Original Article

Rapid Degradation of Methyl Orange by Heterogeneous Fenton Process Using $Fewo_4$ Nanocatalyst Prepared by Wet Chemical Route.

V Robert Bellarmin[1]*, Arjun Moorthy[2], M. E Raja Saravanan[3]

[1]*Department of Physics, Periyar University, Salem, Tamil Nadu, India
[2]Independent Researcher, Arjun's nanomaterials research lab, Salem, Tamil Nadu, India. Email: arjunmoorthy97@gmail.com
[3]Government Arts College (Autonomous), Salem, Tamil Nadu, India. Email: merajasaravanan@gmail.

***Corresponding Author:** V Robert Bellarmin

[1]*Department of Physics, Periyar University, Salem, Tamil Nadu, India
DOI: 10.47750/pnr.2022.13.S08.505

Abstract

To remove the hazardous organic adulterants from the wastewater, iron tungstate nanoparticles were prepared by a simple wet chemical route. These nanoparticles characterized to be polydispersed, polycrystalline with irregular spherical morphologies without any notable impurities were used as a catalyst for heterogeneous Fenton reaction, an advanced oxidation process. Their catalytic properties, degradation efficiency, and recyclability were analyzed for methyl orange degradation, a common -reactive azo dye in an acidic aqueous. The rapid fall of absorption peak exhibits the complete degradation of dye within 50 minutes of reaction with discoloration efficiency of ~97% without any additional external exposures such as light or ultrasonic waves. In addition to this, the durability of the $FeWO_4$ nanoparticles catalyst is proved to be maintained over five catalyst reuse cycles, which strongly suggests that at this present scenario of ecological deterioration, the chosen nanomaterial is one of the apt candidates for azo dye removal by heterogeneous dark Fenton process.

Keywords: $FeWO_4$, Fenton process, Catalyst, Methyl orange.

INTRODUCTION

Nowadays, freshwater scarcity is the leading challenge for the economic growth and development of a country. As the groundwater storage is slowly declining, the discharge of dye effluents[1] from the textile, plastic, dyes, cosmetic, agrochemical, paper, and refining industries into the water bodies defile the available water unfit for consumption. While the production and usage of chemicals in various fields are increasing exponentially day by day, the anatomical properties of the chemicals mixed with water manifest carcinogenic, teratogenic, mutagenic, and other toxic effects[2]. Hence the degradation of organic and inorganic chemicals in water is an alarming threat to humanity and other living organisms that requires utmost attention. Furthermore, the coloring components are noted to cause the formation of virulent aniline and phenolic compounds even under anaerobic surroundings which adulterate the soil and ground water[3], triggering the environmental disorder[4,] and health issues. For the eviction of such intractable pollutants, there are numerous conventional technologies such as reverse osmosis, adsorption, precipitation, ion exchange, biodegradation, ultrafiltration, photochemistry, sonolysis, and radiolysis[5] are available. These methods are not only very expensive but their aerobic treatment is proved to be unproductive in the case of aromatic amines under anaerobic situations[6]. In addition to this, the requirements of high precision equipment for the post-treatment of sorbent materials restrict their practical far-reaching execution[7]. These shortcomings are overcome by the advanced oxidation processes, wherein oxidizing radicals are generated to degrade organic compounds[8], developed to treat the contaminated water. Out of all the reported advanced oxidation processes, Fenton oxidation[9-11] is a process that utilizes ferrous ions and hydrogen peroxide in an acid medium to degrade organic compounds with a vast variety of utilization due to its simplicity, inflated production rate of hydroxyl radicals, mineralization rate, easy availability, economical and easy handling[12]. This is proved to be one of the simplest and decisive technologies in environmental reformation[13,14]. In due course, the Fenton process had undergone technological extension such as Electro Fenton, Sono Fenton, Photo Fenton, Sono Photo Fenton, Photo Electro Fenton, and Sono Electro Fenton ever since it is initiated by Horstman Fenton Jackson in the year 1894. The primary Fenton reaction is as follows

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{\bullet} + OH^{-}$$

This Fenton technology mineralizes the pollutants when H_2O_2 and Fe^{2+} combine in the presence of the acidic aqueous medium producing $OH^{\bullet}$[8] which is a highly oxidative hydroxyl radicle to degrade recalcitrant organic pollutants. The ferrous ions involved in oxidation are regenerated again during the reaction is the main advantage of this mechanism to abate organic compounds. However, maintaining an acidic aqueous medium with a narrow pH value and continuous insertion of homogenous catalyst[15] to sustain[16] the reaction are the limitations of the homogeneous Fenton process. Since

the catalyst is a metal salt, fueled to carry out the reaction cannot be retained during the degradation process which accumulates metal ions throughout the reaction, causing slush production and difficulties in post treatment[1,17.] This difficulty is administered very well in heterogeneous Fenton process[18] wherein the iron catalyst permeated at the solid surface[19] will not be dissolved, thus the leaching of iron ions from the heterogeneous catalyst is prevented. The main advantage of this method is that the iron-based catalyst can be separated[8,20] easily from the solution by a magnetic field to reutilize the catalyst further, thus avoiding secondary pollutions by the iron-based catalyst. Though numerous iron-based materials such as magnetite[21], goethite, hematite, Fe-clinoptilolite[22], mesostructured silica[23], fly ash[24], Fe-zeolite[25], activated carbon[26], ceria-based catalysts[19], ball clay[25], etc., are used for this process. new generation heterogeneous catalysts based on nanoparticles are developed due to their inherent properties mainly enhanced catalytic activities which are absent in their bulk form[27,28.] Nanoparticles including iron oxide nanoparticles, manganese oxide nanoparticles, zerovalent iron nanoparticles, supported gold nanoparticles, supported palladium nanoparticles[29] have been tested successfully based on relative efficiency and operating mechanism such as leaching of metal ions, reusability, the concentration of hydrogen peroxide used. The general strategy of heterogeneous catalysts (deposition of small ionic particles on large surface area metal support) is accomplished by these nanoparticles due to their relationship between surface area and catalytic activities. Amidst the numerable iron-based nanoparticles, Iron tungstate ($FeWO_4$) bulk counterpart is widely used as a catalyst for peroxide oxidation while nanomaterials are not explored sufficiently. In this work FeWO4, the nanoparticle is considered as a smart candidate for the Fenton reaction due to its catalytic and ferromagnetic properties, antimicrobial activity, photocatalytic activity cost-effectiveness, and nontoxic are the advantages of $FeWO_4$ nanomaterial over other materials. The proper selection of preparation methods that directly capitulates fine $FeWO_4$ nanoparticles without introducing any enhancement techniques like thermal processes, doping, crafting, etc. is the productive way of increasing hydrogen peroxide's activating ability. Of the known synthesis methods such as hydrothermal[30], solvothermal[31], microwave-hydrothermal[32], spray pyrolysis, and sol-gel method[33], the wet chemical route is the cost-effective, reliable and simple method to synthesize iron tungstate nanoparticles.

Herein $FeWO_4$ particles are synthesized by wet chemical route, with polycrystalline and polydisperse nature (2-25nmsized), also their crystal structure, morphology, and catalytic properties are investigated properly. The degradation efficiency and recyclability are analyzed for methyl orange dye, one of the most common azo dyes, used in leather, food, paint, textile, and paper industries predominantly discharged in the industrial wastewater. The rapid fall of the absorption peak at a wavelength of 520nm exhibits the complete degradation of dye from the aqueous solution at 50 minutes of reaction without any external exposure like light, heat, electric field, etc., with decolorization efficiency of 97% which is remarkable compared to the previously reported results. The fabricated $FeWO_4$ nanoparticles are so effective that their catalytic activity is far better than the catalytic activities reported elsewhere by Photo Fenton or electro Fenton processes.

MATERIAL AND METHODS:

Preparation of $FeWO_4$ catalyst:

Iron tungstate nanoparticles were synthesized by the wet chemical method which was reported previously by our research group[33] in which 120ml of 0.88 g of $NaWO_4$ and 0.43 g of CTAB solution is prepared and stirred for 15 minutes. Then 0.6M $FeSO_4$ solution of 5ml is rapidly injected within the precursor mixture. The mixture turns brown and is heated up to 80^{o}C using a hot plate setup for 15 minutes. Finally, NaOH solution was added quickly showing dark brown $FeWO_4$ nanoparticle formation which was cleaned many times thoroughly using a centrifuge and dried.

The particles shapes, size distribution, and morphology of prepared $FeWO_4$ nanoparticles are analyzed using a highresolution transmission electron microscope (HRTEM- JEOL JEM 2100) and field emission scanning electron microscope (FESEM- Carl Zeiss SIGMA) coupled with an EDS detector (Bruker Quantax 200—Z10). The purity of sample preparation and phase purity is studied by powder X-ray diffractometer (XRD- Bruker D8) using Cu-Kα targets with a 2^o/min scan rate.

Dye degradation studies:

The degradation studies are performed by dispersing 50 mg of the above-prepared catalyst in 50 ml of dye solution (25 mg per liter methyl orange in water), the mixture is ultrasonicated for 15 minutes for better dispersion and left idle in a dark for 20 minutes to obtain adsorption equilibrium. Then the degradation is initiated in dark by adding 75 microliter 30%vol/vol Hydrogen peroxide. By adding sufficient concentrated Hydrochloric acid, the pH of the solution is brought to 2 constantly and 3ml of the dye solution is extracted every 10 minutes to record dye concentration using a visible spectrometer (Labman LMSP-V325). Every time the catalyst was removed using magnetic separation and the decolorization efficiency was calculated using the following equation, Decolorization efficiency = $(C-C_0)/C_0 \times 100$

Where the initial dye concentration value is C_0 and C is the dye concentration at time t.

RESULTS AND DISCUSSION

Fig1(a) shows the XRD pattern of $FeWO_4$ nanoparticles prepared in which all the observed diffraction peaks of XRD patterns are well correlated and in harmony with the diffraction standards (JCPDS 74-1130), indicating that the $FeWO_4$ is a crystalline monoclinic structure with a good degree of purity as no other peaks correspond to impurities are observed.

Also, the broad peaks suggest that the particles are smaller in size. The calculation by the Scherrer equation proved that the average particle size is approximately 17 nm[33]. Fig 1(c),(d) shows the HRTEM images of prepared nanoparticles. The size and morphology of the $FeWO_4$ nanoparticles from the TEM

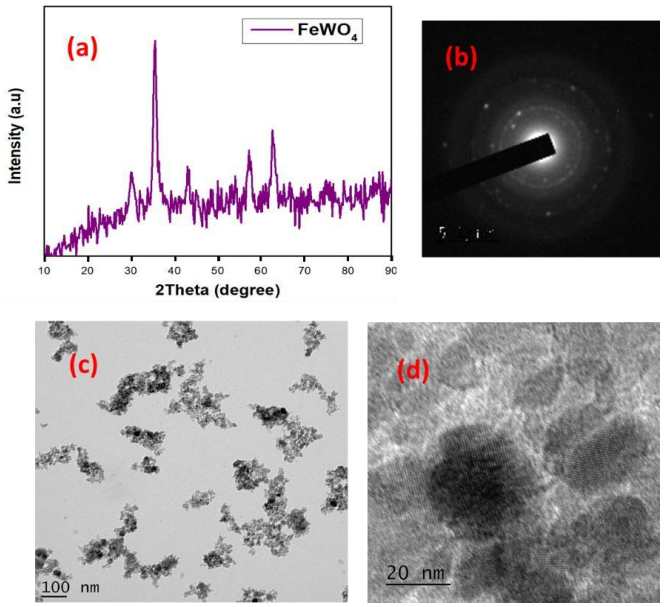

Figure 1. shows the (a) XRD pattern, (b) SAED and (c), (d) HRTEM images of prepared $FeWO_4$ nanoparticles.

The image reveals that they are polydispersed and polycrystalline with sizes ranging from 2nm to 25nm. Also, they are agglomerated into small aggregates. The surface morphology of $FeWO_4$ nanoparticles is revealed by the FESEM image (Fig 2, (a)) showing that the particles are uniformly distributed with irregular shapes and an approximate size of about 17nm. The elemental analysis of the synthesized iron tungstate nanoparticles from the EDS spectrum (Fig 2 (b)) revealed the presence of Fe, W, O, C, and Au. The presence of Au is due to the sputtering of samples to improve electron mobility for FESEM analysis. No other elements were detected in a significant amount showing that the samples are free from impurities. Figure 2(c) shows the variation in the absorption spectrum of methyl orange by heterogeneous Fenton process and its respective decolorization kinetics (Fig. 2(d)) under the suitable operating conditions (C_0= 25mgL^{-1}, pH=2, H_2O_2 concentration 15mM) until 50 min of reaction time. The rapid decrease of the absorption peak at 520 nm is observed which implies that Methyl orange dye was considerably degraded in the aqueous solution, attaining 97% degradation efficiency at 50 min of reaction time. This indicates that -N=N- bonds of the molecules of methyl orange azo dye were annihilated as a result the color of the solution vanishes.

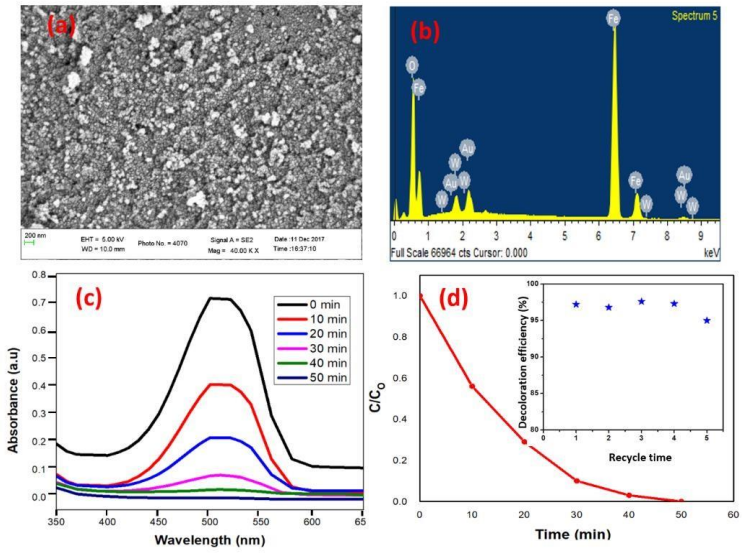

Figure 2 shows the FESEM image, EDAX analysis of as prepared $FeWO_4$ catalyst. Fig (c) and (d) show the absorption graph of MO and change in concentration concerning reaction time. The inner image of Fig.2(d) shows the decoloration efficiency concerning recycling time.

Figure 2 (d) explains the kinetics of the degradation process of methyl orange. This graph plotted with a ratio of initial concentration to concentration at time t as a function of reaction time, shows a straight line, specifying zero-order reaction. The Fenton process could be further understood by the reaction as follows

$$OH^{\bullet} + RH \text{ (methyl orange)} \rightarrow R^{\bullet} + H_2O$$
$$R^{\bullet} + Fe^{3+} \rightarrow R^{+} + Fe^{2+}$$

According to this, ferrous iron was promptly oxidized to ferric ions, at the same time ferrous iron is regenerated during the reaction between ferric ions and H_2O_2. To study the durability of the $FeWO_4$ catalyst, the separated and collected residue catalyst using a magnetic field was washed with distilled water and dried at room temperature. This recycled catalyst was again utilized and the same experiment was repeated for 5

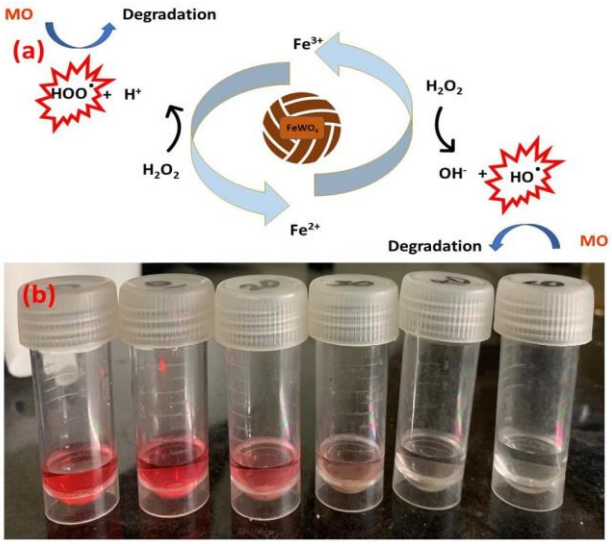

Figure 3(a) shows the graphical representation of the Fenton process using $FeWO_4$ nanoparticles, (b) shows the optical image of MO Dye solution extracted every 10 minutes interval in the Fenton process.

cycles. Fig 2. (d) inner images showing decoloration efficiency concerning several cycles. This explains that the decolorization efficiency changes as 97.2%, 96.8%, 97.6%, 97.3%, 95% in 1,2,3,4,5 cycles respectively which indicates the sustainability and oxidative capacity of the $FeWO_4$ catalyst for methyl orange azo dye. Fig 3 (a) shows the graphical representation of the appropriate mechanism for the Fenton process using $FeWO_4$ nanoparticles, Fig 3(b) shows the realtime sample of MO dye which was collected after every 10 minutes interval of the reaction. The decolorization of methyl orange is visible through the naked eye.

CONCLUSIONS

$FeWO_4$ nanoparticles were prepared by the wet chemical route and were found to be polycrystalline, polydispersed with a fine size of 2-25nm. The prepared catalyst showed no notable impurities and exhibited good catalytic activity for degradation of MO dye by heterogeneous Fenton process. The Catalyst showed 97% efficiency, without any external stimuli such as light, heat, electric, and sonic waves, within 50 minutes is outperforming other reports on Iron tungstate used as a catalyst for photo Fenton and electro Fenton processes. Also, the sustainability of the catalytic activity reported up to the five cycles of reuse demonstrates that $FeWO_4$ could be a promising and potential catalyst for the treatment of azo dye-containing wastewater by a heterogeneous Fenton process.

ACKNOWLEDGMENTS

The authors are thankful to STIC (Sophisticated Test and Instrumentation Center) and SITRA (South Indian Textile Association) for helping us to do microscopic analysis (HRTEM and FESEM).

REFERENCES

1. Z. Han, Y. Dong and S. Dong, J. Hazard Mater., 189, 241-248 (2011).
2. R.D Combes and R.B. Haveland-Smith, Mutation Research., 98,101-248 (1982).
3. K. Swaminathan, S. Sandhya, S. A. Carmalin, K. Pachhade, and Y.V Subrahmanyam, Chemosphere., 50, 619-625(2003).
4. G. Zhang, F. Yang, and L. Liu, J. Electroanalytical Chemistry., 632, 154-161(2009).
5. J.R. Dominguez, J. Beitran and O. Rodriguez. Catal Today., 101, 389-395 (2005).
6. C. Radulescu, I. Ionita, E. I. Moater and C. Stihi, OUAC., 20(1), 66-71 (2009).
7. N. Panda, H. Sahoo and S. Mohapatra, J. Hazard Mater.,185, 359-365 (2011).
8. J.J Pignatello, Environmental Science and Technology.,26(5) 944-951 (1992).
9. A. Georgi , A. Schierz, U. Trommler, C. P. Horwitz, T. J. Collins and F.-D. Kopinke, Appl.Catal.B.,72,2636(2007)

10. D. F. Laine, A. Blumenfeld and I. F. Cheng, Ind. Eng. Chem. Res., 47, 6502-6508 (2008)
11. Y. Seol and I. Javandel, Chemosphere.,72537-542(2008)
12. S. Karthikeyan, M. Ezhil Priya, R. Boopathy, M. Velan, A. B. Mandal and G. Sekaran, Environ.Sci.Pollut.Res.,19,1828-1840(2012)
13. L.F Liotta, M. Gruttadauria, G. D. Carlo, G. Perrini and V. Librandod, J. Hazard Mater.,162,588-606(2009)
14. A. Ziylan and N. H. Ince, J. Hazard. Mater.,187,24-36 (2011).
15. A. Corma, and H. Garcia, Chem. Rev.,103, 4307 – 4366(2003).
16. Y. Chen, G. Li, F. Yang and S-M. Zhang, Polym.Degrad.Stab.,96,863-869(2011).
17. H. Hassan and B. H. Hameed, Int.J.Environ.Sci.Tecnol.,2, 218-222 (2011).
18. S.R. Pouran, A. A. A Raman and W.M.A.W Daud, J. Cleaner Production., 64, 24-35 (2014).
19. A.F. Rossi, N. Amaral-Silva, R.C. Martins and R.M. Quinta-Ferreira, Appl. Catal. B., 111-112, 254-263 (2012) .
20. A.N Soon and B. H. Hameed, Applied Catalysis A: General.,450, 96-105 (2013)
21. S. P. Sun, A and T. Lemley, J. Mol. Catal. A Chem.,349,71-79(2011)
22. M. Bayat, V. Sohrabi and S.J. Royaee, J. Ind. Eng. Chem., 18,957-962(2012).
23. X. Zhong, S. Reyer, H. Zhang, Q. Huang, L. Xiang, S. Valange, and J. Barrauli, Sep.Puri.Technol.,80,163-171(2011).
24. N. Zhang, J. Wang, P. Zhou, Jiang and G. Liu, J. Hazard. Mater 201-202,68-73(2012).
25. H. Hassan and B. H. Hameed, Desalination., 276,45-52(2011)
26. X. Liang, Y. Zhong, H. He, P. Yuan Zhu,S.Z.Z.Jiang,Chem.Eng.J.,191,177-184(2012).
27. E. G. Garrido-Ramirez, B. K. G. Theng, M. L. Mora, Appl. Clay Sci., 47,182-192(2010)
28. J. M. Perez, Nat. Nanotechnol., 2, 535 – 536(2007)
29. Amarajothi Dhakshinamoorthy, Sergio Navalon, Mercedes Alvaro, Hermenegildo Garcia, ChemSusChem.,5,46-64(2012)
30. J. Guo, X. Zhou, Y. Lu, X. Zhang, S. Kuang and W. Hou, J.Solid State Chemistry., 96, 550-556(2012)
31. Y. X. Zhou, H. B. Yao, Q. Zhang, J. Y. Gong, S. J. Liu and S.H.Yu, Inorganic Chemistry., 48,1082-1090(2009)
32. M.A. P. Almeida, L. S. Cavalcante, C. Morilla-Santos, P. N. Lisboa Filho, A. Beltran, J. Andres, L. Gracia and E. Longo, Materials Characterization.,73 124-129(2012)
33. Arjun Moorthy, V.Robert Bellarmin, Balaji Kumaran, M.E. Raja Saravanan, Inorganic and Nano-metal Chemistry.,50,10(2020)