

Synthesis & Characterization of Maghemite (γ -Fe₂O₃) Nanoparticles

Prof. S. T. Patil¹ Miss. Priyanka R. Patil²

^{1,2}Tatyasaheb Kore Institute of Engineering Technology Warananagar, Shivaji University, Kolhapur, Maharashtra, India

Abstract— The range of environmental cleaning technologies has been introduced in wastewater treatment which uses iron oxide nanomaterials as Nano sorbents and photo catalysts. Nanostructured iron oxide will be synthesized using cost-effective chemical methods. This Nanostructured iron oxide will be characterized by various characterization techniques viz., X-ray diffraction (XRD), Fourier, Transmission Electron Microscope (TEM) etc. The primary parameters for nanostructures of iron oxide will be optimized.

Key words: Nanostructures, XRD, TEM, Chemical Methods, Iron Oxide

I. INTRODUCTION

Nanotechnology is the science, engineering, and technology related to study, understanding and control of matter of approximately 1 to 100 nanometers at the length scale. At this range material exhibits unique characteristics due to a small size and high surface area to volume ratio than their bulk counterparts. Iron oxide nanoparticles have one more special property in the form of super magnetism along with small size and high surface area. The large surface area of the magnetic nanoparticles dramatically changes the magnetic properties and shows super magnetism phenomena and magnetization. A magnetic fluid is a stable colloidal suspension of magnetic nanoparticles dispersed in a carrier liquid. The properties of the material strongly depend on the particle size, the degree of dispersion of the nanoparticles and the particle matrix interaction. The magnetic particle without any coating tends to aggregate to form large clusters. It is, therefore, necessary to functionalize the surface of nanoparticles for their application in the fields of separation technology [1]. Based on their physical, thermal, and mechanical properties, they find application in different areas such as color imaging, detoxification of biological fluids, drug delivery, and heavy metal ion separation from wastewater. Currently, iron oxide nanoparticles with novel properties and functions have been widely studied in the field of separation due to its cost-effective synthesis, easy coating and surface modification and ability to control or manipulating materials on nanoscale dimensions provide amazing versatility in separation techniques. Apart from these, low toxicity, chemical inertness, and biocompatibility make it good adsorbent for heavy metal removal. After magnetic separation, they can also be reused in removing the adsorbed toxic contaminants. Also, their surface can be modified by attachment of organic molecules and inorganic shells that not only stabilize but also prevent oxidations of nanoparticles. Moreover, these surface functionalities provide sites that uptakes specific or selective metal ions and, thus, resulting in enhanced removal efficiency [2]. Various wet chemical processes have been used to synthesize maghemite nanoparticles including thermolysis by organic metallic decomposition and carbonyl decomposition [8]. Chemical precipitation is one of the oldest and simple techniques for the synthesis of nanoparticles [8]. In precipitation processes, the metal precursors (e.g. FeCl₃ or

FeCl₂) are dissolved in a solvent and a precipitating agent (e.g. NH₄OH) is added to form nanoparticles. Even though chemical precipitation is simple and manufacturable, this process is difficult to control and yields nanoparticles with a broad size distribution and irregular morphology. Thermolysis can produce monodispersed maghemite nanoparticles with good crystallinity by thermal decomposition of iron cupferron complexes in octylamine and thermal decomposition of iron pentacarbonyl in the presence of oleic acid, respectively [9,10]. Although thermolysis in the presence of capping agents offers monodisperse nanoparticles with good crystallinity, these methods operate at a higher temperature (100–300°C) and require toxic and expensive precursors. These methods have limited controllability of particle morphology and size causing the variation of magnetic properties. Electrodeposition is a promising alternative technique for fabrication of nanoparticles, because it is simple, manufacturable, inexpensive, fast, operates at near room temperature, and its ability to control composition, crystallinity, and properties of the deposit by adjusting deposition conditions. Iron oxide thin films were both cathodically and anodically electrodeposited [11–19]. In the case of anodic formation of iron oxides, the different phases of the iron oxides oxyhydroxides thin films were obtained by adjusting deposition potentials and solution composition [11]. The cathodic electro deposition of amorphous Fe₂O₃ thin films by reduction of Fe (III) per chlorate in oxygenated acetonitrile where ferric ions reduced with dissolved oxygen to form amorphous Fe₂O₃. Amorphous Fe₂O₃ thin films were later converted to γ -Fe₂O₃ (i.e. maghemite) thin films after heat treatment. Electrodeposited amorphous and nanocrystalline γ -Fe₂O₃ (i.e. maghemite) thin films from electrolytes containing 5mM FeCl₃ + 1M H₂O₂ + 5mM NaF + 0.1M KCl at 50°C [18]. The reduction of hydrogen peroxide at the cathode caused an increase in local pH on the surface of the cathode which later directed the surface precipitation of Fe (OH)₃. Ferric hydroxides were later transformed to Fe₂O₃ by the thermal annealing in air. The synthesized amorphous maghemite nanoparticles by anodic dissolution of sacrificial Fe anode are followed by chemical reaction in an organic medium [19].

II. EXPERIMENTAL METHOD

A. Materials & Chemicals

Making Electrolyte solution of Ferric Chloride (AR Grade), H₂O₂ (30 wt %), NaF (LR Grade), KCl and Distilled Water etc. by using Sigma Aldrich Grades.

B. Experimental Set Up

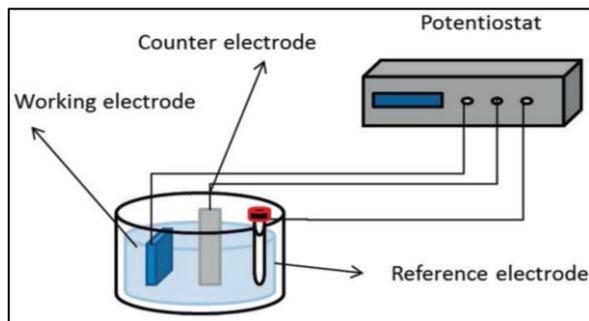


Fig. 1: Electro Deposition Set Up

C. Experimental Procedure

To prepare an electrolytic solution containing 5mMFeCl₃ + 1MH₂O₂ + 5mMKF + 0.1MKCl at 50°C. Maghemite nanoparticles were cathodically electrodeposited from electrolytes with FeCl₃ concentrations under galvanostatic control at 20°C. The electrochemical cell was a 150 ml glass jar with a working volume of 100 ml, an open to the atmosphere. Steel rods served as both the cathode and anode. The surface area of the cathode was fixed at 4 cm². The pH of the solution was adjusted to 2 by adding HCl or NaOH. The current densities were varied from 150 to 2000mAcm⁻². All reagents used in this study were reagent grade. Ultrapure water was used in the preparation of solutions. To produce γ -Fe₂O₃ through annealing having temperature 150°C. Make a fine powder by crush in crushing unit.

III. RESULTS & DISCUSSIONS

The phases were identified by the means of X-ray diffraction (Bruker D 8 advance diffractometer with Pb K- α radiation). Surface morphology was characterized using (JEOL JSM-6360A) scanning electron microscope and energy dispersive spectroscopy was carried out. Transmission electron microscope (Philips CM200) was used to study particle size.

A. X-ray Diffraction (XRD)

Crystallographic structure of the magnetic nanoparticles was measured using X-ray diffraction. Bruker D-8 Advance spectrometer (Cu target/40 kV/30 mA, wavelength $\lambda=0.1504$ nm) was used for powder X-ray diffraction (XRD) measurements. The XRD pattern change was plotted by intensity vs. 2θ in the range of 20°C-80°C. Debye-Scherrer's formula was used to calculate the average crystal size. The XRD patterns of the samples heat-treated under different conditions are presented in the figures below. Bare iron oxides nanoparticles have high chemical activity and easily oxidized in the air especially magnetite, generally resulting in loss of magnetism and dispensability. In addition, magnetite nanoparticles are not very stable under ambient conditions and are easily oxidized to maghemite. Widened diffraction line demonstrates the extremely small size of particles. It is interesting that the structure of the final iron oxide product depends on how we dry and exposure to the air atmosphere of obtained electro deposition product. As in figure 2, the sample was dried at 150°C showing the effect of concentration in the formation of different phases of nanoparticles. In figure 2, the diffraction peaks at $\theta=29^\circ$, 35° and 62° can be assigned to (2 2 0), (3 1 1) and (4 4 0) (JCPDS

79-0418) giving cubic spinel structured magnetite nanoparticles and sharp peak at $\theta=23^\circ$ is assigned to (2 1 0) giving presence of γ -Fe₂O₃ phase.

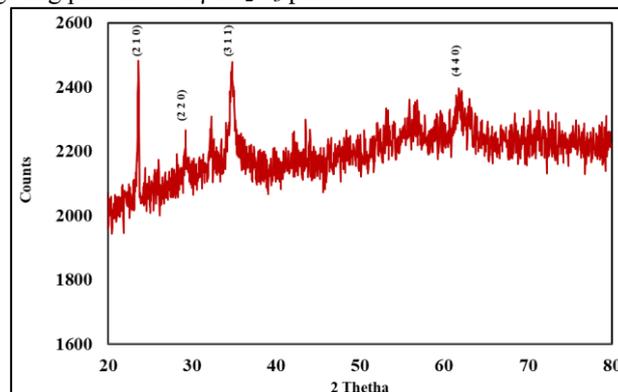


Fig. 2: X-Ray Diffraction Patterns of the Maghemite IONP at 500mAcm⁻²

B. SEM Images

Scanning electron microscope (JEOL JSM-6360A) was used to study surface morphology. Figure 3 shows how morphology changes at various current density and concentration effect for 0.01M concentration. It is observed in figure 3 (A), that the particles are approximately spherical in shape. However figure 3 (B) and 3 (C), shows approximately double layer particles with few micro pores on the surface, whereas in figure 3 D, we see in some parts sphere are well dispersed.

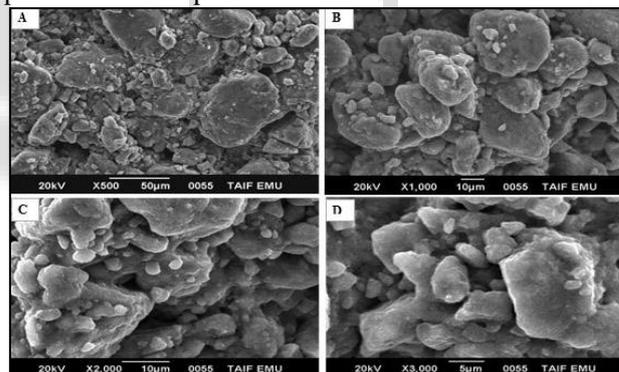


Fig. 3: SEM Images of Maghemite nanoparticles at different magnification

C. TEM Images

Transmission electron microscopy (TEM) was utilized to investigate the shape and size dependence of maghemite nanostructures as functions of current density and electrolyte compositions (Fig.4). The shape and size of nanoparticles were strongly influenced by electrolyte composition and applied current density. The change in morphology and size with the increase in current density might be attributed to the (1) higher nucleation rate; (2) shift reaction control from kinetic control to mass transfer control; and (3) non-uniform electric field cause by nanostructure formation at the electrode surface. At relatively high deposition current density (e.g. 150mAcm⁻² in 0.01M FeCl₃), the local current density at the electrode is not uniform because of the higher electrical field at the edge of the growing deposit, which favors the nucleation at the tip of the deposit. These conditions can lead to the formation of dendrites. When the

deposition current density is very high (e.g. $>500\text{mAcm}^{-2}$), powdered deposits (i.e. micro or nanoparticles) are formed on the cathode due to the high nucleation rate. The deposit morphology shifts from dendritic to powdery deposits similar to other electro deposition systems. These results clearly demonstrate that the shape and size of maghemite nanoparticles can be controlled by adjusting electrolyte compositions and deposition current density.

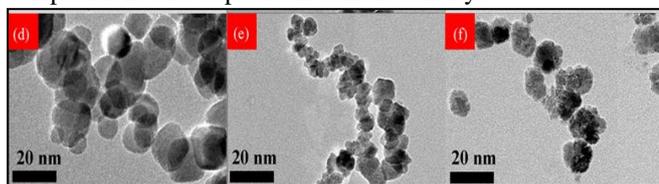


Fig. 4: TEM images of Maghemite Iron Oxide Nanoparticles at current density 500mAcm^{-2}

IV. CONCLUSION

Randomly oriented polycrystalline maghemite (γ -Fe₂O₃) nanoparticles were electrodeposited from environmentally benign electrolytes. The morphology and production rate of nanoparticles could be precisely controlled by adjusting the current density and the electrolyte compositions. Transmission electron microscopy (TEM) images showed that the size of particle decreased when increasing the current density and the FeCl₃ concentration. Compared to other methods, electro deposition is often a cost-effective bulk quantity production method to synthesize nanoparticles with good controllability over size, shape, and crystallinity.

REFERENCES

- [1] K. Raj, B. Moskowitz, R. Casciari, Advances in ferrofluid technology, *J. Magn. Magn.* 149 (1995) 174-180.
- [2] J. Popplewell, L. Sakhnini, The dependence of the physical and magnetic-properties of magnetic fluid on particles-size, *J. Magn. Magn.* 149 (1995) 72-78.
- [3] D. Kim, Y. Zhang, K. Rao, Synthesis and characterization of surfactant coated supermagnetismmonodispersed iron oxide nanoparticles, *J. Magn. Magn.* 225 (2001) 30-36.
- [4] S. Shi, J. Hwang, Microwave assisted wet chemical synthesis: advantages, significance, and step to industrialization, *J. Mine. Mater. Charct. Engg.* 2 (2003) 101-110.
- [5] F. Fenglian, Q. Wang, Removal of heavy metal ions from wastewater, *J. Enviro. Manage.* 92 (2011) 407-418.
- [6] J. Pope, Activated carbon and some applications for the remediation of soil and groundwater pollution, Virginia Tech, Virginia, (1996).
- [7] A.K. Shrivastava, A review on copper pollution and its removal from water bodies by pollution control technologies, *Indian J. Environ. Protection* 29 (2009) 552-560.
- [8] F.V. Pereira, L.V.A. Gurgel, S.F. de Aquino, and L.F. Gil, Removal of Zn²⁺ from electroplating wastewater using modified wood sawdust and sugarcane bagasse, *ASCE*, 135 (2009) 341-350.
- [9] ElShafey, M. Cox, A. Pichugin, Q. Appleton, Application of a carbon sorbent for the removal of cadmium and other heavy metal ions from aqueous solution, *J. Chem. Technol. Biotechnol.* 77 (2002) 429-436.
- [10] L. Norton, K. Baskaranand, T. Mckenzie, Biosorption of zinc from aqueous solutions using biosolids, *Adv. Environ. Res.* 8 (2004) 629-635.
- [11] D. Pentari, V. Perdikatsis, D. Katsimicha, and A. Kanaki, Sorption properties of low calorific value Greek lignites: removal of lead, cadmium, zinc and copper ions from aqueous solutions, *J. Hazard. Mater.* 168 (2009) 1017-1021.
- [12] Shafaei, F. Z. Asthiani, T. Kaghazchi, Equilibrium studies of the sorption of Hg (II) ions onto chitosan, *Chem. Engg. Journa.* 133 (2007) 311-316.
- [13] N.K. Srivastava, C.B. Majumder, Novel biofiltration methods for the treatment of heavy metal ions from industrial waste water, *J. Hazard. Mater.* 151 (2008) 1-8.
- [14] K.R. AswinSidhaarth, J. Jeyanthi, N. Suryanarayan, Comparative studies of removal of lead and zinc from industrial waste water and aqueous solution by iron oxide nanoparticles performance and mechanism, *European J. Sci. Res.* 70 (2012) 169-184.
- [15] Reife, H.S. Fremann, Environmental chemistry of dyes and pigments, John Wiley & Sons Inc, New York (1996).
- [16] M. Mohaptra, S. Anand, Synthesis and application of nano- structured iron oxide/ hydroxides- a review, *Int. J. Eng. Sci. Tech.* 2 (2010) 127-146.
- [17] K. Choo, S. Kang, Removal of residual organic matter from secondary effluent by iron oxides adsorption, *Desalination.* 154 (2003) 139-146.
- [18] K. Raj, R. Moskovitz, Commercial applications of ferrofluids, *J. Magn. Magn. Mater.* 85 (1990) 233-245.
- [19] R. Cornell, U. Schwertmann, The iron oxides structure, properties, reactions, occurrence and uses, VCH Verlagsgesellschaft Weinheim (1996).
- [20] J. Dutta, H. Hofmann: Nanomaterials. Springer Verlag. (2008) 37-58.