

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/318500906>

# Visible Light Induced Heterogeneous Photo-Fenton Oxidation of Direct blue 71 using Mesoporous Fe/KIT-6

Article in *Research Journal of Pharmacy and Technology* · May 2017

DOI: 10.5958/0974-360X.2017.00257.8

CITATIONS

2

READS

187

4 authors:



Ar Sasieekhumar

Vinayaka Missions Kirupananda Variyar Engineering College

5 PUBLICATIONS 23 CITATIONS

SEE PROFILE



Thirunavukkarasu Somanathan

Vels University

63 PUBLICATIONS 794 CITATIONS

SEE PROFILE



Abilarasu Annamalai

Sri Sivasubramaniya Nadar College of Engineering

20 PUBLICATIONS 327 CITATIONS

SEE PROFILE



Manivannan Shanmugam

roquette india private limited

8 PUBLICATIONS 48 CITATIONS

SEE PROFILE

**RESEARCH ARTICLE**

## Visible Light Induced Heterogeneous Photo-Fenton Oxidation of Direct blue 71 using Mesoporous Fe/KIT-6

A.R. Sasiyekhumar<sup>1,2</sup>, T. Somanathan<sup>2\*</sup>, A. Abilarasu<sup>2</sup>, M. Shanmugam<sup>2</sup>

<sup>1</sup>Department of Chemistry, AVS College of Technology, Chinnagoundapuram, Salem – 636 106, Tamilnadu, India

<sup>2</sup>Department of Chemistry, School of Basic Sciences, Vels University, Pallavaram, Chennai, 600 117, Tamilnadu, India.

\*Corresponding Author E-mail: [soma\\_nano@yahoo.co.in](mailto:soma_nano@yahoo.co.in)

### ABSTRACT:

The present study deals with the synthesis of mesoporous Fe/KIT-6 and catalyst has been successfully tested for the heterogeneous photo-Fenton degradation of organic dye solutions under direct sun light. The physico-chemical properties of the catalyst were analyzed by XRD, N<sub>2</sub> sorption studies, SEM and TEM. From the results we infer that the catalyst reveal excellent catalytic property for 97% removal of direct blue 71 within 75mins, which could be attributed to the adsorptive power of Fe/KIT-6. With the advantages of rapid degradation and efficient magnetic separation, the synthesized material could gain a potential application in wastewater treatment and organic pollutant.

**KEYWORDS:** Mesoporous material, XRD, visible light driven catalyst, photo fenton, wastewater treatment.

### INTRODUCTION:

Now a day's removing organic pollutant from the industrial wastewater is most important aspect in environmental technology. Dyes are the major industrial pollutants and water contaminants<sup>1,2</sup>. During the dyeing process about 20% of the dye is not fixed on the fabric and enters into the environment. The conventional physical-chemical and biological treatment methods for removal of pollutant from industrial effluent are unsuccessful, often resulting in a colored discharge from the treatment plants<sup>3</sup>. Thus advance treatment methods are essential for the degradation of long lasting organic pollutant or converting them to harmless products in water<sup>4</sup>. Advanced oxidation processes (AOPs) have been developed to removal of organic pollutant from industrial waste. AOP produce an oxidizing agent hydroxyl radical, which remove the organic compound in effluent rapidly and non-selectively<sup>5</sup>.

Fenton process is a most important oxidation system amongst advanced oxidation processes, which has its own advantages such as high removal efficiency, and usage of low cost materials<sup>6</sup>. However, homogeneous fenton system have own drawbacks such as recovery of catalyst and maintaining narrow pH<sup>7</sup>. The use of zeolite-immobilized Fe ions<sup>8</sup>. Fe pillared clay<sup>9</sup>, or polymer supported Fe has been studied for the removal of organic pollutant<sup>10</sup>. Nowadays, mesoporous materials (such as SBA-15, MCM-41 and KIT-6) were widely used as the catalytic support material for the metal oxide, because it has more specific area, controllable pore volume, narrow pore distribution, and easy surface modification<sup>11-14</sup>. KIT-6 mesoporous materials show enhanced characteristics for metal immobilization due to *Ia3d* pore architecture to better diffusion within the interconnected cubic structure<sup>15</sup>. The aim of this study to investigate catalytic efficiency of iron loaded KIT-6 as a heterogeneous fenton type catalyst using sunlight for removal of direct blue 71 dyes.

Received on 18.03.2017

Modified on 24.03.2017

Accepted on 06.04.2017

© RJPT All right reserved

Research J. Pharm. and Tech. 2017; 10(5): 1455-1458.

DOI: 10.5958/0974-360X.2017.00257.8

## MATERIALS AND METHODS:

TEOS (tetraethyl orthosilicate), P-123 poly (ethylene glycol)-block- poly (propylene glycol)-block-poly (ethylene glycol) triblock copolymer, hydrochloric acid, n-butanol, ferric nitrate and methanol were purchased from sigma-aldrich for the synthesis of nanocatalyst. Deionized water was used during the experiment.

### Synthesis of Fe/KIT-6:

According to our previous report,<sup>16</sup> we have synthesized iron loaded mesoporous KIT-6 catalysts by wet impregnation method. In a typical synthesis, 4 g amphiphilic triblock copolymer (Pluronic P123) in 144 ml water was stirred for 1 h. Thereafter, 7.9 g of hydrochloric acid solution was added to it and the gel was stirred for 4 h<sup>17</sup>. Then, 4 g n-butanol was added to it and the stirred for 1 h at 35°C. Then 8.6 g of tetra ethyl ortho silicate (TEOS) was added to it and then continuously stirring for 24 h at 35°C. The mixture was finally heated in an autoclave at 100°C for 24 h. Thus, the solid product obtained was filtered, dried at 100 °C and then calcined at 550°C in air to expel the template. The loading of iron (10 wt%) into KIT-6 was carried out as follows: 1 g of KIT-6 was treated with required amount of 1 M iron nitrate solution as per loading in ethanol solution (total volume ~25 ml) under stirring at room temperature for 3 h followed by filtration and drying at 80 °C. The obtained materials were then calcined at 450 °C in air.

### Photo catalytic Experiments:

Photo degradation of direct blue 71 (DB) was carried out to evaluate the catalytic activity of Fe/KIT-16 according to our previous report<sup>18</sup>. The experiments were performed in a 100 ml beaker in presence of sun light irradiation, suspended catalyst and dye solution stirred under darkness to attain adsorption/desorption equilibrium and expose to the sunlight. At the given time intervals, 2 ml of the suspensions were separated, and then centrifuged to remove the catalyst. The amount of direct blue present in the water was calculated by Shimadzu UV-3600 Model UV-Visible Spectrophotometer (Japan) and the wavelength of maximum absorption at  $\lambda_{max} = 587 \text{ nm}$  was monitored.

## RESULTS AND DISCUSSION:

### XRD Pattern of Fe/KIT-6:

Fig. 1 shows the small angle powder XRD pattern of Fe/KIT-6. The high intensity peak in the  $2\theta$  range  $1^\circ$ - $3^\circ$  due to (211) reflection plane indexed to a body centred cubic  $Im\bar{3}m$  space group.

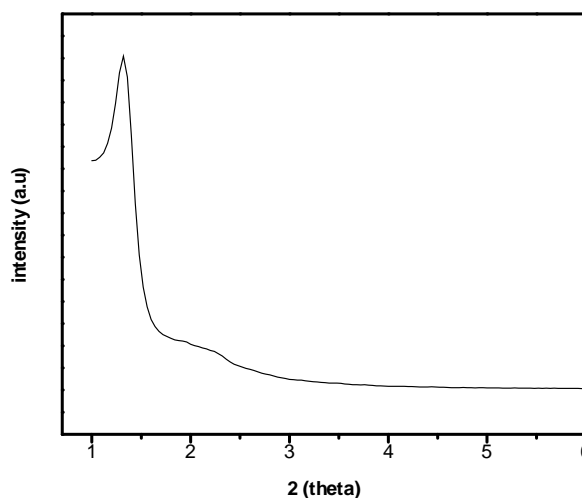


Figure 1: XRD pattern of Fe/KIT-6

### Morphological study:

Typical SEM image shows the morphology of the sample is shown in Fig.2. The deposition of iron oxide on the surface of the catalyst formed agglomerations with irregular shapes and were responsible for heterogeneity of the catalyst<sup>19-20</sup>.

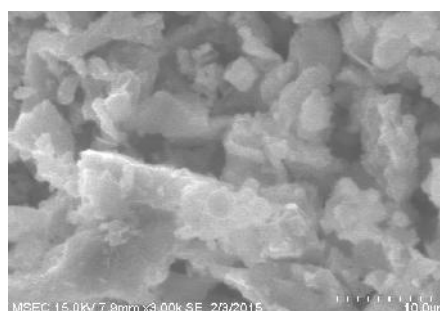


Figure 2: SEM Image of Synthesized Catalyst

### Photo catalytic activity of the synthesized Fe/KIT-6 catalyst:

The degradation efficiency of synthesized material was studied using DB as the target compound under sun light irradiation. The control experiments were performed under different conditions it's shown in Fig.3 From the results we infer that negligible amount of degradation was achieve with sun light irradiation and catalyst alone, it's clearly shows that DB was very stable in typical condition. The Fe/KIT-6 catalyst associate with sunlight has a significant influence on the degradation efficiency of DB. Photo catalytic activity can be influenced by various operating parameters, which could be optimized.

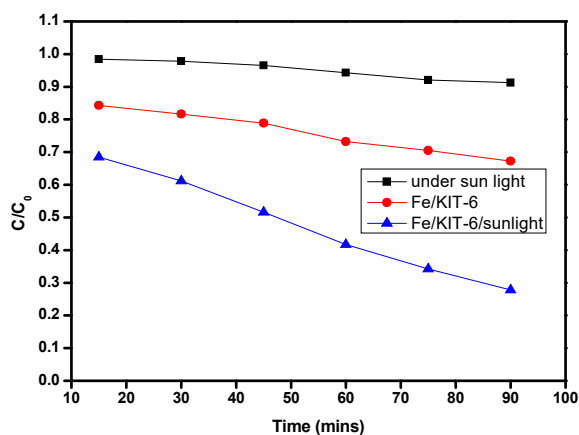


Figure 3: Degradation of Direct Blue 71 by different process

**Influence of catalyst dosage:**

The influence of the Fe<sup>3+</sup> ions on decolourization of DB under direct sun light using Fe/KIT-6 was evaluated by varying the catalyst concentration between 10% and 40% at 100 mg of DB concentration. The degradation efficiency increases on increasing the concentration of Fe<sup>3+</sup> ions due to enhanced generation of OH radicals (Fig.4). Further increase in the concentration, degradation efficiency decrease because of Fe<sup>3+</sup> act as a filter of sun light<sup>21</sup>.

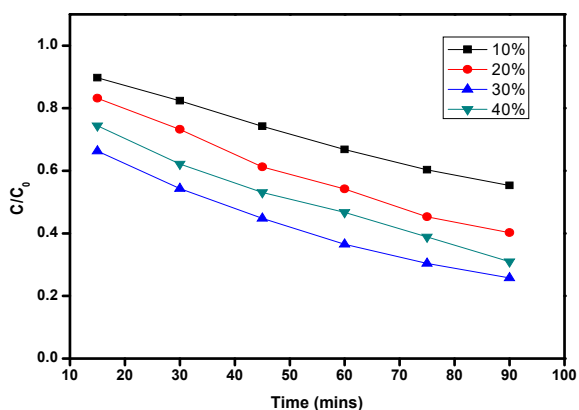


Figure 4: Effect of Fe<sup>3+</sup> concentration on degradation

**Effect of H<sub>2</sub>O<sub>2</sub> :**

The effects of H<sub>2</sub>O<sub>2</sub> concentrations on the degradation rate were investigate to explain the role of H<sub>2</sub>O<sub>2</sub>. Fig.5 illustrates the degradation efficiency at various concentrations of H<sub>2</sub>O<sub>2</sub>. It was observed that the degradation efficiency initially increased with an increase in the H<sub>2</sub>O<sub>2</sub> concentration up to 6ml/L. At low concentration, H<sub>2</sub>O<sub>2</sub> cannot generate enough hydroxyl radicals so rate of the reaction is low. Above optimum level of H<sub>2</sub>O<sub>2</sub> concentration the decrease in decolourization occurs due to the scavenging effect of excess H<sub>2</sub>O<sub>2</sub>, which decreases the number of hydroxyl radicals in the solution<sup>22-24</sup>.

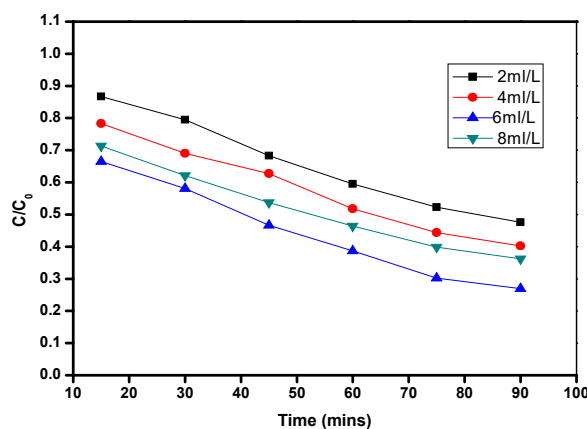


Figure 5: Effect of H<sub>2</sub>O<sub>2</sub> on degradation efficiency

**CONCLUSION:**

In summary, we synthesized Fe/KIT-6 photo catalyst by wet chemical method. The synthesized material was characterized using XRD, HRSEM. Hence, the catalytic efficiency of the synthesized sample was studied on the removal of direct blue 71 under sun light and optimized various parameters like H<sub>2</sub>O<sub>2</sub> and catalyst dosage. From the results we confirmed the synthesized material shows to be highly efficient for removal of organic dyes in water by catalytic degradation.

**ACKNOWLEDGEMENTS:**

The author A. R. Sasieekhumar would like to thank the Department of Chemistry, School of Basic Sciences for providing infrastructure facilities to complete the research work.

**REFERENCE:**

1. Brown DH, Hitz HR and Schafer L. The assessment of the possible inhibitory effect of dye stuffs on aerobic wastewater: experience with a screening test. Chemosphere. 10; 1981: 245–261.
2. Muruganandham M, Sobana N and Swaminathan M.: Solar assisted photocatalytic and photochemical degradation of Reactive Black 5. Journal of Hazardous Materials B. 1; 2006: 1371–1376.
3. Huang CH etal. Characterization and application of Ti-containing mesoporous silica for dye removal with synergistic effect of coupled adsorption and photocatalytic oxidation. Journal of Hazardous Materials. 186; 2011: 1174–1182.
4. Krishnakumar B and Swaminathan M. Influence of operational parameters on photocatalytic degradation of a genotoxic azo dye Acid Violet 7 in aqueous ZnO suspensions. Spectrochimica Acta A. 81; 2011: 739–744.
5. Neelakandeswari N et al. Spectroscopic investigations on the photodegradation of toluidine blue dye using cadmium sulphide nanoparticles prepared by a novel method. Spectrochimica Acta A. 78; 2011: 1592–1598.
6. Guo S, Zhang G and Wang J. Photo-Fenton degradation of rhodamine B using Fe<sub>2</sub>O<sub>3</sub>-Kaolin as heterogeneous catalyst: Characterization, process optimization and mechanism Journal of Colloid and Interface Science. 433; 2014: 1–8.
7. Liu SQ et al. Magnetic nickel ferrite as a heterogeneous photo-Fenton catalyst for the degradation of rhodamine B in the

- presence of oxalic acid. *Chemical Engineering Journal*. 203; 2012: 432–439.
8. Kuznetsova E et al. The catalytic and photocatalytic oxidation of organic substances using heterogeneous Fenton-type catalysts. *Water Science and Technology*. 49; 2004: 109–16.
  9. Chen Q et al. Heterogeneous photo-Fenton photodegradation of reactive brilliant orange X-GN over iron-pillared montmorillonite under visible irradiation. *Journal of Hazardous Materials*. 168; 2009: 901–8.
  10. Liang H et al. Diatomite coated with Fe<sub>2</sub>O<sub>3</sub> as an efficient heterogeneous catalyst for degradation of organic pollutant. *Journal of the Taiwan Institute of Chemical Engineers*. 000; 2014: 1–8.
  11. Baldrian P et al. Degradation of poly cyclic aromatic hydrocarbons by hydrogen peroxide catalyzed by heterogeneous polymeric metal chelates. *Applied Catalysis B*. 59; 2005: 267–74.
  12. Shanmugam M, Abilarasu A and Somanathan T. Transesterification of waste chicken fat oil using mesoporous Mg-KIT-6 catalyst. *Advanced Science Engineering and Medicine*. 8; 2016: 1–7.
  13. Shen Z et al. Photocatalytic properties of TiO<sub>2</sub> supported on SBA-15 mesoporous materials with large pores and short channels. *Materials Letters*. 65; 2011: 3354–3357.
  14. Hinda L et al. Photocatalytic activity of TiO<sub>2</sub>-SBA-15 under UV and visible light. *Journal of Photochemistry and Photobiology A: Chemistry*. 226; 2011: 1–8.
  15. Cyril P et al. Tunable KIT-6 Mesoporous sulfonic acid catalysts for fatty acid esterification. *ACS Catalysis*. 2; 2012: 1607–1614.
  16. Somanathan T et al. Fabrication of multiwalled carbon nanotubes in the channels of iron loaded three dimensional mesoporous material by catalytic chemical vapour deposition technique. *Applied Surface Science*. 257; 2011: 2940–2943.
  17. Chandrasekar G, Hartmann M and Murugesan V. Preparation of SBA-15 extrudates: Evaluation of textural and mechanical properties. *Journal of Porous Materials*. 16; 2009: 175–183.
  18. Abilarasu A, Saravanan A and Somanathan T. Synthesis of cobalt manganese ferrite and  
it used as a visible active fenton catalyst for dye degradation. *Journal of Chemical and Pharmaceutical Sciences*. 7; 2014: 111–112.
  19. Liany DL et al. Hydrotalcite-TiO<sub>2</sub> magnetic iron oxide intercalated with the anionic surfactant dodecylsulfate in the photocatalytic degradation of methylene blue dye. *Journal of Environmental Management*. 156; 2015: 225–235.
  20. Huang Z et al. Enhancement of photocatalytic degradation of dimethyl phthalate with nano-TiO<sub>2</sub> immobilized onto hydrophobic layered double hydroxides: a mechanism study. *Journal of Hazardous Materials*. 246–247; 2013: 70–78.
  21. Vaishnav P et al. Photo oxidative degradation of azure-B by sono-photo-Fenton and photo-Fenton reagents. *Arabian Journal of Chemistry*. 7; 2014: 981–985.
  22. Ersöz G, Napoleoni A. and Atalay S. Comparative study using chemical wet oxidation for removal of reactive black 5 in the presence of activated carbon. *Journal of Environmental Engineering*. 139 (12); 2013: 1462–1469.
  23. Bokare AD and Choi W. Review of iron-free Fenton-like systems for activating H<sub>2</sub>O<sub>2</sub> in advanced oxidation processes. *Journal of Hazardous Materials*. 275; 2014: 121–135.
  24. Tehrani-Bagha AR, Gharagozlou M and Emami F. Catalytic wet peroxide oxidation of a reactive dye by magnetic copper ferrite nanoparticles. *Journal of Environmental Chemical Engineering*. 4 (2); 2016: 1530–1536.