

SYNTHESIS OF MOF FOR ORGANIC REACTIONS

**Submitted in partial fulfillment of the requirements for the award
of Master of Science in CHEMISTRY**

By

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SATHYABAMA

INSTITUTE OF SCIENCE AND TECHNOLOGY

(DEEMED TO BE UNIVERSITY)

Accredited with Grade "A" by NAAC

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APRIL-2021



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BONAFIDE CERTIFICATE



This is to certify that this Project Report is the bonafide work of **M.AMBIKA (39910002)** who carried out the project entitled "**SYNTHESIS OF MOF FOR ORGANIC REACTIONS**" under our supervision from February 2021 to March 2021.

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Submitted for Viva voce Examination held on _____

Internal examiner

External Examiner

DECLARATION

I **M.AMBIKA** student of **SATHYABAMA INSTITUTE OF SCIENCE AND TECHNOLOGY** hereby declare that the Project Report entitled **“SYNTHESIS OF MOF FOR ORGANIC REACTIONS ”** done by Me under the guidance of **Dr. V. KAVITHA, M.Sc., M.Phil., Ph.D., Professor, Department of Chemistry, Sathyabama Institute of Science and Technology** is submitted in partial fulfilment of the requirements for the award of **Master of Science degree in CHEMISTRY.**

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ACKNOWLEDGEMENT

I am pleased to acknowledge my sincere thanks to Board of Management of **SATHYABAMA** for their kind encouragement in doing this project and for completing it successfully. I am grateful to them.

I convey my thanks to **Dr. M. Sundareswari Ph.D.**, Dean, School of Science and Humanities and **Dr. J. Karthikeyan, M.Sc., Ph.D.**, Head of the Department, Dept. of Chemistry for providing me necessary support and details at the right time during the progressive reviews.

I would like to express my sincere and deep sense of gratitude to my Project Guide **Dr. V. Kavitha M.Sc., Ph.D.**, for her valuable guidance, suggestions and constant encouragement paved way for the successful completion of my project work.

I wish to express my thanks to all Teaching and Non-teaching staff members of the Department of Chemistry who were helpful in many ways for the completion of the project.

M.AMBIKA

ABSTRACT

Metal-Organic Framework, Fe-BDC was synthesized by solvothermal method from iron salt and terephthalic acid using N, N-Dimethylformamide as the solvent. The aim of this study is to see if the Fe-BDC metal organic framework can be used for the Biginelli reaction. Further spectral studies were done which Fourier Transform-Infrared Spectroscopy, X-ray Diffraction, Scanning Electron Microscopy, Energy Dispersive X-ray analyser.

KEYWORDS: Metal organic framework, iron, benzene dicarboxylic acid, DMF.

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LIST OF ABBREVIATIONS

ABBREVIATIONS	EXPANSIONS
BDC	Benzene dicarboxylic acid
DMF	Dimethylformamide
MOF	Metal organic frameworks
FT-IR	Fourier Transform Infrared X- ray
XRD	X-ray diffraction
SEM	Scanning Electron Microscopy
EDX	Energy Dispersive X-ray

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CHAPTER 1

INTRODUCTION

MOFs are organic-inorganic hybrid crystalline porous materials made up of a standard array of positively charged metal ions surrounded by organic 'linker' molecules. The metal ions form nodes, which join the arms of the linkers to form a cage-like structure. MOFs have a very wide internal surface area due to their hollow nature. MOFs with a surface area of more than 7800 square metres per gram have been generated by researchers.

In comparison to other porous materials, MOFs have a remarkable structural diversity: uniform pore structures, atomic-level structural uniformity, tunable porosity, a wide range of varieties, and versatility in network topology, geometry, dimension, and chemical functionality. This enables researchers to successfully monitor the topology, porosity, and functionality of frameworks.

The special structure nature and tunability of MOFs – crystalline porous materials made up of both organic and inorganic components in a rigid periodic networked structure – is not readily available in traditional porous materials, such as solely inorganic zeolites.

They are commonly used in adsorption, catalysis, sensing, energy storage, and drug delivery, among other applications. Many MOF materials, on the other hand, can be used only.

Metal–organic frameworks (MOFs) have attracted the attentions of adsorption researchers in recent years due to the existence of a standard nanoporous structure with a high porosity and surface area, which are critical for the storage, transport, and separation of various gases such as methane (CH₄), carbon dioxide (CO₂), and hydrogen (H₂).

Metal–organic frameworks are crystalline polymeric materials made up of metal atoms or clusters connected by polydentate ligands. Coordination polymers of this subclass are well known for their structural versatility, which allows them to form a variety of structures, each with its own set of physical properties.

Metal–organic frameworks are crystalline polymeric materials made up of metal atoms or clusters connected by polydentate ligands.

The structural flexibility of this subclass of coordination polymers is well established, resulting in a variety of structures, each with its own set of physical properties. Since MOFs have such a wide range of design possibilities, choosing a starting point is crucial.

The aim of this study was to build a metal–organic framework based on the transition metal, iron, which has a high adsorption activity.

The ligand BDC from terephthalic acid was chosen to achieve the required structural-energy characteristics of Fe–MOF.

The best solvent for metal–ligand coordination is N,N-dimethylformamide. This method allows for the development of a high-activity metal–organic framework structure, Fe–MOF, with a large micropore volume and sufficient surface area for the adsorption of energetic gases including CH₄ and H₂.

They also discovered that the presence of Fe³⁺ ions in the MOF structure increases the hydrogen–MOF interaction significantly.

H₂ interaction is twice as strong in the MOF–Fe system as it is in the MOF–Cu and MOF–Zn systems. The metal site of MOFs can be used to increase the interaction energy of H₂ in the MOF structure, according to this research.

The Fe-MOF structure synthesized with the BDC ligand forms a more stable compound than other Fe–MOFs synthesized with other organic acids, according to data from the thermo gravimetric study.

CHAPTER 2

LITERATURE SURVEY

2.1 Synthesis of MIL-53(Fe) Metal-Organic Framework Material and Its Application as a Catalyst for Fenton-Type Oxidation of Organic Pollutants

Under different conditions, the iron (III) benzene dicarboxylate metal-organic framework content (MIL-53(Fe)) was synthesized using either the solvent-thermal or hydrothermal process. The effect of solvent form, precursor-to-solvent molar ratio, temperature, and reaction time on the structure of MIL-53(Fe) was investigated. X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HR-TEM), X-ray photoelectron spectroscopy (XPS), and the N₂ adsorption/desorption isotherm were used to characterize the sample. In N-methylformamide (DMF), and methanol (MeOH), but not in water, the MIL-53(Fe) structure developed. The crystal structure of MIL-53 was significantly affected by the molar ratio of precursors and solvent, temperature, and reaction time in DMF (Fe). MIL-53(Fe) has high crystallinity and a wide specific surface area ($S_{\text{BET}} = 88.2 \text{ m}^2/\text{g}$) under ideal conditions. The MIL-53(Fe) obtained could be used as a heterogeneous catalyst for the oxidation of phenol (PN), rhodamine B (RhB), and methylene blue (MB) in the Fenton-like reaction system at the different solution pHs. The MIL-53(Fe) metal-organic framework material can be successfully synthesized using the solvent-thermal process with DMF or MeOH as solvents, with DMF being the better option. Moreover, the molar ratio of precursors and solvents, temperature, and reaction time all affect MIL-53 formation (Fe). MIL-53(Fe) has high crystallinity, a wide specific surface area ($S_{\text{BET}} 88.2 \text{ m}^2/\text{g}$), and an even porous structure when made in DMF with a Fe (III)/BDC molar ratio of 1:2. MIL-53(Fe) is a possible heterogeneous Fenton catalyst for the oxidation of organic compounds in aqueous environments by hydrogen peroxide at pH 2–12. (Pham Dinh and Pham Ngoc Hoai-2021)

2.2 Iron based metal organic framework for efficient removal of methylene blue dye from industrial waste

This study aims to see whether the Fe-BDC metal-organic system can be used to extract the toxic dye methylene blue from industrial waste. The effect of contact time, dye concentration, amount of adsorbents, and temperature on the

adsorption characteristics and dye removal efficiency of Fe-BDC MOF has been investigated. By growing the adsorbent dose and temperature, up to 94.74 percent dye removal was achieved. After 24 hours, applying 25 mg of FeBDC MOF to a dye solution of MB with a concentration of 5 mg/L resulted in a maximum dye removal of 94.74 percent. The isotherm models of Langmuir, Freundlich, and Tempkin have been used to assess the ongoing adsorption process. It was discovered that the Freundlich adsorption isotherm is best suited to the adsorption process. Using pseudo-first-order, pseudo-second-order, and intra particle diffusion kinetic equations, various kinetic parameters have been calculated. The best fit for adsorption of methylene blue on FeBDC MOF is a pseudo-second-order kinetic model with a rate constant (k_2) 4.9×10^2 g/mg min, suggesting that the dye is removed primarily by chemisorption. Using batch and column techniques, an iron-based metal-organic system Fe-BDC MOF effectively extracted methylene blue dye from its aqueous solution. The effect of various parameters on the removal of MB, such as contact time, adsorbent dose, pH, temperature, and initial dye concentration, has been studied. At 50 °C temperature, 92% MB dye was removed from 5 ppm dye solution within 6 h. In an acidic medium, excess H^+ ions present in the dye solution inhibit the adsorption. The equilibrium adsorption data showed a significant correlation to Freundlich's adsorption isotherm. The results indicate that the FeBDC MOF can be used for the removal of the entire range of concentrations of methylene blue dye. The adsorption mechanism is spontaneous and endothermic, and it continues by chemisorptions, according to thermodynamic parameters. There are three kinetic model. The interaction behavior of the MOF surface with the MB dye was interpreted using pseudo-first-order, pseudo-second-order, and intra-particle diffusion models, with the pseudo-second-order model proving to be the most suitable for interpreting the interaction between MB dye and Fe MOF. (Charu Arora, Sanju soni-2019).

2.3 Fe-based MOFs for photo catalytic N₂ reduction: Key role of transition metal iron in nitrogen activation

In photo catalytic nitrogen fixation, nitrogen activation is the Achilles' heel. For the first time, metal-organic frameworks (MOFs) are proposed as a solution to the aforementioned bottleneck in this paper. Photocatalytic nitrogen fixation activity

was demonstrated in a series of Fe-based MOFs (MIL-101(Fe), MIL-100(Fe), and MIL-88(Fe), MIL-101(Cr) and MIL-101(Fe), which have the same molecular structure except for the central metal ions, were chosen for device comparison to gain insight into the reaction mechanism. MIL-101(Fe) and MIL-101(Cr) have photocatalytic nitrogen fixation activities of 50.355 mol L⁻¹ h⁻¹ and inactive, respectively. This meant that the Fe catalytic core was responsible for nitrogen fixation. Fe catalytic centers have a higher electron density, lower reaction activation energy, and more generation of N–H bond than Cr catalytic centers, according to in situ FTIR and quantum computation performance. Due to the similar outer electron configurations of Cr and Fe, it was hypothesized that two extra d-orbitals electronics of Fe are the primary cause of the high photocatalytic nitrogen fixation operation. This study introduces a new application of MOFs in the field of photocatalytic nitrogen fixation, emphasizing the importance of d-orbitals electronics in the nitrogen activation process. In summary, we used a variety of Fe-based MOF materials for photocatalytic nitrogen fixation, including MIL-88(Fe)-40.035 mol L⁻¹ h⁻¹, MIL-100(Fe)-46.532 mol L⁻¹ h⁻¹, MIL-101(Fe)-50.355 mol L⁻¹ h⁻¹, and MIL-102(Fe)-50.355 mol L⁻¹ h⁻¹. This will open up new possibilities for low-energy green ammonia production. MIL-101(Cr) (inactivity) and MIL-101(Fe) (activity) were chosen for device comparison because they have the same molecular structure except for the central metal ions. Fe catalytic centers have a higher electron density, lower reaction activation energy, and more generation of N–H bond than Cr catalytic centers, according to in situ FTIR and quantum computation performance. Due to the similar outer electron configurations of Cr and Fe, it was hypothesized that two extra d-orbitals electronics of Fe are the driving force behind the high photocatalytic nitrogen fixation operation. This study introduces a novel application of MOFs in the field of photocatalytic nitrogen fixation, emphasizing the importance of d-orbitals electronics in the nitrogen activation process. (Guoqiang Li, Feifei Li-2020)

2.4 In-situ ethylenediamine-assisted synthesis of a magnetic iron-based metal-organic framework MIL-53(Fe) for visible light photocatalysis

An in-situ ethylenediamine (EDA)-assisted solvothermal process was used to make a novel magnetic MIL-53(Fe) photocatalyst (MAG-MIL). The c-Fe₂O₃ nanoparticles embedded in the MAG-MIL system lead to a red change of the light

absorption edge as well as the superparamagnetism property. An in-situ ethylenediamine (EDA)-assisted solvothermal method was used to make a superparamagnetic MIL-53(Fe) photocatalyst with a red-shifted light

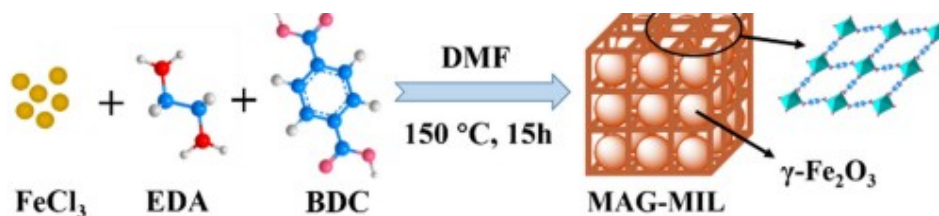


Fig 2.4.1 A super paramagnetic Mil-53(Fe) Photo catalyst with a Red shift of the light absorption edge was synthesized by an in-situ ethylenediamine (EDA) assisted solvothermal method

absorption tip. The increased light-harvesting ability of MOFs from ultraviolet light (UV) to visible light for further enhancement of photocatalytic activity is a major challenge. The photocatalytic activity of MOFs such as NH₂-MIL-125(Ti), NH₂-MIL-88B(Fe), and UiO-66-NH₂ (MIL and UiO stand for two kinds of MOFs) has been stated to be increased by ammoniating or hydroxylating the organic linkers. By adding ethylenediamine, a magnetic iron-based metal-organic framework was successfully fabricated using an in-situ solvothermal process. The procedure was simpler and more convenient than previously published methods. As a ligand, ethylenediamine has the potential to react with Fe³⁺ and form magnetic c-Fe₂O₃ nanoparticles. Ethylenediamine, as a stabilizer, also regulated the size of magnetic particles to fit the pores of MIL-53 (Fe). As a result, c-Fe₂O₃ and MIL-53(Fe) could shape at the same time, saving time over the previously stated step-by-step assembly process. In comparison to the MIL-53 catalyst, the synthesized MAG-MIL catalyst with many c-Fe₂O₃ nanoparticles injected into the matrix had a wider absorption peak in the visible light field (Fe). Under visible light irradiation, the surface area normalized photocatalysis degradation rate of MB on MAG-MIL was higher than that of MIL-53(Fe) and registered Fe₃O₄@MIL-100 (Fe). Moreover, the superparamagnetism property made it simple to extract MAG-MIL particles from the solution. Recycle tests also revealed that MAG-MIL was much more reusable and stable for dye degradation than MIL-53 (Fe). Furthermore, the

preparation method described here can be applied to the synthesis of other magnetic MOF materials.(Xiangwen Feng,Huan Chen-2017)

2.5 Metal organic frameworks of lanthanum and iron using BDC linker as catalysts for glucose conversion into 5-hydroxymethylfurfural (5-HMF)

Lanthanum and Iron-Metal Organic Frameworks (La-MOFs, Fe-MOFs) have been successfully synthesized and used as catalysts to transform glucose into 5-Hydroxymethylfurfural using a solvothermal process (5-HMF). 5-HMF is a promising energy source that is widely used in the chemical and polymer industries. MOF is used as a source of Lewis and Brnsted acids, which can help improve the conformation of 5-HMF during the glucose transformation process. X-Ray Diffractometer (XRD), Scanning Electron Microscopy-Energy Dispersive X-Ray (SEM-EDX), Fourier Transform Infrared (FTIR), and Brunauer-Emmelt-Tellers were used to determine the XRD pattern, surface morphology, chemical composition, absorption spectra, and surface area (BET). On the XRD pattern, the unique peaks of La-MOF corresponded to MIL-88B structure at $2\theta = 8^\circ$, while Fe-MOF corresponded to MIL-88B structure at $2\theta = 9^\circ$. The morphology of La-MOF and Fe-MOF was revealed by SEM analysis to be rod-like and rhombic. The broadening peak for O-H stretching vibrations was found in the FTIR spectrum of La-MOF at 3526 cm^{-1} , while the sharp peak strength for C-H bending vibrations was found in the FTIR spectrum of Fe-MOF at 749 cm^{-1} . The surface area of the La-MOF was 107.107 m^2/g and the surface area of the Fe-MOF was 215.435 m^2/g , respectively. The behavior of La-MOF and Fe-MOF as catalysts was tested in a 10 mL vial glass reactor at $T = 403 \text{ K}$ for 0–8 hours with a catalyst loading of 8–12 mg. The product was analyzed using High-Performance Liquid Chromatography (HPLC), which revealed that Fe-MOF had higher activity, yielding 26.79 percent versus 19.2 percent for La-MOF in a 6 h reaction period with 10 mg catalyst in DMSO as solvent.

For the conversion of glucose to 5-hydroxymethylfurfural, La-BDC and Fe-BDC MOF were used as catalysts (5-HMF). The catalytic experiments were carried out

in a 10 mL vial glass reactor at $T = 403\text{ K}$ for 0, 3, 6, and 8 hours, with different quantities of catalysts (0, 8, 10, and 12 mg). The reactor was then filled with 2 mL of a 10% wt. glucose solution in H_2O or DMSO, which was combined with the catalyst. The experiment was conducted without the use of a catalyst. To stop the reaction, the vial was immediately put in an ice bath at $5\text{ }^\circ\text{C}$ after being heated for different reaction periods. The product was analyzed with High-Pressure Liquid Chromatography using LC200 Quantine Isocratic Pump with Inertsil ODS column packaged, UV detector with 285 nm wavelengths (for 5-HMF), and UV detector with 285 nm wavelengths (for 5-HMF). The solvothermal method was used to successfully synthesize La-BDC and Fe-BDC using DMF and H_2O as solvents. According to the findings, the XRD pattern of the materials has similar peaks to MIL-88B. The La-BDC was rod-like, while the Fe-BDC was rhombic, according to SEM photographs, with a specific surface area of $107.107\text{ m}^2/\text{g}$ for La-BDC and $215.28\text{ m}^2/\text{g}$ for Fe-BDC. According to this research, the best conditions for glucose conversion to 5-HMF are 10 mg of catalysts mixed with glucose in 10 mL of DMSO (10% w/v solution) and heated to 403 K for 6 hours, yielding 19.21 percent for La-BDC MOF and 26.79 percent for Fe-BDC MOF, respectively. To summarise, Fe-BDC MOF is a more active catalyst for converting glucose to 5-HMF. (N Riezzati et al-2020)

2.6 Design and development of amine functionalized iron based metal organic frameworks for selective fluoride removal

Because of their large surface area and high porosity, metal-organic frameworks (MOFs) play a critical role in the adsorption process. A trivalent metal ion, iron (Fe^{3+}), was used to fabricate benzene-1,4-dicarboxylic acid (BDC) and 2-aminobenzene-1,4-dicarboxylic acid (ABDC), resulting in Fe@BDC and Fe@ABDC dependent metalorganic frameworks (MOFs) for selective fluoride resorption. The Fe@BDC and Fe@ABDC MOF composites had enhanced defluoridation capacities (DCS) of 4.90 and 4.92 mg g^{-1} toward fluoride adsorption, respectively. The Fe@BDC and Fe@ABDC MOF composites were characterized using FTIR, TGA, SEM, BET, EDAX, XPS, and XRD. The batch

level investigated the responsible parameters for the defluoridation process, such as adsorption time, solution pH, initial fluoride concentration, adsorbent dosage, interfering anions, and temperature. For fluoride adsorption, the adsorption isotherms, kinetics, and thermodynamic parameters of Fe@BDC and Fe@ABDC MOF composites were investigated. The process of fluoride adsorption in Fe@BDC and Fe@ABDC MOF composites was thoroughly discussed. Field test applicability and recyclability of Fe@BDC and Fe@ABDC MOF composites were also investigated. The fluoride removal studies were successfully carried out using the produced Fe@BDC and Fe@ABDC MOF composites. The strengthened DC of Fe@BDC and Fe@ABDC MOF composites against maximum fluoride adsorption was 4.90 and 4.92 mg g⁻¹, respectively. The surface-atmosphere of the synthesized Fe@BDC and Fe@ABDC MOF composites is primarily affected by the adsorbate pH of the fluoride concentration solution. Furthermore, enhanced DC was obtained in a neutral pH setting. Bicarbonate ions were found in potable water and competed with fluoride sorption for the most part. The prepared Fe@BDC and Fe@ABDC MOF composites were investigated using characterization methods such as TGA, EDAX, FTIR, XPS, BET, XRD, and SEM. Adsorption isotherm studies confirmed the chemical adsorption existence of Fe@BDC and Fe@ABDC MOF composites against fluoride adsorption, confirming the Langmuir isotherm as a valid model for defluoridation systems. Moreover, kinetic studies show that the pseudo-second-order and intraparticle diffusion models are more applicable to defluoridation. The results of the thermodynamic parameters showed that the fluoride adsorption mechanism was feasible and endothermic. Electrostatic attraction and complexation mechanisms dominated the fluoride adsorption mechanism of Fe@BDC and Fe@ABDC MOF composites. The Fe@BDC and Fe@ABDC MOF composites were recycled for six cycles, and field tests of Fe@BDC and Fe@ABDC MOF composites confirmed that they are suitable for use in the field. (Antonyamy Jeyaseelan-2020)

2.7 Functionalization effect of Fe-type MOF for methylene blue adsorption

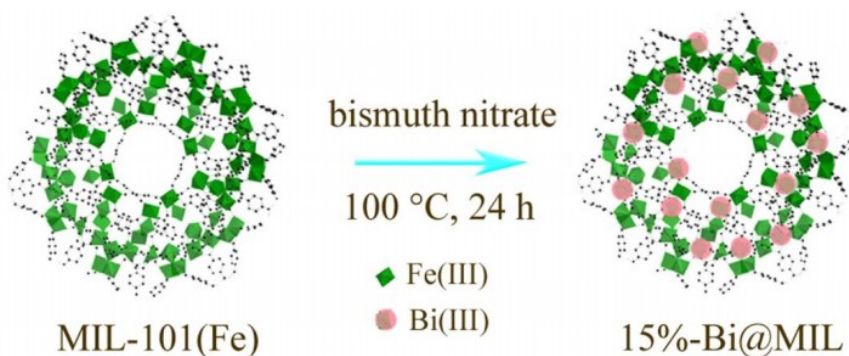
Pollutants in the water, such as dyes, posed a threat to the water's safety. Porous materials have a lot of potential for dye adsorption from water sources these days. The iron-based metal-organic structure (MOF-Fe) of MIL-101 is

synthesized using a simple solvothermal method in this analysis. The adsorptive removal of methylene blue (MB) from MOF-Fe (amine-MOF-Fe) is investigated using the amine-functionalization effect of the MOF-Fe (amine-MOF-Fe). Because of the porous MOF-Fe structure's pore-filling mechanism, the adsorption behavior showed rapid MB adsorption within the first hour of the operation. The high adsorption potential was due to the electrostatic interaction between the amino group of amine-MOF Fe and MB. The amine-functionalization effect also revealed that amine-MOF-Fe has a two-fold higher adsorption potential than non-functionalized MOF-Fe when used with a two-fold lower loading. The maximum equilibrium adsorption capacities for MOF-Fe and amine-MOF-Fe, respectively, were 149.25 and 312.5 mg/g, with optimum MOFs loading of 0.8 and 0.4 g/L. Electrostatic contact, pore filling, hydrogen bonding, and π -stacking are all proposed as adsorption mechanisms. The MOFs could be recycled without affecting the removal efficiency, according to the regeneration report. As a result, the findings suggest that the MOFs have desirable reusability for the practical adsorption of cationic dyes due to their quick absorption and high capacity properties. The adsorption process can effectively extract hazardous dye (MB) from polluted water. The cationic MB adsorption potential of the MOF-Fe and amine-MOF-Fe synthesized in this study was 149.25 mg/g and 312.5 mg/g, respectively. The effect of amine functionalization demonstrated that the amine group was crucial in the adsorption process, as it resulted in a two-fold increase in MB ion adsorption capacity. Furthermore, when the MOF-Fe is functionalized with an amine group, the MOF loading can be cut in half.

The Langmuir isotherm was found to be the best fit for MOF-Fe in the adsorption isotherm. Meanwhile, the Freundlich isotherm for amine-MOF-Fe had been better identified. Furthermore, both MOFs adopted the pseudo-second-order kinetics model, according to the adsorption kinetics. Attempts to reuse both MOFs showed that after two cycles, the amine-MOF-Fe could retain adsorption efficiency. Regardless, both MOFs are promising adsorbents for the removal of cationic dyes from aqueous solutions. (Syafikah Huda Paiman-2020)

2.8 Facile synthesis of mesoporous Fe-based MOFs loading bismuth with high speed adsorption of iodide from solution

To improve the uptake effect of iodide anions from aqueous solution, mesoporous Fe-based MOFs (Bi@MIL) were made by solvothermal synthetically mixing Bi(III) and MIL-101(Fe) in a Teflon-lined autoclave. The crystal structure of MIL-101(Fe) was preserved when the addition of Bi(III) species in the synthesis of Bi@MIL was less than 5.0 percent, as determined by IR, XRD, SEM, BET, and XPS. Mesoporous Fe-based MOFs were obtained when the amount of Bi(III) reached 15.0 percent. The adsorption equilibrium was reached in 20 minutes in 200 mg L⁻¹ of iodide anions solution concentration at neutral medium in Bi@MIL composites with fast adsorption kinetics. The adsorption of iodide anions was affected by the pH of the solution, and the highest adsorption capacities were found at pH 3.



2.8.1 Mesoporous Fe-based MOFs loading bismuth with high speed adsorption of iodide from solution

Mesoporous Fe-based MOFs (Bi@MIL) were rendered by solvothermal synthetically mixing Bi(III) and MIL-101(Fe) until the amount of Bi(III) reached 15.0 percent. The adsorption kinetics of Bi@MIL composites were quick, and the adsorption equilibrium was reached in 20 minutes. 15 percent -Ni@MIL has a maximum adsorption capacity of 189.6 mg g⁻¹. Finally, a new method for producing mesoporous MOF materials is presented. The adsorbents (Bi@MIL) were easily made by solvothermal synthetically integrating Bi(III) into MIL-101(Fe). The crystal structure of Bi@MIL was almost unchanged when the sum of Bi(III) species in the synthesis was less than 5.0 percent. When the concentration reached 15.0 percent, the MOFs crystal structure became defective, resulting in the formation of mesoporous MOFs. In a 200 mg L⁻¹ iodide anions solution at neutral medium, Bi@MIL composites have fast

adsorption kinetics, with adsorption equilibrium achieved in just 20 minutes. The adsorption potential of iodide anions is affected by the pH of the solution, with overall adsorption capacities of 189.6 mg g⁻¹ in a 200 mg L⁻¹ iodide anions solution at pH 3. Bi@MIL composites have a promising future in the field of rapid iodide ion aggregation, such as that of radioactive iodide ions.(Wenjing Xu-2018)

2.9 Synthesis and Structural-Energy Characteristics of Fe-BDC Metal-Organic Frameworks

Using N, N-dimethylformamide as the solvent, a metal-organic structure, Fe-BDC, was synthesized by solvothermal process from iron salt and terephthalic acid. The data from the Dubinin-Radushkevich, Kelvin, and BET equations were used to measure structural-energy characteristics. SBET = 2240 m² /g and W0 = 0.83 cm³/g are the specific surface areas and micropore volumes of the Fe-BDC sample. This sample's morphological and X-ray characteristics were investigated. The inorganic iron salt hydrate, terephthalic acid, and N, N-dimethylformamide as the solvent was used to make the Fe-BDC metal-organic system structure. The structural-energy characteristics of the microporous structure were calculated for each sample using the Dubinin–Radushkevich equation based on nitrogen adsorption data at 77 K.

The Fe-BDC sample has the following adsorption parameters: W0 = 0.83 cm³/g micropore length, SBET = 2240 m²/g, x0 = 0.90 nm, E0 = 13.4 kJ/mol normal characteristic energy of benzene adsorption and a0 = 23.87 mmol/g limit nitrogen adsorption in micropores. The mesopore volume was Wme = 0.47 cm³/g, the mesopore surface area was Sme = 110 m², and the total pore volume was Ws = 1.30 cm³/g, according to the Kelvin equation. Over 200°C, the synthesized Fe-BDC structure is thermally unstable, and the adsorption behavior is unstable in cyclic adsorption processes.(M. K. Knyazeva-2018)

2.10 Ultrasound-assisted biodiesel production by a novel composite of Fe (III)-based MOF and phosphotangestic acid as efficient and reusable catalyst

Esterification of oleic acid by various alcohols is achieved with high yields under ultrasonic irradiation. MIL-53, a novel heterogeneous catalyst made of heteropoly acid and Fe(III)-based MOF, was used in this reaction (Fe). Ultrasound irradiation at room temperature and pressure was used to synthesise and encapsulate MIL-53. The prepared composite was characterised using a variety of techniques, including XRD, FT-IR, SEM, BET, and ICP, and showed excellent catalytic activity while being extremely simple to make. The results showed that ultrasound irradiation could be used to make biodiesel efficiently and effectively. Finally, we have successfully fabricated PTA-MOF composite as a novel catalyst using a functional method suitable for oleic acid-based biodiesel processing. High yields of esterification of oleic acid by different alcohols are achieved under ultrasonic irradiation and completely heterogeneous conditions. The materials were extremely catalytic and easy to separate from the reaction medium. (Ahmad Nikseresht-2017)

CHAPTER 3

AIM AND SCOPE

3.1 AIM:

The aim of the project is to compare the preparation of Iron-Benzene dicarboxylic acid Metal organic framework from chemical precursor .

3.2 SCOPE:

The aim of this study was to create a metal–organic framework based on a transition metal, such as iron, that has a high adsorption activity. The ligand BDC from terephthalic acid was chosen to achieve the necessary Energy Dispersive X-ray analyser characteristics of Fe-BDC MOF. The best solvent for metal–ligand coordination is N, N-dimethylformamide. This method allows for the development of a high-activity metal-organic framework structure, Fe-MOF, with a large microspore volume.

Main objectives of the study

- To prepare Iron-benzene dicarboxylic acid Metal Organic Framework as a catalyst from chemical precursor.
- To characterize the prepared catalyst by Fourier Transform – Infrared Spectroscopy (FT-IR), Powder X-ray Diffractometry (XRD), Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray Analyzer (EDX).

CHAPTER 4

MATERIALS AND METHODS

4.1 CLEANING OF APPARATUS

All the apparatus were washed in sulphuric acid, washed with tap water followed by distilled water. It is cleaned with acetone and dried before using them.

4.1.1 MATERIALS AND CHEMICALS REQUIRED

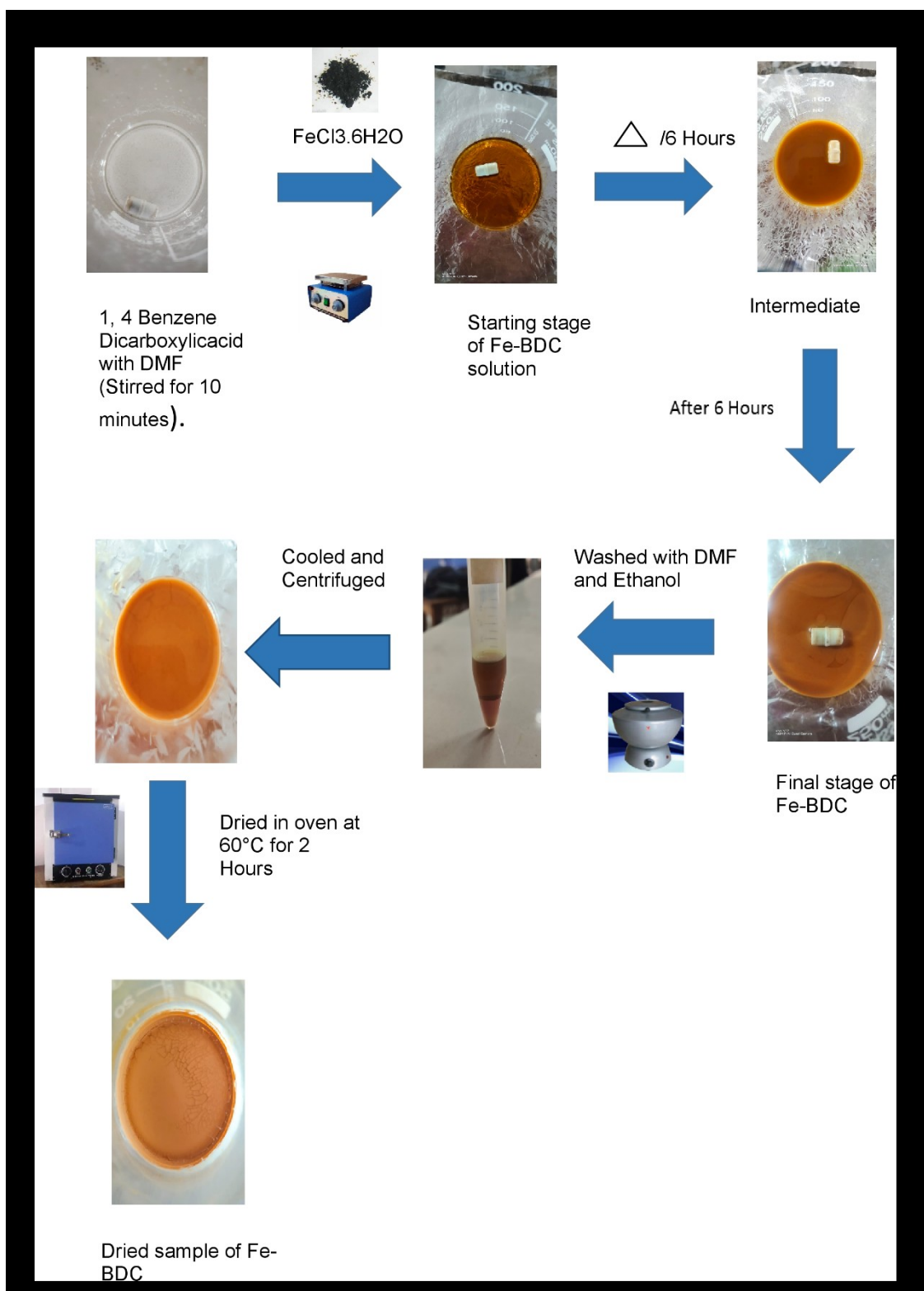
- Ferric Chloride Hexa hydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$)
- 1,4 Benzene dicarboxylic acid ($\text{C}_6\text{H}_4(\text{CO}_2\text{H})_2$)
- N, N-dimethylformamide ($\text{C}_3\text{H}_7\text{NO}$)
- Ethyl alcohol ($\text{C}_2\text{H}_5\text{OH}$)(LR)

4.2 METHODS

4.2.1 PREPARATION OF Fe-BDC

0.4g of Ferric Chloride Hexahydrate taken in 100 ml Beaker. 0.21g of 1, 4 Benzene dicarboxylic acid is taken in another 100ml beaker with 15 ml of N, N dimethylfarmamide as a solvent. The solution of mixed solvent is added to $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$. The beaker solution is kept in magnetic stirrer for 6 hours at 30% of temperature. When the solution reaches the intermediate stage 15 ml of ethanol is added. After 6 hours the solution cooled and centrifuged. The obtained precipitate is added with 2.5ml of DMF and 2.5ml of ethanol approximately and dried in hot air oven at 150 for 1 hour. Fe-BDC ($\text{C}_8\text{H}_6\text{FeO}_4$) is obtained by recrystallizing the dried sample with Ethanol.

The same procedure is repeated for 1:1, 3:1, 4:1 proportions of Fe: BDC respectively.



4.2 Schematic flowchart of preparation of Fe-BDC

Table 1. Description of the resulting MOF sample, Fe–BDC, and starting compounds used in the synthesis

Substance name	Chemical formula	Molecular weight	Appearance
Fe-BDC metal-organic framework	$C_8H_6FeO_4$	604 g/mol	Pink-brown particles
Source of metal cation: Iron(III) Chloride Hexa hydrate	$FeCl_3 \cdot 6H_2O$	270.29 g/mol	Brownish yellow solid
Organic ligand: terephthalic acid	$C_8H_6O_4$	166 g/mol	Colourless crystals
Organic solvent: <i>N,N</i> -dimethylformamide	C_3H_7NO	73.09 g/mol	Colourless liquid

4.3 CHARACTERIZATION TECHNIQUES

4.3.1. Fourier Transform - Infrared Spectrometer

Fourier Transform Infrared Spectrometer (FTIR) is primarily used to measure the light absorption at mid-infrared region, with a wavelength range of 4,000 to 400 cm^{-1} (wavelengths of 2.5 to 25 μm), in order to distinguish and quantify different materials.

FTIR spectroscopy is a molecular spectroscopy which is employed to characterize each organic and inorganic sample. The sample is bombarded with infrared radiation. Once the frequency of the infrared radiation matches

the natural frequency of the bond, the amplitude of the vibration will increase and therefore the infrared is absorbed.

The characteristics peak is observed for each functional group or a part of the molecule. The graph is plotted relative absorbance versus wave number

The attenuated total reflection (ATR) technique can be used to analyze strongly infrared adsorbing materials like rubbers, silicone films, and aqueous solutions. ATR analysis needs little to no sample preparation. 450ZnSe and 450Ge are the two types of crystals we have in our lab.

The KBr disc approach was used to generate infrared spectra on a spectrum 100 FT-IR spectrophotometer (Perkin-Elmer, USA).

4.3.2 Powder X-Ray Diffraction

When an X-ray is incident on a crystal, it diffracts in a pattern characteristic of the structure. In powder X-ray diffraction, the diffraction pattern is obtained from a powder of the material than an individual crystal. Powder X-Ray diffraction (XRD) also obtains a diffraction pattern for the bulk material of a crystalline solid than a single crystal. The purity of a sample can also be determined from its diffraction pattern and the composition of impurities present.

Powder X-ray diffraction (PXRD) on a Rigaku smartlab diffractometer with Cu K α radiation ($\lambda = 1.5406$) confirmed the crystalline structure. To record the pattern in the 2θ range of $5-90^\circ$, a scan speed of 8° min^{-1} was used.

4.3.3 Scanning Electron Microscope

SEM can produce very high-resolution images of a sample surface, revealing details less than one nm in size. The signals employed by a scanning electron microscope provide an image resulting from the interactions of the electron beam with atoms at varied depths within the sample. Various forms of signals are produced together with secondary electrons (SE), reflected or back-scattered electrons (BSE), characteristic X-

rays and light (cathode luminescence, CL), absorbed current (specimen current) and transmitted electrons. Secondary electron detectors are standard equipment in all SEM.

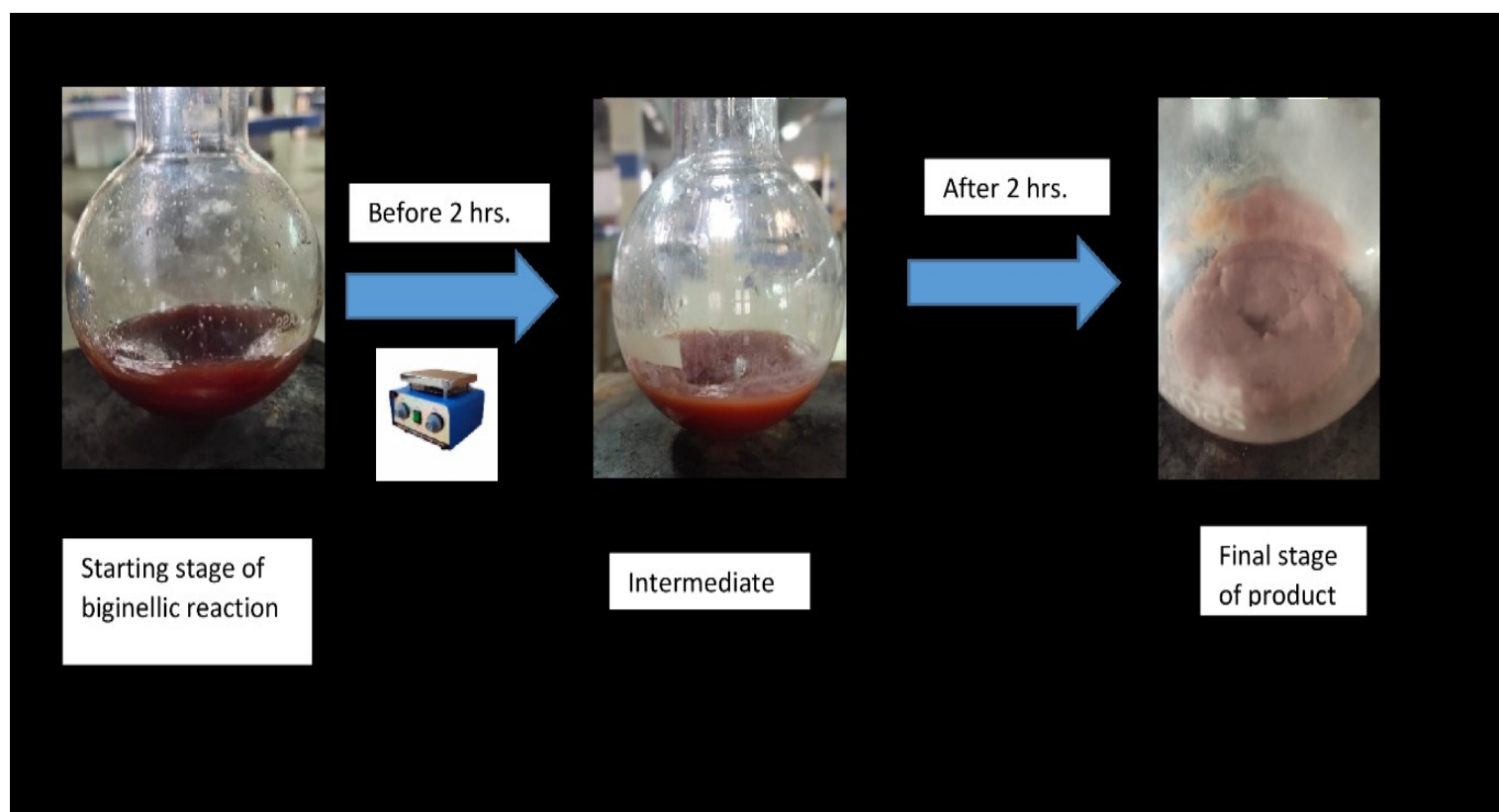
JSM-6700F scanning electron microscopy was used to assess the micro morphologies of the materials (SEM, JEOL Ltd., Japan). The samples' precise surface area was determined by nitrogen adsorption on a specific surface analyzer (ASAP 2420, Micrometrics, USA).

4.3.4 *Electron Dispersive X-ray Spectroscopy*

EDX (energy dispersive X-ray spectroscopy) is an analytical technique for determining the chemical or analytical properties of materials. EDX devices are typically used in conjunction with an electron microscope, such as a transmission electron microscope (TEM) or a scanning electron microscope (SEM). The EDX method is based on the emission of a specimen's unique X-rays. The investigated sample is bombarded with a beam of high-energy charged particles (electrons or protons). As an electron from a higher binding energy electron level falls into the core hole, it emits an X-ray with the energy of the difference between the binding energies of the electron levels. The peaks correlated to the elemental composition of the examined saline are shown in an EDX spectrum.

4.4 Biginelli reaction

A weighted amount of 5 mL Benzaldehyde, 10 mL of acetonitrile, 6 mL of ethyl acetoacetate, 3grams of urea and again 10 mL of acetonitrile is taken in round bottom flask. To this round bottom flask prepared amount of 0.5 gram Fe - BDC is added. This round bottom flask is placed in a magnetic stirrer for 2 hours. The end product was recrystallized with ethanol.



4.4 Schematic flowchart of preparation of Biginelli Reaction

CHAPTER 5

RESULTS AND DISCUSSION

Experiments were conducted to synthesize iron-BDC (Fe-BDC) as described in the section 3.5 by varying the amount iron and BDC ratio. The as-synthesized samples are named as Fe-BDC (1:1); Fe-BDC (2:1) and Fe-BDC(3:1) which represents the ratio of iron and bdc in 1:1; 2:1 and 3:1. The synthesized samples were characterized by FTIR, XRD and SEM. The prepared Fe-BDC was used as a catalyst for biginelli reaction for the preparation of dihydropyrimidones.

Characterization of Fe-BDC

5.1 FOURIER TRANSFORM-INFRARED SPECTROMETER (FTIR)

The Fe-BDC samples were scanned in the range of 4000cm^{-1} to 400cm^{-1} to explore the nature of functional groups present in the molecule and the results are presented in Fig. The peak at 1673 cm^{-1} , 1538 and 1525 cm^{-1} was due to C-O bond stretching of COOH group in BDC. The sharp peaks at 1409 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 734 cm^{-1} indicates the C-H bending vibration of benzene in BDC. The emergence of new peak in the finger print region at 677cm^{-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 677cm^{-1} increases as the ratio of iron increases as witnessed in Fe-BDC (3:1).

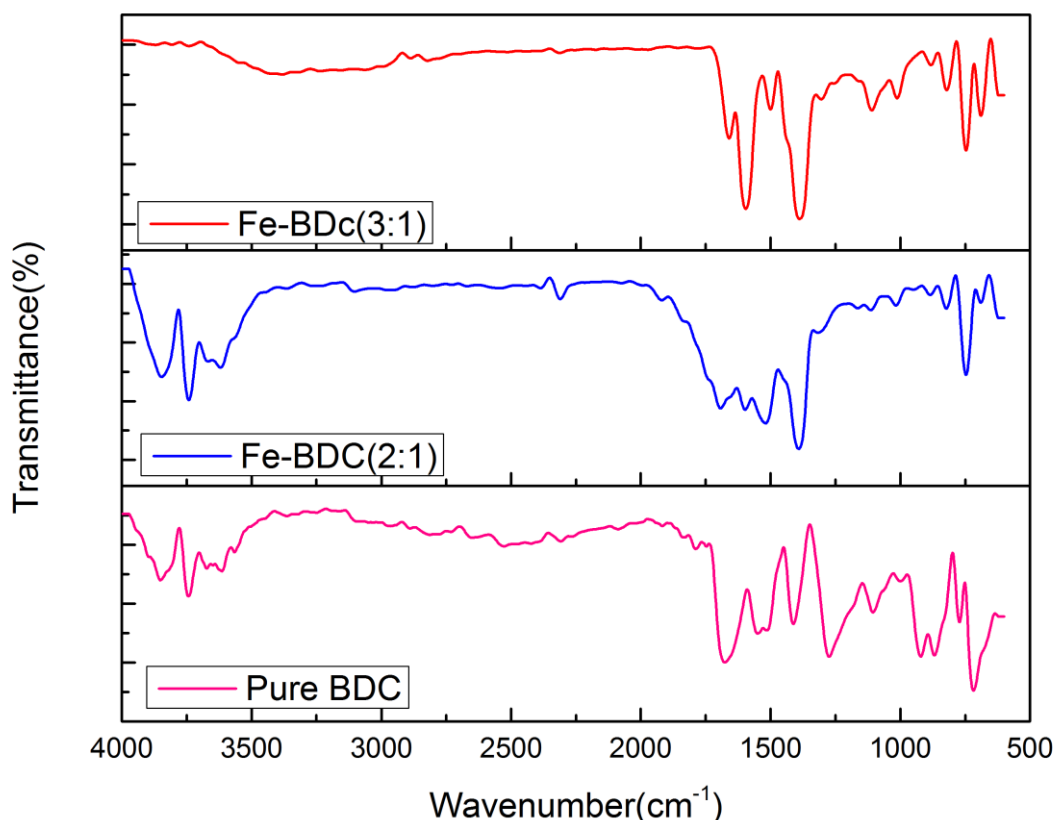


Fig 5.1 FTIR Spectrum for 3:1 of Fe-BDC, 2:1 of Fe-BDC and pure BDC

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°/sec. A sharp peak at 2θ values of 9.74°; 12.52°; 18.70°; 21.93° 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 (**M**ateriaux de l'**I**nstitut **L**avoisier). The observed peaks in Fe-BDC at lower than 10° (9.74°) indicates the crystalline nature of the sample. 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.

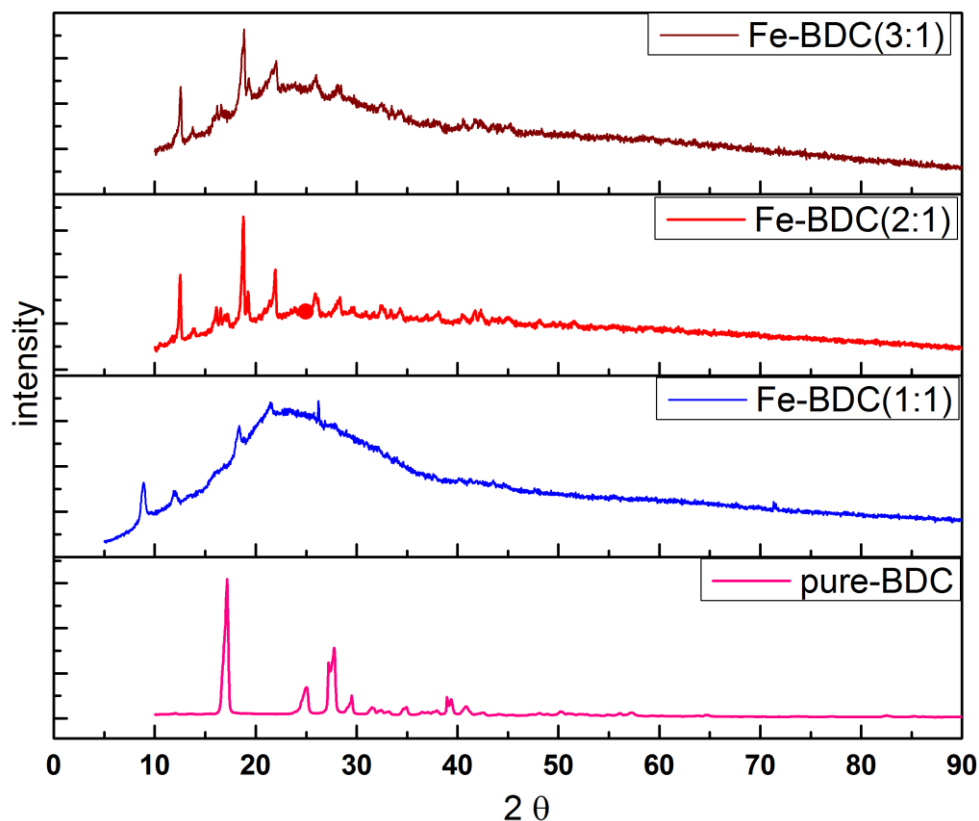


Fig 5.2 XRD Pattern for 1:1 Fe-BDC, 2:1 Fe-BDC, 3:1 Fe-BDC and pure BDC

The average crystallite size for synthesized Fe-BDC by Scherer was found to be 126nm, 278nm and 366nm indicating the crystalline nature of Fe-BDC and the crystalline size found from Williamson-Hall plot for Fe-BDC (2:1) is presented in Table

Sample	Crystallite size (nm)	Lattice strain	Crystallinity (nm)
Fe-BDC (2:1)	366	2×10^{-3}	608

The crystalline and strain induced due to line broadening (β) can be deduced by Williamson-Hall method. The line broadening in Fe-BDC structures is a combination of both size and strain and is given by,

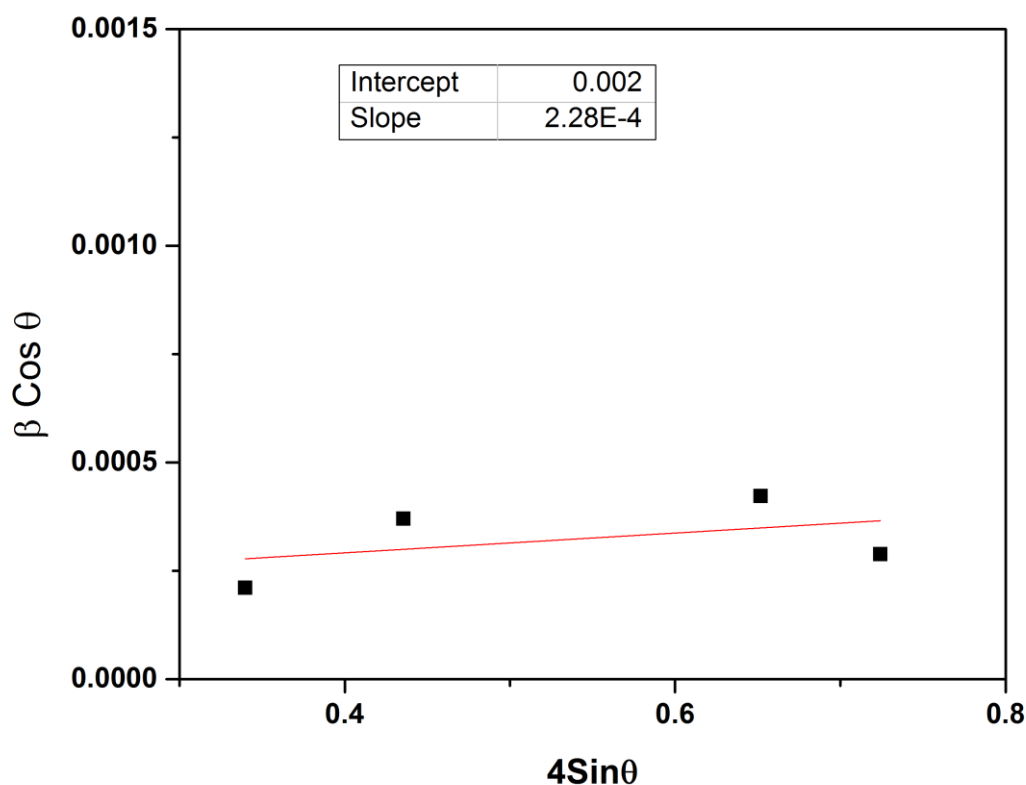
$$\beta \cos \theta = \beta_{\text{size}} + \beta_{\text{strain}}$$

On rearranging the equation can be represented as,

$$\beta \cos \theta = (k\lambda/D) + 4\epsilon \sin \theta.$$

where 'k' is the shape factor assumed to be 0.9 for crystalline materials; ' λ ' is the wavelength of the K_{α} -line = 1.5406 Å; 'D' is the size of the crystal and ' ϵ ' is the strain induced.

A plot of $\beta \cos \theta$ as y-axis and $4 \sin \theta$ as x-axis gives a straight line with slope gives the value of strain and intercept = $k\lambda/D$ can be used to determine the crystal size. The Williamson-Hall plot for Fe-BDC (2:1) is plotted and is depicted in the Fig. The linear graph is plotted by taking into considering the major XRD peaks of Fe-BDC (2:1). The intercept ' ϵ ', the intrinsic strain was found to be 2×10^{-3} . The positive value of the intrinsic strain indicates that the crystals experience tensile strain. The intercept value of 2.28×10^{-4} was used to determine the crystal size and is presented in the above table.



5.3 Williamson-Hall plot for Fe-BDC

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) and pure BDC 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 triangular rod shape with an average diameter of 700nm in the sample ratio of 2:1. Similar bulky rod like structures were obtained in the other samples of Fe-BDC. An histogram of average crystal size of Fe-BDC is shown in the Fig. As seen from the Fig, the frequency of crystal size is in the range of $0.7\mu\text{m}$ i.e 700nm.

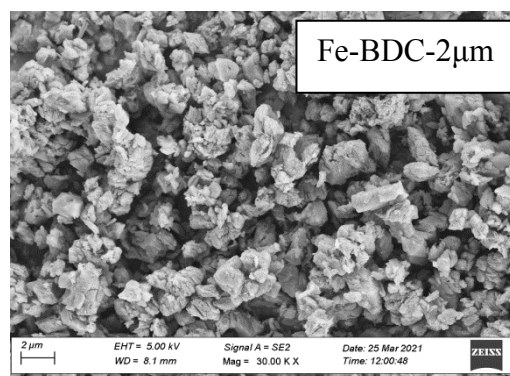
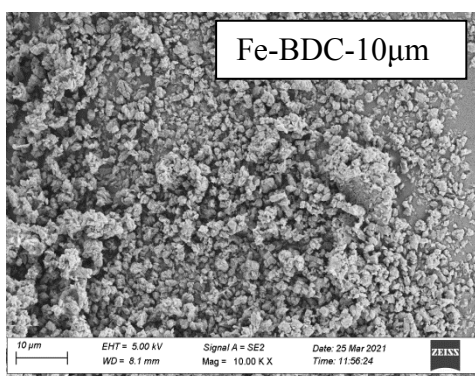
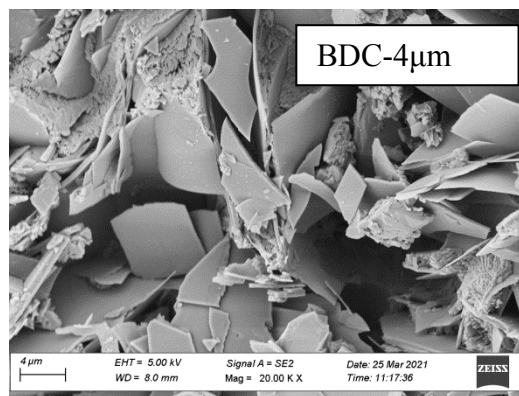
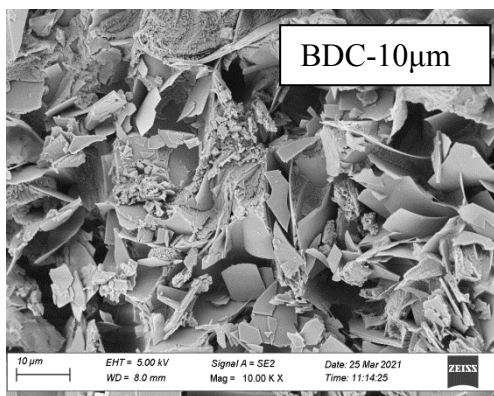
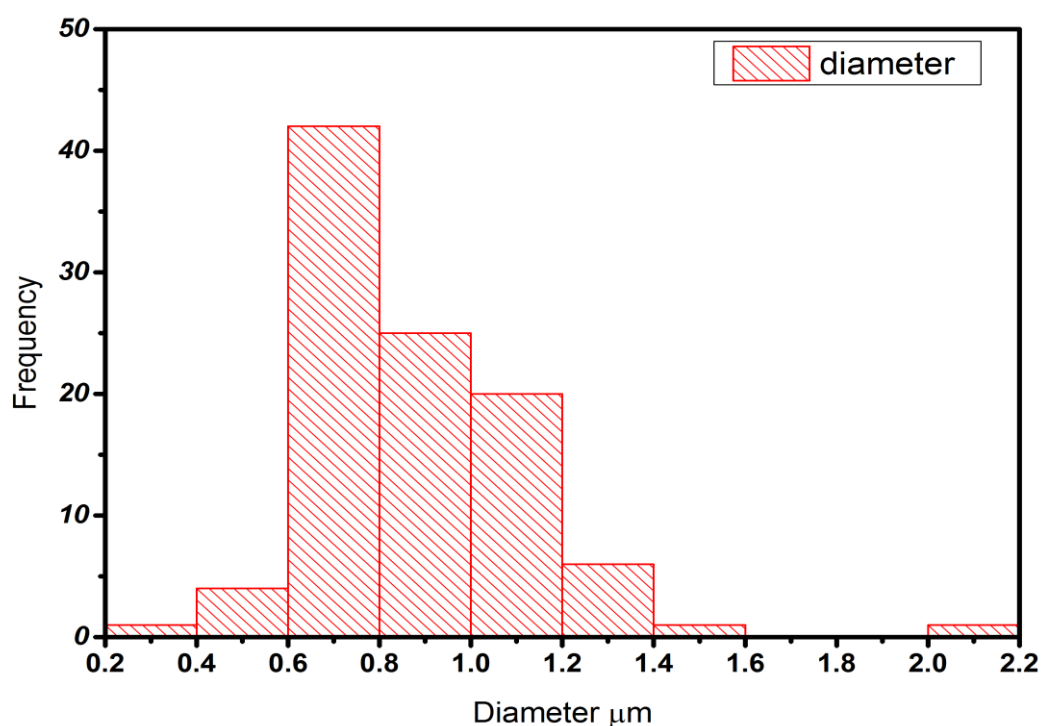


Fig 5.4 SEM images of Fe-BDC and BDC

The average crystal size for Fe-BDC (2:1) obtained from the SEM images coincides well with the crystal size calculated from XRD data using Williamson-Hall plot which is around 608nm.



5.5 Histogram for Fe-BDC

5.4 ENERGY DISPERSIVE X-RAY ANALYZER (EDX)

The elemental composition of the synthesized Fe-BDC is monitored by EDX and is presented in the fig. 5.4. The EDX of BDC confirms the absence of Fe while in Fe-BDC, the presence of iron is confirmed by the peak at 0.67Kev and at 6.78Kev. The atomic weight % of Fe was determined as 2.58% which corresponds to 4Fe atoms in the crystal structure of Fe-BDC.

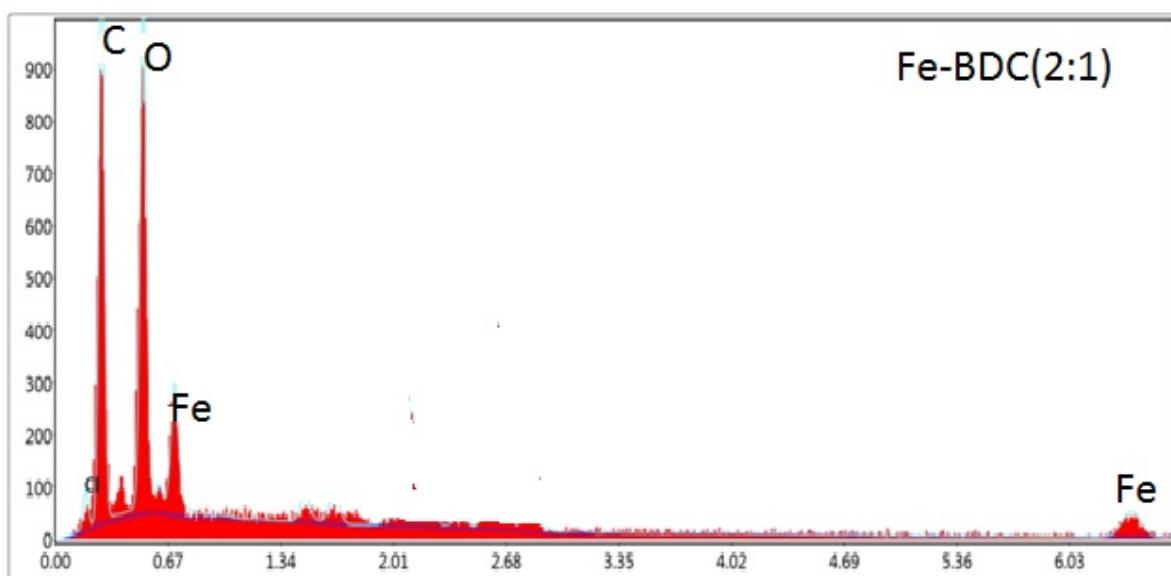
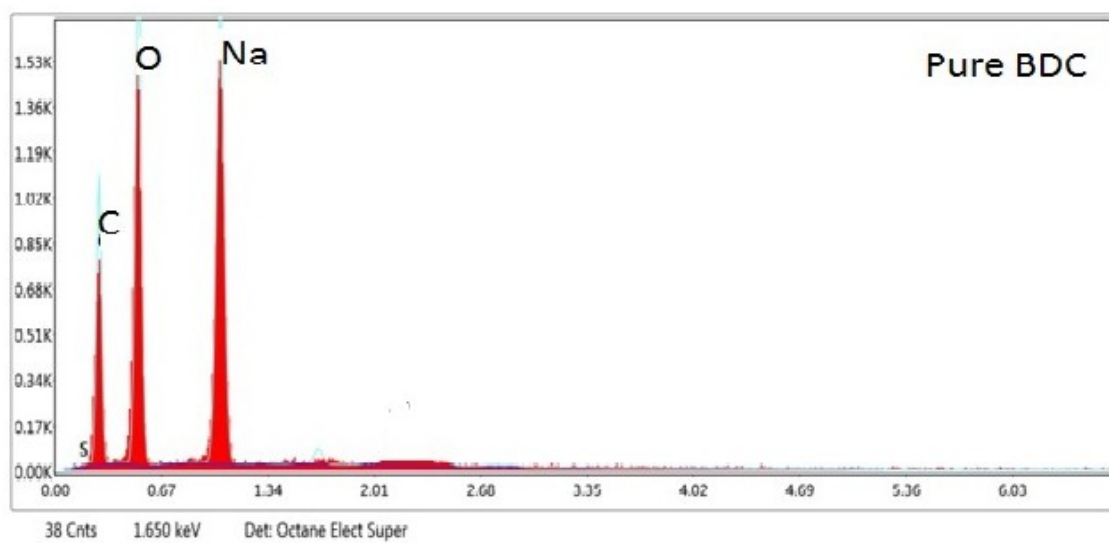


Fig 5.6 EDX graph for Fe-BDC and pure BDC

5.5 BIGINELLI REACTION

Biginelli reaction is a multiple-component Chemical Reaction that creates 3, 4-dihydropyrimidin-2(1H)-ones from Benzaldehyde, Ethyl acetoacetate, Urea, Acetonitrile and Prepared catalyst of Fe-BDC. The yield product of Biginelli Reaction is 3.5 grams.

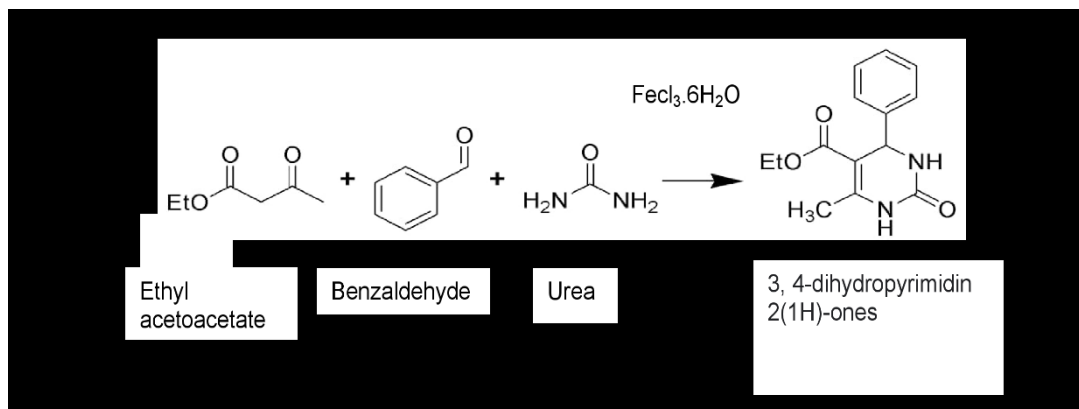


Fig 5.7 Reaction scheme of Biginelli reaction

CHAPTER 6

SUMMARY AND CONCLUSION

The Fe-BDC metal-organic framework structure was synthesized using the inorganic iron salt hydrate, terephthalic acid and N, N-dimethylformamide as the solvent. We have synthesized the metal organic framework Fe-BDC using the effective solvothermal method with optimized synthesis conditions.

- The FTIR shows the vibrational frequencies 1673 cm^{-1} , 1538 and 1525 cm^{-1} for C-O bond, 1409 cm^{-1} for $-\text{O}-\text{C}-\text{O}-$ groups, 3734 cm^{-1} and 3870 cm^{-1} for OH groups, 734 cm^{-1} for C-H bending vibration and 677 cm^{-1} for Fe-O bond.
- The X-ray diffraction of the sample shows the peaks 9.74° ; 12.52° ; 18.70° and 21.93° .
- SEM image displays Triangular rod shape structure of Fe-BDC and Flake structure for pure BDC.
- EDX shows peak at 0.67Kev and at 6.78Kev which confirms the presence of iron in Fe-BDC.
- It can be applied for the Biginelli reaction for the preparation of the dihydropyrimidinones.

REFERENCES

1. Ahsan, Md Ariful, Eva.D, Olivia F.D, Huiyao.W, Michael L. Curry, Ahmed A. El-Gendy, and Juan C. Noveron, "Fe nanoparticles encapsulated in MOF-derived carbon for the reduction of 4-nitrophenol and methyl orange in water," *Catalysis Communications* volume 130, 2019, page No.105753.
2. Ai, Lunhong, Caihong.Z, Lili.L, and Jing Jiang. "Iron terephthalate metal–organic framework: revealing the effective activation of hydrogen peroxide for the degradation of organic dye under visible light irradiation." *Applied Catalysis B: Environmental* vol. 148, 2014,Pg.no. 191-200.
3. Bai, Yi-Wen, Guimei Shi, Jun Gao, and Fa-Nian.S, "Synthesis, crystal structure of a iron-manganese bimetal MOF and its graphene composites with enhanced microwave absorption properties," *Journal of Physics and Chemistry of Solids* vol.148,2021, Pg.no. 109657.
4. Feng, Xiangwen, Huan Chen, and Fang.J, "In-situ ethylenediamine-assisted synthesis of a magnetic iron-based metal-organic framework MIL-53 (Fe) for visible light photocatalysis," *Journal of colloid and interface science* vol.494, 2017, Pg.no. 32-37.
5. Ghosh, Arnab, and Gopal. D, "Green synthesis of Sn (II)-BDC MOF: Preferential and efficient adsorption of anionic dyes", *Microporous and Mesoporous Materials* vol.297, 2020, Pg.No.110039.
6. Haldar, Dibyajyoti, Prangan.D, and Mihir Kumar Purkait, "MOFs for the treatment of arsenic, fluoride and iron contaminated drinking water: A review," *Chemosphere* vol.251, 2020, Pg.no. 126388.
7. Hayati, Bagher, Niyaz Mohammad M, Mina O, Atefeh P, Mohammad B, Sepideh Langari, Kumars. S.S, and Hasan M, "Synthesis of iron based-metal-organic framework nanocomposite and visible light pollutant degradation ability," *Materials Research Bulletin* vol.138,2021, Pg.No.111243.
8. Iqbal, Bushra, Andrea Laybourn, and Muhammad Z, "Size-controlled synthesis of spinel nickel ferrite nanorods by thermal decomposition of a bimetallic Fe/Ni-MOF," *Ceramics International*, 2021.

9. Jeyaseelan, Antonysamy, Mu Naushad, Tansir A, and Natrayasamy Viswanathan, "Design and development of amine functionalized iron based metal organic frameworks for selective fluoride removal from water environment," *Journal of Environmental Chemical Engineering* 9, vol. 1 .2021, Pg.No.104563.
10. Knyazeva, M.K., et al, "Synthesis and Structural-Energy Characteristics of Fe-BDC Metal-Organic Frameworks", *Protection of Metals and Physical Chemistry of Surfaces*, vol.54.6, 2018, Pg .No. 1004-1009.
11. Lee, Yu-Ri, Jun Kim, and Wha-Seung.A, "Synthesis of metal-organic frameworks: A mini review," *Korean Journal of Chemical Engineering* 30, vol no. 9, 2013, Pg.No.1667-1680.
12. Li, Guoqiang, Feifei L, Jianxin L, and Caimei F, "Fe-based MOFs for photocatalytic N₂ reduction: key role of transition metal iron in nitrogen activation," *Journal of Solid State Chemistry* vol.285, 2020, Pg.No. 121245.
13. Liu, Chao, Jing W, Jingjing W, and Chengzhong Y, "MOF-on-MOF hybrids: Synthesis and applications," *Coordination Chemistry Reviews* vol.432, 2021, Pg.No.213743.
14. Liu, Jianqiang, and Ying P, "Mixed-metal systems for the synthesis of MOFs." In *Metal-Organic Frameworks for Biomedical Applications*, pp. 45-68. Woodhead Publishing, 2020.
15. Liu, Yuanjun, Cheng Wang, Suxiao J, Mo L, Aihua Yuan, and Guoxing Z, "FeCo-based hybrid MOF derived active species for effective oxygen evolution," *Progress in Natural Science: Materials International* 30, vol no. 2, 2020, Pg.No. 185-191.
16. Nguyen, Duyen T.C, Hanh T.I.N, Trung Sy D, Van Thinh P, Lam Dai T, Van Thi T.H, Thuan Van Tran et al, "Metal-organic framework MIL-53 (Fe) as an adsorbent for ibuprofen drug removal from aqueous solutions: response surface modeling and optimization," *Journal of Chemistry* ,2019.
17. Omkaramurthy, B. M., G. Krishnamurthy, and N. L. Prasad, "Two new Zn (II) bdc Metal-Organic Frameworks based on benzene 1, 4-dicarboxylic acid: Synthesis, Crystal structures, Luminescent properties and Electrochemical studies," *Materials Today: Proceedings* vol.22, 2020, Pg.No.2179-2190.
18. Paiman, Syafikah Huda, Mukhlis A. Rahman, T.Uchikoshi, Norfadhilatuaadha A, Mohd Hafiz Dzarfan O, Juhana Jaafar, Khairul Hamimah A, and Ahmad

- Fauzi Ismail, "Functionalization effect of Fe-type MOF for methylene blue adsorption," *Journal of Saudi Chemical Society* 24, no. 11, 2020, Pg.No. 896-905.
19. Pan, Chengcheng, Zhicheng L, and Minghua H, "2D iron-doped nickel MOF nanosheets grown on nickel foam for highly efficient oxygen evolution reaction," *Applied Surface Science* vol.529, 2020, Pg.No. 147201.
 20. Riezzati, N., Y. K. Krisnandi, and A. Zulys, "Metal organic frameworks of lanthanum and iron using BDC linker as catalysts for glucose conversion into 5-hydroxymethylfurfural (5-HMF)," In *IOP Conference Series: Materials Science and Engineering*, vol. 902, no. 1, Pg.No.012044, IOP Publishing, 2020.
 21. Sharanyakanth, P. S., and R. Mahendran, "Synthesis of metal-organic frameworks (MOFs) and its application in food packaging: A critical review," *Trends in Food Science & Technology*, 2020.
 22. Soni, Sanju, P. K. Bajpai, Jyoti M, and Charu Arora, "Utilisation of cobalt doped Iron based MOF for enhanced removal and recovery of methylene blue dye from waste water," *Journal of Molecular Liquids* vol.314, 2020, Pg.No. 113642.
 23. Tran, Hoang V, Hue Thi Minh D, Luyen Thi Tran, Chau Van Tran, and Chinh Dang Huynh, "Metal-Organic Framework MIL-53 (Fe): Synthesis, Electrochemical Characterization, and Application in Development of a Novel and Sensitive Electrochemical Sensor for Detection of Cadmium Ions in Aqueous Solutions," *Advances in Polymer Technology* 2020 .
 24. Wan, Yongjie, J. W, Joe R. Zhao, Yan W, Ting Luo, Shou Yang, and Yaxin Liu, "Facile preparation of iron oxide doped Fe-MOFs-MW as robust peroxydisulfate catalyst for emerging pollutants degradation," *Chemosphere* vol.254, 2020, Pg.No.126798.
 25. Wei, Huijie, Yu Tian, Qian C, Diana E, Peng X, Hua-Xin Peng, and Faxiang Qin, "Microwave absorption performance of 2D Iron-Quinoid MOF," *Chemical Engineering Journal* vol.405, 2021, Pg.No. 126637.
 26. Wu, Qiangshun, Muhammad Saboor S, and Wenzheng Y, "Iron-nickel bimetallic metal-organic frameworks as bifunctional Fenton-like catalysts for enhanced adsorption and degradation of organic contaminants under visible light: Kinetics and mechanistic studies," *Journal of Hazardous Materials* vol.401, 2021, Pg.No.123261.

27. Xia, Tianliang, Yingchao Lin, Weizun Li, and Meiting J, "Photocatalytic degradation of organic pollutants by MOFs based materials: A review," Chinese Chemical Letters 2021.
28. Xiang, Huan, Ahmed Ameen, Patricia G, R. Siperstein, Stuart M. Holmes, and Xiaolei Fan, "Selective adsorption of ethane over ethylene on M (bdc)(ted) 0.5 (M= Co, Cu, Ni, Zn) metal-organic frameworks (MOFs)," Microporous and Mesoporous Materials vol.292,2020, Pg.No.109724.
29. Yang, Dongxu, Yuanfu Chen, Zhe Su, Xiaojuan Zhang, Wanli Zhang, and Katam S, "Organic carboxylate-based MOFs and derivatives for electrocatalytic water oxidation," Coordination Chemistry Reviews vol.428, 2021,Pg.No. 213619.
30. Yang, Shuliang, Vikram V. Karve, Anita J, I Kochetygov, Jordi E, Mehrdad A, O.Trukhina, Daniel T. Sun, Li Peng, and Wendy L. Queen, "Enhancing MOF performance through the introduction of polymer guests," Coordination Chemistry Reviews vol.427,2021, Pg.No. 213525.
31. Yaqoob, Lubna, Tayyaba N, Naseem I, H. Nasir, Neelam Z, and Khalid T, "Electrochemical synergies of Fe–Ni bimetallic MOF CNTs catalyst for OER in water splitting," Journal of Alloys and Compounds vol.850, 2021, Pg.No. 156583.
32. Zhu, Guocheng, Yongning B, Andrew S. Hursthouse, Shengnan X, Nana Xiong, and Peng W, "The role of magnetic MOFs nanoparticles in enhanced iron coagulation of aquatic dissolved organic matter," Chemosphere vol.247, 2020, Pg.No.125921.