

Efficient Degradation of Methyl Orange by Fenton Process with Fc-based Metal-Organic Framework

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Abstract : Herein, we report the unique property of MOF as a photo catalyst: ferrocene (Fc) based Co-MOF (probe R1) prepared by a simple method was able to react with H₂O₂ to achieve high efficiency in photocatalytic Fenton process. In selective heterogeneous Fenton process using Fc based Co-MOF; the results suggest that the combination of Fe²⁺/Fe³⁺ cation and H₂O₂ can significantly improve the photocatalytic proficiency at room temperature. It could completely remove MO azo dye in the presence of a certain amount of H₂O₂ under visible light within 40 minutes. The activity performed by varying different parameters, such as dye and catalyst concentration, pH, H₂O₂ dosage. MOF catalyst shows better adsorption at acidic medium. When the quantity of photo catalyst R1 increased, then the decolorization of the azo dyes enhanced. The degradation diminishes with increasing the concentration of dyes as well as pH range. This work reveals that Fc based Co-MOF materials hold countless potential for assertions in the field of radiation-energy exchange into chemical energy. The photo catalyst probe-R1 perceived that was a perfect photo catalyst from the degradation/adsorption of Methyl Orange in the presence of visible radiation.

Keywords- Degradation, Fenton Catalyst, H₂O₂, MOF, Visible light.

Introduction

Industrial processes release large amounts of organic dye or pigments in environment. These are poisonous and non-biodegradable and when it released the natural water recourses, the approaching photosynthetic action of aquatic plant life seriously threatens the whole ecosystem. Sources of dye pollution have expanded from textile industries to paper, cosmetic, food, leather pharmaceutical and printing companies. These dyes are not treated appropriately get gathered in the environment and become a hazard to the ecosystem. The treatment of wastewater from synthetic dyeing is a major environmental problem that has received great consideration^{1 2 3}. In recent decades, various physical⁴, chemical⁵, and biological methods have been developed to remove dye from the wastewater. Conventional treatment methods, such as coagulation⁶, flocculation, adsorption⁷, absorption⁸, ultrafiltration, reverse osmosis⁹, and membrane technology¹⁰, simply target or transfer organic compounds from one phase to another phase. Photo catalysis is a very vital process for water splitting¹¹, degradation of pollutants^{12 13}, solar cells¹⁴, hydrogen generation¹⁵ and CO₂ conversion.

Advanced oxidation processes (AOP) are strategies dependent on the development of hydroxyl radicals, which are exceptionally receptive oxidizing agents. AOP can oxidize a wide

range of compounds that would otherwise be difficult to decompose. The Fenton heterogeneous procedure utilizing H_2O_2 as the precursor oxidizer is one of the most grounded AOPs and, after the disintegration of H_2O_2 , produces amazing hydroxyl radicals that can break down most natural contaminations under reasonable circumstances.^{16 17}

The metal-organic frameworks (MOFs) are rapidly growing class of materials for their various network architectures in a 3D space. The network architectures constructed from metal ions or clusters are linked together by multifunction organic bridging ligands, which can expose more metal active sites with inherent a large specific surface area, uniform but tunable cavity, porosity, and are easy to functionalize with different ligands have allowed them to show a variety of potential applications.³⁻⁹

Actually, several studies that demonstrate the successful applications of MOFs in photocatalysis, mostly for photocatalytic dye degradation or hydrogen production, have emerged.^[11, 12]

Earlier many photo catalyst systems synthesized such as carbon-based nanomaterials, semi conducts TiO_2 , ZnO , WO_3 , CdS , some nanotubes, graphene, and nanocomposites also have concerned prominent attention. Ferrocene $Fe(C_5H_5)_2$ ¹⁷ is a highly stable organometallic compound which is nontoxic, due to the rich application of the iron(II) center it has been extensively used in many areas in present days.²⁰ Fc has an electron donor-acceptor conjugated arrangement; it has redox reversible moiety which is having high catalytic capacity. Here we used ferrocene based MOF as a visible-light-driven photo catalyst for absorption/degradation of waste product azo dye Methyl Orange.²¹

1. Materials and method

$Co(NO_3)_2 \cdot 6H_2O$, ferrocene dicarboxylic acid (FcDCA), 4,4'-bipyridyl, NaOH, MeOH and all the dyes. All materials were procured from Merck and used in the experiments as received. The solvents were used without any further purification.

1.1.Synthesis of Catalyst probe R1

According to the reported literature (shown in Fig.-1) Fc Based Co-MOF (R1) was successfully synthesized by using an aqueous solution of $Co(NO_3)_2 \cdot 6H_2O$ was prepared.²² On the other side methanolic solution of 4,4-bipyridyl mixed with an aqueous solution of the sodium salt of FcDCA and the resulting solution stirred for 1 hr. to make a clear solution. After that 2.5 ml of mixed ligand solution was gradually and carefully added into $Co(NO_3)_2 \cdot 6H_2O$ solution. Then, the orange-red colored solid compound was recovered by filtration, washed with MeOH and finally dried overnight at under vacuum.

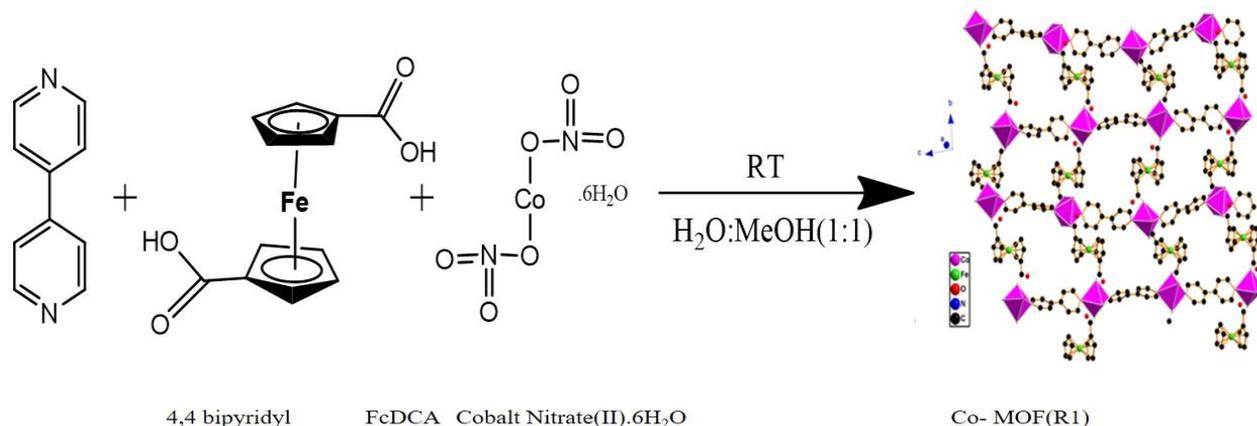


Fig. 1 The structural formula is 3,7-bis (Dimethylamino)-phenothiazin5-ium chloride.

1.2. Photocatalytic degradation of MO

The Fe-based photocatalytic MOF evaluations were examined by removing the MO dye under a Xenon 500-watt lamp at room temperature. The space between the light source and the beaker surrounding the reaction mixture was permanently at 10.0 cm. Photo catalysts R1 (10.00 mg) were dissolved in an aqueous solution of 40.0 ml MO (10.0 ppm) in a 50.0 ml beaker. Before exposure, the reaction mixture was magnetically stirred in the dark for 1 hr. to confirm the creation of adsorption /absorption equilibrium. After the equilibrium, the addition of H₂O₂ is permitted. Stirring continued during the photo construction experiment. The samples were removed at regular intervals and centrifuged to separate the photo catalyst from the reaction mixture. Changes in the concentration of MO were observed by measuring the absorption intensity at wavelength $\lambda = 463$ nm using a spectrophotometer.

2. Results and discussion

Experiments on photocatalytic degradation of the MO dye in visible light were performed as a function of time. The photocatalytic activity of the R1 probe was studied by the adsorption/degradation of the MO dye. MO has been selected as the standard dye because it exhibits maximum degradation in the shortest time possible. MO has a characteristic peak at 463 nm. The R1 probe offers enough surface area for further investigations to experiment with photo catalysis. Fig.2 shows an optimization experiment to terminate MO in the presence of R1 and H₂O₂ probes without irradiation. The same experiment was performed only in the presence of R1

and H_2O_2 probes. Under two conditions, no significant change in the corrosion of MO was found.

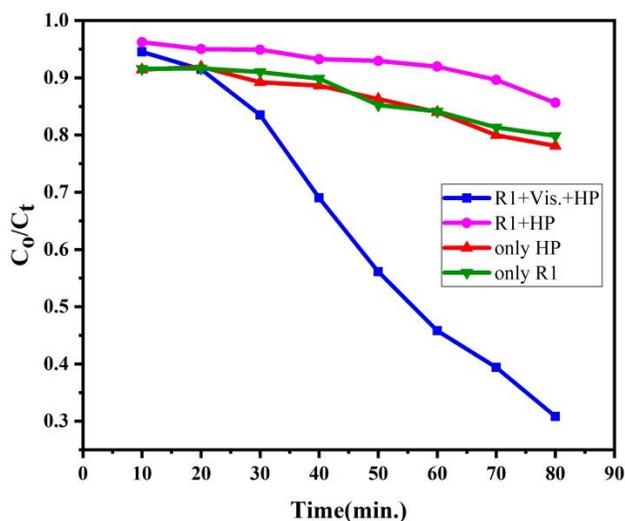


Fig. 2 Comparison between R1+visible light+HP, R1+ HP, HP alone, R1 alone

In the photo catalytic experiments carried out in the presence of visible light and catalyst R1 with H_2O_2 , remarkable changes in absorption occurred. About 90% of the MO was removed in 50 minutes. This is shown in Fig.3.

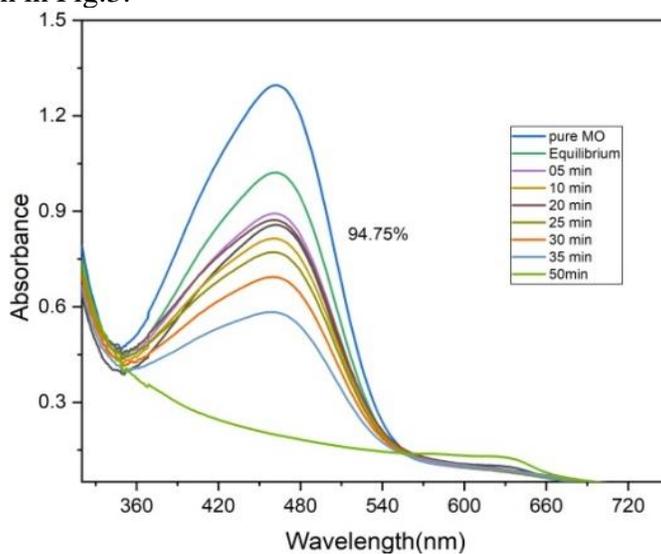


Fig.3 Absorption spectra of Methyl orange (MO) solution under Visible light in the presence of photo catalyst probe R1 (10 mg).

The surface charge of the R1 played an important part in the photocatalytic process. The MO indicates greater adsorption on the surface of the R1 in the acidic medium due to attraction between oppositely charged species. The degradation of MO can be shown by observing the dye solution with the naked eye.

Effect of H₂O₂ dosage

In the Fenton process, H₂O₂ is a source of ^{*}OH radicals. The degradation of MO was studied with varying dosage of H₂O₂ from 0.5ml to 3.0 ml and results are shown in Fig.4.

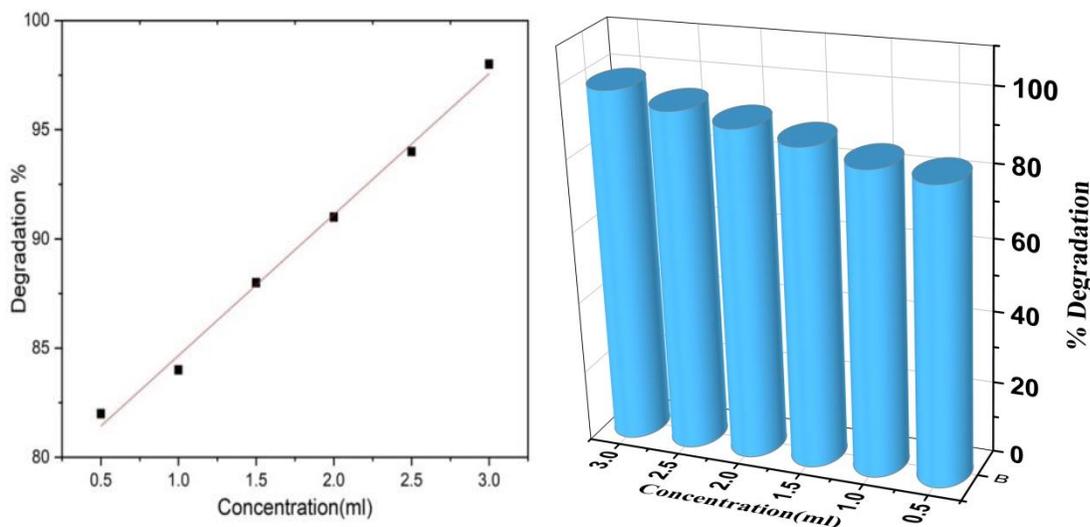


Fig.4 (a) Effect of H₂O₂ concentration 0.5ml to 3ml (MO-10mgL⁻¹, catalyst-10mg) (b) Comparison of degradation % of MO with varying H₂O₂ dosages

It reveals that increasing the dosage of H₂O₂, the degradation of MO is enhanced due to the improvement of availability of active radical OH^{*} which degrades MO dye.

Effect of dye concentration & Catalyst dosage

Keeping the catalyst loading concentration constant at 10 mg/40 ml of the dye solution, the results of varying the amounts of the dye (from 10 ppm to 25 ppm) were examined, as shown in Fig. 5

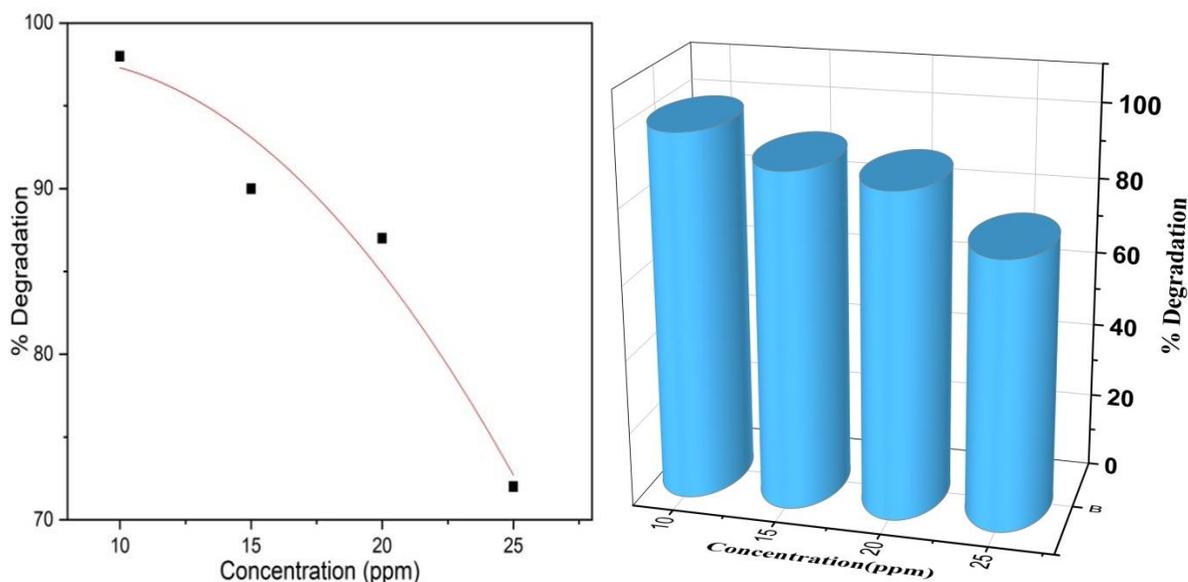


Fig.5 (a)Effect of dye concentration 10-25 ppm (HP- 0.5ml, catalyst-10 mg) (b)Comparison of degradation % of MO with varying dye concentration.

The number of dye molecules increases, then the amount of light (photons) that enter in the dye solution which affects the catalyst surface and reduces the active sites due to the obstruction of the light path. The amount of catalyst was then varied from 10 mg to 40 mg/40 ml of constant dye solution with a concentration of 10 ppm. We observed that as the amount of catalyst increased, the reaction kept faster due to an increase in the number of active surfaces on the catalyst. However, the reaction rate decreased from 25 mg, which could be due to the obstruction of the light path to reach the dye molecules, as shown in Fig.6. Light scattering may dominate at higher catalyst loads.

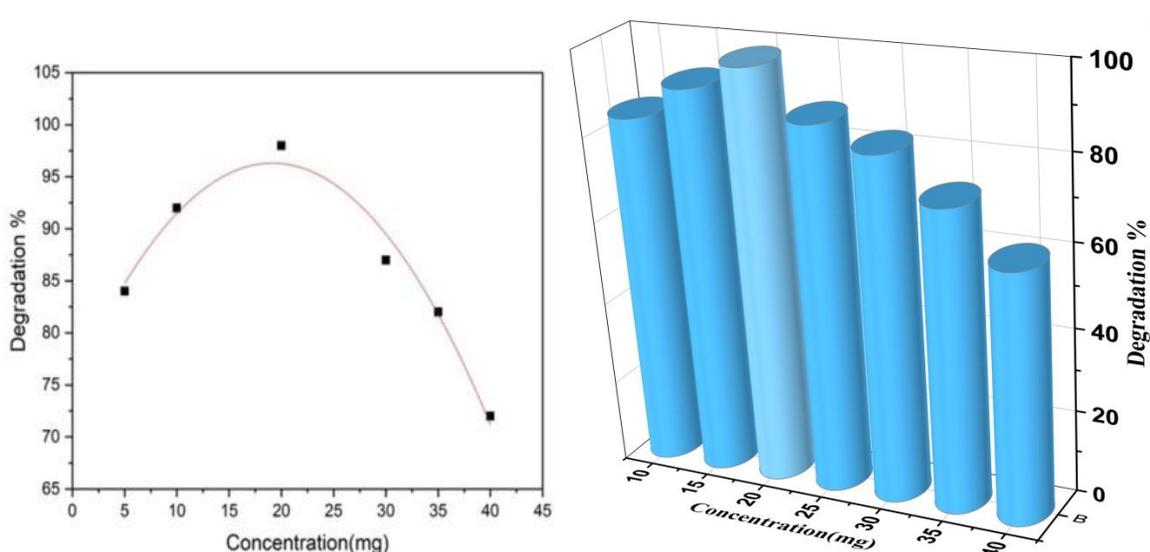


Fig.6 (a) Effect of varying the catalyst dosages from 10mg to 40 mg ($\text{MO}-10 \text{ mg L}^{-1}$, $\text{HP}-0.5\text{ml}$)
(b) Comparison of degradation % of MO with various concentration of R1

Effect of pH

The photo degradation response was likewise studied under changing pH conditions (2 to 10 pH). It reveals that increasing the pH (alkaline) range of the solution; it could diminish the degradation of MO diminished, shown in Fig.7.

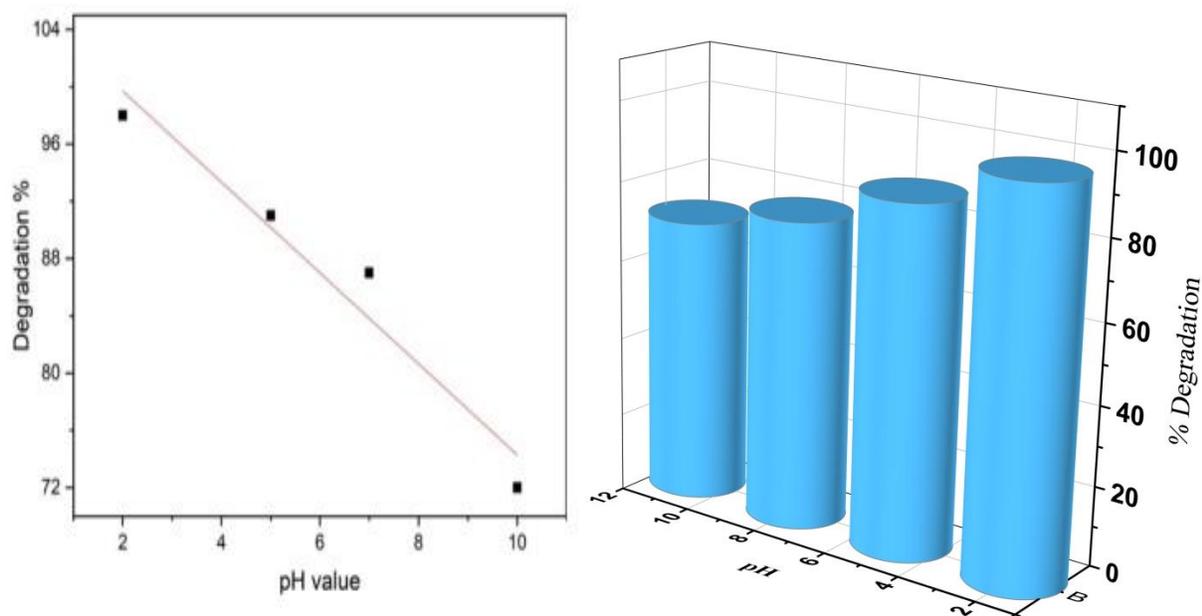


Fig.7 (a) Effect of pH 2 to 10 ($\text{MO}-10 \text{ mgL}^{-1}$, $\text{HP}-0.5\text{ml}$, catalyst-10 mg) (b) Comparison of degradation % of MO with varying pH range.

In an acidic medium, the surface of the catalyst produces ferrous ions, which creates the HO^* radical. As per the report, the acidic condition favors the heterogeneous Fenton catalysis. HO^* radicals attack on the bonds which are present in the dye molecules which may be in arrange on the impetus surface. The cleavage of the azo bond ($-\text{N}=\text{N}-$) is the reason for the degradation of the MO dye solution. The acidic conditions are encouraged for the arrangement of receptor intermediates which are hydroxyl radicals and are essentially improved, which further monitors/contributes to improving the response rate.

Conclusion

In summary, it could be said that Co-MOF based on ferrocene was successfully synthesized in the literature described above. Probe R1 was also considered as a photocatalyst and H_2O_2 enhanced their activity which shows R1 is a suitable candidate for the Fenton process. The large surface area, the smaller particle size and the heterogeneous activities make this Co-MOF a

suitable candidate for the adsorption/degradation of organic azo dyes under visible light. Besides, better re-usability and high stability support practical application in the industrial sector.

Acknowledgements

The author SR gratefully acknowledges to Mr. Shaikh M. Mobin Assistant Professor of IIT Indore for his excellent guidance. S.R. sincerely gratefully acknowledges to Sophisticated Instrumentation Centre (SIC), IIT Indore, for providing characterization facilities. We are very thankful to Mrs Richa Rajak for their support. Special thanks to M.P. Council of Science & Technology, Bhopal to provide Young Scientist Fellowship.

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