JETIR.ORG ISSN: 2349-5162 | ESTD Year : 2014 | Monthly Issue
JOURNAL OF EMERGING TECHNOLOGIES AND INNOVATIVE RESEARCH (JETIR)
An International Scholarly Open Access, Peer-reviewed, Refereed Journal

Comparative Study on Photocatalytic degradation against methylene blue dye using CuO, Fe (Zero valent) Nanoparticles

[1]Aswini.R, [2]S.Kothai[*]

PG & Research Department of Chemistry, Ethiraj College For Women, Chennai- 600 008.

Abstract : Water pollution is a major issue for the environment and can disturb the entire ecosystem. To eradicate this problem, utilize an efficient photocatalyst for the degradation of toxic pollutants. Thus, we synthesized the CuO, Fe (Zero valent) nanoparticles by chemical method. The CuO, Fe (Zero valent) nanoparticles were characterized by X-ray diffraction (XRD), Field Emission Scanning Electron Microscopy (FESEM), Energy Dispersive X-ray Analyser (EDX), Fourier Transform Infrared Spectroscopy (FTIR), UV-Visible Spectroscopy (UV-Visible). The average crystallite size of the CuO (13 nm), Fe (Zero valent) nanoparticles (24 nm) was examined by XRD. The surface morphology was determined by FESEM. The comparative study of photocatalytic degradation of synthesized CuO, Fe (Zero valent) nanoparticles against methylene blue in two different environments like solar light, mercury light irradiation and results reveals that the synthesized CuO nanoparticles show 90 % photocatalytic degradation efficiency under mercury light irradiation was achieved within 180 minutes.

Keywords : **Nanoparticles, Surface Morphology, Methylene blue, Photocatalytic degradation, Irradiation.**

I. INTRODUCTION:

Nanotechnology is gaining a tremendous impulsion in the present century due to its capability of modulating metals into their nanosize. The use of iron-based technologies is a rapidly developing field, with a range of technologies proposed which use iron as a reductant or a sorbent, which have been tested at various scales of application. Nanotechnology is the manipulation of individual atoms and molecules to create materials and devices with vastly different properties[1]. Water pollution is the major cause of the environmental issues raised by the degradation of aquatic ecosystems. This may lead to a wide range of physical changes such as elevated temperatures, chemicals[2] etc., An aquatic pollution (water pollution) is the pollutant of water bodies. For example rivers, aquifers, reservoirs, lakes [3]etc., In 2017, a study reveals that 1.8 million people were died due to polluted water spreading gastrointestinal diseases, parasitic infections[4]. The major contribution to environmental pollution is organic dyes due to their non-biodegradability, high toxicity, carcinogenic effects[5,6]. During the process of degradation, the destruction of organic pollutants with reactive oxygen species to create electron-hole pairs[7,8].

The photocatalytic degradation property of copper oxide and zero-valent iron nanoparticles are discussed as follows. Muthuvel *et al*., (2020) reported the two different methods of copper oxide nanoparticles to examine their photocatalytic property. The results reveal that 85 % for chemically synthesized copper oxide nanoparticles and 97 % for biosynthesized copper oxide nanoparticles respectively [9]. Phang *et al*., (2021) studied the green synthesis of copper oxide nanoparticles for photocatalytic degradation exposure of UV irradiation and they found that 66 % degradation was achieved after 3 hours under UV irradiation [10]. Naincy Sahu *et al*., (2019) reported the optimum effect on photocatalytic degradation. The synthesized zero-valent iron

nanoparticles are highly active for the adsorptive treatment against methylene blue [11]. Moosavi *et al*., (2020) evaluated the photocatalytic activity of the doped magnetic materials under methylene blue dye [12].

In this study, we report the synthesized CuO and Fe (Zero valent) nanoparticles by chemical method and examine their photocatalytic degradation against methylene blue dye in the presence of solar light and mercury light irradiation.

II. MATERIALS AND METHODS:

Copper Sulphate, Ferrous Sulphate, Sodium Borohydride, Sodium hydroxide pellets, Methylene Blue and 30 % of Hydrogen Peroxide were purchased from Sigma Aldrich, Merck.

2.1 Synthesis of Copper Oxide Nanoparticles :

1 M solution of is Copper Sulphate mixed with Sodium hydroxide solution and stirred for 1 hour. Initially, the blue color of the reaction mixture slowly changes to black color. It is then filtered, dried at 80^{o}C for 4 hours[13].

2.2 Synthesis of Iron (Zero valent) Nanoparticles :

Iron Nanoparticles were prepared by chemical reduction method[14]. 0.1 M solution of Ferrous sulfate was prepared by using distilled water and it is stirred for 10 minutes. To the above mixture, add 0.75 M solution of sodium borohydride with continuous stirring for 30 minutes. The black color particles were filtered using Whatman filter paper and then dried at room temperature.

2.3 Experimental Setup for the Photocatalytic Degradation Study:

The Photocatalytic degradation of methylene blue was analyzed by using CuO, Fe (Zero valent) nanoparticles as a catalyst in the presence of solar light and mercury light irradiation. In this experiment, 100 mL of methylene blue dye were mixed with 50 mg of catalyst and 2 mL of 30 % H_2O_2 was taken in a 250 mL beaker. The above aqueous suspension was stirred in a dark environment for 40 minutes to attain adsorption-desorption equilibrium. And then the suspension was irradiated in the presence of solar light and Mercury light (Mercury Lamp of 500 W) irradiation.

The photocatalytic degradation of CuO, Fe (Zero valent) nanoparticles was measured by a UV-Visible spectrophotometer. At regular time intervals of 1 hour, 5 mL of dye was taken out from the reaction mixture and then centrifuged. The concentration was determined by UV absorbance at 665 nm for Methylene blue dye. The photocatalytic degradation efficiency of methylene blue was calculated by the general formula[15]

$$\% \text{ Photocatalytic Degradation Efficiency} = C_0\text{-}C_t \,/\, C_0 \times 100$$

Where C_0 is the initial concentration of methylene blue dye after the adsorption-desorption equilibrium and C_t is the absorbance of the solution after the photocatalytic reaction at a time ‘t’.

III. CHARACTERISATION:

XRD analysis was performed by Powder X-ray Diffractometer-PANalytical, Xpert3 instrument. It is used to predict the average crystallite size for the sample. Field Emission Scanning Electron Microscopy was performed by Desktop Mini-FESEM (SNE-3200, SEC FESEM). SEM analysis is used to predict the magnification images of a sample’s surface topography. Fourier Transform Infrared Spectroscopy was performed by Shimadzu Instrument. The FTIR spectrum shows the presence of a functional group. The UV-Visible spectroscopy and Photocatalytic degradation study were determined by UV-Visible Spectrophotometer (Shimadzu).

IV. RESULTS AND DISCUSSION:

4.1 X-ray Diffraction Analysis:

XRD patterns for the Copper Oxide, Iron (Zero valent) nanoparticles were recorded with the CuKα radiation with the diffraction angle. The average crystallite size D was calculated from the Sherrer equation.

The X-ray diffraction pattern for CuO nanoparticles was shown in Fig.1. The diffraction peaks of CuO Nanoparticles are 32.5^{o} (110), 35.5^{o} (002), 38.7^{o} (111), 48.7^{o} (202), 53.4^{o} (020), 58.1^{o} (202), 61.5^{o} (113), 66.2^{o} (311), 68^{o} (220), 72.3^{o} (311), 75^{o} (222) planes of monoclinic (JCPDS File 41-0254) which confirms the phase formation of CuO Nanoparticles[16,17]. The average crystallite size of CuO Nanoparticles was found to be 13 nm.

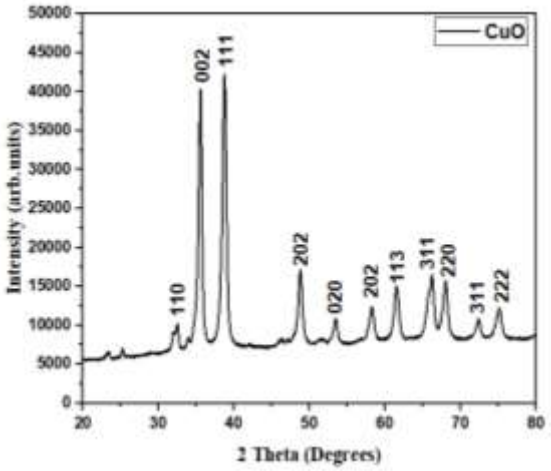

Fig. 1 XRD pattern for CuO Nanoparticles

The X-ray diffraction pattern of Fe (Zero valent) Nanoparticles was shown in Fig.2. The synthesized iron nanoparticles are in the cubic system with the lattice constant of a=b=c= 2.82 Å. The hkl values for iron nanoparticles are (110) and (200) planes (JCPDS File 87-0721) respectively. The diffraction peak is around 45º which corresponds to the iron nanoparticles[18]. The average crystallite size for Fe (Zero valent) nanoparticles was found to be 24 nm.

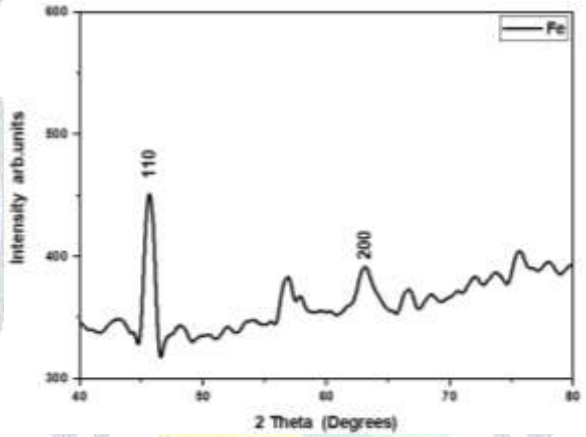

Fig. 2 XRD pattern for Fe (Zero valent) Nanoparticles

4.2 FESEM & EDX Analysis :

Field Emission Scanning Electron Microscopy was implied to examine the surface morphology of CuO, Fe (Zero valent) nanoparticles which are depicted in Fig.3. The FESEM images of CuO nanoparticles showed spherical with slight needle shape morphology. For the Iron nanoparticles showed a flower-like morphology. The surface morphology of CuO, Fe (Zero valent) nanoparticles are uniformly distributed with an average particle size ranging from 100 to 300 µm [5].

Energy Dispersive X-ray analysis examined for the synthesized CuO, Fe (Zero valent) nanoparticles were shown in Fig.4. The EDX analysis confirms the existence of Cu and O in the prepared CuO nanoparticles and also confirms the presence of Fe (Zero valent) in the synthesized iron nanoparticles.

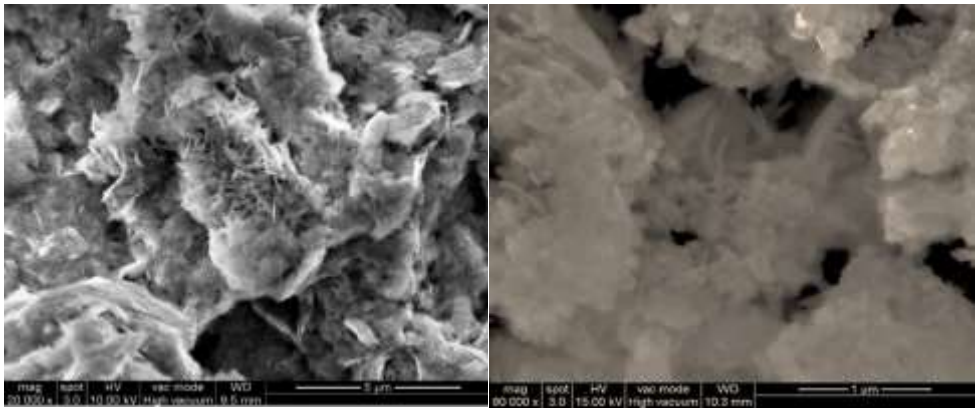

Fig. 3 SEM images of CuO & Fe (Zero valent) Nanoparticles

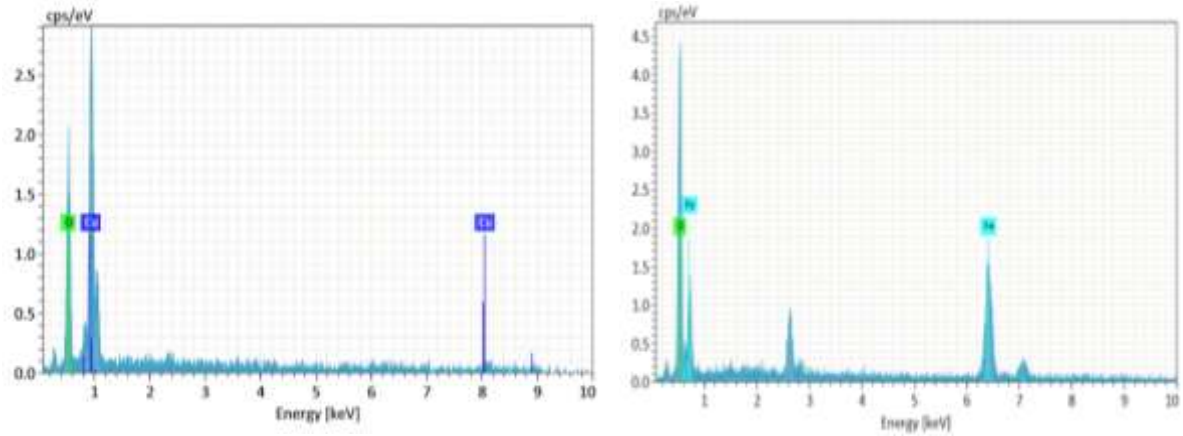

Fig. 4 EDX spectra of CuO & Fe (Zero valent) Nanoparticles

4.3 FTIR Spectroscopy :

The Fourier Infrared spectra of CuO and Fe (Zero valent) Nanoparticles were shown in Fig 5. The C=C stretching vibration was observed at 1505 cm^{-1}. The absorption peak at 613 to 878 cm^{-1} corresponds to the aromatic C-H bending vibrations and the peaks at 530 and 579 cm^{-1} which confirms the formation of Cu-O bond respectively [16,17]. The absorption peaks at 529 and 670 cm^{-1} correspond to zero-valent iron nanoparticles [18,19]. The OH stretching frequency was observed at 3398 cm^{-1}.

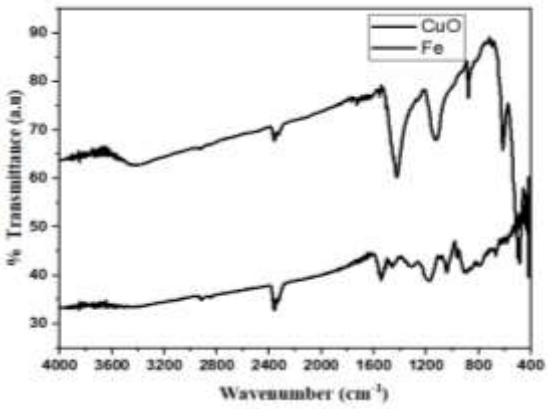

Fig. 5 FTIR Spectra of CuO, Fe (Zero valent) Nanoparticles

4.4 UV-Visible Spectroscopy

The electronic transition of synthesized CuO Nanoparticles was shown in Fig. 6. The characteristic peak at 410 and 455 nm corresponds to the formation of CuO Nanoparticles [13]. The UV-Visible spectrum of Fe (Zero valent) nanoparticles was shown in Fig.6. The absorption peak at 306, 365 nm confirms the formation of Fe (Zero valent) nanoparticles[20]

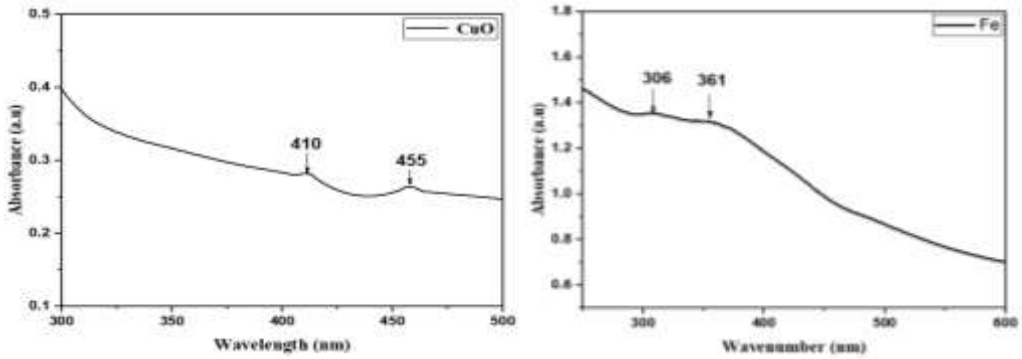

Fig .6 UV-Visible Spectrum of CuO, Fe (Zero valent) Nanoparticles

4.5 Photocatalytic Degradation Study

The absorption spectra of CuO, Fe (Zero valent) nanoparticles for the degradation of MB dye under solar light were shown in Fig.7. The synthesized CuO nanoparticles adsorbed 67 % whereas the Fe (Zero valent) nanoparticles adsorbed 77 % against methylene blue dye, due to their increase in the surface area. The highest photocatalytic degradation of methylene blue containing CuO nanoparticles as a catalyst significantly develops the electron pairs and increases the photoinduced charge carrier of nanoparticles.

The absorption spectra of CuO & Fe (Zero valent) nanoparticles for the degradation of MB dye under the mercury light were shown in Fig.7. The Synthesised CuO nanoparticles adsorbed 90 % in 180 minutes (up to 3 hrs) due to their increase in the surface area. The Fe (Zero valent) nanoparticles adsorbed 6.7 % in 300 minutes (up to 5 hrs) against methylene blue dye. The highest photocatalytic degradation of methylene blue containing CuO nanoparticles as a catalyst significantly develops the electron pairs and increases the photoinduced charge carrier of CuO nanoparticles.

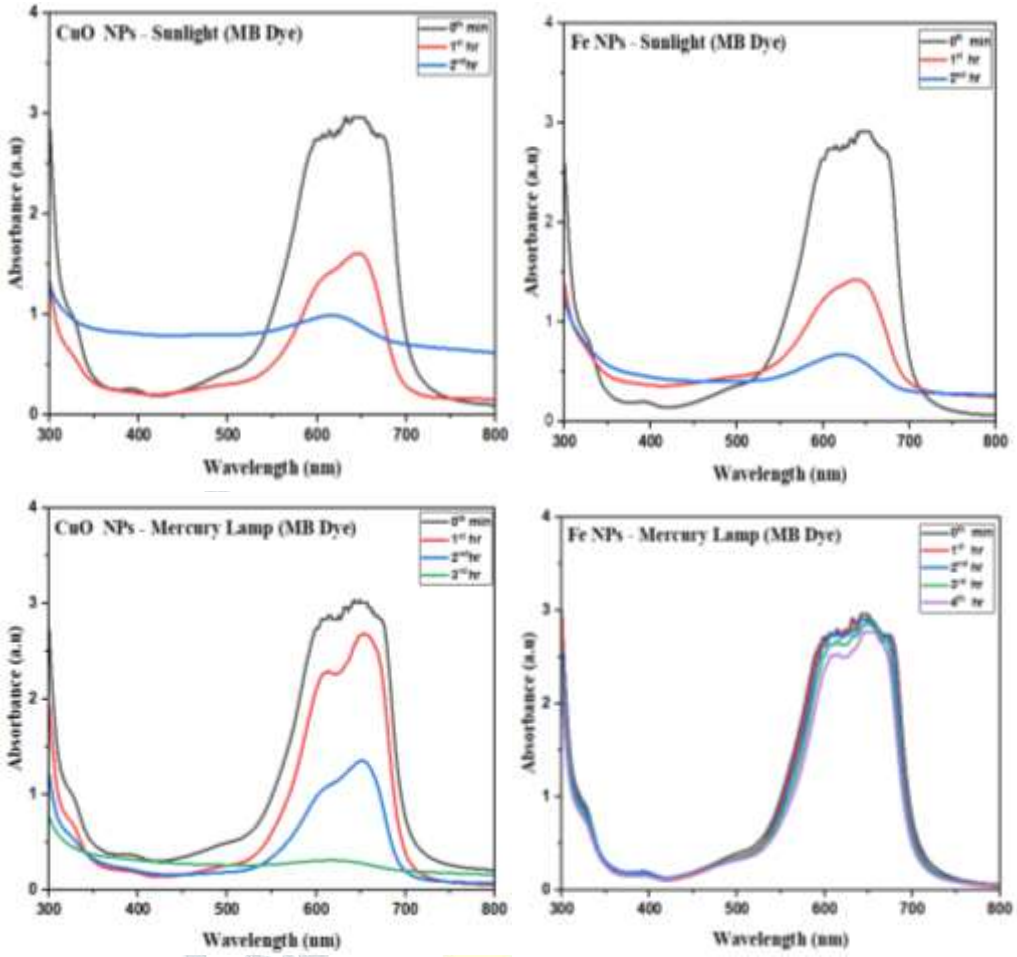

Fig.7 Photocatalytic Degradation efficiency of CuO, Fe(Zero valent) nanoparticles under Sunlight and mercury light irradiation (MB Dye)

V. CONCLUSION

The Present study demonstrated the synthesis, characterization and photocatalytic degradation of CuO and Fe (Zero valent) nanoparticles. The X-ray diffraction analysis reveals that the monoclinic phases for CuO nanoparticles and cubic phases for the Fe (Zero valent) nanoparticles. The Field Emission Scanning Electron Microscopic images of synthesized CuO & Fe (Zero valent) nanoparticles exhibit spherical and flower-like morphology. The synthesized CuO and Fe (Zero valent) nanoparticles confirm the formation of EDX, FTIR, UV-Visible spectroscopy. The photocatalytic degradation of CuO, Fe (Zero valent) nanoparticles using methylene blue dye by comparing the two different environments like solar light and mercury light irradiation. It reveals that the degradation efficiency of CuO nanoparticles is higher than the, Fe (Zero valent) nanoparticles in both solar and mercury light irradiation.

VI. ACKNOWLEDGEMENT:

The authors are thankful to Ethiraj College for Women for providing a research facility to carry out this part of the research work. And also we thank SRM University, Anna University for SEM, XRD analysis.

REFERENCES

1. Wang. C., Zhang. W.: Synthesis of nanoscale iron particles for rapid and complete dechlorination iron particles for rapid and complete dechlorination of TCE and PCBs. Environmental Science & Technology. 31(7), 2154-2156(1997). doi: https://doi.org/10.1021/es970039c.
2. Moss B. Water pollution by agriculture. Philos Trans R Soc B Biol Sci. 2008; 363(1491): 659–66.
3. Marcos von Sperling. Wastewater Characteristics, Treatment and disposal, Biological Wastewater treatment series. 1. 2007. 292.
4. "Global WASH Fast Facts | Global Water, Sanitation and Hygiene | Healthy Water | CDC". www.cdc.gov. April 2, 2021. Retrieved September 19, 2021.
5. Murali S K, N Suprajaa, E David. Photocatalytic Activity of Methylene Blue Using Zinc Nanoparticles Synthesized from Gymnema Sylvestre And Antimicrobial Assay. Advancements Bioequivalent, 2(4),2019, 161-167. doi: 10.31031/ABB.2019.02.000542.
6. Cheng W, Wang SG, Lu L, Gong WX, Liu XW, et al. Interaction between congo red and copper in a binary adsorption system: Spectroscopic and kinetic studies. Biochem Eng J, 538-546, 2008.
7. Yan Li, Dewen Ye, Mingxi Li, Ming Ma, and Ning Gu, Adaptive Materials Based on Iron Oxide Nanoparticles for Bone Regeneration, Chem Phys Chem. doi : http://dx.doi.org/10.1002/cphc.201701294.
8. Veiseh O, Gunn JW, Zhang M. Design and fabrication of magnetic nanoparticles for targeted drug delivery and imaging. Adv Drug Deliv Rev. 2010; 62(3): 284–304. doi : http://dx.doi.org/10.1016/j.addr.2009.11.002.
9. M.Muthuvel. Jothibas C.Manoharan. Synthesis of copper oxide nanoparticles by chemical and biogenic methods: photocatalytic degradation and in vitro antioxidant activity, Nanotechnology for Environmental Engineering, 2020, 5:14. Doi: https://doi.org/10.1007/s41204-020-00078-w.
10. Phang, Y.-K.; Aminuzzaman,M.; Akhtaruzzaman, M.; Muhammad,G.; Ogawa, S.; Watanabe, A.; Tey,L.-H. Green Synthesis and Characterization of CuO Nanoparticles Derived from Papaya Peel Extract for the Photocatalytic Degradation of Palm Oil Mill Effluent (POME). Sustainability 2021, 13, 796. Doi : https://doi.org/10.3390/su13020796
11. Naincy Sahu, Shalu Rawat, Jiwan Singh Rama Rao Karri, Suhyun Lee, Jong-Soo Choi and Janardhan Reddy Koduru, Process Optimization and Modeling of Methylene Blue Adsorption Using Zero-Valent Iron Nanoparticles Synthesized from Sweet Lime Pulp Appl. Sci. 2019, 9, 5112; Doi: http://dx.doi:10.3390/app9235112
12. Moosavi, Seyedehmaryam, Li, Rita Y, Lai, Chin W, Yusof, Yusliza, Gan, Sinyee, Akbarzadeh, Omid Chowhury, Zaira Z. Yue, Xiao-Guang, Johan, Mohd R.Methylene Blue Dye Photocatalytic Degradation over Synthesised Fe3O4/AC/TiO2 Nano-Catalyst: Degradation and Reusability Studies, Nanomaterials, 2020, 10(12), 2360. Doi :http://dx.doi.org/10.3390/nano10122360
13. Manyasree D, Peddi KM, Ravikumar R. CuO nanoparticles: Synthesis, characterization and their bactericidal efficacy. Int J Appl Pharm. 2017; 9(6): 71.
14. Huang KC, Ehrman SH. Synthesis of iron nanoparticles via chemical reduction with palladium ion seeds. Langmuir. 2007;23(3):1419–26.
15. Ali I, Kim J. Continuous-Flow Photocatalytic Degradation of Organics Using Modified TiO2 Nanocomposites, Catalysts, 8, 4(3), 1- 13, 2018.
16. Tadjarodi A, Akhavan O, Bijanzad K. Photocatalytic activity of CuO nanoparticles incorporated in mesoporous structure prepared from bis (2-aminonicotinato) copper ((II) microflakes. Trans Non-ferrous Met Soc China [Internet]. 2015;25(11):3634–42. Available from: http://dx.doi.org/10.1016/S1003-6326(15)64004-3
17. Srivastava R, Prathap MUA, Kore R. Colloids and Surfaces A : Physicochemical and Engineering Aspects Morphologically controlled synthesis of copper oxides and their catalytic applications in the synthesis of propargylamine and oxidative degradation of methylene blue. Colloids Surface A Physicochem Eng Asp. 2011;392(1–1):271–82. doi: http://dx.doi.org/10.1016/j.colsurfa.2011.10.004

18. Vemula Madhavi, Prasad, T.N.V.K.V., Gajulapalle Madhavi.: Synthesis and Spectral Characterization of Iron-Based Micro and Nanoparticles. Iranica Journal of Energy & Environment. 4 (4), 385-390 (2013). doi: 10.5829/idosi.ijee.2013.04.04.10
19. Kharat, H.J., Kakde, K.P., Savale, P. A., Datta, K., Ghosh, P., Shirsat, M.D.: Synthesis of iron oxide films for the development of ammonia sensor. Polymers for Advanced Technologies. 18, 397-402 (2007). doi: https://doi.org/10.1002/pat.903
20. Yana Bagbi, Ankur Sarswat, Sachchidanand Tiwari, Dinesh Mohan, Arvind Pandey, Pratima R.Solanki, L-cysteine stabilized Zero valent iron nanoparticle and their application for the remediation of lead ions from water, Environmental Nanotechnology, Monitoring and management, 11, 2016. doi: http://.org/doi:10.1016/j.enmm.2016.11.008