



## Comparative Study of Magnetic Nanoparticles Synthesized ( $\text{Fe}_3\text{O}_4$ ) By 1, 2, 3-Tri Substituted Stereoisomeric Imidazolium Ionic Liquids and its Anti-Oxidant Properties

Rajathi K<sup>1\*</sup>, Chandran P<sup>1</sup>, Sridhar S<sup>2</sup>

<sup>1</sup>Department of Chemistry, Government Arts College, Tamil Nadu, India

<sup>2</sup>Department of Botany, Government Arts College, Tamil Nadu, India

### ABSTRACT

Nanotechnology is a growing field that has contributed to all areas of human life. The conventional synthesis of nanoparticles is complicated and suffers from serious problems such as high temperature, low yield, long reaction time, and the use of highly sensitive and toxic compounds. The green synthesis of nanoparticles has revealed better methods and approaches in the field of medicine. This article studies the synthesis of stable  $\text{Fe}_3\text{O}_4$  nanoparticles by co-precipitation method using two stereoisomeric ionic imidazolium liquids as green solvents. The synthesized nanoparticles were characterized by UV-visible spectroscopy, Fourier transforms infrared (FT-IR) spectroscopy, X-ray diffraction (XRD) analysis, Transmission Electron Microscopy (TEM), Energy-dispersive X-ray spectroscopy (EDX) analysis and magnetization measurements. The functional groups present in  $\text{Fe}_3\text{O}_4$  nanoparticles were examined by FT-IR study. The formation of  $\text{Fe}_3\text{O}_4$  nanoparticles has been confirmed through UV-visible spectroscopy by the change of colour owing to surface Plasmon resonance. X-ray diffraction (XRD) and transmission electron microscopy (TEM) were used to characterize the size, crystalline nature and morphology of the synthesized  $\text{Fe}_3\text{O}_4$  nanoparticles. The magnetic nature of the synthesized particles was found by magnetization measurements. Moreover, the synthesized nanoparticles ( $\text{Fe}_3\text{O}_4$ ) were also screened for their antioxidant activities. From the experimental results, it has been examined that the size of the particles plays a vital role in Anti-Oxidant properties.

**Keywords:** Antioxidant properties; EDX analysis;  $\text{Fe}_3\text{O}_4$  nanoparticles; Stereoisomeric imidazolium ionic liquids;

Transmission electron microscopy

### INTRODUCTION

Nanotechnology is developing very rapidly due to the unique physical and chemical properties of nanoparticles (NPs) compared to bulk solids. Magnetic Iron Oxide (MNP) nanoparticles have received a great deal of research interest in recent years due to their inherent properties such as large area and rapid response under an applied external magnetic field, superparamagnetism, force high coercive and low temperature [1-3]. Moreover, magnetic nanoparticles (MNPs) have potential applications in materials science and biomedicine. MNPs can be functionalized by modifying their surfaces with different materials to achieve specific goals. Recently, shell-core MNPs coated

with carbon, aluminum oxide and surfactants have been used to preconcentrate inorganic/organic contaminants in environmental and biological samples [4]. On the other hand, recent studies show that magnetic nanoparticles are excellent catalysts for organic reactions [5-7]. Besides, the magnetic properties compete with the recovery of the catalyst using an external magnetic field. These advantages are even more interesting when such reactions can be carried out in an aqueous medium. Imidazole derivatives are a very interesting class of heterocyclic compounds because they have many pharmacological properties and play important roles in biochemical processes [8,9]. In recent years the synthesis of 2,4,5-trisubstituted imidazoles [10,11] and 1,2,4,5-tetrasubstituted imidazoles [12-14] have been performed and used as a catalyst in many reactions.

In this study, we employed stereoisomeric imidazolium ionic liquid as a solvent for the synthesis of  $\text{Fe}_3\text{O}_4$  nanoparticles and investigated the role of these solvents in the yields, sizes, morphologies, magnetic nature and anti-oxidant properties.

## MATERIALS AND METHODS

All AR grade 1-Methylimidazole, 1-Bromobutane, Bromoethane, Sodium hydride, Acetonitrile, Ether, Dichloromethane, Ethyl acetate, Ethanol, Sodium hydroxide, Hydrochloric acid, Ferrous sulfate, Ferric chloride, De-ionized water were purchased from Merck, SD Fine chemicals limited, Sigma Alrich and used without further purification. The homogeneity of the products was checked on TLC plates coated with silica gel-G and visualized by exposure to iodine vapors.

### Synthesis of $\text{Fe}_3\text{O}_4$ Nanoparticles

The ILs used in this study were synthesized according to the procedures reported in the journalism [15]. The precipitation technique is the easiest way to get iron oxide ( $\text{Fe}_3\text{O}_4$ ) particles. Iron oxide nanoparticles were made by adding 0.01 mole of ionic liquid, 0.04 mole of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  and 0.02 mole of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  in 50 ml of 0.5 M HCl solution and then the solution was stirred vigorously for uniform dissolution at  $80^\circ\text{C}$  in Figure 1a and 1b. Then 500 ml of 1.5 M NaOH were added drop-wise to the stirring solution. The  $\text{Fe}_3\text{O}_4$  precipitate obtained was separated off with a magnet and washed several times with de-ionized water. Finally, the precipitant was dried at  $50^\circ\text{C}$  for 8 hours for further characterization. The anti-oxidant studies were performed according to Oyedemi et al. methodology [16].

## RESULTS AND DISCUSSION

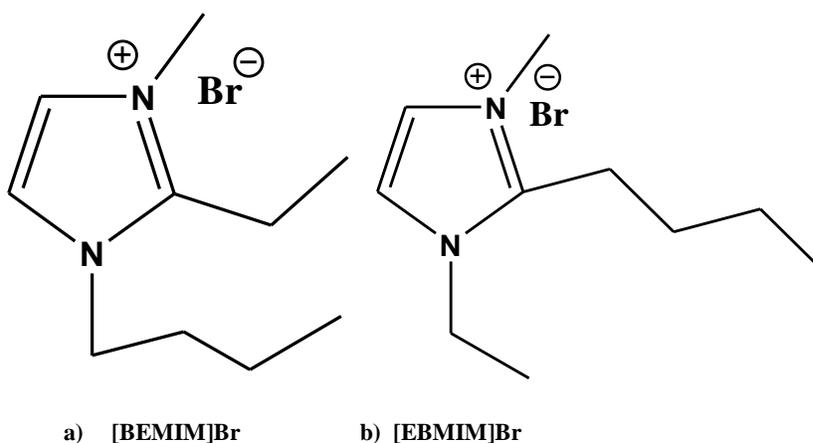


Figure 1: Stereoisomeric imidazolium ionic liquids

### The FT-IR Studies

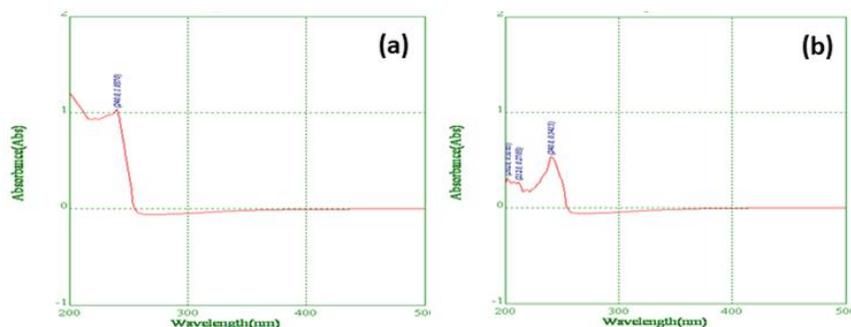
The assignments of the main peaks in the FT-IR spectra of Fe<sub>3</sub>O<sub>4</sub> nanoparticles synthesized by stereoisomeric ionic liquids are presented in Table 1. The above results show that the presence of the same substituents at different positions on the imidazolium ring of ionic liquid solvent did not produce remarkable changes in the absorbed frequencies of the synthesized Fe<sub>3</sub>O<sub>4</sub> nanoparticles.

**Table 1: Interpretation of FT-IR spectrum of Fe<sub>3</sub>O<sub>4</sub> nanoparticle synthesized by ILs**

Peak Assignment	Frequencies of absorption bands, cm-1 of Fe <sub>3</sub> O <sub>4</sub> nanoparticle (IL-1)	Frequencies of absorption bands, cm-1 of Fe <sub>3</sub> O <sub>4</sub> nanoparticle (IL-2)
Fe-O stretching Frequency	559	558
-C=N-, stretching Frequency	1588	1549
C-H stretching Frequency	2920	2921

### UV Studies

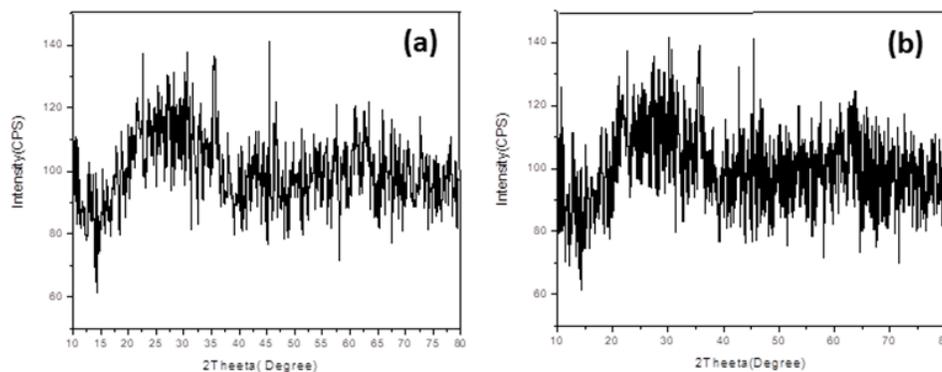
The formation and stability of iron oxide nanoparticles in an aqueous colloidal solution is confirmed by UV-Visible spectral analysis. The IL was mixed with a solution of FeCl<sub>3</sub>•6H<sub>2</sub>O and FeSO<sub>4</sub>•7H<sub>2</sub>O, causing the solution to change from brown to black due to the formation of iron oxide nanoparticles. The colour changes come from the excitation of the surface plasma resonance phenomenon (SPR), typically from iron oxide nanoparticles [17]. The optical absorption spectrum of metallic nanoparticles depends on the particle size, shape, state of matter and the surrounding dielectric medium [18]. The absorption spectrum obtained showed a strong surface plasmon resonance band maximum at 240 nm (Figure 2a and 2b), a characteristic peak of Fe<sub>3</sub>O<sub>4</sub> nanoparticles.



**Figure 2: UV spectrum of Fe<sub>3</sub>O<sub>4</sub> nanoparticle synthesized by (a) [BEMIM] Br (IL-1) AND (B) [EBMIM] Br (IL-2)**

### XRD Analysis

Figure 2 shows the XRD diffraction patterns of the produced MNPs. In Figure 3, the weak diffraction peaks at  $2\theta$ ; 21.74°, 35.54° and 60.82° were observed for Fe<sub>3</sub>O<sub>4</sub> synthesized by IL-1, indicating that the Fe<sub>3</sub>O<sub>4</sub> particles have an amorphous structure. All reflection peaks could be indexed for Fe<sub>3</sub>O<sub>4</sub> (JCPDS # 82-1533) on the face-centered cubic (FCC).

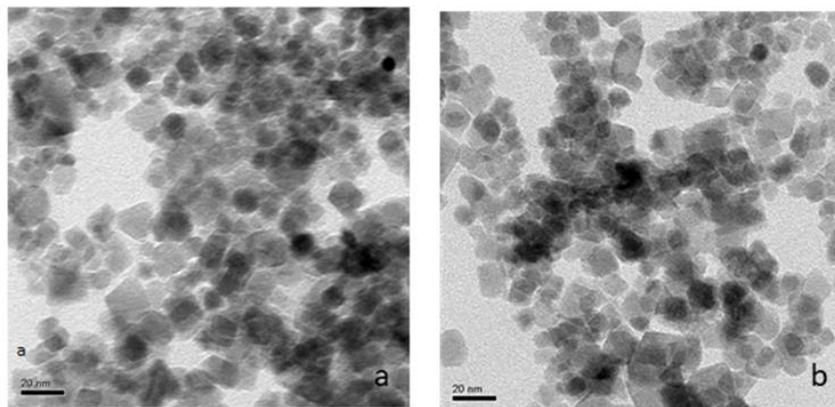


**Figure 3: The powder XRD pattern of  $\text{Fe}_3\text{O}_4$  nanoparticle synthesized by (a) [BEMIM] Br (IL-1) and (b) [EBMIM] Br (IL-2)**

Figure 2b is the XRD model of  $\text{Fe}_3\text{O}_4$  MNs using IL-2. It is clear that the two peaks of these patterns correspond to the values of the standard JCPDS values (file no 89-0950) and it has a face-centered cubic structure. Furthermore, this corresponds to the pattern of the  $\text{Fe}_3\text{O}_4$  nanoparticles synthesized by IL-1. Indeed, the same substitution at different positions on the solvent imidazolium ring did not change the structure of the as-synthesized  $\text{Fe}_3\text{O}_4$  nanoparticles, but rather influenced the size of the nanoparticles. Moreover, the crystal size of the synthesized nanoparticles was calculated from the Debye-Scherrer equation  $D = K\lambda / \beta \cos\theta$ . Where D is the crystallite size of iron oxide nanoparticles,  $\lambda$  is the wavelength of the X-ray source (0.1541 nm),  $\beta$  is the full width at half maximum of the diffraction peak, K is the Scherrer constant with a value of 0.9, and  $\theta$  is the half diffraction angle-Bragg angle. The average crystal size of the iron oxide nanoparticle was found to be 8.48 nm for IL-1 and 28.68 nm for IL-2.

### TEM Analysis

The morphologies and dispersity of synthesized nanostructured  $\text{Fe}_3\text{O}_4$  samples by ionic liquids were investigated by Transmission electron microscope (TEM). A typical transmission electron microscope (TEM) image of  $\text{Fe}_3\text{O}_4$  nanoparticles derived from IL-1 and IL-2 are presented in Figure 4a and 4b. Analysis of the micrographs indicates that the morphology of the nanoparticles was a cubic shape with smooth surfaces. The obtained nanoparticles were in the range of sizes approximately 7-10 nm. From the results, it has been learned that the position of substituents on the imidazolium ring did not play a vital role in the morphologies of nanoparticles. But it plays an important role in size determination.  $\text{Fe}_3\text{O}_4$  nanoparticles synthesized by [BEMIM] Br gave particles with a smaller size than [EBMIM] Br.



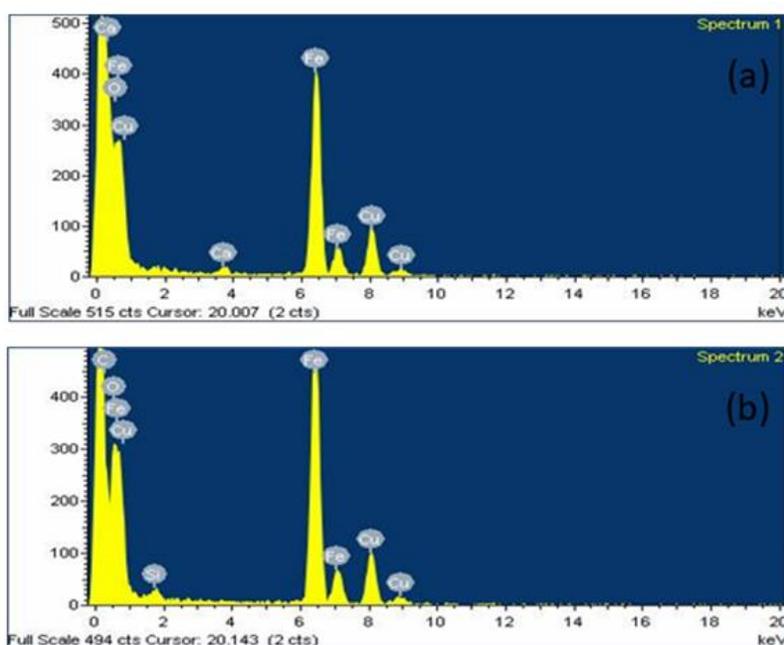
**Figure 4: TEM images of Fe<sub>3</sub>O<sub>4</sub> nanoparticle synthesized by (a) [BEMIM] Br (IL-1) and (b) [EBMIM] Br (IL-2)**

### EDX Pattern

The purity and composition of the products (Fe<sub>3</sub>O<sub>4</sub> nanoparticles synthesized by [BEMIM]Br and [EBMIM]Br) were studied quantitatively and qualitatively by energy-dispersive X-ray spectroscopy (EDX). The results are displayed in Figure 5a and 5b. Only iron and oxygen signals are observed in the spectral studies. It implies that the nanoparticles are made up of only Fe and O. It is clear that the Fe<sub>3</sub>O<sub>4</sub> nanoparticles prepared were sufficiently pure. The other peak in the figure, which corresponds to copper and carbon, was due to the carrier material and was not taken into account in the elementary analysis of the products.

**Table 2: EDX weight ratio of Fe<sub>3</sub>O<sub>4</sub> nanoparticles synthesized by [BEMIM] Br and [EBMIM] Br**

Compound	Fe		O	
	Weight %	Atomic %	Weight %	Atomic %
Fe <sub>3</sub> O <sub>4</sub> nanoparticles by [BEMIM] Br	66.68	53.81	10.44	29.41
Fe <sub>3</sub> O <sub>4</sub> nanoparticles by [EBMIM] Br	61.8	38.52	8.92	19.41

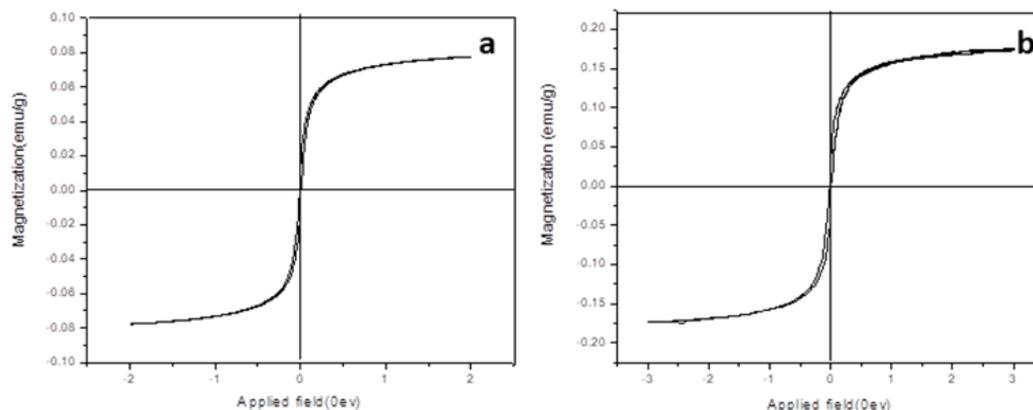


**Figure 5: EDX pattern of Fe<sub>3</sub>O<sub>4</sub> nanoparticle synthesized by (a) [BEMIM] Br (IL-1) and (b) [EBMIM] Br (IL-2)**

The details of the two EDX spectra of the electrospun values, measured in atomic and weight %, are shown in Table 2. From the EDX spectrum and Table 2 results, it has been confirmed that, compared to [EBMIM]Br ionic liquid, Fe<sub>3</sub>O<sub>4</sub> nanoparticles synthesized by [BEMIM]Br ionic liquid, gave quantitatively good yield. The spectral result is very much agreed with the preparation yield.

### Magnetization Measurements

The magnetization curve of the  $\text{Fe}_3\text{O}_4$  nanoparticles is shown in Figure 6. The graphs of magnetization versus magnetic field (MH loop) at  $250^\circ\text{C}$  obtained with a superconducting interference device (SQUID) showed a very low hysteresis value in the two  $\text{Fe}_3\text{O}_4$  nanoparticles (Figures 5a and 5b), which indicates that the MNPs were superparamagnetic.

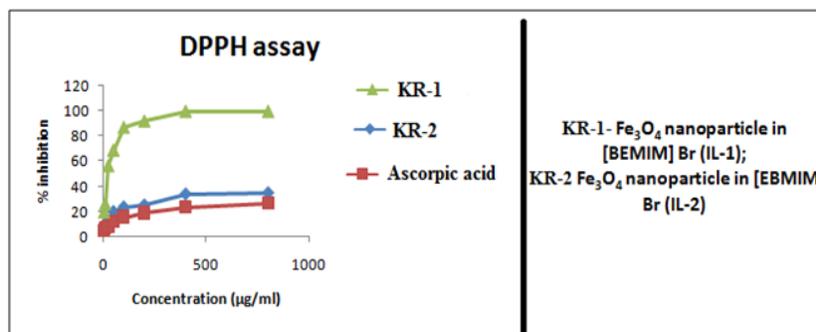


**Figure 6: Magnetization of  $\text{Fe}_3\text{O}_4$  nanoparticle synthesized by (a) [BEMIM] Br (IL-1) and (b) [EBMIM] Br (IL-2)**

Measurements of the specific magnetization curve at room temperature ( $M$ ) against the applied magnetic field ( $H$ ) of the sample show a magnetization saturation value ( $M_s$ ) of  $64.60 \text{ emu g}^{-1}$ . We can also see that the magnetization curve follows a Langevin behaviour in the applied magnetic field and the coercive force ( $H_C$ ) can be ignored, which can be seen as superparamagnetism [19].

### Anti-Oxidant Study (DPPH Radical Scavenging Activity)

DPPH radical scavenging assay report of  $\text{Fe}_3\text{O}_4$  nanoparticles by ILs are shown in Figure 7. The synthesized nanoparticles (KR-1, KR-2) by both ILs are more active in comparison with standard drug ascorbic acid. When compared among the nanoparticles, nanoparticles synthesized by IL-1 is more active than nanoparticles by IL-2. From the XRD report, it has been inferred that nanoparticles synthesized by IL-1 were small in size than by IL-2. Moreover, if the size of the particles is smaller, the larger will be the surface area available for the reaction site. Because of the above-said reason, nanoparticles synthesized by IL-1 is more active than by IL-2.



**Figure 7: Comparison of anti-oxidant properties of standard drug and synthesized Fe<sub>3</sub>O<sub>4</sub> nanoparticles in ILs**

### CONCLUSION

In conclusion, we have described a simple, efficient and greener methodology for the synthesis of Fe<sub>3</sub>O<sub>4</sub> nanoparticles by stereoisomeric solvents. The synthesized nanoparticles (Fe<sub>3</sub>O<sub>4</sub>) were examined by various techniques. From the various characterization studies such as FT-IR, UV, XRD, TEM and Magnetization studies it has been confirmed that the as-synthesized Fe<sub>3</sub>O<sub>4</sub> nanoparticles by stereoisomeric solvents did not show any vast variation in their absorbed frequencies, crystalline nature, morphology and magnetic nature. Instead, it affects only the size and antioxidant activities of the nanoparticles. Nanoparticles synthesized by IL-1 had smaller in size compared to IL-2. Moreover, its antioxidant activity had higher for nanoparticles synthesized by IL-1. This is because as particle size decreases, the surface area per unit volume increases.

### REFERENCES

- [1] Morel AL, Nikitenko SI, Gionnet K, et al. J American Chemical Society. 2008; 2, 847-856.
- [2] Wei Y, Han B, Hu X, et al. Elsevier. 2012; 27, 632-637.
- [3] Kim YS, Kim YH. IAEA. 2003; 267, 105-110.
- [4] Li Y, Tang N, Inagaki F, et al. J Chem. 2013; 1, 1-7.
- [5] Hu A, Yee GT, Lin W. J American Chemical Society. 2005; 127(36), 12486-12487.
- [6] Senapati KK, Borgohain C, Phukan P. J Molecular Catalysis. 2011; 339, 24-31.
- [7] Lim CW, IS Lee. J Chem. 2010; 5(5), 412-434.
- [8] A Puratchikody and M Doble. Bio med chem. 2007; 15, 1083-1090.
- [9] Safari J, Khalili SD, Rezaei M, et al. J Pharm. 2010, 141, 1339-1345.
- [10] Sharma GVM, Jyothi Y, Lakshmi SP. J Che. 2006, 36, 2991-3000.
- [11] Wang L, Cai C. J Sem Scholar. 2009; 140, 541-546.
- [12] Kantevari S, Vuppapapati SVN, Biradar DO. and L Nagarapu. J Molecular Catalysis. 2007; 266, 109-113.

- [13] Heravi MM, Derikvand F, Bamoharram FF. *J Molecular Catalysis*. 2007; 263, 112-114.
- [14] Sadeghi B, Mirjalili BBF, Hashemi MM. *Sci Res*. 2008; 49(16), 2575-2577.
- [15] Rajathi K, Rajendran A. *J Chem*. 2013; 2(1), 36-41.
- [16] Oyedemi SO, Afolayan AJ. *J tropical med*. 2011; 4(2), 952-958.
- [17] Shankar SS, Rai A, Ankamwar B. *Nature Materials*. 2004; 3, 482-488.
- [18] Petla RK, Vivekanandhan S, Misra M. *J nanobiotechnology*. 2012; 3, 14-19.
- [19] Jiang Y, Gao JQ, Ruan M, et al. *Nanotechnology*. 2008; 19, 75714-75719.