

**Synthesis of mesoporous magnetic MFe_2O_4 ($M = Co, Mn, Ni$)
nanoparticles
for the photodegradation of pesticides**

A

Dissertation

Submitted by

SATYA RANJAN SAHOO

ROLL NO-413CY2017

Under the guidance of

Dr. Sasmita Mohapatra



**Department of Chemistry
National Institute of Technology, Rourkela
Odisha 769008
INDIA**

ACKNOWLEDGEMENT

I express my cordial gratitude to my respected teacher and supervisor Dr. Sasmita Mohapatra, Assistant Professor, Department of Chemistry, National Institute of Technology, Rourkela, for her continuous supervision, assiduous cooperation, moral support and constant encouragement through out my project work.

It is my great pleasure to acknowledge to Prof. N.Panda, Head of the Chemistry Department, National Institute of Technology, Rourkela for providing me the necessary facilities for making this research work a success.

I am highly indebted to all our teachers of this department for their kind help and expert suggestions. I express our profound gratitude to Mrs. Swagatika Sahu, Mr. Smruti Ranjan Rout, Mr. Rahul Kumar Das and Ms. Ranjita Mohapatra, Y. Arun Kumar, for their ceaseless encouragement, immense help and hearty encouragement during our project work.

I wish to thank all of friends for making our stay in this institute a memorable experience. Finally, I am honestly grateful to my family members for their endless love, unending support & blessings.

SATYA RANJAN SAHOO
NIT ROURKELA

Dr. Sasmita Mohapatra
Assistant Professor,
Department of Chemistry
National Institute of Technology
Rourkela
Odisha-769008



CERTIFICATE

This is to certify that the dissertation entitled “**Synthesis of mesoporous magnetic MFe_2O_4 (M = Co, Mn, Ni) nanoparticles for the photodegradation of pesticides**” submitted by Satya Ranjan Sahoo for the award of Master of Science in Chemistry (August 2014 - May 2015) is a record of research work carried out by him under my supervision for training purpose. To the best of my knowledge, the matter embodied in this dissertation has not been previously submitted for any degree in this/any other institute.

Date:

Dr. Sasmita Mohapatra

CONTENTS

	Page no
1. Abstract	01
2. Introduction	02
3. Objective	04
4. Experimental Details	04
5. Results and Discussion	06
6. Conclusion	10
7. Reference	10

ABSTRACT

A facile synthesis method was employed to prepare monodisperse, magnetic mesoporous inverse spinel ferrites MFe_2O_4 (Co,Mn,Ni) nanoparticles of size 35–50 nm. The synthesis method involves thermal decomposition of metal chloride precursors in presence of ethylene glycol, sodium acetate and ethanolamine. Synthesized spinel ferrites were well characterized by XRD, SEM, and UV-DRS analysis. The as synthesized material showed photocatalytic activity towards Imidacloprid (IMP) degradation. Magnetic property of the ferrites defines it to be easily separable for repeated applications.

Keywords: Photocatalyst, magnetic nanoparticles, Imidacloprid

1. INTRODUCTION

The pesticides used in agriculture are the most notorious contaminants in aquatic environments. Modern agriculture requires tons of pesticides and insecticides worldwide to protect plants from pests and insects. It is estimated that about 2 million tons of organophosphorus (OP) pesticides are used in a year throughout the world ^[1,2]. Because of indiscriminate and extensive use of pesticides, they persist in soil, ground, surface waters, air, and agricultural products. Depending on their aqueous solubility, pesticides either remain in the soil or enter surface waters and groundwaters. The compounds that result from pesticide degradation can remain in animals, vegetables, and water sources, and they can become more concentrated as they move up the food chain. Because of the toxicity of these compounds—even at trace levels—there is increasing interest in the development of systems to sense, monitor, break down, and/or remove them. It is also very much essential to understand the pathways of degradation of pesticides and the toxicity of the transformed products in order to design better nanomaterials based remediation strategies.

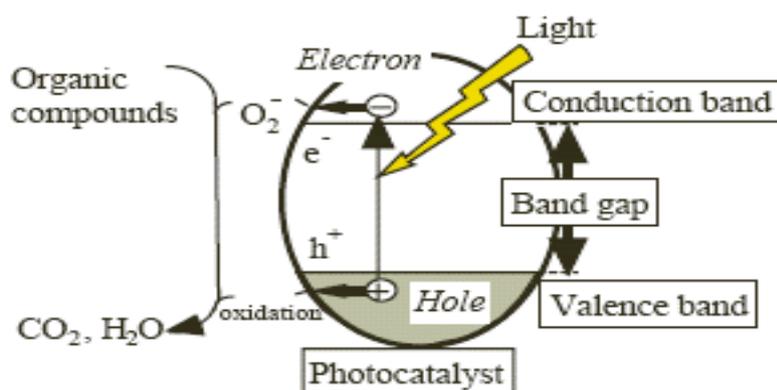
2. Magnetic nanoparticles/ nanocomposites used for the degradation of Dyes and Pesticides

Recently, magnetic nanoparticles and nanocomposites are used extensively for catalytic purposes to sense and degrade the dyes and pesticides. Photocatalysts utilize photon energy to carry out oxidation and reduction reactions. When irradiated with light energy, an electron (e^-) is excited from the valence band (VB) to the conduction band (CB) of the photocatalyst, leaving a photogenerated hole (h^+). This creates hydroxyl ions in aqueous solution thus facilitating catalytic activities^[3,4]. For a material to qualify as a good photocatalyst needs a relatively large band gap, larger surface area, and nonagglomeration of particles. Agglomeration of particles can be avoided by coating the surface with a surfactant. However, it considerably reduces the magnetic moment of the materials and cannot be reused due to low value of magnetization. That is why development of MNP-based catalyst without surfactant requires greater attention. In particular, tremendous progress has been made in the preparation and processing of MNP-supported catalysts, in view of their high surface area resulting in high catalyst loading capacity ^[5], high dispersion ^[6], excellent stability ^[7], and controllable catalyst recycling without loss in their properties. Magnetic separation renders the recovery of catalyst from liquid-phase reactions

much easier and thus dramatically reduces the cost. To fulfill the requirements for various applications, these particles must have suitable magnetic properties (large saturation magnetization (MS), moderate coercivity (HC), and high blocking temperature) and also controllable size and shape [8].

Among all ferrites, Spinel ferrites (MFe_2O_4 , $M=Co, Ni, Mn$) offers the advantages of having a band gap capable of absorbing visible light, as well as the spinel crystal structure, which enhanced efficiency due to the available extra catalytic sites by virtue of the crystal lattice [9]. It can be seen that each of the ferrites have a band gap of approximately 2 eV or lower making them effective under visible light irradiation. It is also important to note that these ferrites also have band gaps that are smaller than other commonly used visible light catalysts such as WO_3 (2.8 eV), CdS (2.4 eV), or $AgVO_3$ (2.2 eV). This is significant in that their ability to absorb visible light is enhanced with a smaller band gap rather than those photocatalysts with a band gap that more effectively encompasses the UV and visible regions, but may not be as highly efficient.

Recently, mesoporous magnetic nanocomposites have received much attention since these composites not only retain the catalytic activity of the metal nanoparticles but also possess the photocatalytic activity.[10-12] In this regard, several investigators have employed standard nanoparticle preparation methods for dye degradation. Recently, $Fe_3O_4@C@Cu_2O$ magnetic core-shell composites with bean-like morphology have been explored to have visible-light-photocatalytic activity for the degradation of organic pollutants[13]. Panda et al. demonstrated catalytic activity of the Fenton-like mesoporous $Fe_2O_3-SiO_2$ composite towards successful decolourisation of methyl orange. [14] In addition, Zhang et al. have synthesized superparamagnetic Fe_3O_4 nanoparticles as catalysts for the catalytic oxidation of phenolic and aniline compounds from aqueous solution. [15] Fe_3O_4 -poly(3,4ethylene-dioxythiophene) core-shell nanoparticles as heterogeneous Fenton catalysts have been synthesized by acid etching-mediated chemical oxidation polymerization. [16]



Mechanism of Photocatalysis

The electron of the photocatalyst valence band becomes excited when illuminated by light. The excess energy of this excited electron promotes the electron to the conduction band of the photocatalyst thus creating the negative-electron (e-) and positive-hole (h+) pair. This stage is referred as the semiconductor's 'photo-excitation' state. The energy difference between the valence band and the conduction band is known as the 'Band Gap'. Wavelength of the light necessary for photo-excitation is: $1240 \text{ (Planck's constant, h) / 3.2 eV (band gap energy) = 388 nm}$ and higher. The positive-hole of the photocatalyst breaks apart water molecules to form hydrogen gas and hydroxyl radicals. The negative-electron reacts with oxygen molecules to form super oxide anions. The super oxide anions and hydroxyl free radicals oxidize the germs, chemical contaminants and odors into harmless carbon dioxide and water. This cycle continues indefinitely as long as light is available and the catalyst does not become depleted.

3. OBJECTIVE OF THE PRESENT WORK

Currently, tremendous effort has been devoted for the synthesis of high surface area, recyclable photocatalyst for the degradation of a variety of organic pollutants. We feel that there sufficient scope to develop a highly water soluble magnetic spinel ferrites for visible light absorption which applicable for degradation of pesticides and dyes. In this regards, our present investigation is addressed on the followings

- Synthesis of mesoporous magnetic spinel Metal ferrites $\text{MFe}_2\text{O}_4(\text{Co}, \text{Mn}, \text{Ni})$ photocatalyst.
- Characterization of the phase, morphology, particle size, zeta potential and surface area using standard characterization techniques like X-ray diffraction technique, Scanning electron microscope (SEM), UV-visible-DRS and BET surface area etc.
- Investigation on catalytic efficiency MnFe_2O_4 in photocatalytic degradation of organic pollutants under UV light.

4. EXPERIMENTAL

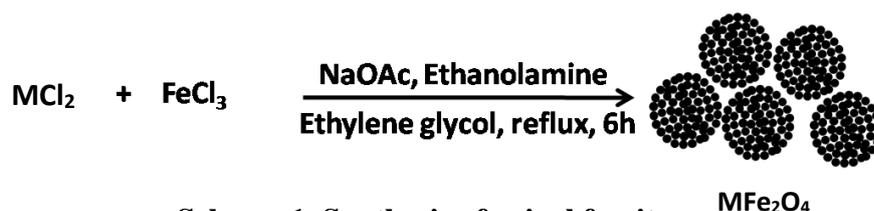
4.1. Materials

All chemicals used here were of analytical grade and used without further purification. Ethylene glycol, ethanol amine, sodium acetate, ferric chloride, cobalt chloride hepta

hydrate, nickel chloride, manganese chloride tetra hydrate were procured from Merck, Germany.

4.2. Synthesis of Spinel MFe_2O_4 (M = Co, Mn, Ni) nanoparticles

Spinel ferrite nanoparticles MFe_2O_4 nanoparticles were synthesized by thermal decomposition of MCl_2 (M= Co, Mn, Ni) and $FeCl_3$ in ethylene glycol in the presence of sodium acetate and ethanolamine. Briefly, anhydrous $FeCl_3$ (4 mmol) and $MCl_2 \cdot 7H_2O$ (2 mmol) were taken in 30 ml ethylene glycol and 0.5 g of sodium acetate was added to it. The black color solution thus obtained was stirred for 30 min at 80 °C followed by the addition of 15 ml of ethanolamine. The entire solution was heated at 150°C for 6h during which fine black colloidal particles appeared reaction mixture. Then it was cooled down to room in the temperature. The particles were recovered using a magnetic separator (DynaMag2, Invitrogen) washed with Millipore water (5×5 ml) and dried in hot air oven at 80 °C for 2 h.



Scheme 1. Synthesis of spinel ferrites

4.3. Characterization

The identification of the crystalline phase of the synthesized ferrite particles was performed by an Expert Pro Phillips X-ray diffractometer. The morphology were analyzed using scanning electron microscope (HITACHI COM-S-4200) operated at 300 KV. The hydrodynamic size and dispersion stability of particle aggregates were investigated through dynamic light scattering using a Malvern ZS90 zetasizer. Hydrodynamic size was measured by dispersing 0.1 mg of sample in 3 ml of distilled water. The surface charge was determined through zeta potential measurements. The pH was adjusted between 4 and 9 using dilute NaOH/HCl solutions for both HD size and zeta potential measurements. The surface chemistry of the nanoparticles was studied using FTIR spectroscopy (Perkin Elmer (BX 12)).

5. RESULTS AND DISCUSSION

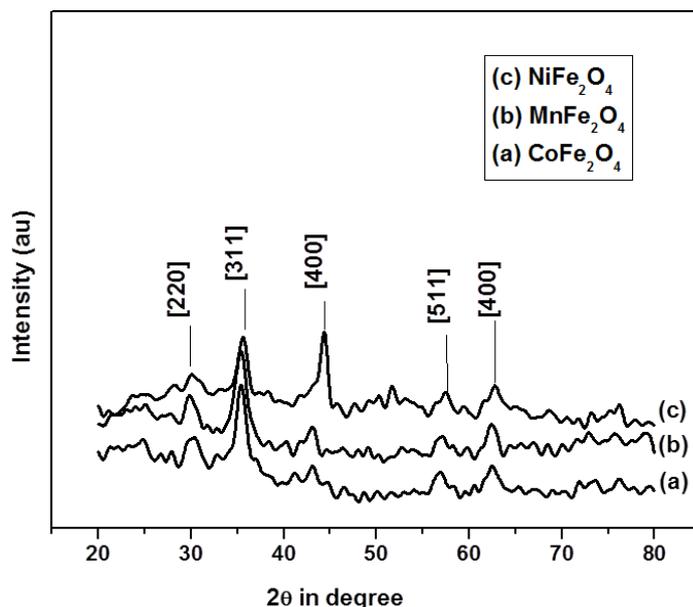


Fig.1 XRD patterns of MFe₂O₄ (M=Co,Mn,Ni) nanoparticles.

X-ray diffraction analysis (Fig. 1) shows that in all metal cases the diffraction pattern perfectly matches with the expected cubic spinel structure of Co, Mn and Ni ferrites and has been identified as CoFe₂O₄ (JCPDS no.03-0864), MnFe₂O₄ (JCPDS no.10-0319) and NiFe₂O₄ (JCPDS no. 03-0875) respectively. The crystallite sizes were calculated using Scherer's equation taking into account broadening each diffraction peak and are summarized in Table 1. The lattice parameters calculated from reflection of [400] plane is 8.36Å, 8.4 Å and 8.32Å for CoFe₂O₄, MnFe₂O₄ and NiFe₂O₄ respectively. Most importantly, the broad peaks in case of all ferrites indicate fine nanocrystalline nature of samples.

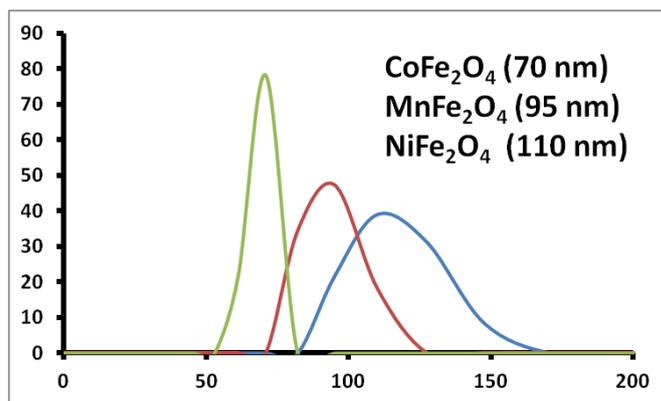


Fig.2 Particle size distribution of ferrite nanoparticles

The aqueous dispersion stability of magnetic nanoparticles is an important factor for their utilization in photocatalyst. The hydrodynamic size was calculated from the diffusional properties of the particle is an indicative of the apparent size of the dynamic hydrated/solvated particle. It was observed that the hydrodynamic (HD) size of CoFe_2O_4 , MnFe_2O_4 and NiFe_2O_4 was found to be 70 nm, 95 nm and 110 nm by DLS. These particles shows a a narrow distribution of size with polydispersity 0.2 (Fig.2). When measured against time, it was found that there was absolutely no change in mean HD size up to 3 day.

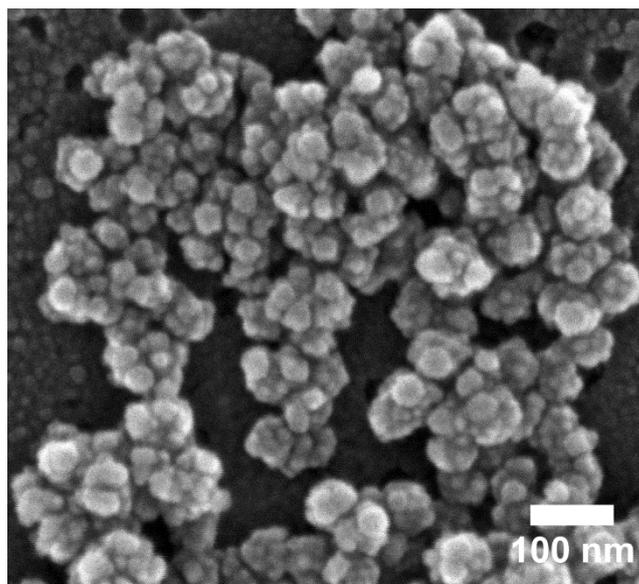


Fig 3. FESEM image of MnFe_2O_4 nanoparticles

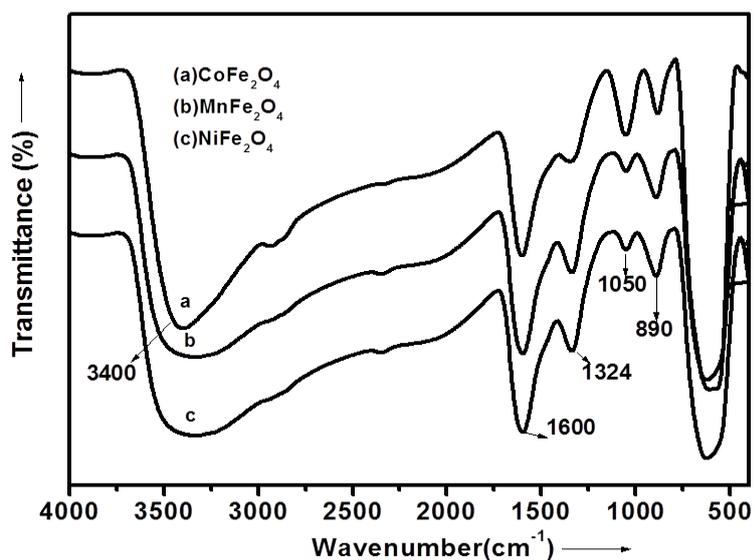


Fig 4. FTIR spectra of CoFe_2O_4 , MnFe_2O_4 , NiFe_2O_4 nanoparticles

Fig 3. shows FESEM image of MnFe_2O_4 NPs which corresponds to the particle size displayed in the particle size analysis. Fig 4. shows FTIR spectra of synthesized ferrite nanoparticles.

The strong band at low frequency region (500–800 cm^{-1}) in each sample is ascribed to the M–O stretching in the oxide nanoparticles. The appearances Of peaks at 890 and 1324 cm^{-1} correspond to the out of plane bending vibration of –N–H bond in primary amine and C–N stretching. This indicates that ethanol amine acting as good capping agent on the surface of metal ferrites and prevent from particle aggregation.

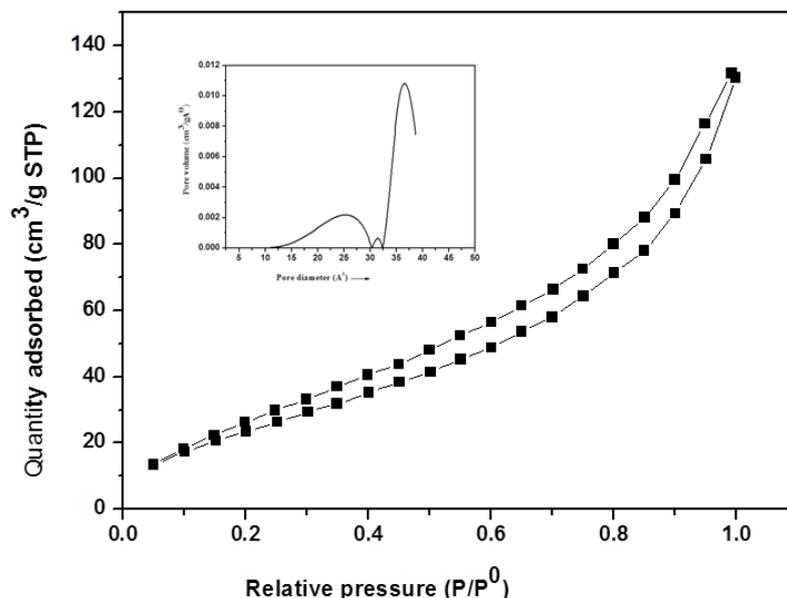


Fig 5. Nitrogen adsorption-desorption isotherm of MnFe_2O_4 nanoparticles. The inset is the pore size distribution curve.

Nitrogen sorption experiment was performed to check the porous nature of the MnFe_2O_4 nanoparticles. The isotherm plot identified as type III, which indicates the mesoporous nature of the sample (Fig. .). From BJH pore size distribution, the pore diameter of the sample was found to be 3 nm. The BET surface area of the MnFe_2O_4 nanoparticles was found to be 105 m^2/g . Hence this synthetic route provides high surfcae area of ferrite nanoparticles and it would be particularly beneficial for catalytic application. The band gap of the spinel ferrites was measured by using the following equation derived by Tauc and Devis Mott independently.

$$\alpha h\nu = K (h\nu - E_g)^n$$

where α was the absorption coefficient, $h\nu$ was the energy of the incident light, E_g was the optical energy gap or the band gap and n was a number which characterized the optical absorption processes. For direct transition $n=1/2$ and for indirect transition $n=2$.

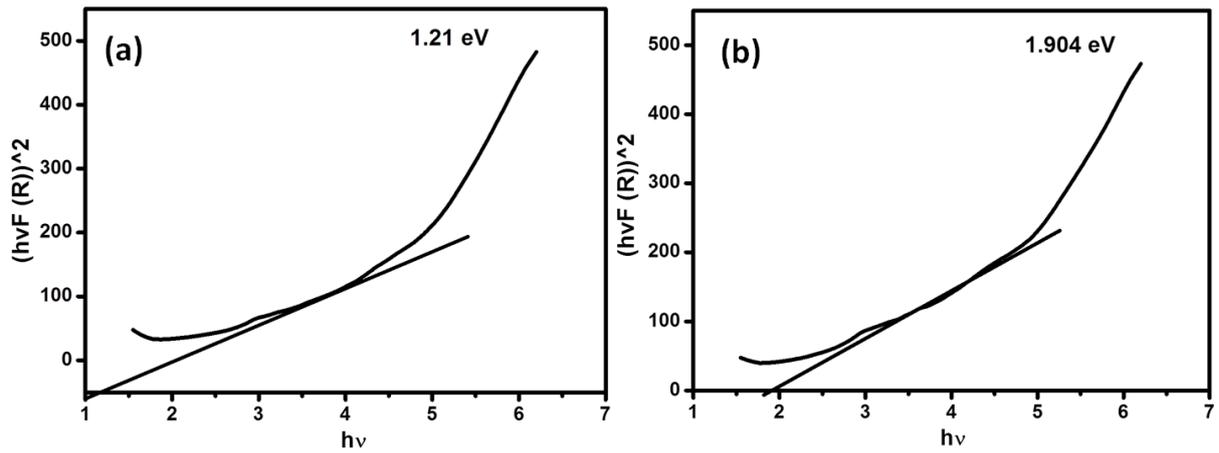


Fig. 6. Tauc plot of (a) CoFe_2O_4 and (b) MnFe_2O_4 for determination of band gap energy.

For high absorbing region, where α obeyed the above equation, by plotting $(\alpha h\nu)^2$ as a function of photon energy ($h\nu$) (Fig. 6) and extrapolating the linear regions of this curve to $(\alpha h\nu)^2 = 0$, the value of band gap for the material CoFe_2O_4 1.21 eV and MnFe_2O_4 1.90 eV. Such tuned band gap of the synthesised nanocomposite is suitable for exhibiting high photocatalytic activity.

After successful synthesis of the nanocomposite, the degradation experiments were carried out in sunlight to explore the photocatalytic efficiency taking imidacloprid (IMP) as a model pesticide. The effect of the three different catalysts while maintaining a constant IMP concentration is shown in Fig. 7. The amount of IMP degradation was found to be better in case of CoFe_2O_4 NPs. The detail investigation on photocatalytic degradation and reusability of the catalyst is under process.

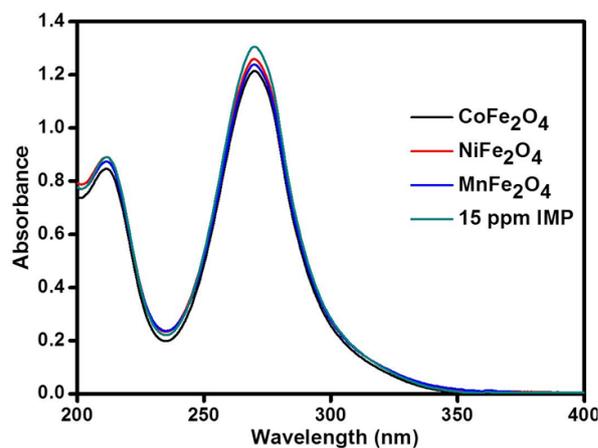


Fig. 7. Degradation of imidacloprid (IMP) by different spinel ferrites

6. CONCLUSION

Mesoporous magnetic inverse spinel metal ferrites MFe_2O_4 ($\text{M} = \text{Co}, \text{Ni}, \text{Mn}$) have been prepared Thermal decomposition of respective metal chlorides in ethylene glycol and ethanolamine. The formation of spinel ferrites was confirmed by XRD. The narrow

band gap of the synthesised nanocomposite sensitized the wide band gap of the prepared ferrites was in the visible region, confirmed by UV–DRS. In addition, the synthesised photocatalyst exhibits removal efficiency for IMP under solar light, easy separation and good stability. These results suggest that the designed photocatalyst may be further explored as a general and competent platform for the removal of pesticides.

7. REFERENCES

1. H. Kyung, J. Lee, and W. Choi, *Environmental Science and Technology*, 2005, **39**, 2376–2382.
2. H. Zollinger, VCH Publishers, New York, NY, USA, 1987.
3. MA. Valenzuela, P. Bosch, J. Jimenez-Becerrill, O. Quiroz, A.I. Paez, *J. Photochem. Photobiol.*, 2002, **148**, 177–182
4. L. Zhang, X. Zhou, X. Guo, X. Song, X. Liu, *J. Mol. Catal. A: Chem.* 2011, **335**, 31–37.
5. H. Zhang, G. Chen, D.W. Bahnemann, *J. Mater. Chem.* 2009, **19**, 5089–5121
6. Mandal, K. Ojha, A.K. De, S. Bhattacharjee, *J. Chem. Eng.* 2004, **102**, 203–208.
7. S. Li, Y. Lin, B. Zhang, C. Nan, Y. Wang, *J. Appl. Phys.* 2009, **105**, 5601–5604
8. L. Kao, T. Hsu and K. Cheng, *J. Colloid Interface Sci.*, 2010, **341**, 359–365.
9. Y. Noda, B. Lee, K. Domen and J. N. Kondo, *Chem. Mater.*, 2008, **20**, 5361–5367.
10. J. C. Yu, L. Zhang, Z. Zheng and J. Zhao, *Chem. Mater.*, 2003, **15**, 2280–2286.
11. S. K. Li, F. Z. Huang, Y. Wang, Y. H. Shen, L. G. Qiu, A. J. Xie and S. J. Xu, *J. Mater. Chem.*, 2011, **21**, 7459–7466.
12. N. Panda, H. Sahoo and S. Mohapatra, *J. Hazard. Mater.*, 2011, **185**, 359–365.
13. S. Zhang, X. Zhao, H. Niu, Y. Shi, Y. Cai and G. Jiang, *J. Hazard. Mater.*, 2009, **167**, 560–566.

14. S. Xavier, R. Gandhimathi, P. V. Nidheesh and S. T. Ramesh, *Desalination and Water Treatment*, 2015, **53**, 311.
15. S. Zhang, X. Zhao, H. Niu, Y. Shi, Y. Cai and G. Jiang, *J. Hazard. Mater.*, 2009, **167**, 560.

