IOSR Journal of Applied Physics (IOSR-JAP)
e-ISSN: 2278-4861.Volume 10, Issue 2 Ver. III (Mar. – Apr. 2018), PP 52-56
www.iosrjournals.org

Synthesis and Characterization of Biopolymer capped Zinc ferrite nanoparticles by a thermal treatment method

D. O. Okoroh [1], S. O. Aisida[2*], P. U. Asogwa[2]
[1]*Federal College of education (Tech) Omoku, River state*
[2] *Department of Physics and Astronomy, University of Nigeria Nsukka, Nigeria*
**Correspondence Author: S. O. Aisida*

Abstract: *Zinc ferrite(ZF) nanoparticles was synthesized by the thermal treatment method, followed by calcination from zero to 500^0 C. The ZF was stabilized using polyvinyl alcohol (PVA) to prevent agglomeration. The ZF obtained was characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and Vibrating sample magnetometer (VSM). The XRD confirmed the good crystallinity of the sample with an average estimated crystalline size ranging from 5 to 14 nm.The SEM confirmed the morphology of the sample, with a less agglomeration for the higher concentration of the polymer and the annealed samples. The VSM confirmed the superparamagnetic nature of the sample capped with a polymer with an increase in saturation magnetization (SM) from 2.07 emu/g (un-annealed) to 6.56 emu/g (annealed). Consequently, surface encapsulation and calcination process of the ZF gave a more homogeneous size for various applications.*

Date of Submission: 14-04-2018 Date of acceptance: 30-04-2018

I. Introduction

Magnetic nanoparticles (MNPs) are a class of nanoparticle which can be controlled by an external magnetic field and often form the core of nano-biomaterial. Various types of metal and metallic oxide magnetic nanoparticles (MNPs) such as iron, silver, gold, copper Oxide and zinc oxide with variety of morphology are attracting increasing attention due to their capabilities and negligible side effects[1].

Their applications which span through*in vivo* and *in vitro* in different fields via (1) industries (magnetic energy storage [2], magnetic recording media, information storage and spintronics [3], magnetic toners in xerography, magnetic ink and paints [4], giant magneto-resistance (GMR) sensors, enhancing the capacity of magnetic storage devices such as magnetic tapes and computer hard disc [5]. (2) Agricultures [6, 7, 8] and (3) biomedicine (such as: diagnostics, therapeutics and theranostic e.g magnetic resonance imaging (MRI) contrast enhancement [9 - 15] magnetic fluid hyperthermia (MFH), immunoassay [16], drug delivery [17 - 21] are increasing daily due to their unique capabilities, negligible side effects [22, 23] and as a result of the advent of nanotechnology with much attention focusing on their physical, chemical and mechanical properties such as (optical, electrical/electronic, magnetic, strength, hardness and catalytic properties).

One of the most commonly studied MNPs is spinel ferrite (SF) nanocrystals a very important inorganic nanomaterials sequel to their optical, electronic, electrical and magnetic properties. SF belong to the class of oxides with exceptional magnetic properties. SF have the crystal structure of the natural spinel AB_2O_4 in which A and B display tetrahedral and octahedral cation sites respectively, and O indicates the oxygen anion site [24]. Generally, metal spinel ferrite nanoparticles (SFN) have the general molecular formula MFe_2O_4 (where M is a divalent cation of either Ni, Fe, Zn, Mn, Ni, Cr, Co or Mg) with a face-centered-cubic (fcc) close packing structure [25]. Ferrite nanoparticles composition can be strongly modified while the basic crystalline structure remains unchanged. Among the SFN, Zinc ferrite (ZF) ($ZnFe_2O_4$) has received enormous interest due to its high electromagnetic performance, excellent chemical stability, mechanical hardness, low coercivity and moderate saturation magnetization. All these enhanced it for various applications. A typical example of a ferrite is $Zn_xNi_{1-x}Fe_2O_4$ for $0 \leq x \leq 1$. When x = 0, we have Ni-Fe_2O_4 (inverse spinel) with ferromagnetic property and, when x = 1, we have Zn-Fe_2O_4 (normal spinel) with antiferromagnetic property.Variousinorganic synthetic methods have been used for the synthesis of ZFNPs, such as: hydrothermal [26], sol-gel [27], sputtering [28], microemusion [29], thermal decomposition [25, 30]and chemical co-precipitation [31].

This work employs the use of biopolymers as an effective capping agent which enhanced the biocompatibility and eco-friendly synthesis of ZFNPs. Many work has been reported about the uncoated and un-annealed properties of ZF, but the encapsulation of ZF under annealing has not been fully explored. Hence, this paper investigates the effect of the biopolymer and the annealing temperature to produce a nanometer sized on the structural stability, crystallization and magnetic properties of ZFNPs.

II. Materials and method

Materials

Iron nitrate Fe $(NO_3)_3.9H_2O$ (MW =404) and Zinc nitrate, Zn $(NO_3)_2.6H_2O$ (MW = 297.48), poly(vinyl alcohol) (PVA) (MW = 14000), were purchased from Sigma Aldrich and were used without further purification.

Preparation of Iron nitrate and Zinc nitrate

0.2mM of iron nitrate was dissolved in 100ml of distilled water (DW) and 0.1mM of Zinc nitrate was dissolved in 50mol of distilled water the combination was vigorously stirred with magnetic stirrer for 2 hours respectively to obtain a clear transparent solution. The mixed reaction was obtained in the ratio (Fe: Zn = 2:1) and stirred with magnetic stirrer for 2 hours to obtained a homogeneous solution.

Preparation of PVA

0.1g, 0.15g and 0.2g concentration of PVA was dissolved respectively in 100 ml DW at 90^0c and constantly stirred with magnetic stirrer for 2 h until a colorless, transparent solution was obtained

Biosynthesis of Zinc ferrite nanoparticles

Biosynthesis of ZF were performed usingIron nitrate and Zinc nitrate prepared in the ratio (Fe:Zn = 2:1) solution and slowly added into an aqueous solution of the biopolymer **(**PVA) and stirred continuously for 2h with a magnetic stirrer until a colourless, transparent solution was obtained. The mixture was poured into an evaporating dish and heat at 80^oC in an evaporating heater to evaporate the water and later transferred to the oven for 24h to complete the drying. The dried, orange, solid ZF that remained was crushed and ground in a mortar to form powder. The ZF powder and the biopolymer ZF powder were annealed at 500^0C for 3h to enhance the crystallinity of the nanocrystals and the decomposition of organic compounds.

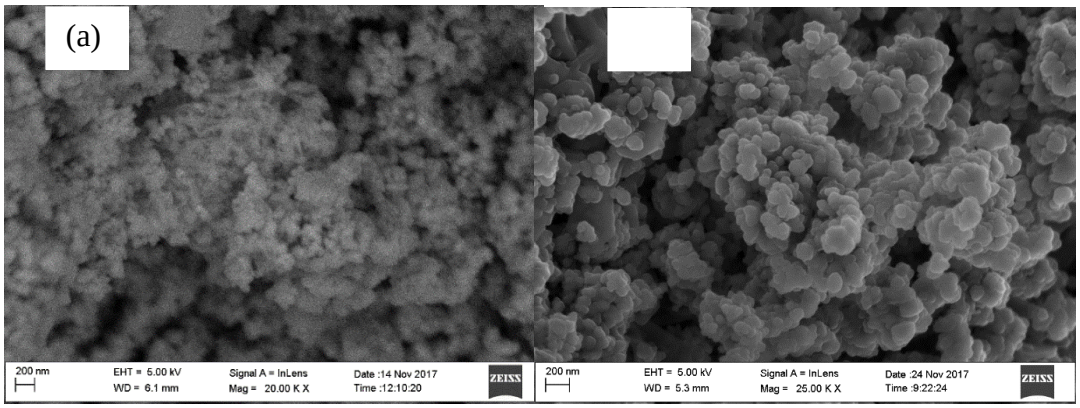
Characterization

The ZF encapsulated PVA was characterized using XRD, EDX, SEM, and VSM. The structure of the ZFNPs was analyzedusing powder crystalline samples at room temperature by the XRD technique employing a Shimadzu diffractometer model XRD 6000 using CuK_α (0.154nm) radiation in a 2θ range of 10^o - 80^o. The morphology of the samples was determined from SEM images that were obtained using JEOL_SEM1010 SEM instrument. The magnetization via hysteresis loop at room temperature were conducted using a vibrating sample magnetometer (VSM) (lake shore 4700) with a magnetic field range from -5 KOe to 5KOe.

III. Results and Discussion

SEM Micrograph Analysis

The SEM micrograph analysis shows the presence of nanoparticles with aggregation of un-annealed samples as shown in figure 1 (a) and (b) while the annealed (heat treatment) samples as shown in figure 1 (c) and (d) clearly exhibit low aggregation which decreases as the concentration increases. Hence, these micrographs showed that the microstructure of the materials was affected by the annealed temperature. Also, the EDX spectra shown in figure 1 (e) and (f) revealed the presence of iron, Zinc, oxygen and carbon in the respective samples with iron and zinc dominating an indication of the presence of ZF with a suitable atomic ratio of Fe/Zn to the stoichiometric value of ferrite chemical formulation.



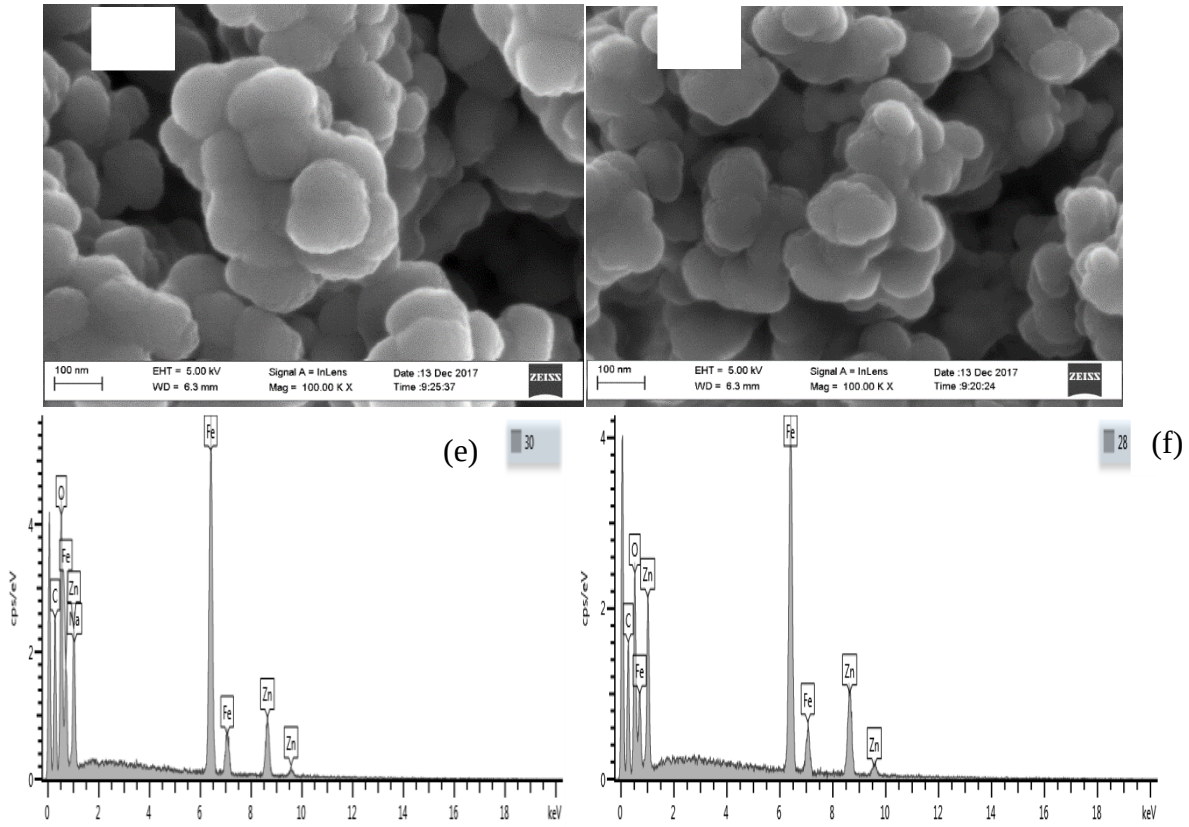


Figure 1. SEM images of Zinc ferrite nanoparticles capped with PVA Un-annealed (a) 0.1g (b) 0.2g and the annealed (c) 0.1g (d) 0.2g. The EDX images are shown in (e) 0.1g and (f) 0.2g

XRD graph analysis

The XRD diffraction patterns of the sample as prepared and the annealed samples are shown in the figure 2. The results revealed that the un-annealed samples show more of broad peaks with no sharp difraction patterns while the annealed samplesshow sharp diffraction peaks patterns with reflection plane (220), (311), (222), (511) and (440) an indication of face-centered cubic spinel structure a characteristic of nano-sized crystallites. The average particle diameter was analyzed by the Scherer formula:

$$\Omega = \frac{0.9\lambda}{\beta \cos\theta} \qquad (1)$$

Where Ω is the crystalline size (nm), β is the full width of the diffraction line (line broadning) at half the maximum intensity measured in radians, λ is the X-ray wavelength, θ is the Bragg angle and k is the Scherrer constant (shape factor), which is a dimensionless factor related to the shape of crystallites, with a value close to unity (~0.9) [32]. The average diameter estimated ranged from 5 to 14 nm with $5 \pm 1nm$ for B, $7 \pm 1nm$ for C, $10 \pm 1nm$ for D and $14 \pm 1nm$ for E samples. The annealed temperature influences the particle average size.

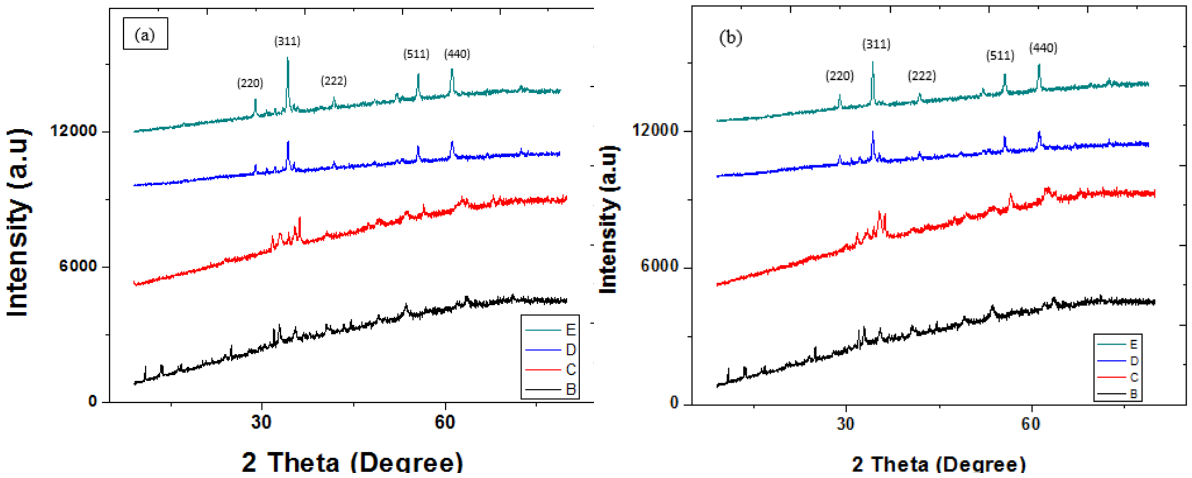


Figure 2. XRD patterns of ZF NPs (a) 0.1g and (b) 0.2gcalcined at 0 and 500^{0C} where (B is ZF only_unannealed, C is ZF capped PVA_unannealed, D is the ZF only_annealed and E is the ZF capped PVA_annealed)

VSM graph analysis

The magnetization curves of ZFNPs as prepared and annelled at 500^{o}C in the range of approximately -5 to +5 KOe was shown in figure 3.The coercivity fields (Hc) are almost negligible for the un-annealed sample while the annealed sample exhibit superparamagnetic behaviour with no remanence and coercivity values. The saturation magnetization increases from 2.07 to 6.56 for un-annealed and annealed samples respectively.This super paramagnetism made it suitable for biomedication applications such as drug delivery.

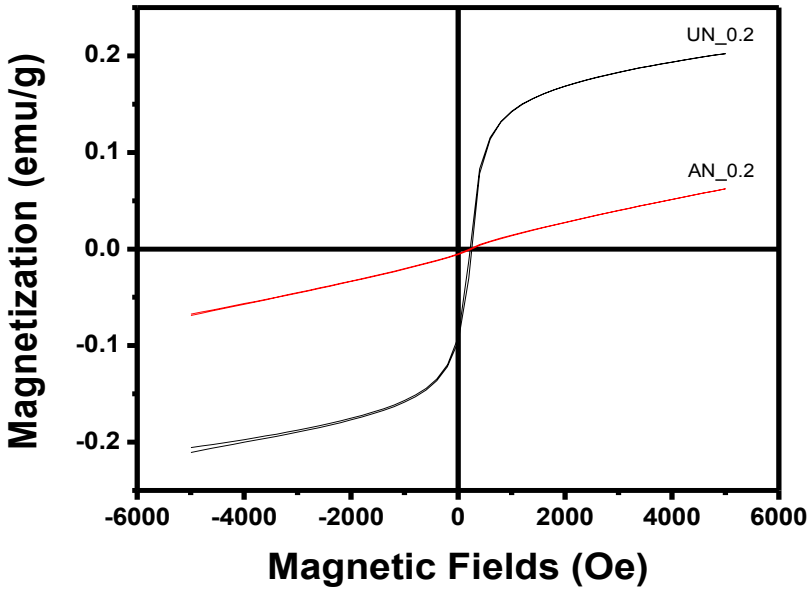


Figure 3. Magnetization curves for ZFNPs as prepared and at 500^{0C}

IV. Conclusion

A simple, environmentally benign and cost effective biopolymer thermal treatment procedure for ZFNPs capped with PVA was successfully synthesized. XRD, SEM, EDX and VSM were used to investigate the effect of polymer and annealing on the morphology, crystallinity and magnetic properties of ZF. The particle size was observed with an increase from 5nm to 14nm. The agglomeration was prevented by the application of capping agent (Biopolymers) and calcination temperature. Hence the agglomeration was reduced, creating a uniform and spherical particle size distribution sequel to the capping agent and the calcination temperature. The EDX confirmed the presence of Fe, Zn. O and C in the samples. The magnetic study analyzed by VSM gave a

good superparamagnetic behavior for the sample. This approach observed for the first time enhanced the properties ZFNPs for various applications.

References

[1]. Morteza, M., Shilpa, S., Ben, W., Sophie, L., & Sen, T. (2011). Superparamagnetic iron oxide nanoparticles (SPIONs): Development, surface modification and applications in chemotherapy. *Advanced Drug Delivery Reviews, 63*, 24-46.

[2]. Frey, N., Peng, S., Cheng, K., & Sun, S. (2009). Magnetic nanoparticles: Synthesis, functionalization, and application in bioimaging and magnetic energy storage. *Chem. Soc. Rev., 38*, 2532-2542.

[3]. Singamaneni, S., Bliznyuk, V., Binekc, C., & Tsymbalc, E. (2011). Magnetic nanoparticles: Recent advances in synthesis, self-assembly and applications. *J. Mater. Chem., 21*, 16819-16845.

[4]. Park, S., Kim, S., Lee, S., Khim, Z., Char, K., & Hyeon, T. (2000). Synthesis and magnetic studies of uniform iron nanorods and nanospheres. *J Am Chem Soc., 122*, 8581–8582.

[5]. Skumryev, V., Stoyanoy, S., Zhang, Y., Hadjipanayis, G., Givord, D., & Nogues, J. (2003). Beating the superparamagnetic limit with exchange bias. *Nature, 423*, 850-853.

[6]. Rai, M., & Ingle, A. (2012). Role of nanotechnology in agriculture with special reference to management of insect pests. *Appl Microbiol Biotechnol, 94*, 287–293.

[7]. Mohammadinejad, R., Karimi, S., Iravani, S., & Varma, R. (2016). Plant-derived nanostructures: types and applications . *Green Chem, 18*, 20.

[8]. Siddiqi, K., & Husen, A. (2016). Engineered gold nanoparticles and plant adaptation potential. *Nano Res Lett., 11*, 400.

[9]. Larsen, B. A., Haag, M., Serkova, N., Shroyer, K., & Stoldt, C. (2008). Controlled aggregation of superparamagnetic iron oxide nanoparticles for the development of molecular magnetic resonance imaging probes. *Nanotechnology, 19*.

[10]. Zhu, D., Liu, F., Ma, L., Liu, D., & Wang, Z. (2013). Nanoparticle-based systems for T1-weighted magnetic resonance imaging contrast agents. *Int. J. Mol. Sci., 14*, 10591-10607

[11]. Kessinger, C. W., Togao, O., Khemtong, C., Huang, G., Takahashi, M., & Gao, J. (2011). Investigation of in vivo targeting kinetics of alpha (v) beta (3)-specific superparamagnetic nanoprobes by time-resolved MRI. *Theranostics., 1*, 263-73.

[12]. Khemtong, C., Kessinger, C. W., Ren, J. M., Bey, E. A., Yang, S. G., & Guthi, J. S. (2009). in vivo off-resonance saturation magnetic resonance imaging of alpha(v)beta(3)-targeted superparamagnetic nanoparticles. *Cancer Res., 69*, 1651-1658.

[13]. Reimer, P., & Weissleder, R. (1996). Development and experimental application of receptor-specific MR contrast media. *Radiology, 36*, 153–163.

[14]. Chouly, C., Pouliquen, D., Lucet, L., Jeune, J. J., & Jallet, P. (1996). Development of superparamagnetic nanoparticles for MRI: Effect of particle size, charge and surface nature on biodistribution. *J. Microencapsulation, 13*, 245–255.

[15]. Weissleder, R., Bogdanov, A., Neuwelt, E. A., & Papisov, M. (1995). Longcirculating iron oxides for MR imaging. *Adv. Drug Delivery Rev., 16*, 321–334.

[16]. Zhang, G., Liu, Y., Zhang, C., Hu, W., Xu, W., Li, Z., . . . Wang, Y. (2009). Aqueous immune magnetite nanoparticles for immunoassay. *J. Nanopart. Res., 11*(2), 441–448.

[17]. Salata, O. (2004). Applications of nanoparticles in biology and medicine. *Journal of Nanobiotechnology, 2*, 3.

[18]. Guthi, J. S., Yang, S. G., Huang, G., Li, S., Khemtong, C., & Kessinger, C. W. (2010). MRI-visible micellar nanomedicine for targeted drug delivery to lung cancer cells. *Mol Pharm, 7*, 32-40.

[19]. Nasongkla, N., Bey, E., Ren, J., Ai, H., Khemtong, C., & Guthi, J. S. (2006). Multifunctional polymeric micelles as cancer-targeted MRI-ultrasensitive drug delivery systems. *Nano Lett., 6*, 2427-2430.

[20]. Jain, T., Morales, M., Sahoo, S., Leslie-Pelecky, D., & Labhasetwar, V. (2005). Iron oxide nanoparticles for sustained delivery of anticancer agents. *Mol Pharm, 2*, 194–205.

[21]. Gupta, P. K., & Hung, C. T. (1989). Magnetically controlled targeted microcarrier systems. *Life Sci., 44*, 175–186.

[22]. Jurgons, R., Seliger, C., Hilpert, A., Trahms, L., Oden-bach, S., & Alexiou, C. (2006). Drug loaded magnetic nanoparticles for cancer therapy. *J Phys: Cond Mat, 18*, S2893–S2902.

[23]. Ai, H., Flask, C., Weinberg, B., Shuai, X. T., Pagel, M. D., Farrell, D., . . . Gao, J. (2005). Magnetite-loaded polymeric micelles as ultrasensitive magneticresonance. *probes. Adv Mat, 17*, 1949–1952.

[24]. Bragg, W. H. (1915). The structure of the spinel group of crystals. *Philosophical Magazine, 30*(176), 305–315.

[25]. mahmoud, G. N., Elias, B. S., Mansor, H., & Abdul, H. S. (2011). Synthesis and characterization of Zinc ferrite nanoparticles by a thermal treatment method. *Solid state communications, 151*, 1031-1035.

[26]. Yu, S.-H., Fujino, T., & Yoshimura, M. (2003). *J. Magn. Magn. Mater. , 256*, 420.

[27]. Ho, J. C., Hamdeh, H. H., Chen, Y. Y., Lin, S., Yao, Y. D., Willey, R. J., & Oliver, S. A. (1995). *Phys. Rev. B , 52*, 10122.

[28]. Nakashima, S., Fujita, K., Tanaka, K., & Hirao, K. (2005). *J. Phys.: Condens. Matter, 17*, 137.

[29]. Grasset, F., Labhsetwar, N., Li, D., Park, D., Saito, N., Haneda, H., . . . Etourneau, J. (2002). *Langmuir , 18*, 8209.

[30]. Wu, W., He, Q., & Jiang, C. (2008). Magnetic iron oxide nanoparticles: synthesis and surface functionalization strategies. *Nanoscale Res. Lett., 3*, 397–415.

[31]. Laurent, S., Forge, D., Port, M., Roch, A., Robic, C., Vander, E. L., & Muller, R. (2008). Magnetic iron oxide nanoparticles: synthesis, stabilization, vectorization, physicochemical characterizations, and biological applications. *Chem. Rev., 108*, 2064–2110.

[32]. Cullity, B. (1978). *Element of X-ray Diffraction* (2nd ed.). Addison-Wesley, London.

S. O. Aisida "Synthesis and Characterization of Biopolymer capped Zinc ferrite nanoparticles by a thermal treatment method." IOSR Journal of Applied Physics (IOSR-JAP) , vol. 10, no. 2, 2018, pp. 52-56.