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Green Synthesis of Fe_3O_4, ZnO & Fe_3O_4-ZnO NP's Stabilized by a Lemon Fruit (Citrus limon) Peel Extract for Antioxidant Activity

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ABSTRACT

Now a days, nano materials have replaced all other materials in every field because of their unique physical and chemical properties, which facilitate extraordinary applications. That's why finding the most convenient way for the synthesis is very important, so in the process, researchers found the simplest way for the synthesis to be the "Green method or biological method". It is the most rapid, simple, cheap, and eco-friendly way among all the chemical and physical methods [1]. In this present work, the Fe3O4, ZnO, and Fe3O4-ZnO NPs were synthesised by the Green method using lemon fruit peel extract as a stabilizing agent [2]. The synthesised NPs were characterised by UV-VIS, FTIR, XRD, TGA, and SEM techniques. And further, the antioxidant activity of all prepared NPs [3] was studied.

Keywords: Green Synthesis: Metal Oxide NP's, Antioxidant property

1. INTRODUCTION

NPs are those whose at least one dimension should be smaller than 100nm. By virtue of their larger surface area, they have unique physical and chemical properties [4], and their nanosize facilitates cellular and molecular-level biological interactions [5]. In recent decades, nanotechnology has occupied most all fields. Especially metal oxide NPs have drawn greater interest as they have shown remarkable applications to various fields such as the medical field, pharmaceuticals, diagnosis, anticancer, antibiotics, drug delivery, cell therapy, tissue engineering, hyperthermia, etc. [6]. In agriculture fields [7], in sensing fields to sense poisonous gases [8], and as a catalyst in waste water treatment [9]. In the research field, efforts are going on to enhance solubility, bioavailability, stability, suppress toxicity, and improve pharmacological activity [10]. Due to their wide range of applications, determining the most convenient method for the synthesis of NPs is very important. As such, we have physical, chemical, and biological methods for synthesis, but physical and chemical methods are generally expensive, require much energy, and use toxic and hazardous chemicals, the residuals of which pose a threat to the environment [11]. To overcome these limitations and disadvantages, synthesis recently introduced a biological method (green synthesis), which is simple, low-cost, eco-friendly, and requires less time and energy [12].

This method uses natural organisms (bacteria, algae, viruses, etc.) or plant extracts as they contain proteins, enzymes, amino acids, carbohydrates, alkaloids, terpenoids, tannins, saponins, phenol compounds, sugar, and vitamins. They act as stabilising, reducing, and capping agents [13] and have the capability to control the size and shape of the NPs [14].

Here, the lemon fruit peel is used for synthesis. The lemon plant can be grown in California. West Indies, Italy, Spain, Sicily, Portugal, Florida, California, Jamaica, Australia, and grown all over India, particularly in home gardens and small orchards. Lemon peel contains volatile oil (2.5%), vitamin C, hesperidin and other flavone glycosides, mucilage, pectin, and calcium oxalate [15]. The important constituents of the volatile oil are limonene (90%), citronellal, geranyl acetate, -pinene, camphene, linalool, terpineol, methyl heptenone, octyl and nonyl aldehydes, -terpinene, -pinene, neral, and geranial [16]. The peels also contain the flavonoids eriocitrin, epigenin, luteolin, chrysoeriol, quercetin, isorhamnetin, limocitrin, limocitrol, isolimocitrol, hesperidin, coumarins scopoletin and umbelliferone, sinapic acid, and -coumaric acid [17]. Lemon peel is used as a flavouring agent, perfume, stomachic, and carminative. Externally, the oil is a strong rubefacient, and if taken internally in small doses, it has stimulating and carminative properties [18].

2. Materials and Methodology :

2.1 Materials :

Lemons were collected from the local market Shivamogga, Karnataka, India. The $FeCl_3.6H_2O$, $FeCl_2.4H_2O$, $Zn(NO_3)_2$ $3H_2O$ and 2,2-Diphenyl-1-1-Picryllhydrazyl (DPPH) were procured from Sigma-Aldrich, India. Ethanol and acetic acid were purchased from SD-fine Chemicals, India. Double distilled water will be used throughout the experiment. Chemicals and compounds used are analytical grade and used directly as received without further purification.

2.1.1 Preparation of Lemon Fruit Peel Extract

The extract of Lemon fruit peel was obtained using a reported method. Briefly, the fruit peels were washed several times to remove dust, followed by drying at ambient temperature. A total of 10 g of the fruit peel was ground and mixed with 100 ml of double deionised water at 80°C using an oil bath under constant stirring at 250 rpm for 1 h. The crude extract solution (10 mV) was filtered with filter paper (Fioroni 601) and oven-dried at 45°C for 24 h. The dried extract powder was termed S5 and stored at 4°C for further processing.

2.1.2 Green Synthesis of Fe_3O_4 NPs by Lemon Fruit Peel Extract:

A simple co-precipitation method and the extract of Lemon fruit peel as a novel stabilising and capping agent were used to synthesise Fe_3O_4 NPs. The crude extract of Lemon fruit peel and iron salts are used as stabilisers, iron sources, and reducing agents, respectively. Four different extract solutions (wt.%) were prepared. In total, 1, 2, 5, and 10 g of the dried extract powder were added into four different beakers containing, respectively, 99, 98, 95, and 90 g of double deionised water and stirred for 15 minutes at room temperature. $FeCl_3.6H_2O$, 97% (2.53 g), and $FeCl_2.4H_2O$, 99% (0.99 g), at a molar ratio of 2:1, respectively, were added to each solution. After that, Fruit peel extract (11.2 pH) was drop wise added into the respective solutions to adjust the pH to 11, followed by vigorous stirring for another 30 min. Finally, the samples were centrifuged three times at 14,000 rpm for 12 min, and the collected precipitates were oven-dried at 70°C. The same procedure without using the extract was carried out for the preparation of bare Fe_3O_4 NPs. The synthesised Fe_3O_4 NPs with 0, 1, 2, 5, and 10 wt.% concentrations of the peel extract were termed S0, S1, S2, S3, and S4, respectively, and the peel extract powder alone was termed S5.

2.1.3 Green Synthesis of ZnO NPs by Lemon Fruit Peel Extract:

Finely cut fruit peels were dried into a 40-gramme powder that was soaked with 100 ml of deionised water and boiled for 50 minutes until the colour of the aqueous solution changed from watery to light yellow. The mixture was then filtered to obtain aqueous leaf extract and boiled to 60–80 ^{0}C with stirring. To this was added 2 g of copper nitrate trihydrate [$Zn(NO_3)_2$ $3H_2O$] in 100 ml of deionised water under vigorous stirring until black precipitate separated. After the formation of NPs, stop stirring and leave the precipitate to settle. Filter and repeatedly wash with deionised water and absolute ethanol for several times until pH reaches 7. Subsequently, washed material is dried at 80 °C for 16 h in an oven, followed by calcination at 500 °C for 4 h

2.1.4 Green Synthesis of ZnO NPs by Lemon Fruit Peel Extract:

Finely cut fruit peels were dried into a 40-gramme powder that was soaked with 100 ml of deionised water and boiled for 50 minutes until the colour of the aqueous solution changed from watery to light yellow. The mixture was then filtered to obtain aqueous leaf extract and boiled to 60–80 ^{0}C with stirring. To this was added 2 g of iron chloride hexahydrate [FeCl3. 6H2O] and copper nitrate trihydrate [$Zn(NO_3)_2$ $3H_2O$] in a 1:1 molecular ratio and 100 ml of deionised water under vigorous stirring until black precipitate separated. After the formation of NPs, stop stirring and leave the precipitate to settle. Filter and repeatedly wash with deionised water and absolute ethanol for several times until pH reaches 7. Subsequently, washed material is dried at 80 °C for 16 h in an oven, followed by calcination at 500 °C for 4 h.

2.2 Ultraviolet-visible Spectroscopy (UV-Vis):

Ultraviolet-visible spectroscopy (UV-Vis) refers to absorption spectroscopy in the UV-Vis spectral region. This means it uses light in the visible and adjacent (near-UV and near-infrared) ranges. The absorption in the visible range directly affects the perceived colour of the chemicals involved. In this region of the electromagnetic spectrum, molecules undergo electronic transitions. UV-Vis spectroscopy was used to investigate the formation, stability, surface modifications, and light barrier properties (opacity, transparency, and percent transmittance) of the prepared metal oxide NPs (Shimadzu, UV-1800, USA).

2.3 Fourier Transforms in Infrared Spectroscopy:

The FT-IR spectra of the prepared NPs were acquired in the range of 4000–400 cm1 using an attenuated total refraction Fourier Transform Infrared (ATR FT-IR) spectrophotometer (Thermo Scientific, Nicolet iZ10). FT-IR functional group detection helps to analyse the structural changes that take place in the nanocomposite FLMs.

2.4 X-ray Diffraction (XRD) Analysis:

The crystalline and amorphous behaviour of the synthesised metal oxide NPs can be determined by X-ray diffraction (XRD) using a Rigaku Miniflex Diffractometer in reflection mode with Cu K radiation at an accelerating voltage of 30 kV with an operating current of 10 mA.

2.5 Thermogravimetric analysis:

The thermal stability and decomposition temperature of the FLM samples were evaluated using thermogravimetric analysis (TGA) (TA-SDT650 instruments, USA). The FLM sample (4–4.5 mg) was heated in the temperature range 25–600 °C at an incremental rate of 10 °C/min under a nitrogen atmosphere (50 ml/min). TA Instruments, made in the USA, were used to perform the differential scanning calorimetry (DSC). The 1.5–2.0 mg of the FLM sample was sealed in an aluminium crucible and heated in an inert nitrogen atmosphere (50 ml/min) from 25 to 400 °C at a heating rate of 10 °C/min.

2.6 Scanning Electron Microscopy (SEM):

TESCAN (Czech Republic) was used to examine the surface morphology of the prepared NPs. Before further treatment, the samples were covered with a thin palladium-platinum conductive coating. A sputter coating was used to produce the layer. A secondary electron detector with a 30 kV accelerating voltage was used to view the surface of the sample.

2.7 Antioxidant activity:

The antioxidant activities of the samples are measured on the basis of their free radical scavenging activity using the DPPH method. The stock solution of DPPH was prepared by dissolving 3.9432 mg of DPPH in 100 ml of methanol and storing it at 40 °C until use. 2 ml of DPPH solution was mixed with 1 ml of five different concentrations (20, 40, 60, 80, and 100 g mL^{-1}) of the samples and standard, respectively. A mixture of 1 ml of distilled water and 2 ml of DPPH solution was used as the control. The reaction mixture was mixed, kept in the dark for 30 minutes, and incubated at room temperature. The absorbance was recorded spectrophotometrically at 517 nm. An antioxidant activity was estimated based on the percentage of DPPH radicals scavenged in the following equation:

Scavenging effect % = [control absorbance - sample absorbance] X 100

[Control absorbance]

3. Results and discussion ;

Present work demonstrated the synthesis of Fe_3O_4, ZnO & Fe_3O_4-ZnO NP's by greener method using Lemon Fruit (Citrus limon) Peel Extract, and prepared NPs was confirmed by various techniques.

3.1.Physico-chemical characterization of Fe_3O_4, ZnO & Fe_3O_4-ZnO NP's :

To inspect the formation of NPs and to control the reaction was collected UV-visible absorption of λ_{max}. The absorption spectra showed a distinct peak at 252nm, 254nm, 250 nm for Fe_3O_4, ZnO, Fe_3O_4-ZnO NP's [19-22]. They are also overlapped in Fig.1. The absorption spectra are distinctly separated and it's clear that, the formation of a Fe_3O_4, ZnO & Fe_3O_4-ZnO NP's were takes place by the frut peel extraction method. It has been well established by researchers, the fruit peel contains phytoconstituents like flavonoids, polyphenols, tannin, phytosterols and many more active ingredients are responsible for the formation of NPs[23].To check the chemical composition of the prepared Fe_3O_4, ZnO & Fe_3O_4-ZnO NP's, employed FTIR using KBr pellet method for to find stretching frequencies. The FTIR spectrum as shown in Fig.2. of Fe_3O_4, ZnO, Fe_3O_4-ZnO NP's were found characteristic peak at 3485, 3488, 3490 cm^{-1} are attributed to the stretching vibrations of –OH group. 2987,2990,2992cm^{-1} are attributed to the stretching vibrations of C-H stretching and 2255,2256, 2258cm^{-1} of $–CH_2$ group present in phenolic compounds of lemon peel extract [24]. The peak at 1651,1653,1656 and 1479,1483,1484 cm^{-1} corresponds to the asymmetric and symmetric stretching of the Fe-O and Zn-O bond The band appeared at 1140.1143,1145 cm^{-1} was assigned to the C-O stretching vibration of alcohol and ester present in the extract [25-27]. The characteristic peak at 562.565,567 cm^{-1} was associated with the Fe-O, Zn-O stretching vibration of NPs [28]. Fig.3. represents the XRD pattern of prepared Fe_3O_4, ZnO & Fe_3O_4-ZnO NP's, showing prominent characteristic diffraction at 24.22º,27.15º,29.34º which corresponds to the unit cell of (110). 29.4º,32.42º,32.48º which corresponds to the unit cell of (111). 32.51º,32.62 º,34.45º. which corresponds to the unit cell of (111). 36.65º, 37.28º, 37.66º which corresponds to the unit cell of (202). 42.93º,39.52º,39.82º which corresponds to the unit cell of (020). 48.44º,44.92º,43.55º which corresponds to the unit cell of (202). 52.08º,51.98º 57.64º which corresponds to the unit cell of (022/31-1). 56.07º,56.98º,61.92º which corresponds to the unit cell of (113/22-0). 63.38º,63.88º,65.45º which corresponds to the unit cell of (311). 71.47º,78.51º,77.13º which corresponds to the unit cell of (004/22-2) crystallographic planes respectively (JCPDS: 48-15148) [29-30]. The average particle size of the Fe_3O_4, ZnO & Fe_3O_4-ZnO NP's was found to be 17.32 nm,15.63nm and 14.61nm respectively was obtained by applying Debye-Scherer procedure [31]. The SEM image obtained for the prepared Fe_3O_4, ZnO & Fe_3O_4-ZnO NP's was appended in Fig. 5. Fig. 6. Fig. 7. Respectively. It is observed that, the Fe_3O_4, ZnO & Fe_3O_4-ZnO NP's have a well-defined morphology and are nearly spherical in shape. The spectrum depicted major peaks for Fe, Zn and O, which confirms the presence of Fe_3O_4, ZnO & Fe_3O_4-ZnO NP's. This data was also in accordance with the reported Fe_3O_4, ZnO & Fe_3O_4-ZnO NP's from Lemon fruit peel[32].The TGA analysis Fig.4.of green synthesized Fe_3O_4, ZnO & Fe_3O_4-ZnO NP's reveals the bond breakdown and weight loss in three stages during heat operation[33]. The first phase of weigt loss occurred at 70º -120º is due to the loss of water abosorbed by NP's[33] where as the second phase at 125º-640º which could have arisen due to the breakdown of bonds and destruction of biomolecule structure[34]. And the third phase at above 700º is due to bond breakdown in NP's[35].

3.2. Antioxidant Activity study of Green synthesized Fe_3O_4, ZnO & Fe_3O_4-ZnO NP's :

Antioxidant properties of green synthesized Fe_3O_4, ZnO & Fe_3O_4-ZnO NP's and their activities in food and biological systems and the ability to capture free radicals were measured on the basis of free radical scavenging activity by DPPH method. To evaluate free radical inhibition (hydrogen donating) ability of synthesized NP's the DPPH radicals were used[36]. The DPPH scavenging % and half maximum inhibitory concentration (IC_{50}) of prepared NP's is as shown in Fig. 8. As the DPPH radicals ability was decreased considerably when the concentration of NP's were increased[37] (free radicals suppressing ability follws the order IC_{50} value of NP's follows the order as ZnO> Fe_3O_4> Fe_3O_4-ZnO NP's.

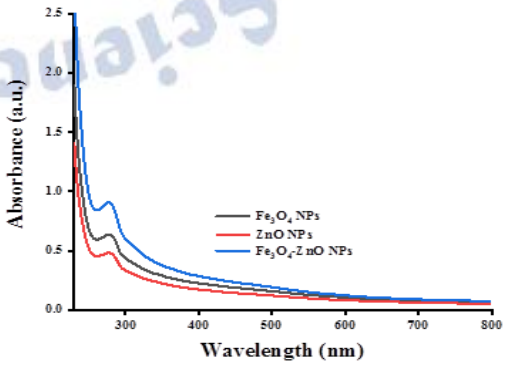

Fig. 1.**UV-Vis Spectra of synthesized Fe_3O_4, ZnO & Fe_3O_4-ZnO NP's.**

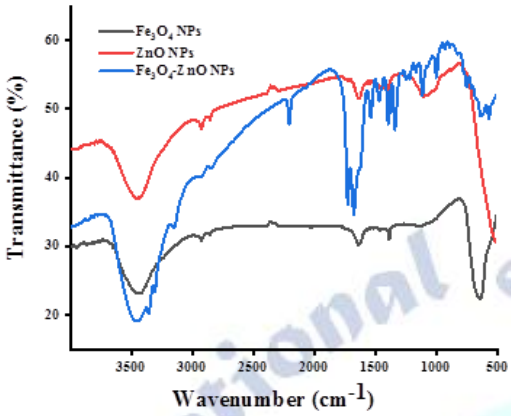

Fig. 2. **FTIR Spectra of synthesized Fe_3O_4, ZnO & Fe_3O_4-ZnO NP's.**

ZnO < Fe_3O_4< Fe_3O_4-ZnO NP's) of the As a result the NP's have lower IC_{50} than standard ascorbic acid[38]. The

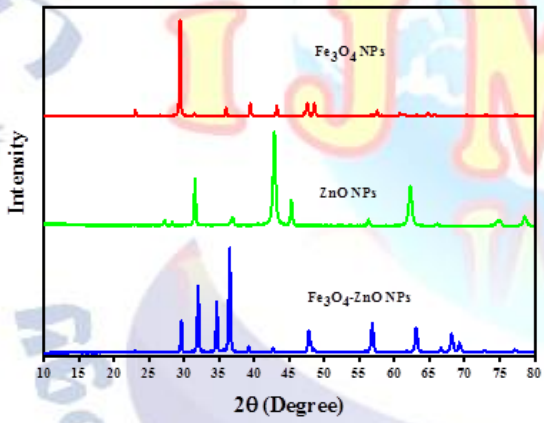

Fig. 3. **XRD Spectra of synthesized Fe_3O_4, ZnO & Fe_3O_4-ZnO NP's.**

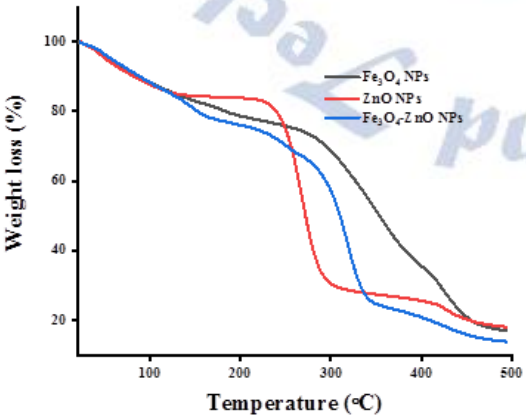

Fig. 4. **TGA Spectra of synthesized Fe_3O_4, ZnO & Fe_3O_4-ZnO NP's .**

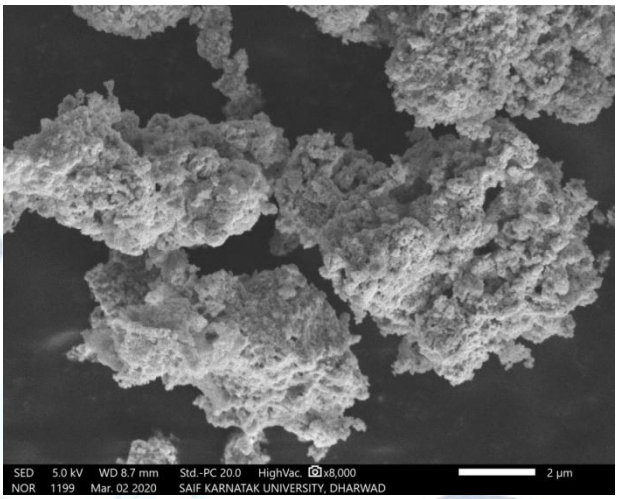

Fig. 5. **SEM Image of synthesized Fe_3O_4 NP's .**

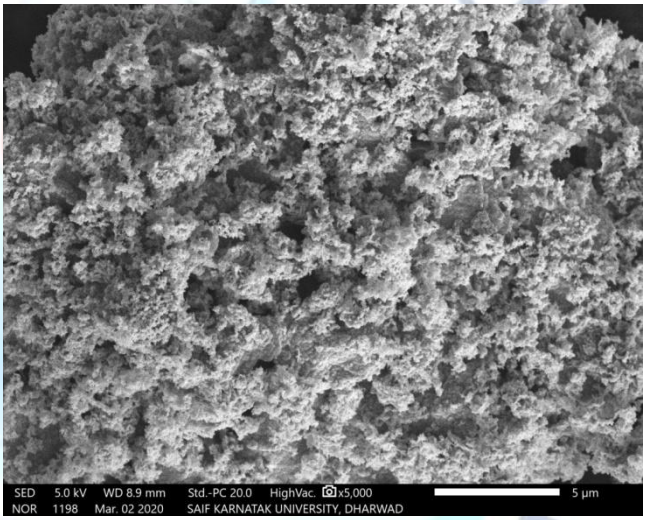

Fig. 6. **SEM Image of synthesized ZnO NP's .**

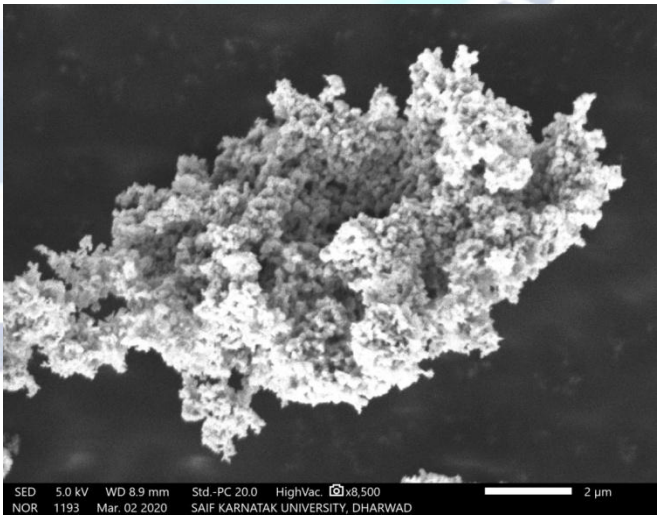

Fig.7. **SEM Image of synthesized Fe_3O_4-ZnO NP's .**

bonds which confirmed the alcoholic, phenolic compounds presents in lemon peel which involved in NP's formation. Thr XRD spectra confirmed the crystallographic nature of NP's. and SEM images established the well-defined morphology and nearly spherical in shape of NP's. and The average particle size of the Fe_3O_4, ZnO & Fe_3O_4-ZnO NP's was found to be 17.32 nm,15.63nm and 14.61nm respectively which is obtained by applying Debye-Scherer procedure.TGA confirms the weight loss of NP's with various temparatures. And further the Antioxidant property

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Material	Concentration (μgmL^{-1})	Radical scavenging activity (%)	IC50 (μgmL^{-1})	Correlation coefficient
Standard Ascorbic acid	20	39.281± 2.120	25.74	0.989
	40	51.612±0.965		
	60	70.289±3.056		
	80	81.765±2.028		
	100	90.878±1.909		
ZnO NPs	20	40.856± 0.970	42.85	0.987
	40	52.224± 1.336		
	60	69.888± 1.270		
	80	72.212± 1.560		
	100	80.145± 1.418		
Fe_3O_4 NPs	20	41.745± 0.978	39.25	0.985
	40	58.178± 1.350		
	60	62.789± 1.266		
	80	72.830± 1.488		
	100	81.666± 1.515		
Fe_3O_4-ZnO NPs	20	42.455± 0.966	35.12	0.993
	40	60.248± 1.039		
	60	67.288± 1.670		
	80	74.965± 1.598		
	100	83.505± 1.450		

Conclusion:

In this present work, successfully synthesised the Fe_3O_4, ZnO & Fe_3O_4-ZnO NP's by using Lemon fruit peel extract as a stabilising agent. Thus the structural and thermal properties were examined by various advanced techniques such as UV-vis, FTIR, XRD, TGA, SEM. The UV-vissible absorption of λ_{max} peaks were showed at 252nm, 254nm, 250 nm for Fe_3O_4, ZnO & Fe_3O_4-ZnO NP's respectively. The FTIR showed the peaks for stretching vibrations of –OH, –CH, –CH2, C–O groups and also showed the asymmetric and symmetric stretching peaks for Fe-O and Zn-O study demonstrated the more activity for Fe_3O_4-ZnO NP's than Fe_3O_4, ZnO NP's.

Conflict of interest statement

Authors declare that they do not have any conflict of interest.

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