Functionalized by L- cysteine: Adsorption and Desorption Behavior for Rare
Earth Metal Ions (2016).
5. Lu A H, Salabas E L and Schuth F (2007); Magnetic nanoparticles: synthesis, protection, functionalization, and application Angew. Chem. Int. Edn 46 1222.
6. Aleksandr Marinin; Synthesis and characterization of superparamagnetic iron oxide nanoparticles coated with silica; School of Information and Communication Technology Royal Institute of Technology(2012)
7. Wei Wu, Quanguo He, Changzhong Jiang; Magnetic Iron Oxide Nanoparticles: Synthesis and Surface Functionalization Strategies; Nanoscale Res Lett (2008) 3:397–415.
8. An-Hui Lu, E. L. Salabas, and Ferdi Sciuth; Magnetic Nanoparticles: Synthesis, Protection, Functionalization, and Application; Angew. Chem. Int. Ed. 2007, 46, 1222–1244.
9. Sun Sheng-Nan et al; Magnetic iron oxide nanoparticles:Synthesis and surface coating techniques for biomedical applications ;Chin.Phys.B Vol.23,No.3 (2014) 037503.
10. U.T. Lam, R. Mammucari, K. Suzuki, N.R. Foster, Industrial & Engineering Chemistry Research 47 (3) (2008) 599-614.
11. A. Tavakoli, M. Sohrabi, A. Kargari, Chemical Papers (2007) 61 (3) 151-170.
12. Y.X. Pang, X.J. Bao, Journal of Materials Chemistry 12 (12) (2002) 3699-3704.
13. V. Pillai, P. Kumar, M.J. Hou, P. Ayyub, D.O. Shah, Advances in Colloid and Interface Science 55 (1995)241-269
14. P. Tartaj, L.C. De Jonghe, Journal of Materials Chemistry 10 (12) (2000) 2786-2790.
15. I. Capek, Advances in Colloid and Interface Science 110 (1-2) (2004) 49-74.
16. F.A. Tourinho, R. Franck, R. Massart, J. Mater. Sci. 25, 3249 (1990).
17. A.B. Chin, I.I. Yaacob, J. Mater. Process. Technol. 191, 235 (2007).
18. Xia T, Wang J, Wu C, Mengm F, Shi Z, Lian J, Feng J and Meng J (2012) ;CrystEngComm. 145741

19. Sun S and Zeng H 2002 J. Am. Chem. Soc. 1248204.

20. J. Park,K. An, Y. Hwang, J.-G. Park, H.-J. Noh, J.-Y. Kim,J.-H. Park, N.-M. Hwang, T. Hyeon, Nat. Mater. 2004, 3, 891.

21. Vijaya Bhaskar Reddy a,b, Zulkifli Yusop and others(2016); Recent Progress on Fe-based nanoparticles: Synthesis, Properties, Characterization and Environmental Applications.

22. http://www.rsc.org/learnchemistry/collections/spectroscopy/introduction#IRSpectroscopy.

23. Introduction to Fourier Transform Infrared Spectrometry, Madison: Thermo Nicolet Corporation, 2001.

24. Mohapatra and Anand ; Synthesis and applications of nano-structured iron oxides/hydroxides – a review ;International Journal of Engineering, Science and Technology, Vol. 2, No. 8, 2010, pp. 127-146.

25. S. Giri, B. G. Trewyn, M. P. Stellmaker, V. S.-Y. Lin, Angew. Chem. 2005, 117, 5166; Angew. Chem. Int. Ed. 2005, 44, 5038.

26. C. Bergemann, D. Muller-Schulte, J. Oster, L. Brassard, A. S. Lubbe, J. Magn. Magn. Mater. 1999, 194, 45.

27. L. Nunez, M. D. Kaminski, J. Magn. Magn. Mater. 1999, 194, 102.

28. R. B. Bedford, M. Betham, D. W. Bruce, S. A. Davis, R. M. Frost, M. Hird, Chem. Commun. 2006, 1398

29. J. Lee, D. Lee, E. Oh, J. Kim, Y.-P. Kim, S. Jin, H.-S. Kim, Y. Hwang, J. H. Kwak, J.-G. Park, C.-H. Shin, J. Kim, T. Hyeon, Angew. Chem.2005, 117, 7593; Angew. Chem.Int. Ed.2005, 44, 7427

30.J. Kim, J. E. Lee, J. Lee, J. H. Yu, B. C. Kim, K. An, Y. Hwang, C.-H. Shin, J.-G. Park, J. Kim, T. Hyeon, J. Am. Chem. Soc. 2006, 128, 688.

31. Wang et al.; Facile Synthesis and Characterization of Iron Oxide Semiconductor Nanowires for Gas Sensing Application; J. Phys. Chem. C, Vol. 112, No. 39, 2008.

32. Sun et al.; Synthesis of Mesoporous r-Fe2O3 Nanostructures for Highly Sensitive Gas Sensors and High Capacity Anode Materials in Lithium Ion Batteries; J. Phys. Chem. C 2010, 114, 18753–18761

33. K. J.Widder,A. E.Senyei,D. G.Scarpelli,Proc.Soc.Exp.Biol. Med. 1978, 58, 141.

34. A. K. Gupta, M. Gupta, Biomaterials 2005, 26, 3995.

35. T. Neuberger, B. SchPpf, H. Hofmann, M. Hofmann, B. von Rechenberg, J. Magn. Magn. Mater. 2005, 293, 483.

36. Alexiou, C.; Schmid, R. J.; Jurgons, R.; Kremer, M.; Wanner, G.; Bergemann, C.; Huenges, E.; Nawroth, T.; Arnold, W.; Parak, F. G. Eur. Biophys. J. 2006, 35 (5), 446.

37. Kohler, N.; Sun, C.; Fichtenholtz, A.; Gunn, J.; Fang, C.; Zhang, M. Small 2006, 2 (6), 785.

38. Gallo, J. M.; Varkonyi, P.; Hassan, E. E.; Groothius, D. R. J. Pharmacokinet. Biopharm. 1993, 21 (5), 575.

39. S. Wang, Y. Boyjoo, A. Choueib, and H. Zhu, “Removal of Dye from Solution using Fly Ash and Red. Mud,” Water Research, vol. 39, pp. 29-38, 2005.

40. S. Senthilkumaar, P. Kalaamani, K. P. R. Varadarajan, and S. V. Subburaam, “Adsorption of dissolved reactive red dye from aqueous phase onto activated carbon prepared from agricultural waste,” Bioresour. Technology, vol. 97, pp. 1618-1625, 2006.

41. I. A. W. Tan and B. H. Hameed, “Adsorption isotherm, kinetics, thermodynamics and desorption studies of basic dye on activated carbon derived from oil palm empty bunch,” Journal of Applied Science, vol. 10, no. 21, pp. 2565-2671, 2010.

42. J. Wu, J. Wang, H. Li, Y. Du, K. Huang, B. Liu, Designed synthesis of hematite-based nanosorbents for dye removal, J. Mater. Chem. A 1 (2013) 9837-9847.

43. S. Samiee, E.K. Goharshadi, Graphene nanosheets as efficient adsorbent for an azo dye removal: kinetic and thermodynamic studies, J. Nanopart. Res. 16 (2014) 1-16.

44. Y.-S. Lu, B.P. Bastakoti, M. Pramanik, V. Malgras, Y. Yamauchi, S.-W. Kuo, Direct Assembly of Mesoporous Silica Functionalized with Polypeptides for Efficient Dye Adsorption, Chem. Eur. J. 22 (2016) 1159-1164.

45. T. Mahvelati-Shamsabadi, E.K. Goharshadi, Photostability and visible-light-driven photoactivity enhancement of hierarchical ZnS nanoparticles: The role of embedment of stable defect sites on the catalyst surface with the assistant of ultrasonic waves, Ultrason. Sonochem. 34 (2017) 78-89.

46. R. Ahmad, Z. Ahmad, A.U. Khan, N.R. Mastoi, M. Aslam, J. Kim, Photocatalytic systems as an advanced environmental remediation: Recent developments, limitations and new avenues for applications, J. Env. Chem. Eng. 4 (2016) 4143-4164.

47. J. Lu, Sh. Yang, K. Ming, Ch. Su, Ch. Yeh, Y. Wu, D. Shieh, Nanotechnology, 17 (2006) 5812.

48. X. Batlle, A. Labarta, J. Phys. D: Appl. Phys., 35 (2002) 15.

49. J. T. Mayo, et al., “The Effect of Nano Crystalline Magnetite Size on Arsenic Removal,” Journal of Science and Tech Arsenic Removal,” Journal of Science and Technology Materials, vol. 8, pp. 71-75, 2008

50. F. Rosada, M. Otero, A. Moran, and A. I. Garcia, “Adsorption of Heavy Metals onto Sewage Sludge-Derived Materials,” Bioresour Technology, vol. 99, pp. 6332-6338, 2008.

51. B. A. Bolto, “Magnetic Particle Technology for Wastewater Treatment,” Waste Management, vol. 10, pp. 11-21, 1990

52. S. H. Sun and H. Zeng, “Size Controlled Synthesis of Magnetite Nanoparticles,” Journal Am.Chem.Soc., vol. 24, pp. 8204-8205, 2002.

53. S. R. Wan, J. S. Huang, H. S. Yan, and K. L, Liu, “Size controlled preparation of magnetite nanoparticles in the presence of graft copolymer,” Journal Mater.Chem., vol. 16, pp. 298-303, 2006.