

Synthesis and characterization of ZnO doped Fe₃O₄ nanocomposite material and its heterogeneous photocatalytic activity for degradation of phenol

Kale Ganesh K* and Borawake Ganesh A

Post Graduate Department of Chemistry, Jijamata College of Science and Arts, Bhende bk. Tal:- Newasa, Dist: - Ahmednagar, Maharashtra, PIN: 414605

Email: - kalegk111@gmail.com

Manuscript Details

Available online on <http://www.irjse.in>
ISSN: 2322-0015

Editor: Dr. Arvind Chavhan

Cite this article as:

Kale Ganesh K and Borawake Ganesh A.
Synthesis and characterization of zno doped fe₃o₄ nanocomposite material and its heterogeneous photocatalytic activity for degradation of phenol, *Int. Res. Journal of Science & Engineering*, January 2018; Special Issue A3 : 49-55.

© The Author(s). 2018 Open Access

This article is distributed under the terms of the Creative Commons Attribution 4.0 International License

(<http://creativecommons.org/licenses/by/4.0/>), which permits unrestricted use, distribution, and reproduction in any medium, provided you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made.

ABSTRACT

A series of ZnO doped Fe₃O₄ nano-composite materials were synthesized by using co-precipitation method. The surfactant such as CTAB was used during the synthesis of this nano-composite material. This material then characterized with the help of some sophisticated modern techniques such as XRD, FT-IR, and SEM-EDS. According to these all characterizations results suggested the formation of nano-composite highly crystalline materials. The catalytic activities of synthesized materials were successfully tested on degradation of phenol by using hydrogen peroxide at room temperature. The degradation reaction was monitored by using Ultra-Violet visible spectroscopy (UV-Vis) techniques. It was found that 15 wt% ZnO doped Fe₃O₄ nano-composite material shows better activity for the degradation of phenol. The degradation reaction is carried out at room temperature with continuous stirring in presence of sun light irradiation. Thus this degradation reaction is different from conventional heterogeneous catalysis or photocatalysis, in which the degradation reaction is carried out in natural light source. Thus this reported phenol degradation reaction is a quite promising green technology, which could be widely applied in practice.

Keywords: Doping, Heterogeneous catalysis, Photodegradation, Nanocomposite Material

INTRODUCTION

Inorganic chemistry is the branch of chemistry, which deals with the study of synthesis and behavior of inorganic and organometallic compound. This field covers all chemical compounds except the organic compounds (carbon based compounds, usually containing C-H bonds). Important inorganic compounds are the oxides, carbonates, nitrate, sulphates and halides. It is deals with the study of coordination compounds, main group compounds, transition metal compounds, organometallic compounds, cluster compounds, bioinorganic compounds and solid state compounds.

During the last decade, nanosize magnetic materials have been largely studied due to their different magnetic properties compared to their bulk counterparts such as super-paramagnetism which can significantly advance the current clinical diagnostic and therapeutic methods. Each superparamagnetic particle is a single magnetic domain in which thermal energy can overcome anisotropy energy barrier and cause free spin reversal. This is to say that no residual magnetism remains after elimination of external magnetic field.

In this regard, spinel ferrite nanocrystals with general chemical composition MFe_2O_4 (where M= Co, Ni, Mn, Fe, Cu, Zn, etc.) form a group of applicable magnetic materials due to their interesting magnetic, magneto-resistive and magneto-optical properties.

On the overlook at the literature survey, it has been observed that metal oxide and mixed metal oxide play an important role in catalytic processes to speed up chemical reactions, in an eco-friendly manner, cost effective, efficient and clean processes. The main objectives of the present work are:

- 1) To study the effect of various methods on the preparation of metal oxides and mixed metal oxides like co-precipitation, impregnation and sol-gel methods.
- 2) To study the photocatalytic degradation of industrial wastes like phenol, organic dyes with the help of prepared metal oxides.
- 3) To replace the toxic, conventional/classical acid catalysts by means of solid heterogeneous catalyst.
- 4) To develop a clean, efficient and environmentally benign processes for the synthesis of pharmacologically and biologically important heterocyclic compounds.

To take above mentioned aim and objectives here in this research, we successfully synthesized pure ZnO, pure Fe_3O_4 and series of ZnO doped Fe_3O_4 nanocomposite material. We studied the structural and morphological properties of synthesized material by different characterization techniques such as XRD, SEM-EDS and FT-IR. Finally investigates the photocatalytic activity of synthesized material by degradation of phenol.

METHODOLOGY

Chemicals and Reagents:

Ferrous Sulphate, Ferric Sulphate, Zinc Chloride, 1:1 Ammonia, Polyethylene Glycol, Ethanol, etc. All chemicals are Analytical grade and used without further purifications.

1. Synthesis of ZnO:

Dissolve 1.6 gm Zinc Chloride in 50 ml deionised water. Add 10 ml alcohol, then add 5 ml polyethylene glycol. Stirrer it continuously till dissolved it completely, then heat the above solution at 80°C for 5-6 hr. Add drop by drop 1:1 ammonia to maintain pH 8.5. This solution form white precipitate. Then this precipitate is filtered through Whatman filter paper no 41. Wash it with hot water. Dry this residue overnight at 120°C temperature. After drying obtained material is then kept for calcination in high temperature Muffel furnace at the temperature of 120°C for 3 hrs. White coloured final resulting powder is ZnO nanocomposite material.

2. Synthesis of Pure Fe_3O_4 :

Dissolve 3.9 gm ferric sulphate and 2.5 gm ferrous nitrate in 50 ml deionised water in separate clean and dried beaker. Add 10 ml alcohol. Then add 5 ml polyethylene glycol. The solution is heated with continuous stirring at 80°C for 5-6 hr. Add drop by drop 1:1 ammonia to maintain pH 8.5. This solution

form dark brown precipitate. These resulting two solutions are then mixed together with stirring which gives black coloured precipitate. Then this precipitate is filtered through Whattmann filter paper no 41. Wash it with hot water. Dry this residue overnight at 120°C temperature. After drying obtained material is then kept for calcination in high temperature Muffle furnace at the temperature of 500°C for 3 hrs.

3. Synthesis of series of ZnO doped Fe₃O₄.

Take above prepared solutions (3.9 gm ferric sulphate and 2.5 gm ferrous nitrate) in beaker. Add Zinc Chloride solution (0, 1, 5, 10 and 15 wt%) in the same beaker. Then add 5 ml polyethylene glycol with continuous stirring and heat it at 80°C temperature for 4-5 hrs. Filter the total solution through Whattmann filter paper no. 41. Dry this residue in oven at 120°C for overnight. After drying the product was then crushed in mortar pestle to obtain very fine powder. After drying obtained material is then kept for calcination in high temperature Muffle furnace at the temperature of 500°C for 3 hrs. Finally weight is taken off all these products and fill it in sample bottle and labelled it as 1) pure ZnO, 2) pure Fe₃O₄, 3) 1 wt% ZnO doped Fe₃O₄, 4) 5 wt% ZnO doped Fe₃O₄, 5) 10 wt% ZnO doped Fe₃O₄, and 6) 15 wt% ZnO doped Fe₃O₄.

RESULTS AND DISCUSSION

The X-ray diffraction data was acquired in the 2θ range of 20–80° on a Rigaku Multiflex instrument using Cu Kα (λ = 1.5418 Å) radiation source and a scintillation counter detector (SCD). Crystalline phases present in the samples were identified with the help of JCPDF-ICDD.

The Fourier transformation infra-red spectra (FTIR) were recorded on FTIR spectrometer (SHIMADZU-FTIR/4100), Japan in the range 4000–500 cm⁻¹.

The powder morphology was observed by scanning electron microscope (SEM), analysis was performed on a JEOL JSM6700F electron microscope.

1. XRD Analysis:

The XRD pattern of the powder is studied with the diffraction angle 20–80°. All the peaks are in 100%

phase matching with the ZnO hexagonal phase of JCPDF No. 36-1451. It is shown in **Figure 1**. There are no other characteristic impurities peaks were present which also confirm that the product obtained is in pure phase. Similarly high intensity peaks suggested that the synthesized material is highly crystalline material. The peak at 2θ=36.64 is corresponds to the hkl value 101 suggests that ZnO material with hexagonal crystal structure. The line broadening in the peaks determine the crystallite size of ZnO to be less than 25 nm. The values present in the Table 2 are corresponds to the hkl and FWHM of ZnO material. The average crystalline size of the calcined ZnO powder is estimated by the Scherrer's relation (1).

$$D=0.9\lambda/\beta\cos\theta \quad (1)$$

Where D is the average crystalline size λ is the X-ray wavelength of 1.54 Å, θ is the Bragg diffraction angle and β is the FWHM.

The XRD patterns of the synthesized nanoparticles after calcination for various wt.% of ZnO doped Fe₃O₄ are shown in **Fig. 2**. The peak positions agree with those of the spinel structure. Thus the synthesized nanoparticles are Fe₃O₄ phases. The synthesized nanoparticles seem to be Fe₃O₄ phase. In these diffraction patterns, no trace of the reactants and by-products or ZnO material, so on, can be seen, it indicates total incorporation of ZnO material in to the Fe₃O₄. As revealed, diffraction peaks of all samples completely correspond to standard pattern characteristic peaks of the magnetite cubic inverse spinel structure (JCPDS 19-0629). No secondary phase is detected to prove the formation of other Zn-based structures such as ZnO. So, we might conclude that Fe₃O₄ has been formed with high phase purity and Fe ions have been successfully replaced with Zn²⁺ ions.

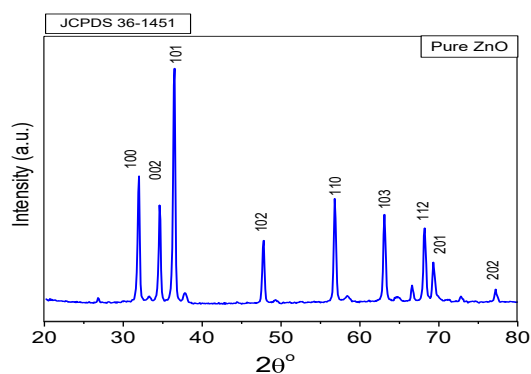


Figure 1: XRD spectrum of Pure ZnO

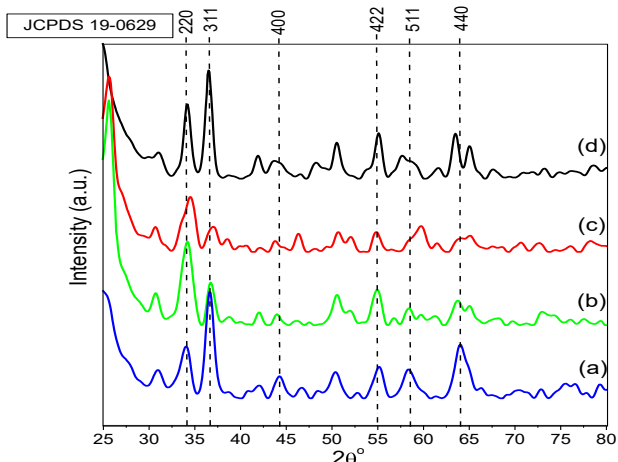


Figure 2: XRD spectrums of (a) Pure Fe₃O₄, (b) 5% ZnO-Fe₃O₄, (c) 10% ZnO-Fe₃O₄, (d) 15% ZnO-Fe₃O₄

2. SEM-EDS Morphology and structure studies:

In order to understand the surface morphology and to know the surface dispersion of the active species on the support, the efficient studies were carried out on the SEM analysis. **Figure 3 (a, b, c and d)** shows SEM morphology photographs for pure ZnO materials with different magnifications which shows highly porous in nature and nanocrystalline structure. In the image of **Figure 3 (c)** clearly shows that ZnO material with 0.5 μm in size.

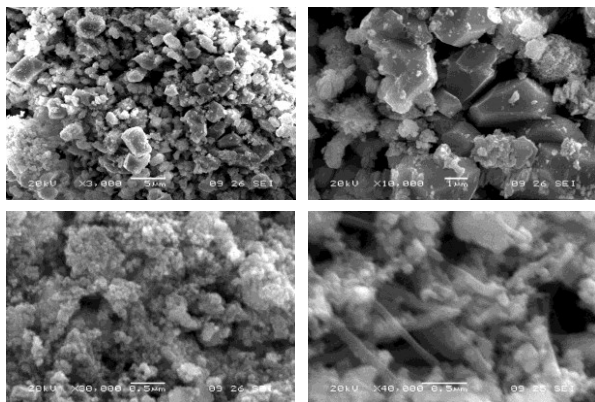


Figure 3 (a, b, c and d): SEM images of Pure ZnO

From the **figure 4 (a, b and c)** it shows good agglomeration of Fe₃O₄ magnetic nanoparticles. It is evident that the sample shows an irregular appearance. From the SEM micrograph of the 15 wt.% ZnO doped Fe₃O₄ material is shown in **Figure 5 (a, b and c)**, it can be clearly seen that effect of addition of ZnO into Fe₃O₄ material clearly shows alteration in

crystallite size, improvement in morphology and increasing the porosity.

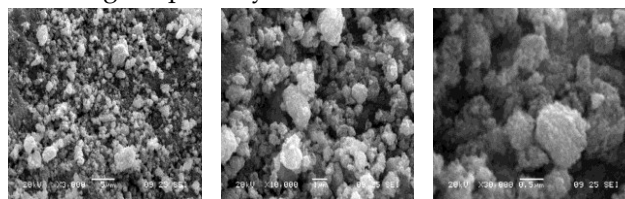


Figure 4 (a,b,c): SEM images of Pure Fe₃O₄

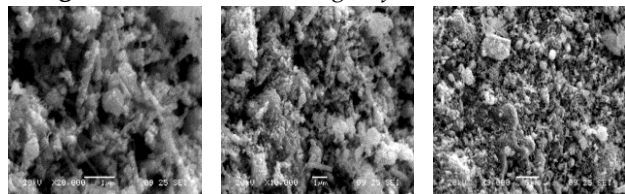


Figure 5: SEM images of 15wt.% ZnO-Fe₃O₄

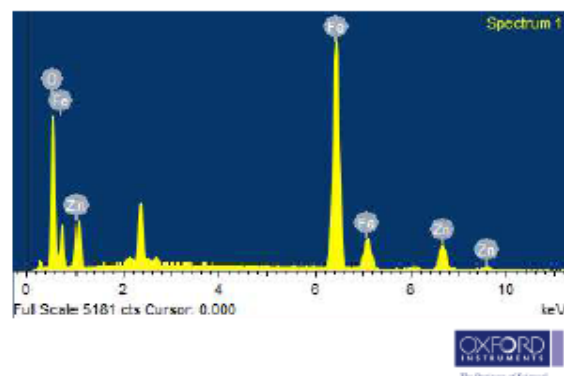
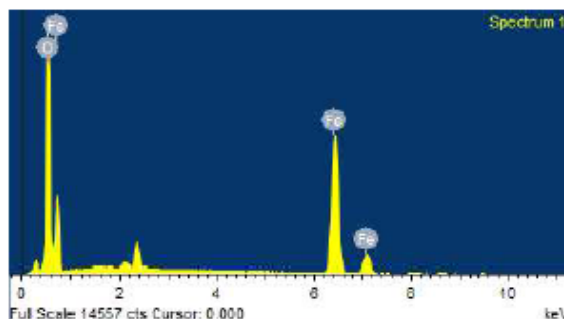
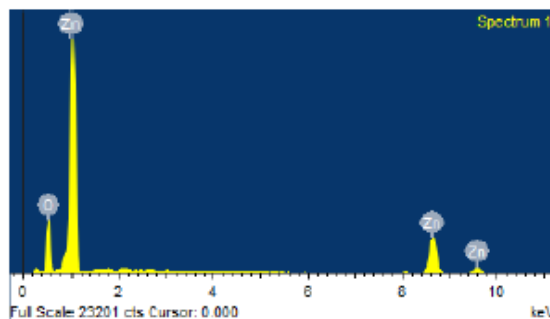
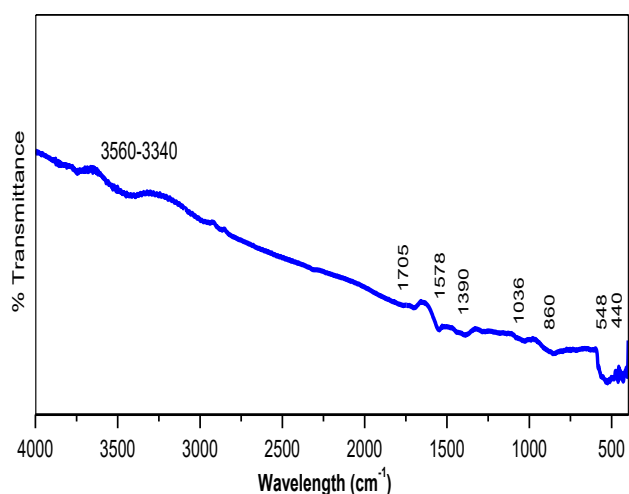
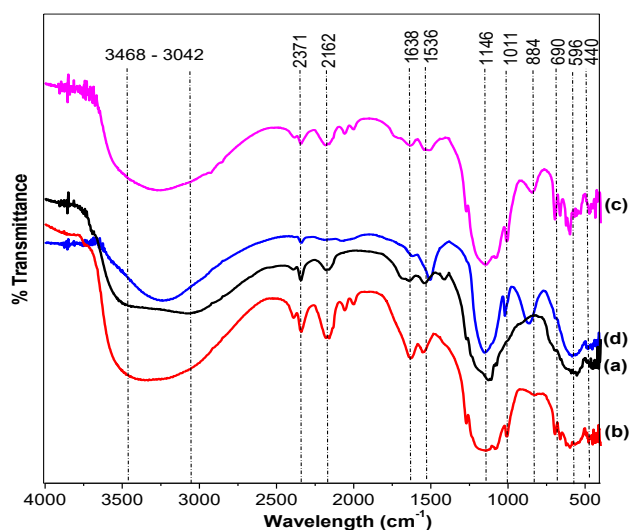


Figure 6: SEM-EDS images of (a) Pure ZnO, (b): Pure Fe₃O₄, (c): 15% ZnO-Fe₃O₄

Table 1: Elemental Data Analysis

Element	Pure Fe ₃ O ₄		Pure ZnO		15 % ZnO-Fe ₃ O ₄	
	Weight %	Atomic %	Weight %	Atomic %	Weight %	Atomic %
O	57.77	82.8	44.08	76.31	36.39	67.32
Zn	0.00	0.00	55.92	23.69	13.37	6.05
Fe	42.23	17.32	0.00	0.00	50.25	26.63
Total	100.00	100.00	100.00	100.00	100.00	100.00

**Figure 7:** FT-IR spectrum of Pure ZnO**Figure 8:** FT-IR spectra of (a) Pure Fe₃O₄, (b) 5% ZnO-Fe₃O₄, (c) 10% ZnO-Fe₃O₄, (d) 15% ZnO-Fe₃O₄

Elemental compositions of pure ZnO, pure Fe₃O₄ and 15 wt. ZnO doped Fe₃O₄ materials are represented in the EDS spectrums shown in **Figure 6** (a, b and c). The elemental quantitative analysis is also shown in **Table 1**. The observed Zn:O; Fe:O and Zn:Fe:O atomic ratios are fairly close to the expected bulk ratios indicating

good distribution of the metal species inside the sample matrix. This observation supports analysis it was shown that, the minimum stoichiometric ratio for the all sample are maintained.

3. Fourier Transformation Infra-Red Spectroscopy Study:

The **Figure 7** shows the FTIR spectrum of pure ZnO material. over the 4000–500 cm⁻¹ range. Two peaks at 1578 and 1390 cm⁻¹ are due to stretching and bending mode of oxygen available in the Zn-O-Zn and the Zn=O indicate that the presence of a ZnO. Two strong vibration bands were detected at 1036, 860 and 548 cm⁻¹, associated to the stretching and bending mode of Zn-O-Zn and the Zn=O indicating the existence of a layered hexagonal ZnO phase. The peak at 1705 cm⁻¹, associated with the vibration mode of the Zn-OH bond. Due to coordinated crystalline water present in material, it gives observed due to OH-stretching at 3300 cm⁻¹. The broad band around 3560–3340 cm⁻¹ is due to O-H stretching vibration modes of the adsorbed water on the surface of the powder.

The **Figure 8** (a-d) shows the FTIR spectrum of series of catalytic material prepared (a) Pure Fe₃O₄, (b) 5% ZnO-Fe₃O₄, (c) 10% ZnO-Fe₃O₄, (d) 15% ZnO-Fe₃O₄ over the range of 4000–500 cm⁻¹. The peaks at 1146,

1011, 884 cm⁻¹ are due to stretching and bending mode of oxygen available in the Fe-O-Fe and the Fe=O indicate that the presence of a FeO and Fe₂O₃. Three strong vibrations were detected at 690, 596 and 440 cm⁻¹, associated to the stretching and bending mode of Fe-Fe and the Fe-O indicating the existence of a layered Fe₃O₄ phase. The peak at 1638 and 1536 cm⁻¹, associated with the vibration mode of the Fe-OH bond. The broad band between the ranges of 3468–3042 cm⁻¹ is due to O-H stretching vibration modes of the adsorbed water on the surface of the powder.

Table 2: Physico-chemical parameters of phenol before and after degradation

	ZnO	Fe ₃ O ₄	5 wt.%	10 wt.%	15 wt.%	Blank
pH	1.40	1.37	1.46	1.44	1.34	1.32
COD	42.24	364.8	595.2	566.4	316.8	345.6
O.C.	0.15	0.28	0.22	0.22	0.22	17.5
E.C.	12.60	15.05	17.43	16.28	13.32	16.70
Flame (Na)	42	54	34	53	46	44
Flame (K)	25	28	17	31	27	25
Phenol Degradation in (%)	8.21	9.47	57.98	60.95	91.59	-

4. Catalytic activity measurements:

Batch degradation control experiments of phenol were carried out at pH = 7.0 in a 25 mL of conical flask placed on a magnetic stirrer at room temperature. The reaction suspension was prepared by adding 0.1 g of catalyst amount into 5 mL of pure phenol (45 mM) and 10 ml of 30% H₂O₂ (100 mM) solution to initiate the reaction. After 1h the reaction mixtures were centrifuged and analyzed in JASCO, V650 UV-Visible spectrophotometer in the range of 200-800 nm. The change in intensity of peak at λ_{max} for phenol at 270 nm was carried out. Each experiment was run in triplicate, and average values and standard deviations are presented.

The catalytic efficiency of the synthesized catalysts was investigated for phenol degradation reaction and the obtained results are shown in **Figure 9**. In each experiment, the reaction suspension was prepared by adding 0.1 g of catalyst amount into 5 mL of pure phenol (45 mM) and 10 ml of 30% H₂O₂ (100 mM) solution to initiate the reaction. As can be seen from the **Figure 9**, that was remarkable decrease in the concentration of phenol was clearly observed using UV-Visible spectra. Among all the catalytic materials, 15 wt.% catalyst was observed higher phenol degradation activity when compared to that of remaining catalysts. It is mainly attributed to increase an availability of more active sites including more surface area, smaller particle size and ample vacancy defects by addition of the ZnO. The colour intensity of the phenol solution was increases to around 80% for the modified with ZnO doped Fe₃O₄ catalytic material when compared with the 0, 5 and 10 wt.%. The change in colour of phenol in the solution from colourless to dark brown is shown which is attributed

to the formation of intermediates like catechol, resorcinol and glycerol etc. during the degradation of phenol in presence of catalyst and H₂O₂ after 1h.



Figure 9: Photographs of phenol degradation process a)5% b) 10% C) 15% d) pure FeO e) pure ZnO f) blank g) Pure phenol after 120 minutes

The efficiency of phenol degradation was performed overall synthesized catalysts under the reaction conditions same as in **Figure 9** and obtained phenol conversions are presented in the **Table 4**. Although the catalytic activity of phenol degradation is very low in the absence of catalyst, the catalytic activity in the presence of catalysts satisfactorily improved. It was found that 15 wt.% ZnO doped Fe₃O₄ catalyst show a higher catalytic performance when compared to that of other series of catalysts. It might be attributed to increase an availability of more active sites by addition of the ZnO metal oxide into Fe₃O₄. We performed the some physico-chemical parameters of phenol before and after degradation reaction such as pH, COD measurement, O.C., Electrical conductance, detection of concentration of Na and K by using Flame photometrically. As well, the measured chemical oxygen demand (COD) for the degradation of phenol before and after the reaction over prepared catalysts

and obtained results are presented in the **Table 2**. The COD values represent the amount of organic compounds in water and a remarkable decrease in the COD value was noticed after the degradation of phenol. The gradual decrease in COD values was observed for all catalysts after 150 minutes of the reaction time. The observed phenol degradation of all catalysts are as ~ 8.21, 9.47, 57.98, 60.95 and 91.59 % for the catalysts such as pure ZnO, pure Fe₃O₄, 5 wt.% ZnO doped Fe₃O₄, 10 wt.% ZnO doped Fe₃O₄ and 15 wt.% ZnO doped Fe₃O₄, respectively. This decrease in COD values shows the degradation of phenol that leads to the conversion of organic compounds into harmless gaseous CO₂ and inorganic ions. This noticeable observation is indeed due to the oxidation and degradation of phenol by radical species into aromatic compounds, low-molecular carboxylic acids, carbon dioxide and water.

CONCLUSIONS

For improving structural and morphological properties of pure Fe₃O₄, ZnO doping effect was studied. XRD pattern of nanoparticles indicated formation of Fe₃O₄ with cubic inverse spinel structure in all samples. Increasing dopant caused to decreasing crystalline size and formation of uniform and spherical shape nanoparticles. The catalytic activities of synthesized materials were successfully tested on degradation of phenol by using hydrogen peroxide at room temperature. The degradation reaction was monitored by using Ultra-Violet visible spectroscopy (UV-Vis) techniques. It was found that 15 wt% ZnO doped Fe₃O₄ nano-composite material shows better activity for the degradation of phenol. The degradation reaction is carried out in natural light source. Thus this reported phenol degradation reaction is a quite promising green technology, which could be widely applied in practice.

REFERENCE

1. Rezai Marand Z, Shahtahmasbia N, Rezaee M, Roknabadia M, Hosseindokht M, Bagheri Mohagheghid M. Helmi Rashid Farimania, R. Etefagh, Proceedings of the 4th International Conference on Nanostructures (ICNS4) 12-14 March, 2012;211-213, Kish Island, I.R. Iran.
2. Zahra Rezay Marand, Mitra Helmi Rashid Farimani, Nasser Shahtahmasebi, *Nanomedicine journal*, 4, 214, 238-247.
3. Yendrapati Taraka Prabhu, Kalagadda Venkateswara Rao, Vemula Sesha Sai Kumar, Bandla Siva Kumari, *Advances in Nanoparticles*, 2013; 2: 45-50.
4. Kotsikau D, Natarov V, Petrova E, Pankov V, *Physics, Chemistry and Application Of Nanostructures*, 2015.
5. Lee JH. *Nature Medicines*, 2007; 13:95.
6. Park J. *Nature Materials*, 2004; 3: 891.