Synthesis and Characterization of Nano-crystaline $CaFe_2O_4$ via Solution Combustion Method from Solid Waste Egg Shells as Source of Calcium

H.Bhagya Lakshmi[1], B. J. Madhu[2], M.Veerabhadraswamy*[3]

[1]Department of Chemistry, Dr. Ambedkar Institute of Technology,Bangalore,Karnataka, India

[2]Post Graduate Department of Physics, Government Science College, Chitradurga, Karnataka, India

[3]Green Chemistry Center, P E S University, BSK 3rd Stage, Bangalore, Karnataka, India

ABSTRACT

The liable application of solid egg shell waste obtained from food processing industry into biocompatible calcium ferrite nano materials will put in significance to the waste generated.Million tons of egg shell waste are produced every day which has contributed to environmental pollution.In this framework blending of nanotechnology with science, ensuing green chemistry moralities has led to arrival of innovative and improved technologies in the field of material science. Our present work aims at synthesis of calcium ferrite nanoparticles by solution combustion method using waste egg shells as source of calcium, ferric nitrate as Fe precursor in presence of urea as fuel at 500°c. Obtained calcium ferrites nanoparticles were annealed 900°c and characterized by X-ray diffraction, Fourier transform infrared spectroscope, Scanning electron microscope, BET, and Vibrating sample magnetometer. XRD results for the sample annealed at 900°c show the formation of calcium ferrites with octahedral structure of crystallite size 10nm and exhibit mixed spherical and capsule morphology. BET surface area of 6.93m2/g with total pore volume of 0.00381 cm^3/g and average pore diameter of 2.19nm is obtained. M-H curve for calcium ferrites annealed at 900°c shows hardly hysteresis behavior under applied magnetic field. Magnetic saturation and Coercive magnetic field strength found to be low which implies that material acts as soft ferrites. Thus their magnetization can easily be reversed without dissipating much energy. Hence the process of transforming eggshell waste into nanocrystaline calcium ferrite is an ecofriendly process, besides; the present work may lead to generation of high valuable ferrite which is applicable in various fields of engineering.

Key words: *Egg shells, Calcium ferrites nano particles, Magnetic property.*

1. INTRODUCTION

Eggs are the nutritious dietary supplement for healthy life but egg shells form a huge waste. Eggshell waste has largely reflected as unusable and is castoff mostly because it pays to pollution. Food processing industries depend on eggs as major ingredient which leads to massive assembly of egg shell waste. Industries are spending vast sum for disposal of waste egg shells in landfills, and the fills are reaching maximum capacity. Main drawback of land fillings is organic layer adhering to the shell attracts rats and other vermin.Thereby, resulting in high environmental impact. Egg shells contain 96% of calcite, with other constituents like magnesium, phosphates, and organic substances [1]. Murakami et al investigate the physical-chemical and thermal behaviour of calcium carbonate obtained from egg shell and comparing to industrial calcium carbonate [2]. Literature work on waste egg shells gives a clear insight of exploiting solid waste egg shells in fabricating value added biomaterials like hydroxyapatite [3], bioactive wollastonite [4]. Catalysis is an energetic part of organic synthesis which is emerging at the boundary of chemistry, physics, biology and mathematics. From past few years chemists have been concentrating on design and use of ecologically caring catalysts. In current ages magnetic nano materials mainly ferrites, due to their easy separation by bid of external magnetic field, have arisen as a beneficial class for catalyst support [6]. Meanwhile Calcium ferrites are also used as catalytic material [5]. Accordingly ferrites an important ceramic material, has been a central part of research studies. As reported in literature, $CaFe_2O_4$ has been synthesized by various methods such as solution combustion [7], sol gel [8], polymeric precursor method [9]. L.Khanna, N.K. Verma reported synthesis of calcium ferrite nano- particles and their magnetic properties at different calcination temperatures [10]. Egg shell waste has potentially been applied in generating calcium ferrites a major component found in magnetic devices, semiconductors, optical memory devises [11], as electrode material especially in lithium ion batteries [12], and effectively utilized as adsorbent of hydrogen sulphide [13]. Recently $CaFe_2O_4$ nano particles prepared by co-precipitation method is been used in grounding of electrode for electrochemical investigation thus finding excessive application in the field of biosensors [14]. In the present work magnetically separable calcium ferrite was successfully synthesized by solution combustion method using waste egg shell as Ca precursor and ferric nitrate as Fe precursor in presence of urea as fuel. Utilizing waste egg shells as Ca source for calcium ferrite synthesis has an added advantage over various other ferrites to use these materials for biological applications owing to its bio-compatibility, thermal stability, and eco-friendly [15].N.H. Sulaiman et al synthesised calcium ferrite nano-particles using sol-gel method for their drug delivery application [16]. The use of eggshell to generate such biocompatible calcium ferrites in medical application will not only lessen the pollution effect but also reduce the economic cost involved for medical expenses thereby resulting in effective waste utilization. This approach has positively revolved untransformed wastes into high value products resulting in wealth from waste.

2. EXPERIMENTAL

Egg shells were collected from local bakeries in Bangalore. Waste egg shells were washed under running water to remove impurities and soaked in hot water for one hour so that egg shell can be separated from egg membrane. Obtained egg shells were repeatedly washed under running water and dried in hot air oven at 120^0 for 24 hrs. Egg shell was then finely powdered by ball milling for 18hrs at 50 rpm.

$CaFe_2O_4$ nano particles were prepared by solution combustion method. Based on oxidizing and reducing valency, stoichiometry of the redox mixture for combustion was calculated. Fine powdered egg shells were used to prepare Calcium nitrate solution by treating egg shells with nitric acid which resulted in clear yellow solution. To the yellow solution of Calcium nitrate stochiometric amount of Ferric nitrate and urea was added and stirred for half an hour to obtain clear homogenous solution. The complete redox mixture was magnetically stirred for half an hour to obtain clear solution. The resulted homogenous mixture was introduced in a pre heated muffle furnace at 500^oc for one hour.$CaFe_2O_4$, obtained as reddish brown powder was then annealed at 900^0c. The overall balanced chemical reaction is represented as

$$\underset{\text{(Waste Egg shells)}}{CaCO_3 + 2HNO_3} \longrightarrow \underset{\text{(Yellow solution)}}{Ca(NO_3)_2}$$

$$3Ca(NO_3)_2 + 6Fe(NO_3)_3.9H_2O + 20\,CO(NH_2)_2 \longrightarrow 3\,CaFe_2O_4 + 20\,CO_2 + 94\,H_2O + 32\,N_2$$

2.1 $CaFe_2O_4$ characterization

$CaFe_2O_4$ prepared by solution combustion method was characterized by techniques such as X-Ray diffraction (XRD), recorded in bruker AXS, model : D8discover diffractometer using Cu-Kα radiation at 2θ rage of 0- 90^o at scan speed of 5^0/min. FTIR spectra was recorded in Carry 630 FT-IR , Agilent instrument KBr pellets from range of 400 to 4000 cm^{-1} . Morphology and chemical composition of the catalyst was analyzed by Scanning electron microscope (Leica, model- S440I) studies. Surface area and total pore volume was analyzed using Quta chrome autosorb IQ instrument. Nitrogen adsorption and desorption studies were carried out and BET (Brunauen-Emmett-Teller) method was applied to adsorption data to obtain surface area measurements, total pore volume was analyzed from liquid nitrogen temperature.. Magnetic measurements on calcium ferrites annealed at 900^{o}c were carried out by Quantum Design SQUID VSM magnetometer.

3. RESULTS AND DISCUSSION

3.1 XRD Analysis

Powder X-Ray diffraction is one of the primary techniques used to determine the material under study. XRD pattern of $CaFe_2O_4$ obtained from chicken egg shells were studied as observed in the figure. $CaFe_2O_4$as prepared shows amorphous nature as no diffraction pattern was observed which depict lack of crystalinity. XRD pattern of sample annealed at 900^{o}c clearly shows crystalinity and average crystallite size is found to be around 10nm. The synthesized calcium ferrite from egg shells has orthorhombic structure, whose space group is Pnam (62), being identified by the JCPDS file number 320168.

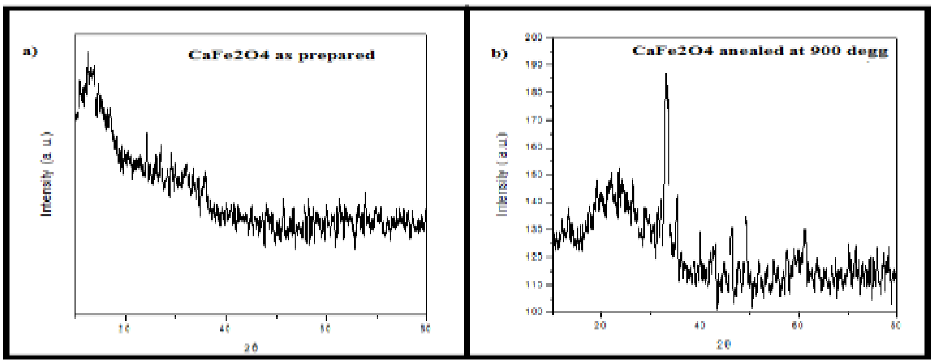

Figure 1(a-b): XRD spectra of a) $CaFe_2O_4$ as prepared at 500^{o}c, b) $CaFe_2O_4$ annealed at 900^{o}c

3.2 FTIR studies

FT-IR studies for the synthesized calcium ferrites annealed at 900^{o}c as shown in figure no.2 was recorded which helps to figure out the nature of chemical bonding. The broad bands at 3454 cm−1 and 1634 cm−1 are assigned to the O–H stretching vibrations. The band at 1064cm−1 corresponds to metal–alloy (Fe–Ca) and bands at 624 and 567 cm−1 are attributed to Fe–O bonds due to the presence of ferrite skeleton. The bands at 875, 712cm−1 are attributed to O–Fe–O, Fe–OH and bands at 451cm−1 correspond to Fe–O bonds. The bands at 526 cm−1 and 495 cm−1 correspond to the stretching vibrations of the metal oxygen bonds (Ca–O).

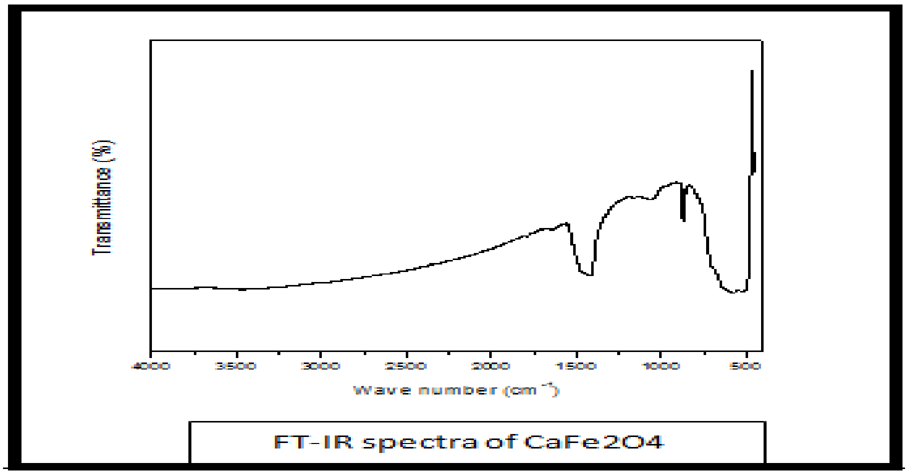

Figure 2: FT-IR spectra of $CaFe_2O_4$annealed at 900^{o}c.

3.3 SEM measurements

SEM results reveal both morphology and particle sizes of the samples. SEM images of $CaFe_2O_4$ samples annealed at 900^{o}c are shown in Fig 3 a-b. It can be observed that SEM images of $CaFe_2O_4$ show mixed morphology of spherical and capsule like. Particles are agglomerated with the average particle size in the range of 290nm to 480nm. Agglomeration may be due to magnetic property of the material. Similar type of results can be observed in the literature.

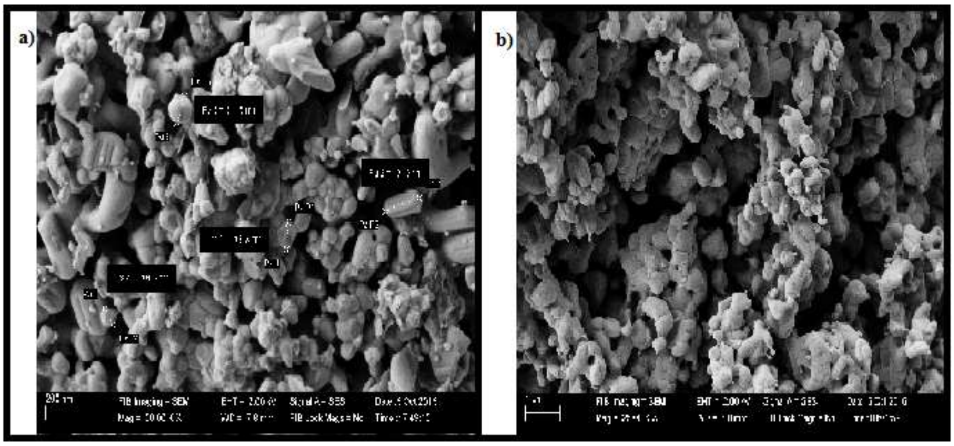

Figure 2(a-b): SEM images of $CaFe_2O_4$annealed at 900^{o}c

3.4 BET surface area analysis

BET surface area of synthesized calcium ferrite annealed at 900^{o}c from solid waste egg shells was evaluated. Practically higher surface area of 6.93 m^2/g was observed with total pore volume 0.00381cc/g and average pore diameter of 2.19nm when compared with the surface area of calcium ferrites reported in literature. N.Rezlescu *et al* has reported synthesis of nano sized calcium ferrites by self-combustion method with BET surface area of about 2.83m^2/g and total pore volume of 0.0049cc/g with average agglomerate size of 440nm[17]. In the similar flow calcium ferrite catalyst ($CaFe_2O_4$) was synthesized by the sol–gel method, which exhibited high catalytic activity for esterification of oleic acid in which BET surface area, average pore diameter and specific pore volume, were 2.48 m^2/g, 96.11 °A, and 0.0078 cc/g, respectively [18]. BET analysis of synthesized calcium ferrites using waste egg shells as calcium source gives a higher surface area when compared with the calcium ferrites as reported in literature.

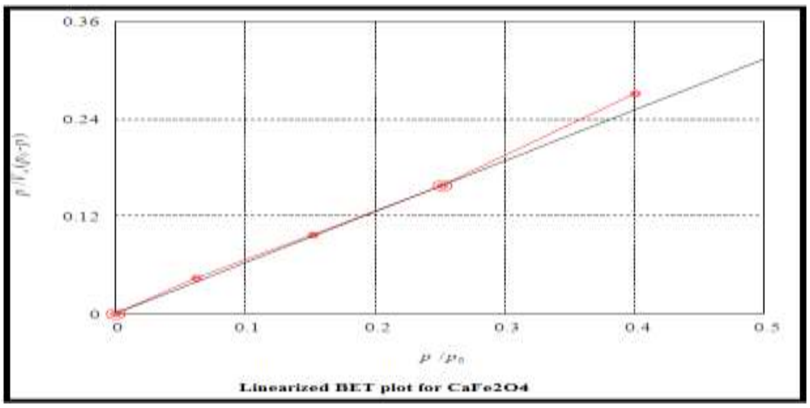

Figure 3: linearized BET plot for calcium ferrites obtained from solid waste egg shells.

3.5 Magnetic measurements study

Magnetic measurements on calcium ferrites annealed at 900^{o}c were carried out by Quantum Design SQUID VSM magnetometer using Quartz sample holder at room temperature. M-H curve is as shown in Figure 5. It can be seen that the magnetization of calcium ferrites exhibits hysteretic behavior under the applied magnetic field. Magnetization of calcium ferrite annealed at 900^{o}c exhibits hardly hysteretic behavior under the applied magnetic field. The values of coercivity (H_c) and saturation magnetization (M_s) of calcium ferrites obtained from waste egg shells as calcium source are 317 and 0.0175 respectively. Similar behavior has been observed for PANI/$Ni_{0.5}Zn_{0.5}Fe_2O_4$ composites [19]. Observed lower values of H_c and M_s for the calcium ferrites annealed at higher temperature may be due to alteration in the structure of the calcium ferrites. Further, various anisotropy mechanisms such as magneto-crystalline anisotropy, surface anisotropy and interparticles interactions also contribute to the magnetic properties.

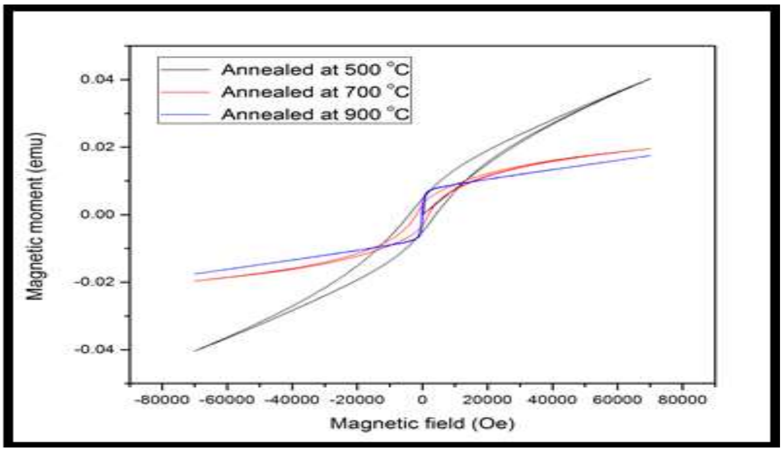

Figure 5: MH plot of $CaFe_2O_4$annealed at 900°c showing hysteresis loop

4. CONCLUSION

In this paper, we account for the preparation of $CaFe_2O_4$ nanoparticles by a solution combustion synthesis using solid waste egg shells as the source of calcium. XRD results shows that obtained calcium ferrites with orthorhombic type. The average crystallite sizes of the studied samples were about 10 nm. FTIR spectra festivities the configuration of chemical bonding in the obtained ferrites. SEM results show the mixed morphology of spherical and capsules with agglomeration. BET outcome depicts an higher surface area when compared with the calcium ferrites reported in literature The magnetic measurements at room temperature of the synthesized $CaFe_2O_4$ annealed at 900°c shows hardly hysteresis with lower value of magnetic saturation and coercivity. Thus calcium ferrites from solid waste egg shell acts as soft ferrites. Obtained Calcium ferrite from waste egg shells can find potential application in microwave absorption area, biomedical application, for designing magneto electronics devices and magnetic data storage. Extending the work, the synthesized calcium ferrites can be used as catalyst in esterification of oleic acid with glycerol, a by-product from biodiesel industry to obtain fine commodity chemicals. Accordingly renewal of solid waste egg shell from food processing industry in synthesising valuable nanocrystaline calcium ferrites materials will add value in waste exploitation thereby bringing about wealth from waste.

ACKNOWLEDGMENT

The authors gratefully acknowledge JNCASR for magnetic data, PPISR for XRD and BET analysis and CMTI for SEM studies. Authors are thankful to Visvesvaraya Technological University (VTU), Belgaum, Karnataka and All India Council for Technical Education (AICTE), India, for providing financial assistance to the project.

REFERENCE

1. D.A.Oliveira, P.Benelli and E.R.Amante , "*A literature review on adding value to solid residues: Egg shells*", J. Cleaner Production, vol. 46, pp.42-47, 2013.
2. Fabio Seigi murakami, Patrik oening rodrigues, Célia maria teixeira de campos and Marcos Antônio Segatto Silva, "Physicochemical study of CaCO3 from egg shells", Ciênc. Tecnol. Aliment., Campinas, vol. 27(3), pp.658-662, jul.-sep 2007.
3. Gre´ta Gergely , Ferenc We´ber , Istva´n Luka´cs , Attila L. To´th , Zsolt E. Horva´th ,Judit Miha´ly and Csaba Bala´zsi "*Preparation and characterization of hydroxyapatite from eggshell*" Ceramics International vol. 36, pp.803–806, 2010.
4. U.Anjaneyulu and S.Sasikumar "*Bioactive nanocrystaline wollastonite synthesized by sol–gel combustion method by using eggshell waste as calcium source"* Bull. Mater. Sci., vol. 37, No. 2, pp.207–212, April 2014.
5. D. Hirabayashi, T. Yoshikawa, K. Mochizuki, K. Suzuki, and Y. Sakai, **"***Formation of brownmillerite type calcium ferrite ($Ca_2Fe_2O_5$) and catalytic properties in propylene combustion"*, Catal Lett. vol. 110, pp.269-274, 2006.
6. Shuai An , Xueyan Liu, Lijun Yang and Lei Zhang, "Enhancement removal of crystal violet dye using magnetic calcium ferrite nanoparticle: Study in single- and binary-solute systems", vol 94, pp. 726–735, Feb 2015.
7. P. Shankar, Bhavyashri, R.S. Raveendra, A. Jayasheelan, C.S. Prakash, B.M. Nagabhushana, H. Nagabhushana and B. Daruka Prasad "*Synthesis, characterization and magnetic properties of CaFe2O4 nanoparticles by solution combustion method*" International journal of advanced scientific and technical research, vol. 1, Jan 2015.
8. Mojgan Jafari Pirouz, Mostafa Hossein Beyki and Farzaneh Shemirani, "*Anhydride functionalised calcium ferrite nanoparticles: A new selective magnetic material for enrichment*

of lead ions from water and food samples", Food Chemistry, vol 170, pp.131–137, March 2015.

9. R.A. Candeia, M.I.B. Bernardi, E. Longo, I.M.G. Santos and A.G. Souza "*Synthesis and characterization of spinel pigment CaFe2O4 obtained by the polymeric precursor method"* Materials Letters, vol 58, pp.569– 572, 2004.
10. Lavanya Khanna and N.K.Verma *"Size-dependent magnetic properties of calcium ferrite nanoparticles"* Journal of Magnetism and Magnetic Materials, vol. 336, pp.1–7, 2013.
11. H.I. Saleh, *"Synthesis and formation mechanisms of calcium ferrite compounds"*, Journal of Materials Science and Technology, vol. 20 (5), pp.530–534, 2004.
12. Sharma, K. M. Shaju, G. V. Subba Rao, and B. V. R. Chowdari, J. Power Sou, vol. 124, pp.204, 2003
13. T.G. Glover, D. Sabo, L. A. Vaughan, J. A. Rossin and Z. J. Zhang, Langmuir, vol. 28, pp.5695−5702, 2012.
14. N.B. Ashoka, B. E. Kumara Swamy, and H. Jayadevappa *" Synthesis, Characterization of Calcium Ferrite Nanoparticles and their Modified Carbon Paste Electrode for the Electrochemical Investigation of Dopamine in Presence of Uric Acid and Folic Acid"* Anal. Bioanal. Electrochem., vol. 7, No. 2, pp.197-209, 2015.
15. Lavanya Khanna and N.K.Verma "Biocompatibility and superparamagnetism in novel silica/$CaFe_2O_4$ nanocomposite", Materials letters, vol. 128, pp. 376–379, August 2014.
16. N.H. Sulaimana, M.J. Ghazalia,b, B.Y. Majlisb, J. Yunasb and M. Razalia *"Superparamagnetic calcium ferrite nanoparticles synthesized using a simple solgel method for targeted drug delivery"* Bio-Medical Materials and Engineering, vol 26 pp.103–110, 2015.
17. N. Rezlescu, E. Rezlescu, P.D. Popa, C. Doroftei and M. Ignat *"Comparative study between catalyst properties of simple spinel ferrite powders prepared by self-combustion route"* Romanian Reports in Physics, vol. 65, No. 4, pp.1348–1356, 2013.
18. Huei Ruey Ong, Md Maksudur Rahman Khan, Abu Yousuf, Nor Amalina Hussain and Chin Kui Cheng *"Synthesis and characterization of a $CaFe_2O_4$ catalyst for oleic acid esterification"* RSC Adv, vol. 5, pp.100362, 2015.
19. B. J. Madhu, M. Gurusiddesh, T. Kiran, B. Shruthi and H. S. Jayanna, "*Structural, dielectric, ac conductivity and electromagnetic shielding properties of polyaniline/$Ni_{0.5}Zn_{05}Fe_2O_4$*

composites", Journal of Materials Science: Materials in Electronics, vol. 27, pp.7760–7766, 2016.

LIST OF FIGURES