

Synthesis and characterization of Iron Metal organic framework for degradation of Rhodamine B dye

Submitted in partial fulfillment of the requirements for the award of

Bachelor of Science Degree in chemistry

by

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DEPARTMENT OF CHEMISTRY

SCHOOL OF SCIENCE AND HUMANITIES

SATHYABAMA

Institute of science and technology

(Deemed to be university)

Accredited with grade "A " by NAAC

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BONAFIDE CERTIFICATE

This is to certify that this Project Report is the bonafide work of M.Divyadharshini(39030008), Ramu(39030025), Sangeetha(39030029) who carried out the project entitled **"SYNTHESIS AND CHARACTERIZATION OF IRON METAL ORGANIC FRAMEWORK FOR DEGRADATION OF RHODAMINE B DYE "** under my/our supervision from December 2021 10 to April 2022

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DECLARATION

M.Divyadharshini (39030008) ,Ramu(39030025), P.Sangeetha(39030029) hereby declare that the project report entitled **“SYNTHESIS AND CHARACTERIZATION OF IRON METAL ORGANIC FRAMEWORK FOR DEGRADATION OF RHODAMINE B DYE”**done by us under the guidance of **Dr.V.KAVITHA** at sathyabama institute of science and technology,Chennai is submitted in partial fulfillment of the requirements for the award of Bachelor of science degree in CHEMISTRY

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ABSTRACT

MOF-METAL ORGANIC FRAMEWORK

Metal organic framework's are a class of compounds consisting of metal ions or clusters coordinated to organic ligands to form one-,two- or three – dimensional structures. MOF'S are crystalline of rigid organic molecules held together and organized by metal ions or clusters.special interests in these materials arise from the fact that many are highly porous and can be eused for storage of small molecules for example,H₂,C₀₂. MOF'S are organic-inorganic hybrid crystalline porous materials that consist of a regular array of positively charged metal ions form nodes that bind the arms of the linkers together to form a repeating ,cage-like structure. That can be used for gas storage,purification and separation as well catalysis and sensing applications.

CHAPTER1-

INTRODUCTION

1:1 METAL ORGANIC FRAMEWORK

Metal-organic frameworks (MOFs) are organic-inorganic hybrid crystalline porous materials that consist of a regular array of positively charged metal ions surrounded by organic 'linker' molecules. The metal ions form nodes that bind the arms of the linkers together to form a repeating, cage-like structure. Researchers have synthesized MOFs that feature a surface area of more than 7800 square meters per gram. To put this into context, if you could lay out the available surface area in a teaspoon of this material it would cover an entire soccer field. MOFs offer unique structural diversity in contrast to other porous materials – uniform pore structures; atomic-level structural uniformity; tunable porosity; extensive varieties; flexibility in network topology, geometry, dimension, and chemical functionality. This allows researchers the successful control of framework topology, porosity, and functionality. MOFs unique structure design and tunability – crystalline porous materials that are composed of both organic and inorganic components in a rigid periodic networked structure – is not readily accessible in conventional porous materials, e.g., purely inorganic zeolites.

1:2 APPLICATIONS:

Metal-organic frameworks (MOFs) are a class of crystalline materials that consist of coordination bonds between transition-metal cations and multidentate organic linkers. The structure of MOFs is characterized by an open framework that can be MOFs can be used for gas storage, purification porous (porous materials and separation, as well catalysis and sensing applications. Numerous applications in many fields are being developed that exploit MOFs' cage-like structure, such as gas storage and separation, liquid separation and purification, electrochemical energy storage, catalysis, and sensing. In addition to direct applications, MOFs have been used as unique precursors for the construction of inorganic functional

materials with unparalleled design possibilities, such as carbons, metal-based compounds, and their composites. Currently, carbonaceous materials are attracting much interest for their extensive applications including adsorption, catalysis, batteries, fuel cells, supercapacitors, and drug delivery and imaging. In addition, some sensors are also one of the important applications of carbonaceous materials, because they are closely related to human health. There are varieties of approaches for the preparation of these carbon materials, but among them, directly carbonizing from organic precursors is the most frequently used method to prepare nanoporous carbons due to its flexibility and simplicity. These materials present certain drawbacks, though, such as low surface areas, disordered structures, and nonuniform sizes, which will greatly limit their applications.

CHAPTER-2

REVIEW AND LITERATURE

2:1 Rajkamal Kuswaha et .al (2018) studied on Degradation of Nile blue sulphate dye onto iron oxide nanoparticles: Kinetic study, identification of reaction intermediates, and proposed mechanistic pathways,suggested

Iron oxide nanoparticles were synthesized and characterized using Fourier transform infrared spectroscopy, X-ray diffraction, vibrating sample magnetometer, nitrogen adsorption–desorption, and transmission electron microscopy. Vibrating sample magnetometer analysis confirmed the supermagnetic behavior of Fe_3O_4 NPs with a specific saturation magnetization value 43 emu g^{-1} . Synthesized Fe_3O_4 NPs exhibited surface area $52 \text{ m}^2 \text{ g}^{-1}$ with pore volume 0.0729 cc g^{-1} and average pore diameter 5.528 nm . The degradation efficiency of Nile blue sulphate dye onto Fe_3O_4 NPs was 86.8% with total organic carbon removal and chemical oxygen demand conversion of 65.6% and 55.9% , respectively, at $5 \text{ mM H}_2\text{O}_2$ and 50 mg l^{-1} of NBS dye concentration for 12 min of reaction time. Rate of degradation of dye onto Fe_3O_4 NPs followed second-order kinetic rate equation with high value of regression coefficient at 303 K . The low activation energy ($19.16 \text{ kJ mol}^{-1}$) obtained from Arrhenius plot showed that of Fe_3O_4 NPs have high catalytic activity towards the degradation of NBS dye during oxidation process. The intermediate products formed during degradation of NBS dye were detected by liquid chromatography–mass spectrometry experiment, and 11 numbers of fragments were detected on the basis of mass to charge ratio (m/z) at 24.186 min . The degradation of NBS dye was attributed to formation of intermediates from destruction of conjugated structure of dye and transformation of these intermediates into small molecules, which were further mineralized to water and carbon dioxide.

2:2 shaohua et.al (2018) studied on Insights into atrazine degradation by persulfate activation using composite of nanoscale zero-valent iron and graphene: Performances and mechanisms,suggested

Atrazine, a herbicide used widely, could not be effectively removed from waters by chemical or biological processes. In this work, the performances and mechanisms for atrazine degradation were examined by persulfate activation with

nanoscale zero-valent iron (nZVI) and graphene composites at various conditions including dosages of nZVI/GR and PS, pH value, temperature and natural organic matters. Results showed that mass ratio of 5:1 for nZVI to GR exhibited the highest efficiency for catalytic degradation of atrazine when 92.1% of atrazine was removed within 21 min. The degradation efficiencies of atrazine increased when PS concentration increased from 0.2 to 1.0 mM, and were favored in acidic pH and high temperature, while was not affected by NOM with a concentration less than 4 mg/L. Electron spin resonance and radical quenching studies showed that both $\cdot\text{OH}$ and $\text{SO}_4\cdot^-$ were mainly produced on the surface of nZVI/GR, while $\text{SO}_4\cdot^-$ was the predominant radicals responsible for the degradation of atrazine. Mechanisms for atrazine degradation were also proposed on the basis of XRD and XPS analysis. And its degradation pathways involved in dealkylation, alkylic hydroxylation, dechlorination-hydroxylation, and alkylic oxidation using LC/MS/MS techniques. These results could provide a better understanding of the application of nZVI/GR-PS system for atrazine removal from waters.

2:3 Chanush Di HE et.al(2018) studied on effects on goods's buffer and ph on the structural transformation on zero valent iron and the oxidative degradation of contaminants,suggested

The presence of Good's buffers caused rapid ZVI corrosion and a dramatic release of Fe(II) leading to the Fe(II)-catalyzed transformation of ferrihydrite to lepidocrocite and/or the direct formation of lepidocrocite from the oxidation of Fe(II) in the pH range 4.0–6.2. In comparison, in the absence of Good's buffers, elution of Fe(II) was insignificant with ferrihydrite being the only Fe(III) oxyhydroxide detected following the oxidative transformation of ZVI.

Presence of The rapid ZVI corrosion in the Good's buffer is possibly due to either

- (i) disruption of the Fe oxide surface layer as a result of attack by Good's buffers and/or
- (ii) interaction of Good's buffer with the outer Fe oxide surface and surface-associated Fe(II)/Fe(III) causing the Fe oxide surface layers to be more porous with both these processes facilitating continuous O_2 access to the Fe(0) core and allowing the diffusion of Fe atoms outward.

Deprotonated forms of Good's buffers and the surface charge of the Fe oxides formed at the ZVI surface strongly affect the sorption of the target compound and hence the oxidation of these compounds via surface-associated Fe(II)-mediated heterogeneous Fenton processes.

2:4 Xiaoguo shi et . al (2018) studied on Degradation of organic dyes by a new heterogeneous Fenton reagent - Fe_2GeS_4 nanoparticle, suggested

The heterogeneous Fenton system has become the hotspot in the decontamination field due to its effective degradation performance with a wide pH range. Based on the unstable chemical properties of pyrite, in this article, Fe_2GeS_4 nanoparticles with better thermodynamic stability were prepared by vacuum sintering and high energy ball milling and its potential as Fenton reagent was investigated for the first time. Three determinants of the heterogeneous Fenton system including the iron source, hydrogen peroxide, pH and the degradation mechanism were investigated. The catalyst dosage of 0.3 g/L, initial H_2O_2 concentration in the Fenton system of 50 mmol/L and pH of 7 were chosen as the best operational conditions. An almost complete degradation was achieved within 5 min for methylene blue and rhodamine b while 10 min for methyl orange. The total organic carbon removal efficiencies of Fe_2GeS_4 heterogeneous Fenton system for methylene blue, methyl orange and rhodamine b in 10 min were 56.3%, 66.2% and 74.2%, respectively. It's found that the degradation ability could be attributed to a heterogeneous catalysis occurring at the Fe_2GeS_4 surface together with a homogeneous catalysis in the aqueous phase by the dissolved iron ions.

2:5 Jing dou et.al (2021) studied on Photochemical degradation of iron(III) citrate/citric acid aerosol quantified with the combination of three complementary experimental techniques and a kinetic process model, suggested

Iron(III) carboxylate photochemistry plays an important role in aerosol aging, especially in the lower troposphere. These complexes can absorb light over a broad wavelength range, inducing the reduction of iron(III) and the $\cdot\text{OH}$, HO_2 , and peroxides in turn reoxidize iron(II) back to iron(III), closing a photocatalytic cycle. In the presence of O_2 , the ensuing radical chemistry leads to further decarboxylation, and the production of $\cdot\text{OH}$, HO_2 , peroxides, and oxygenated

volatile organic compounds, contributing to particle mass loss. This cycle is repeated, resulting in continual mass loss due to the release of CO₂ and other volatile compounds. In a cold and/or dry atmosphere, organic aerosol particles tend to attain highly viscous states. While the impact of reduced mobility of aerosol constituents on dark chemical reactions has received substantial attention, studies on the effect of high viscosity on photochemical processes are scarce. Here, we choose iron(III) citrate (Fe^{III}(Cit)) as a model light-absorbing iron carboxylate complex that induces citric acid (CA) degradation to investigate how transport limitations influence photochemical processes. Three complementary experimental approaches were used to investigate kinetic transport limitations. The mass loss of single, levitated particles was measured with an electrodynamic balance, the oxidation state of deposited particles was measured with X-ray spectromicroscopy, and HO₂ radical production and release into the gas phase was observed in coated-wall flow-tube experiments. We observed significant photochemical degradation with up to 80 % mass loss within 24 h of light exposure. Interestingly, we also observed that mass loss always accelerated during irradiation, resulting in an increase of the mass loss rate by about a factor of 10. When we increased relative humidity (RH), the observed particle mass loss rate also increased. This is consistent with strong kinetic transport limitations for highly viscous particles. To quantitatively compare these experiments and determine important physical and chemical parameters, a numerical multilayered photochemical reaction and diffusion (PRAD) model was developed that treats chemical reactions and the transport of various species. The PRAD model was tuned to simultaneously reproduce all experimental results as closely as possible and captured the essential chemistry and transport during irradiation. In particular, the photolysis rate of Fe^{III}, the reoxidation rate of Fe^{II}, HO₂ production, and the diffusivity of O₂ in aqueous Fe^{III}(Cit)/CA system as function of RH and Fe^{III}(Cit)/CA molar ratio could be constrained. This led to satisfactory agreement within model uncertainty for most but not all experiments performed. Photochemical degradation under atmospheric conditions predicted by the PRAD model shows that release of CO₂ and repartitioning of organic compounds to the gas phase may be very important when attempting to accurately predict organic aerosol aging processes.

2:6 Mohd shoban ansari et.al (2020) studied on Kinetic Studies on the Catalytic Degradation of Rhodamine B by Hydrogen Peroxide: Effect of Surfactant Coated and Non-Coated Iron,suggested

Iron (III) oxide (Fe_3O_4) and sodium dodecyl sulfate (SDS) coated iron (III) oxide nanoparticles were synthesized by the co-precipitation method for application in the catalytic degradation of Rhodamine B (RB) dye. The synthesized NPs were characterized using X-ray diffractometer (XRD), vibrating sample magnetometer (VSM), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and Fourier transform infra-red (FT-IR) spectroscopy techniques and tested in the removal of RB. A kinetic study on RB degradation by hydrogen peroxide (H_2O_2) was carried out and the influence of Fe_3O_4 and SDSFe_3O_4 magnetic NPs on the degradation rate was assessed. The activity of magnetic NPs, viz. Fe_3O_4 and $\text{SDS@Fe}_3\text{O}_4$, in the degradation of RB was spectrophotometrically studied and found effective in the removal of RB dye from water. The rate of RB degradation was found linearly dependent upon H_2O_2 concentration and within 5.0×10^{-2} to 4.0×10^{-1} M H_2O_2 , the observed pseudo-first-order kinetic rates (k_{obs} , s^{-1}) for the degradation of RB (10 mg L^{-1}) at pH 3 and temperature 25 ± 2 °C were between 0.4 and $1.7 \times 10^4 \text{ s}^{-1}$, while in presence of 0.1% w/v Fe_3O_4 or $\text{SDS@Fe}_3\text{O}_4$ NPs, k_{obs} were between 1.3 and $2.8 \times 10^4 \text{ s}^{-1}$ and between 2.6 and $4.8 \times 10^4 \text{ s}^{-1}$, respectively. Furthermore, in presence of Fe_3O_4 or $\text{SDS@Fe}_3\text{O}_4$, k_{obs} increased with NPs dosage and showed a peaked pH behavior with a maximum at pH 3. The magnitude of thermodynamic parameters E_a and ΔH for RB degradation in presence of $\text{SDS@Fe}_3\text{O}_4$ were $15.63 \text{ kJ mol}^{-1}$ and $13.01 \text{ kJ mol}^{-1}$, respectively, lowest among the used catalysts, confirming its effectiveness during degradation. Furthermore, SDS in the presence of Fe_3O_4 NPs and H_2O_2 remarkably enhanced the rate of RB degradation.

2:7 Bharati et.al (2017) studied on Enhanced photocatalytic degradation of dyes under sunlight using biocompatible TiO_2 nanoparticles,suggested

As TiO_2 is one of the most popular photocatalysts, we have studied here the photocatalytic degradation of the most common dyestuffs like rhodamine B (RhB), congo red (CR) and methylene blue (MB), which mainly come from the

textile and photographic industries using nanoparticles of TiO_2 . Nanoparticles of TiO_2 synthesized through a simple and cost effective sol-gel technique crystallizes in the anatase phase, showing a band gap less than that of bulk value. Particles consisting of coherently scattered domains of size 33 nm are found to be agglomerated and polycrystalline in nature. While the degradation rates of MB, CR and RhB after irradiating with a renewable source of energy, i.e. sunlight, show 100% degradation, TiO_2 irradiated with UV light of 4.8 eV shows a much slower degradation rate. To use the waste water after photocatalysis, we examine further the biocompatible nature of the TiO_2 nanoparticles by platelet interaction activity, hemolysis effect and MTT assay. It is worth mentioning here that TiO_2 nanoparticles are found to be highly hemocompatible, show no platelet aggregation, and the level of intracellular ROS in human platelets does not show significant change in ROS level. We conclude that TiO_2 nanoparticles constitute an excellent photocatalyst and biocompatible material, and that after photocatalytic degradation of dye effluents obtained from textile industries, purified water can be used in agriculture and domestic sectors.

2:8 Tadele assefa aragaw et.al (2021) studied on Iron-based nanoparticles in wastewater treatment: A review on synthesis methods, applications, and removal mechanisms,suggested

Nanomaterial is an emerging material with potential technological impacts in various applications. It imposes great opportunities in various disciplines including wastewater remediation. Industrial wastewater is generated with anthropogenic activities and is the most environmental threat that needs remediation to overcome the environmental damages, thereby reducing human risks. Currently, several wastewater treatment techniques are applied and the utilization of nanomaterials for pollutant removal is an emerging technology. This is evident that the publication trends in the field of iron-based wastewater have been drastically increased. In this work, the overview of the preparation of iron-based nanoparticles, such as different polymorphs of iron-oxides, oxyhydroxides, iron hydroxide, and zero-valent iron nanoparticles are reviewed. In addition to the detailed discussion on the preparation of iron-based nanoparticles, their application on waste water treatment, removal mechanisms, advantages, and

limitations are also assessed and discussed. Moreover, the iron-based nanoparticles' removal efficiency for specific pollutants and perspective in environmental remediation are also analyzed. Additionally, the advancements and future perspectives of iron-based nanoparticles are highlighted.

2:9 Soumi dutta et.al (2021) studied on Recent advances on the removal of dyes from wastewater using various adsorbent,suggested

The rapid increase in toxic dye wastewater generated from various industries remains a severe public health issue and prime environmental protection concern, posing a major challenge to existing conventional water treatment systems. Consequently, various physicochemical and biological treatment processes have been studied, which exhibit varying removal abilities depending on their experimental constraints. Among them, adsorption is considered to be the most efficient due to its high removal efficiency, easy operation, cost-effectiveness, and recyclability of the adsorbents. Considering this, the present review article focused on presenting a comprehensive summary of the various types of adsorbents such as commercial activated carbon, metal oxide-based, carbon-based, metal-organic framework, and polymer-based adsorbents used in dye remediation of contaminated water. The effects of several critical factors such as initial dye concentration, solution pH, temperature, and adsorbent dose on the dye adsorption performance are also described. In addition, the adsorption mechanisms responsible for dye removal are explained based on electrostatic attraction, ion exchange, surface complexation, and π - π interactions. Finally, critiques, future perspectives, and a summary of the present article are given. Various adsorbents such as carbon-based materials, metal oxides, bio-adsorbents, and polymer-based materials, have been shown to be efficient for the removal of dye pollutants from wastewater. Thus, it is anticipated that dye removal by adsorption can provide a feasible solution for the treatment of dye-laden water.

2:10 Stanislaw ledakowicz et.al(2021) studied on Recent Achievements in Dyes Removal Focused on Advanced Oxidation Processes Integrated with Biological Methods ,suggested

In the last 3 years alone, over 10,000 publications have appeared on the topic of dye removal, including over 300 reviews. Thus, the topic is very relevant, although there are few articles on the practical applications on an industrial scale of the results obtained in research laboratories. Therefore, in this review, we focus on advanced oxidation methods integrated with biological methods, widely recognized as highly efficient treatments for recalcitrant wastewater, that have the best chance of industrial application. It is extremely important to know all the phenomena and mechanisms that occur during the process of removing dyestuffs and the products of their degradation from wastewater to prevent their penetration into drinking water sources. Therefore, particular attention is paid to understanding the mechanisms of both chemical and biological degradation of dyes, and the kinetics of these processes, which are important from a design point of view, as well as the performance and implementation of these operations on a larger scale.

2:11 Lei Dong et. al (2021) studied on Research Progress on degradation of Organic pollutants in Water Body by Iron-based Materials activated persulfate, suggested

The advanced persulfate oxidation technology has shown great potential in the efficient degradation of organic pollutants in water body, owing to its strong oxidation ability, easy operation and many other advantages. At present, the development of this technology focuses on the choice of activation mode of persulfate, and its essence lies in the cleavage of O-O bond in persulfate. Iron-based catalysts have been widely used in persulfate activation because of their advantages such as earth abundance, eco-friendliness and cost-effectiveness. In this paper, the methods and research progress of activating persulfate by iron-based materials are reviewed. Finally, the existing problems and development direction of persulfate advanced oxidation technology in the current application are analyzed, in order to promote the development of related research work.

2:12 Jianke Tan et.al (2022) studied on MOFs-derived defect carbon encapsulated magnetic metallic Co nanoparticles capable of efficiently activating PMS to rapidly degrade dyes, suggested

In this work, a new defect carbon encapsulated magnetic metallic Co nanoparticles MOFs precursor at 900 °C, and characterized by various

technologies to prove that the Co@DC contains Co^0 , Co^{2+} and Co^{3+} . peroxymonosulfate It was used to activate (PMS) to degrade Rhodamine B (RhB) dye efficiently. Over 99% of 10 mg/L RhB with initial pH of 5.5 was degraded by 100 mg/L PMS activated by 10 mg/L Co@DC within 5 min. The RhB degradation rate constant in the Co@DC/PMS system was 1.1805 min^{-1} , which was approximately 17 times that of DC/PMS system (0.0695 min^{-1}). The Co@DC displayed a good magnetism, stability, and PMS activation ability in a wide pH range of 3 to 10. After four cycles, the RhB removal rate can still maintain over 90% after 10 min reaction. The Co@DC/PMS system can also rapidly degrade the other dyes (acid fuchsin, methylene blue and methyl orange), showing excellent universality. The free radical quenching experiments and EPR trials suggest that both the radicals (sulfate radical, hydroxyl radical, and $\text{O}_2^{\cdot-}$) and non-radical (singlet oxygen) species are involved in the RhB degradation, while the latter plays a major role. In addition to the cobalt ions, the metallic Co^0 also took part in PMS activation and reacted with O_2 to generate Co^{2+} , ensuring the sufficient Co^{2+} to activate the PMS to produce Co^{3+} . The Co^{3+} ions withdraw electrons from HSO_5^- or Co^0 in the Co@DC catalyst, driving a $\text{Co}^{2+}/\text{Co}^{3+}$ cycle to maintain a high performance of the Co@DC/PMS system for RhB removal. The effects of common inorganic anions on RhB removal, the mineralization degree and possible degradation pathway of RhB were studied. Relative to the previous catalysts for PMS activation to degrade RhB, the Co@DC shows lower activation energy of 23.78 KJ/mol. Altogether, this work provides a simple strategy to develop an efficiently magnetic heterogeneous catalyst to activate PMS for the elimination of hardly degradable dyes.

2:13 Liping liang et.al (2020) studied on Efficiency and mechanisms of rhodamine B degradation in Fenton-like systems based on zero-valent iron,suggested

Based on the $\text{Fe}^0/\text{H}_2\text{O}_2$ heterogeneous Fenton system, the degradation of rhodamine B (RhB, an organic dye pollutant) was researched in this paper. The effects of initial pH value, concentration of H_2O_2 , dosage of zero-valent iron (ZVI), and initial RhB concentration on RhB degradation by $\text{Fe}^0/\text{H}_2\text{O}_2$ were studied. The results showed that when the initial pH = 4, dosage of ZVI was 9 mM, and

concentrations of H_2O_2 and RhB were 8 mM and 0.1 mM, respectively, the color of RhB could be completely faded within 30 min, and the total organic carbon (TOC) removal percentage was about 63% after 120 min. The dissolved oxygen (DO) content and oxidation–reduction potential (ORP) were monitored during the reaction. Quenching experiments with methanol confirmed that the degradation of the dye was mainly due to oxidation by the $\cdot\text{OH}$ radical. Besides, the results from UV-Vis spectroscopy showed that the degradation of RhB was mainly due to the destruction of the conjugated oxygen hetero-anthracene in the RhB molecule. The solid-phase characterization of the ZVI samples after reaction confirmed that the original regular and slippery ZVI samples finally were corroded into rough and irregular lepidocrocite and magnetite. Two possible competitive reaction pathways for the degradation of RhB by $\text{Fe}^0/\text{H}_2\text{O}_2$ were proposed by GC-MS analysis, which were attributed to the dissociation of ethyl radicals and the degradation of chromophore radicals.

2:14 Thuy thi thanhe et.al (2020) studied on Photocatalytic Degradation of Rhodamine B by C and N Codoped TiO_2 Nanoparticles under Visible-Light Irradiation,suggested

C and N codoped TiO_2 nanoparticles were synthesized via a solvothermal method. The degradation of Rhodamine B by the photocatalyst C, N- TiO_2 was investigated under visible-light irradiation generated by using a 36 W compact fluorescent lamp which is characterized by wavelengths from 400 to 650 nm. The structure and properties of the obtained photocatalyst have been systematically investigated using X-ray diffraction, TEM, UV-Vis, FT-IR, and BET techniques. The experimental results revealed that C, N codoped TiO_2 nanoparticles were successfully synthesized, with an average diameter of 9.1 nm. C, N- TiO_2 nanoparticles which exhibited an energy band gap of 2.90 eV, were lower than pristine TiO_2 (3.34 eV), C- TiO_2 (3.2 eV), and N- TiO_2 (3.03 eV). The degradation of Rhodamine B by C, N- TiO_2 indicated that, under visible-light irradiation, the optimal dose of the photocatalyst was 1.8 g/L, and the removal of Rhodamine B was almost complete after 3 hours of reaction. The photocatalytic degradation of Rhodamine B in the range of 5–100 mg/L showed that the process followed the first-order kinetics according to the Langmuir–Hinshelwood model. The highest

apparent rate constant (0.0427 min^{-1}) was obtained when the initial concentration of Rhodamine B was 5 mg/L, whereas the former decreased with the increase in the initial concentration of Rhodamine B. Moreover, C and N codoped TiO_2 nanoparticles presented a high potential for recycling, which was characterized by a removal efficiency of more than 86% after three cycles.

2:15 Giang Bach et.al (2022) studied on Photocatalytic degradation of Rhodamine B in aqueous phase by bimetallic metal-organic framework M/Fe-MOF(M = Co, Cu, and Mg),suggested

Bimetallic metal-organic frameworks (MOFs) exhibit outstanding performance in a wide range of applications, including gas catalysis, adsorption, and luminescence sensor. The structure and properties of materials can be designed based on the variation of different metal ions, so this MOFs material system has unique properties. In this study, M/Fe-MOF bimetallic materials (M = Co, Cu, and Mg) were synthesized by solvothermal method and evaluated for photocatalytic activity in the degradation reaction of rhodamine B (RhB) organic pigments. The as-synthesized materials were characterized by using several physicochemical methods such as X-ray diffraction, fourier transform infrared spectroscopy (FT-IR), ultraviolet-visible spectroscopy (UV-Vis), Brunauer–Emmett–Teller (BET), scanning electron microscopy (SEM), and UV-Vis diffuse reflectance spectra. The results show that the Co/Fe-MOF, Cu/Fe-MOF, and Mg/MOF materials have uniform grain grade, high crystallinity, with the surface area of 26.1, 25.9, and 25.9 m^2/g , respectively. When modified with Co, Cu, and Mg, the crystal structure of Fe-MOF materials was unchanged, and all metal ions are inserted inside the structure of the material, as well as replacing Fe ions in the lattice crystals.

CHAPTER 3

AIM AND SCOPE

3:1 AIM

Our project name is "SYNTHESIS AND CHARACTERIZATION OF IRON NANOPARTICLES FOR DEGRADATION OF RHODAMINE B DYE". The main aim of the project is degradation of rhodamine b dye. Iron nanoparticles were synthesized with well-defined morphology at the room temperature by using Mechanochemical method using ferrous chloride, Terephthalic acid, RHB solution and photocalorimeter. Iron nanoparticles were characterized with the help of FTIR, XRD, SEM and to remove the rhodamine b dye from the aqueous solution.

3:2 SCOPE

Synthesizing Iron MOF by Mechanochemical method

Characterization of iron MOF by FTIR, SEM AND XRD

Removal of RHODAMINE B dye from aqueous solution.

Conformation of product formed by characterization by FTIR.

CHAPTER 4

MATERIALS AND METHODS

4:1 PREPARATION OF CATALYSTS AND THEIR OUTPUTS

Materials:

Ferric chloride , Terephthalic acid, Watch glasses, glass rod, Rhodamin B Solution, 250 ml beakers ,Graduate pipette, PH Metry, Polarimeter, Filterpaper, Funnel

Methods:

Catalyst preparation: ($\text{FeCl}_3 + \text{C}_8\text{H}_6\text{O}_4$)

0.16 g Ferric chloride and 3.2g Terephthalic acid should be measured and taken .Put on a grinding stone and grind well for 10 minutes. The salt available after grinding should be transferred to the watch glass. After putting this salt on oven for 2 hours we get the **REDDISH BROWN** colour catalyst.

Catalyst preparation : ($\text{FeCl}_3 + \text{C}_4\text{H}_6\text{O}_6$)

0.16 g Ferric chloride and 0.16g Tartaric acid should be measured and taken .Put on a grinding stone and grind well for 10 minutes. The salt available after grinding should be transferred to the watch glass. After putting this salt on oven for 2 hours we get the **LIGHT GREEN** colour catalyst.

- 1) 0.16g ferric chloride + 0.16g Tartaric acid = Light green ppt
- 2) 0.16 g ferric chloride + 3.2 g Terephthalic acid = Reddish brown ppt

We did 3 type of catalysts in this method using various amount of salt

0.16g FeCl_3 + 0.16g $\text{C}_8\text{H}_6\text{O}_4$ = dark brown colour ppt (1.9g)

0.16g FeCl_3 + 3.2g $\text{C}_8\text{H}_6\text{O}_4$ = Reddish brown colour ppt (3.2g)

0.16g FeCl_3 + 4.8g $\text{C}_3\text{H}_8\text{O}_4$ = brown colour ppt (4.2g)



Fig 4.1 Grinding stone



Fig 4.2 Grinding stone with salt



Fig 4.3 Before grinding

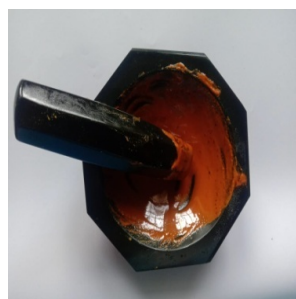


Fig 4.4 After grinding



Fig 4.5 Grinded salt



Fig 4.6 Catalyst

Finally ,we will get 3.2g catalyst



FIG 4.7 Weight of salt

4.2 PREPARATION OF RHB SOLUTION:

Take 2 ml RHB solution and make it 100ml solution with using standard flask.



FIG 4.8 RHB Solution



Fig 4.9 100 ml making solution

4.3 PREPARATION OF PH BUFFER SOLUTION:

Dissolve tablet to 100 ml of distilled water and a solution of the specified PH will be ready .

4.5 ADJUSTING PH

Place electrode in sample solution. Once electrode is placed in sample, PH was ran. Once the reading has stabilized, press the measure button. This is the pH level of sample. If you want increase PH, just add NaOH. If you want decrease PH, just add dilute HCL solution. Rinse your electrode with distilled water and blot or dab dry with a lint-free tissue. You may store your pH meter once clean and dry. We adjusting PH 3,4,5,7 using PH METRY

4.6 EXPERIMENT:

Take, 100 ml RHODAMINE B solution in 250 ml beaker. Again prepare that for blank solution. Then adjust PH like 3,4,5 with using **“PH METRY”**. After adjust PH, put 0.25g catalyst in this solution. Now, we have one Blank solution and one catalyst solution. mixed it well. Keep that beakers to put in **“SOLAR LIGHT”** at 2 hours. Each 15 minutes take that little amount of RHB solutions for taking **“PHOTO CALORIMETER”** reading.

After 30 minutes= It will be change reddish colour

After 1 hour = It will be change light reddish colour

After 2 hours =It will be change colourless

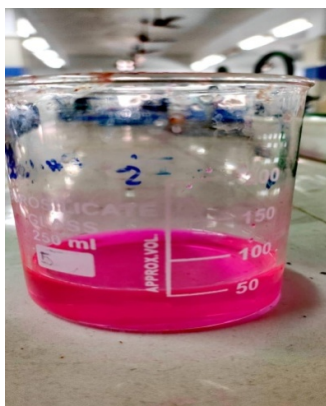


FIG 4.10 Blank solution

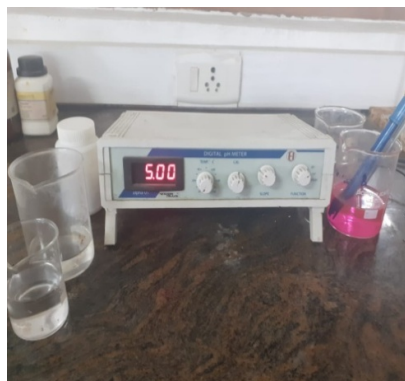


Fig 4.11 Adjusting PH with using PH metry



Fig 4.12 Catalyst solution



Fig 4.13 RHB solution in solar light

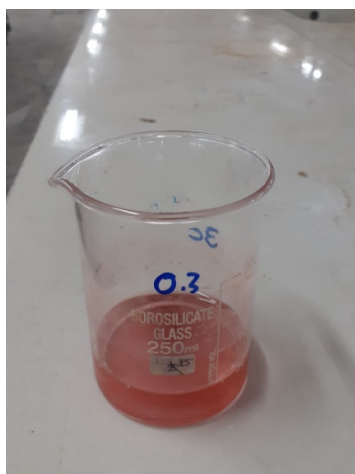


Fig4.14 After 2 hours



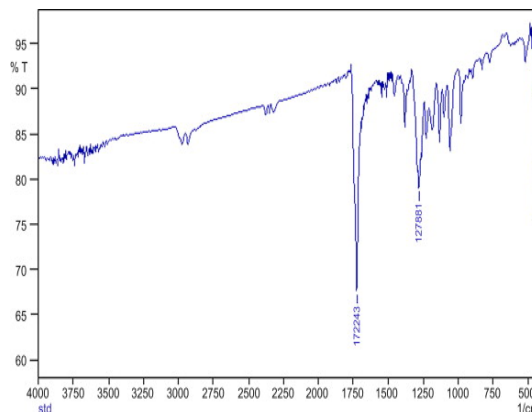
Fig 4.15 Polarimeter reading

We gave the salt for SEM,FTIR,XRD TEST.

4.7 Fourier transform infrared spectroscopy:

Fourier-transform infrared spectroscopy is a technique used to obtain an infrared spectrum of absorption or emission of a solid, liquid or gas. An FTIR spectrometer simultaneously collects high-resolution spectral data over a wide spectral range. This confers a significant advantage over a dispersive spectrometer, which measures intensity over a narrow range of wavelengths at a time. It is used to detect different functional groups in PHB. FTIR spectrum is recorded between 4000 and 400 cm^{-1} . For FTIR analysis, the polymer was dissolved in chloroform and layered on a NaCl crystal and after evaporation of chloroform, the polymer film was subjected to FTIR. The spectrum of PHB shows peaks at 1724 cm^{-1} and 1279 cm^{-1} , which corresponds to specific

rotations around carbon atoms. The peak at 1724 cm^{-1} corresponds to C–O stretch of the ester group present in the molecular chain of highly ordered structure and the adsorption band at 1279 cm^{-1} corresponds to ester bonding.



FTIR is a very versatile tool for surface characterization of nanoparticles. Under specific conditions, the NPs surface chemical composition can be determined, and additionally, the reactive surface sites responsible for the surface reactivity can be identified. FTIR spectroscopy is a technique used to identify the characteristic functional groups from the spectral bands that allow us to know the conjugation between the nanomaterial and the adsorbed biomolecules. FTIR spectrum consists of absorption peaks that correspond to the frequencies of vibration between the bonds of atoms in the nanoparticle. FTIR is an excellent technique for qualitative analysis; the peak intensity is a direct indication of the nature of the materials present.

4.8 X-RAY DIFFRACTION ANALYSIS:

Basic principle: in a crystal the atoms are arranged at well-defined intervals and form a crystal lattice.

The basic model of the defined crystal lattice is repeated periodically. The distances of these periods (lattice spacing) are in the range of 0.02 to 2.5 Å. The lattice spacings define the crystal lattice planes, and their position in the crystal is determined by the integer multiple of the crystal lattice spacing. The radiation is now diffracted on the crystal lattice planes at the corresponding wavelength (x-rays), comparable to the diffraction of light on a grating. Incident x-rays on a

crystals cause a number of reflections, which relate to the incident angle of the rays and the specific crystal lattice planes. Here the Bragg equation applies:

$$n \cdot \lambda = 2 \sin \Theta$$

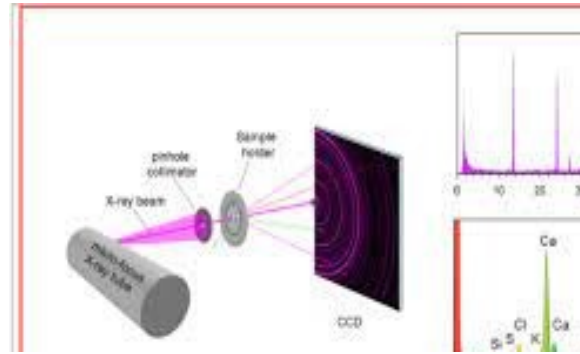
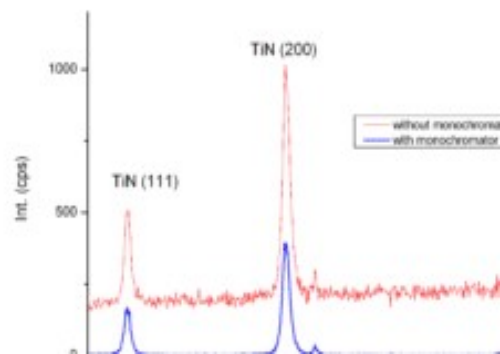
n = integer,

λ = wavelength of the incident x-rays,

d = **interplanar spacing** or spacing between lattice planes

Θ = **glancing or grazing angle**- the angle between the incident ray and the lattice planes.

If the wavelength of the x-rays is known, the crystalline phase can be determined from the position and the intensity of the diffraction reflections. X-ray diffraction cannot provide much information on amorphous, i.e. non-crystalline substances such as glass. In practice it is most common to measure powder samples, because the micro-crystallites are oriented into all direction (statistically). Thus, it is possible to detect nearly all crystal lattice planes without moving the sample (sometimes the **sample holder** is rotated). With certain minerals such as the phyllosilicates, a preferred orientation is obtained on "normal" sample preparation but special measures may prevent this. There are several possibilities for the detection of diffracted radiation. A photographic film with a suitable camera was in the past used for recording the reflections according to the diffraction angle and the intensity of the diffracted radiation. Today the reflections are usually detected with a counter tube or a solid state detector (Goniometer method). The detector determines the intensity of the reflections for each angle with a certain step width covering the desired angle range. The intensity of the x-rays as a function of the angle are recorded in the diffractogram. Today, tables with XRD data are kept in databases available for computer-assisted analysis. These provide a tool for the reliable determination of all crystalline organic and inorganic substances (approx. 50,000 sample plots, 35,000 of these for inorganic substances).



Advantage:

The x-ray diffraction provides a qualitative, a semi-quantitative and in some cases also a quantitative determination of crystalline substances. In conservation and restoration, it delivers particularly good results for the study of pigments, salts, rock samples, corrosion products and ceramic materials. The material quantities needed for analysis, can vary between some milligrams, when using a powder diffractometer, down to a few microgram. Single crystal sample holders using the diffractometer method and Debye-Scherrer- or Guinier- and Gandolfi-method, can. The investigation method is non-destructive, i.e. the sample can be re-used for subsequent investigations.

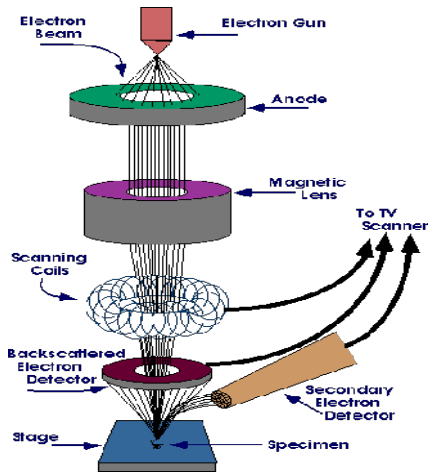
Disadvantage:

For phase mixtures only phases from work with even less a proportion of 1-5% can be detected.

4.9 SCANNING ELECTRON MICROSCOPY:

SEM analysis is a powerful investigative tool which uses a focused beam of electrons to produce complex, high magnification images of a sample's surface topography. Once an area of interest has been identified on the sample and evaluated using SEM, our experts can dive deeper into the detail of the material using energy-dispersive x-ray spectroscopy, or EDX analysis. Performing a visual analysis of a surface using scanning electron microscopy contributes to the identification of contaminants or unknown particles, the cause of failure and interactions between materials. In addition to surface evaluation, SEM analysis is utilized for particle characterization, such as wear debris generated during mechanical wear testing. The high magnification, high-resolution imaging of our

SEM analysis supports the determination of the number, size, and morphology of small particles, allowing clients to understand the wear properties of their material.



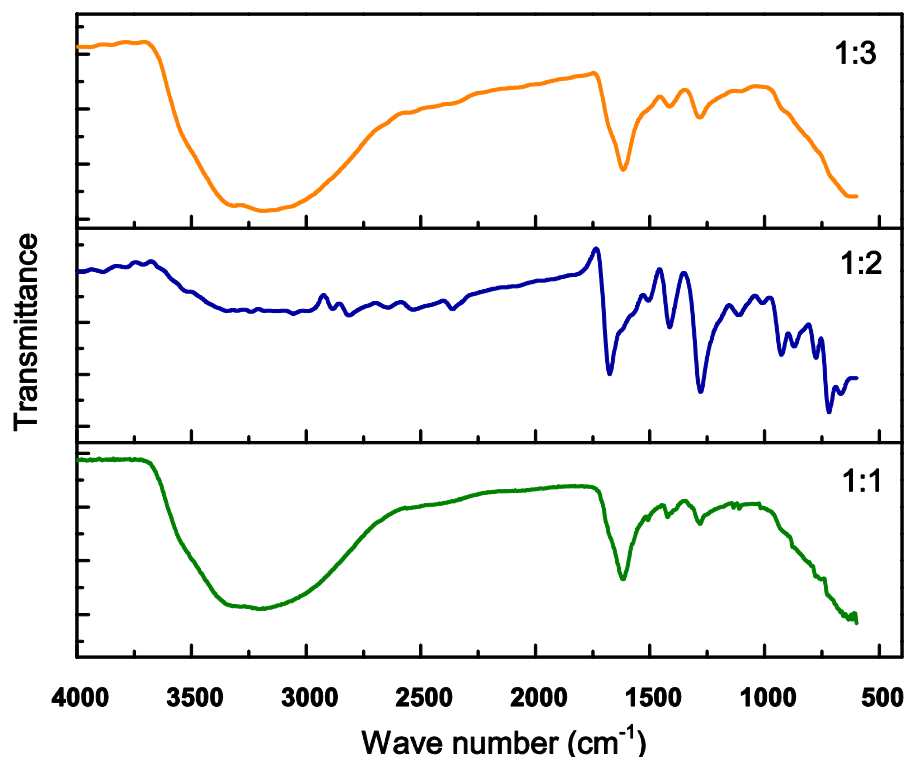
A scanning electron microscope (SEM) projects and scans a **focused stream of electrons over a surface to create an image**. The electrons in the beam interact with the sample, thereby producing various signals that can be used to obtain information about the surface's topography and composition.

CHAPTER 5

RESULT AND DISCUSSIONS

5.1 FTIR SPECTRUM FOR FE-MOF

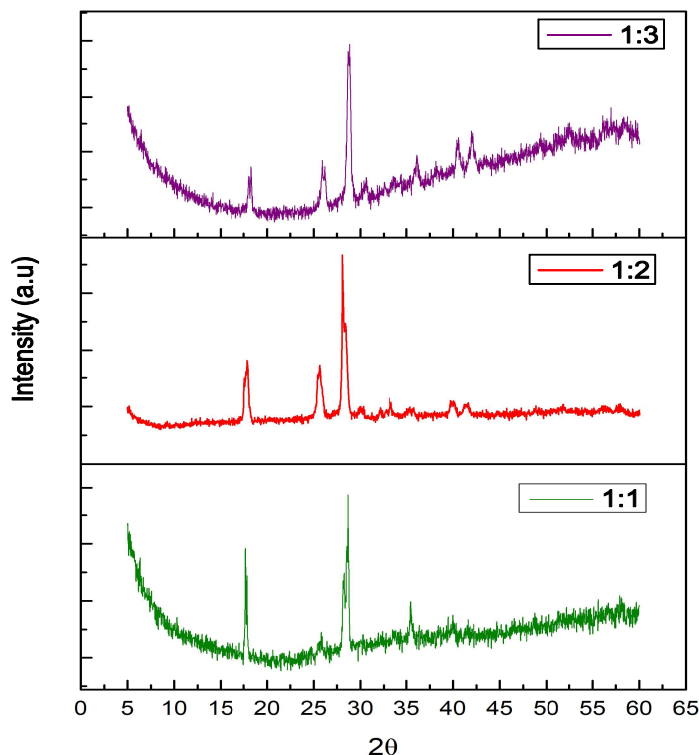
The Fe-BDC samples were scanned in the range of 4000cm^{-1} to 400cm^{-1} to explore the functional groups present in the molecule and the results are presented in Fig. The sharp peaks at 1691 cm^{-1} represents the symmetrical and asymmetrical vibrational bands of -O-C-O- groups. A broad band at 3734cm^{-1} and 3870 cm^{-1} can be assigned to weakly bonded OH groups at the surface indicating the presence of moisture within the framework. The low intensity sharp peak in the finger print region at 723 cm^{-1} indicates the C-H bending vibration of benzene in BDC. The emergence of new peak in the finger print region at 674cm^{-1} in the Fe-BDC spectrum alone reveals the presence of Fe-O bond where the iron is linked to the organic linker BDC through oxygen site. It is further confirmed as the peak intensity at 674cm^{-1} is present only for 1:2 catalyst



Fig(5.1) FTIR spectrum for Fe-MOF

5.2 X-RAY DIFFRACTION (XRD)

XRD is one of the characterization methodology which results from the diffraction pattern of the samples and is associated with the crystallinity of the sample. The XRD diffraction pattern of Fe-BDC synthesized from its chemical organic linker BDC is shown in the Fig. The XRD pattern is obtained by scanning from 5 to 60° with a scan rate of $0.001^\circ/\text{sec}$. A sharp peak at 2θ values of 17.67° ; 25.52° ; 28.14° are typical peaks of Fe-BDC which synchronizes with the Cambridge crystallographic Data Centre (CDCC) with the card no-690315 belongs to monoclinic crystal with a space group of $c1/2/C1$ and nomenclature of MIL-53 (Materaux de l'Institut Lavoisier). The peaks of pure BDC are at 16.75° ; 25.02° ; 27.77° ; which are entirely different from the observed peaks of Fe-BDC which confirms the formation of the product belongs to MIL-53 (Fe) type. As seen from the fig, the peaks at 17.62° ; 25.52° ; 28.14° is increasing with higher concentration of FeCl_3 indicating the presence of MIL-53. The average crystallite size for the 1:2 catalyst is 145-187nm.



Fig(5.2) XRD plot for Fe-MOF

5.3 SCANNING ELECTRON MICROSCOPY (SEM)

The structural morphology of the Fe-BDC crystal along with the crystal size is deduced. The SEM images for Fe-BDC (2:1) is presented in the Fig.5.3. The morphology of pure BDC is in the form of flakes while the Fe-BDC assumes the form of bulky rod shape with a porous structure in the sample ratio of 2:1. Similar bulky rod like structures were obtained in the other samples of Fe-BDC.

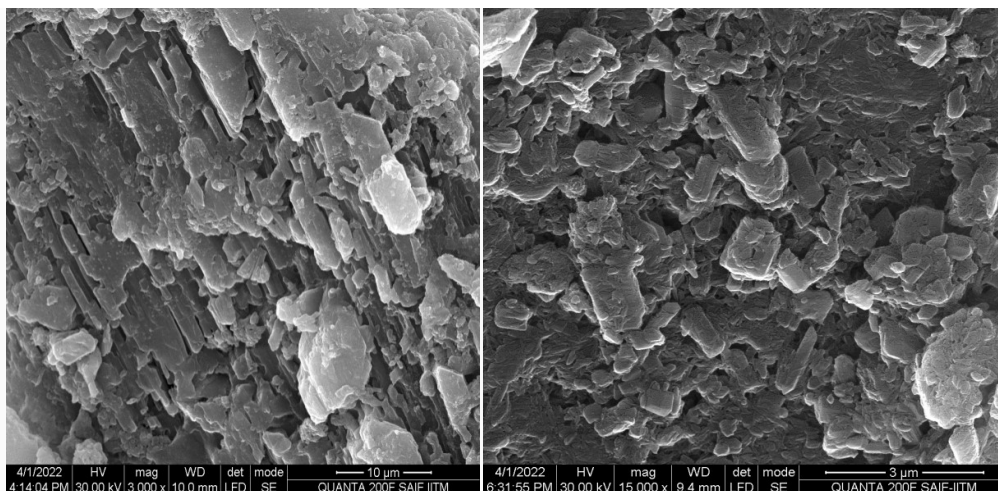


Fig (5.3) SEM image's for FE -MOF

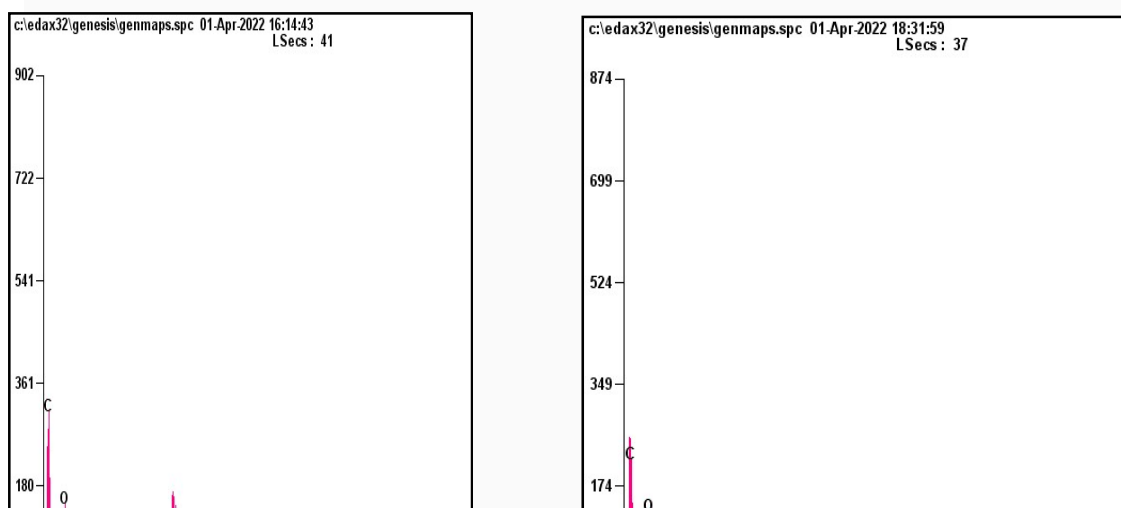


Fig (5.4) EDAX plot for Fe-MOF

5.4 EDOX PLOT FOR FE -MOF

The elemental composition of the synthesized Fe-BDC is monitored by EDX and is presented in the fig. 5.4. The Fe-BDC, the presence of iron is confirmed by the peak at 0.67Kev and at 6.50Kev. The atomic weight % of Fe was determined as 2.58% which corresponds to 4Fe atoms in the crystal structure of Fe-BDC.

<i>Element</i>	<i>Wt%</i>	<i>At%</i>
<i>CK</i>	62.41	71.60
<i>OK</i>	30.53	26.29
<i>AlK</i>	00.43	00.22
<i>ClK</i>	01.75	00.68
<i>FeK</i>	04.88	01.20
<i>Matrix</i>	Correction	ZAF

5.5 SCREENING OF THE CATALYST

Experiments were conducted in solar light at pH 7.0 in order to evaluate the performance of the catalyst. It was found that the catalyst of 1:2 undergoes maximum degradation with rhodamine B at a short interval of time.

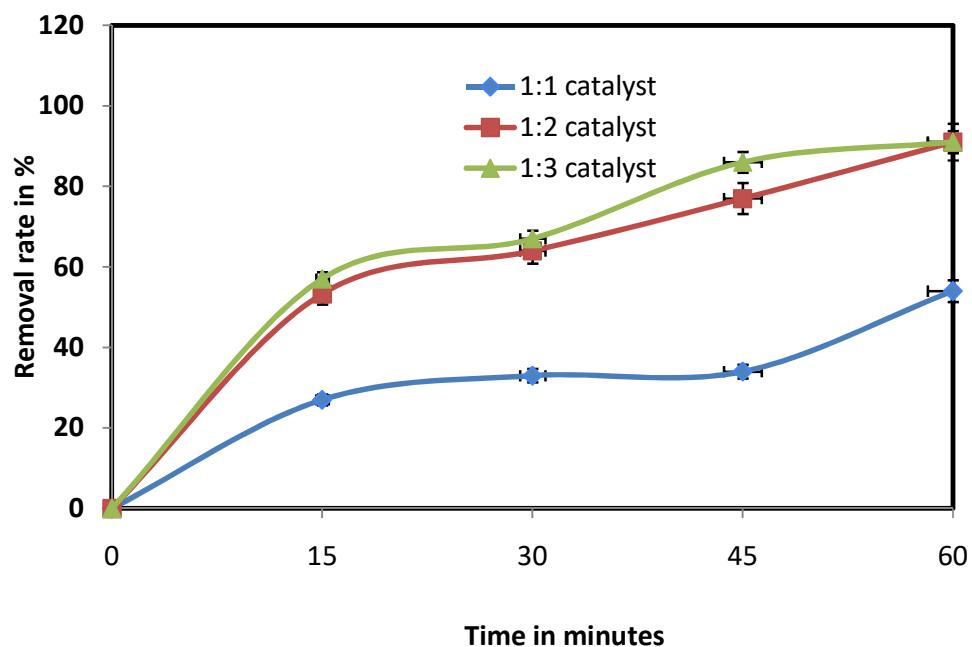


Fig 5.5 Screening of the catalyst for the removal of Rhodamine B.

Optimization of parameters governing the removal of RHB

Experiments were performed to optimize the various parameters governing the reaction like pH, catalyst concentration and dye concentration.

5.6 EFFECT OF PH

Experiments were carried out in 20mg/L of Rhodamine B solution at a catalyst amount of 0.25 g by varying the pH from 2.0 to 6.0. The reactions are performed under solarlight for 120 minutes. The effect of pH on the removal rate of Rhodamine B dye is shown in the Fig. An aliquot of samples were withdrawn at regular intervals and analysed for the dye removal. Maximum degradation of 96% occurred at pH 5.0.

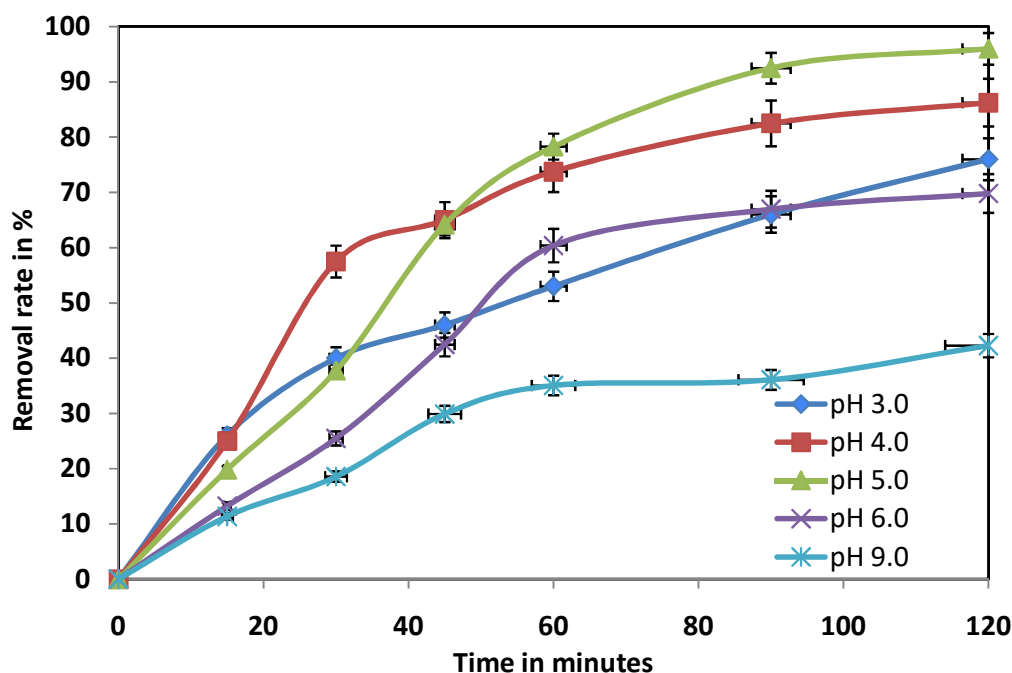


Fig 5.6 Effect of pH on the removal of Rhodamine B

5.6 EFFECT OF CATALYST CONCENTRATION

Experiments were carried out in 20mg/L of Rhodamine B solution at pH 5.0 by varying the catalyst amount from 0.1 to 0.4g. The reactions are performed under solarlight for 120 minutes. The effect of catalyst on the removal rate of Rhodamine B dye is shown in the Fig. An aliquot of samples were withdrawn at regular intervals and analysed for the dye removal. Maximum degradation of 80% occurred at pH 5.0 with catalyst amount of 0.3 g.

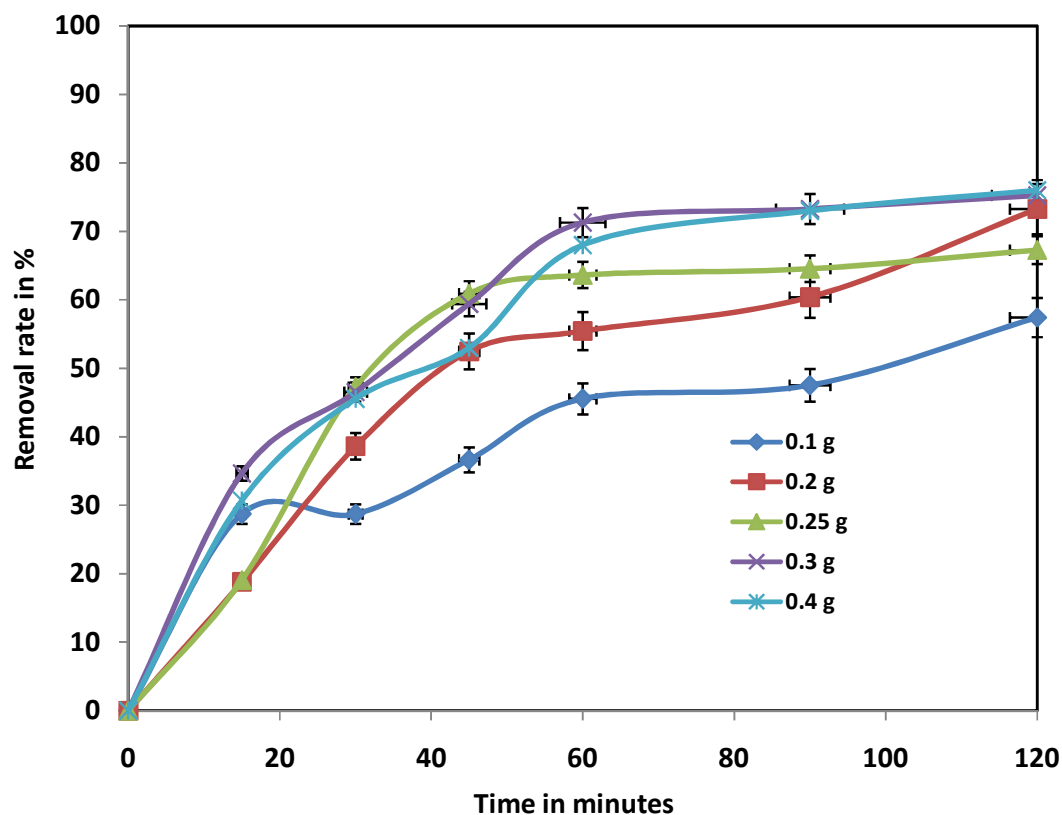


Fig.5.7 Effect of catalyst concentration on the removal of RHB

5.7 EFFECT OF CATALYST CONCENTRATION

Experiments were carried out in different concentrations of Rhodamine B solution at a catalyst amount of 0.3 g and at pH 5.0. The reactions are performed under solar light for 120 minutes. The effect of Rhodamine B conc. on the removal rate is shown in the Fig. An aliquot of samples were withdrawn at regular intervals and analysed for the dye removal. Maximum degradation of 90% occurred at pH 5.0 and at catalyst amount 0.3 g.

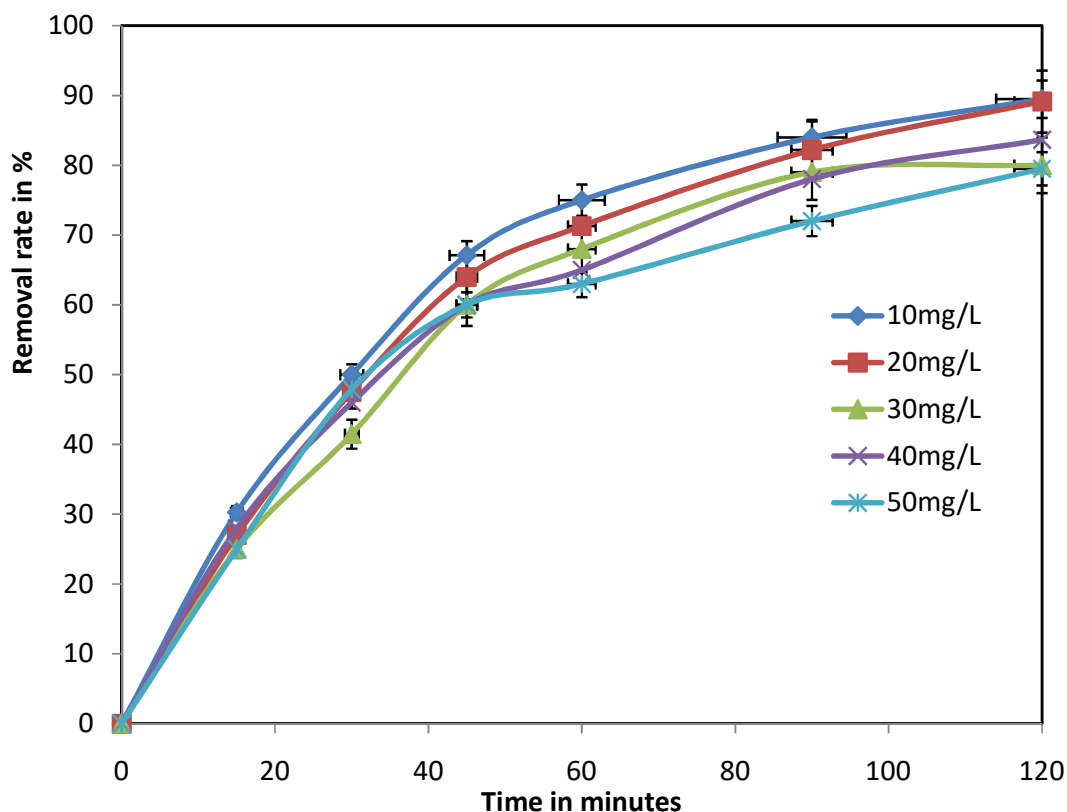


Fig.5.8 Effect of initial concentration on the removal of Rhodamine B

5.8 KINETICS FOR THE REMOVAL OF DYE

Iron MOF catalyst act as a photocatalyst promoting the generation of hydroxyl radical, which degrades/mineralize the rhodamine B dye. The rate of the reaction is dependent on concentration of Rhodamine B dye and hydroxyl radical. Since hydroxyl radical concentration is in excess, the rate equation is reduced to pseudo-first-order rate constant. Kinetic plot for the removal of Rhodamine B is given in the fig. The rate constant for the removal o rhodamine B is found to be $1.9 \times 10^{-2} \text{ min}^{-1}$ and the half-life is found to be 36.47 min.

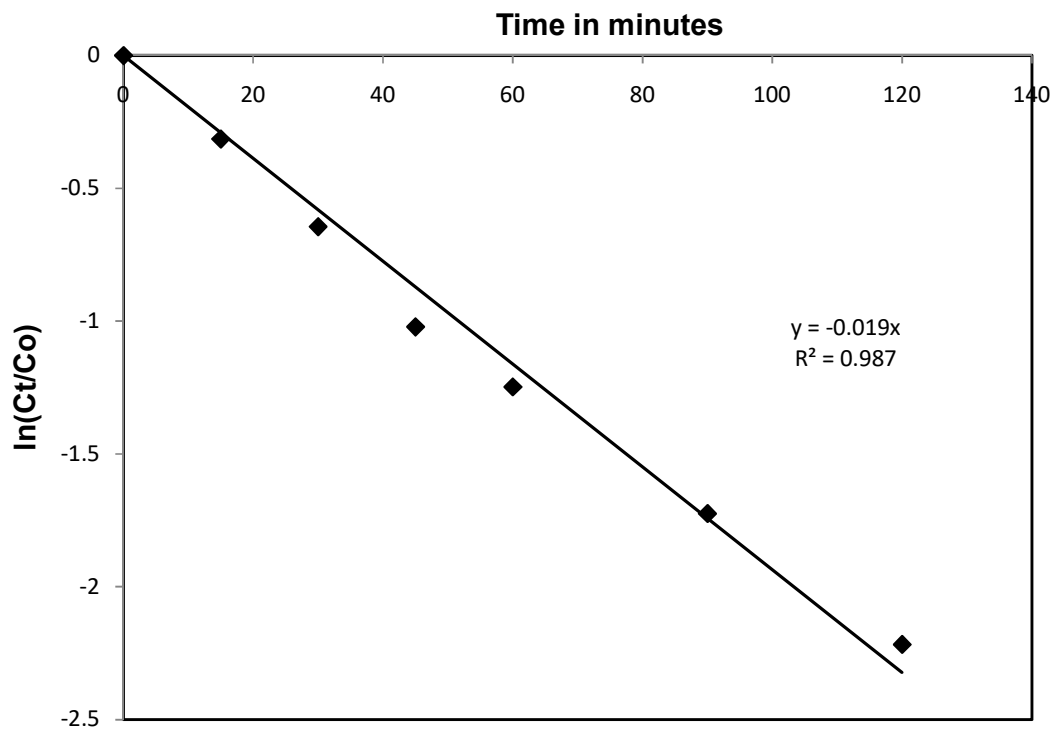


Fig .5.9 Kinetic plot for the removal of Rhodamine B

5.9 REUSABILITY OF THE CATALYST

Stability of the catalyst is studied by the performing the experiments with the same catalyst and determined its performance. The catalyst is stable and its removal rate remains around 85% with three experimental runs.

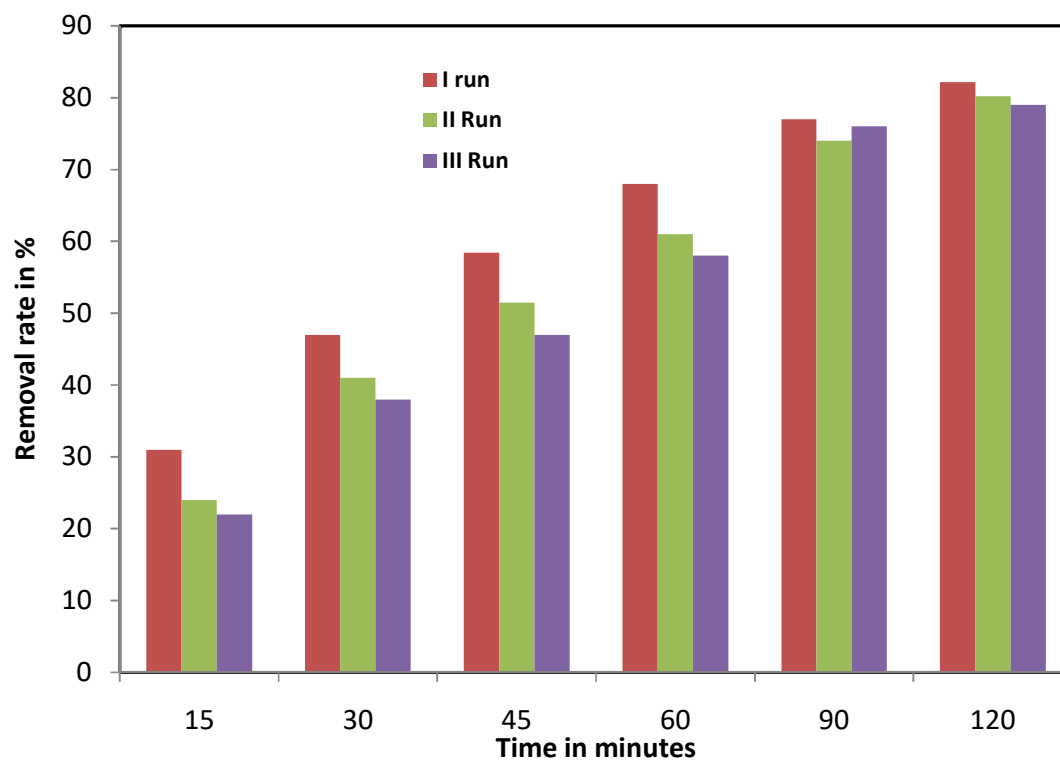


Fig.5.10 Reusability of the catalyst for the removal of Rhodamine B

CHAPTER 6

SUMMARY AND CONCLUSIONS

Summary:

Synthesizing Iron nanoparticles by using Mechanochemical method

Characterization of iron nanoparticles by FTIR, SEM AND XRD

Removal of RHODAMINE B dye from aqueous solution.

Conformation of product formed by characterization by FTIR.

Conclusions:

We used RHODAMINE B solution to removal of dye by optimization method using PH=5

Maximum removal rate of **90 %** was achieved.

The catalyst was found to be stable.

Three runs of three experimental gone.

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