

SYNTHESIS AND CHARACTERIZATION OF IRON MOF FROM WASTE MATERIAL

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

by

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**DEPARTMENT OF CHEMISTRY
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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 **V. Meena (39910011)** who have done the project entitled **“SYNTHESIS AND CHARACTERIZATION OF IRON MOF FROM WASTE MATERIAL”** under our supervision from April 2021.

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Submitted for Viva voce Examination held on _____

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DECLARATION

I **V.Meena** student of **SATHYABAMA INSTITUTE OF SCIENCE AND TECHNOLOGY** hereby declare that the Project Report entitled “synthesis of iron MOF from waste material for organic reaction” 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** submitted in partial fulfillment of the requirements for the award of **Master of Science degree in CHEMISTRY.**

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CANDIDATE**

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ABSTRACT

Metal-organic frameworks (MOFs) have been studied for a variety of new applications, and the creation of cost-effective processes is essential for future practices. Waste PET bottles were used as an acid linker to make value-added metal-organic frameworks containing iron benzene dicarboxylic acid, and the texture properties and hydrogen storage ability were comparable to those obtained from commercial chemicals. This method provides a cost-effective way to eliminate excess PET while still producing value-added products. The ligand of terephthalic acid extracted from waste Polyethylene Terephthalate (PET) bottles was used to design and synthesis a metal organic framework.

KEYWORDS: Metal organic frameworks ,iron ,BDC ,PET ,waste material

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LIST OF ABBREVIATIONS

ABBREVIATIONS

EXPANSIONS

PET	polyethylene terephthalate
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 normally synthesised using analytically pure chemical feed stocks because impurities can have a substantial effect on the results, making scientist understanding and control of the synthesis more difficult. Some widely used MOFs have already had their synthesis conditions extensively investigated. As a result, lower-cost, lower-quality materials may be used as starting materials. MOFs are porous crystalline materials with one-, two-, or three-dimensional networks formed by coordination bonding between metal ions/clusters and multidentate organic linkers. For energy storage, CO₂ adsorption, alkane/alkene separation, and catalysis, they're becoming increasingly common.

This study gives a brief overview of the currently available MOF synthesis methods in order to introduce newcomers to the field of chemical engineering to the rapidly evolving MOF science. Starting with conventional solvothermal/hydrothermal synthesis, microwave-assisted, sonochemical, electrochemical, mechanochemical, ionothermal, dry gel conversion, and microfluidic synthesis methods will be addressed. Despite their various benefits, the implementation of many MOFs is ultimately limited by their stability in harsh environments. The most recent developments in the field of stable MOFs are discussed, including fundamental mechanisms of MOF stability, stable MOF architecture design and synthesis, and their most recent applications.

Typical organic ligands of 1,4-benzenedicarboxylic acid (and its functionalized forms) and 1,3,5-benzenetricarboxylic acid in combination with metal nodes of Zn²⁺, Cu²⁺, Cr³⁺, Al³⁺, Fe³⁺, and Zr⁴⁺ will be used as examples. It contains a lot of iron. Metal-organic frameworks (MOFs) have gotten a lot of attention in the fields of gas separation, catalytic conversion, and drug delivery due to their high surface area and activity, as well as the non toxicity of iron.

The fundamentals of MOF stability divide stable MOFs into two groups: high-valency metal-carboxylate frameworks and low-valency metal-azolate

frameworks. This section introduces some representative stable MOFs, defines their structures, and briefly discusses their properties. The extended applications of stable MOFs in Lewis/Bronsted acid catalysis, redox catalysis, photocatalysis, electrocatalysis, gas storage, and sensing are highlighted. Overall, this research is expected to guide the development of strong MOFs by revealing existing structures, possibly leading to the discovery and development of more advanced functional materials.. PET contains over 85% terephthalic acid in the ester form, which can be hydrolyzed to produce carboxylic acid or carboxylate. Post-consumer PET is a promising reactant for MOF synthesis because it is a relatively pure waste stream.

PET, or polyethylene terephthalate, is a popular plastic that has wreaked havoc on the environment. Since waste PET takes up a ton of room and is difficult to degrade, its indiscriminate disposal causes significant environmental issues. There are many ways to recycle PET terephthalic acid, but only a few are safe and cost-effective.

PET produces terephthalic acid, which can be hydrolyzed to make terephthalic acid, which can then be used to make MOFs. Because of its rigid structure, complex architectures, and different coordination modes under various conditions, terephthalic acid (H₂BDC) is a desirable ligand. Metal organic frameworks (MOFs), also known as crystalline porous architectures, are fascinating materials made up of metal ions and linkers that can be applied to a wide range of applications. Metal–Organic Frameworks (MOFs) are a type of hybrid microporous material made up of metal ions or clusters linked together in a crumb-like structure.

MOFs are normally synthesised using analytically pure chemical feed stocks because impurities can have a substantial effect on the results, making scientist understanding and control of the synthesis more difficult. Many of the most widely used MOFs have already had their synthesis conditions extensively investigated. As a result, lower-cost, lower-quality materials can be investigated as starting compounds. Metal organic frameworks (MOFs) are porous crystalline materials that consist of one-, two-, or three-dimensional networks created by coordination bonding between metal ions/clusters and multidentate organic linkers.

They're gaining popularity as a material for energy storage, CO₂ adsorption, alkane/alkene separation, and catalysis. This study offers a brief overview of the currently available MOF synthesis methods in order to familiarise newcomers to the field of chemical engineering with the rapidly changing MOF research landscape. Chemical processing, thermal treatment methods such as incineration, pyrolysis, and biodegradation are some of the alternative disposal procedures that have been proposed in an attempt to minimise emissions.

PET production doubles every ten years, reaching 300 million ton in 2017, but only 7% of it is recycled. Traditional PET waste management methods are ineffective for closing the loop of processing and recycling. The method included primary recycling, secondary recycling (mechanical, physical reprocessing), and tertiary recycling. Chemical recycling, in particular, is the most realistic approach for repurposing PET waste since it involves depolymerizing PET back into its constituent units. PET can be depolymerized by hydrolysis at high temperatures and pressures, or by microwave heating in some situations. In the presence of acid, alkali, or ethylene glycol, hydrolysis has been reported. However, in order to achieve a viable result, the efficiency of depolymerization conversion must be enhanced further. PET depolymerization requires terephthalic acid (BDC), which has been found in thousands of crystalline porous structures in recent decades. Unlike many depolymerization methods that have been used to convert PET into its monomers, such as glycolysis and methanolysis, hydrolysis is the only direct way to obtain BDC.

Traditional thermal heating or microwave irradiation may be used to conduct hydrolysis in the presence of acids or bases. Since phase-transfer catalysts can be used at atmospheric pressure and low reaction temperatures, it is more convenient and cost-effective than methanolysis. The most significant disadvantage of acid hydrolysis for PET hydrolysis is the acid's high corrosiveness, particularly when concentrated sulfuric acid is used.

During neutral hydrolysis, mechanical impurities found in new PET are left in the recycled BDC, resulting in a lower purity product than alkaline hydrolysis. A divalent or trivalent ion, such as Zn²⁺, Cu²⁺, Ni²⁺, Co²⁺, Mn²⁺, Al³⁺, Cr³⁺, Fe³⁺,

or Mo^{3+} , as well as some lanthanide metals, is the source of a metal cation. Certain inorganic cations or clusters act as coordination sites in MOFs.

The thermal stability of MOFs is determined by the strength of the bonds between the metal cation and the ligand. MOFs formed by divalent ions (Cu^{2+} , Zn^{2+} , Ni^{2+} , Co^{2+} , d^{2+} , and others) have lower metal–ligand bond strength than MOFs formed by higher-charged cations such as Cr^{3+} , Fe^{3+} , Al^{3+} , Mo^{3+} , Ln^{3+} , Ti^{4+} , and others.

As a result, transition metal cations like Fe(III) can improve MOF bond strength during assembly. According to the results, H_2 can be adsorbed on the Fe region of the MOF–Fe cluster. The presence of Fe^{3+} ions in the MOF structure also greatly increases the hydrogen–MOF interaction, according to the researchers. In the MOF–Fe system, the H_2 interaction is twice as strong as in the MOF–Cu and MOF–Zn systems. According to this study, the metal site of MOFs can be used to increase the interaction energy of H_2 in the MOF structure.

CHAPTER 2

LITERATURE SURVEY

2.1 Oleg Semyonov et.al., (2020) have investigated on two emerging problems in recycling polyethylene terephthalate waste (PET) and removing toxic insecticides from water. PET bottles were used as a source and support for the growth of UiO-66 frameworks, and the technology was then used to remove imidacloprid from water. A variety of microscopic and spectroscopic techniques were used to examine the prepared material, confirming the high loading and uniform distribution of UiO-66 across the PET support. the sorbent (PET@UiO-66) provided significant technical benefits, including: sustainable and low-cost preparation; high adsorption capacity and rate; stability and recyclability; 100 times increased permeability compared to UiO-66 powder; and applicability in fixed-bed columns.

2.2 Feng Zhang et.al.,(2019) studied on a lanthanide metal organic framework based on the ligand of terephthalic acid derived from waste polyethylene terephthalate (PET) bottles was designed and synthesized. The Tb-BDC displays a high selectivity and sensitivity towards picric acid (TNP). This is the first time that waste PET materials have been used as the starting precursor of terephthalic acid (BDC) for the fabrication of lanthanide MOF (metal organic framework), which is applied in sensing TNP.

2.3 Xoliswa Dyosiba, et.al., (2016) analysis on Metal-organic frameworks (MOFs) for wide range of new applications, and developing cost-effective processes is critical for future practises. In this analysis, waste PET bottles were used as an acid linker in the preparation of value-added metal-organic frameworks UiO-66 (Zr), with texture and hydrogen storage properties comparable to those obtained from new plastic bottles.

2.4 Ivo Stassen, et.al., (2016) studied Metal–Organic Frameworks (MOFs) are a class of microporous materials built up from metal ions or clusters linked together with organic ligands into a crystalline structure. MOFs are typically synthesized using analytically pure chemical feed stocks as impurities can have a large influence on

the results, making scientific understanding and control over the synthesis more complex. For some widely used MOFs, the synthesis conditions have already been well explored. This makes it possible to investigate cheaper, lower-grade materials as starting compounds. One of these is post-consumer poly(ethylene terephthalate) (PET) which is already an industrially important waste stream.

2.5 Feiyue Jia et.al.,(2018) researched on Metal–organic frameworks (MOFs) based on Fe have recently gotten a lot of attention and are being widely used. It is currently unclear if they can be used to break down tetracycline, one of the most commonly used antibiotics. This work therefore aims to provide such support by comparing the performance of three Fe-based MOFs (namely, Fe-MIL-101, Fe-MIL-100, and Fe-MIL-53) in removing tetracycline. The adsorption and photocatalytic degradation effect improved with increasing time, the optimum dose of Fe-MIL-101 was 0.5 g/L, and the removal efficiency decreased as the initial tetracycline concentrations increased. Furthermore, trapping experiments and ESR tests revealed that the key active species in the photocatalytic degradation of tetracycline were O_2 , OH and h^+ . It may be used as a possible catalyst for the degradation of tetracycline and other antibiotics due to its high removal efficiency and ease of synthesis.

2.6 Antonysamy Jeyaseelana et.al., (2020) have examined, 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 metal organic frameworks (MOFs) for selective fluoridation.

2.7 El-Sayed M. El-Sayed and Daqiang Yuan , 2020 have investigated Greening the synthetic route for metal-organic frameworks (MOFs) has attracted much interest as a decisive step for practical industrial applications. For a more feasible process, employing waste plastic materials as a potential linker source for MOF synthesis is highly encouraging, combining a sustainable and environmentally friendly approach for scale-up production. The process is more economic when the whole MOF synthesis can be achieved based on waste metal and linker resources in the presence of green solvents derived from waste materials as well. Herein, present a valorization waste approach for the preparation of MOFs based

on different recycled polymer waste materials, MOFs based on waste metal sources, and MOFs based on the coupling of waste sources for both organic ligand and metal center. This approach not only recycles discarded products but also produces high value-added wealth materials for different applications. from plastics as a linker building unit in the MOF synthesis, which can be a potential route to the pilot-scale production.

2.8 Chih-Chiung Pan et.al., (2016) analysed series of five isostructural pillared-paddlewheel MOFs, $[M_2(BDC)_2(DABCO)]$ (1-5), (where M = Fe(II) (1), Co(II) (2), Ni(II) (3), Cu(II) (4) and Zn(II) (5); BDC = benzene-1,4-dicarboxylate; and DABCO = 1,4-diazabicyclo[2.2.2]octane) have been synthesized by using waste polyethylene terephthalate (PET) material as a direct BDC source. The optimal reaction condition has been achieved for all the MOFs with 100% depolymerization of waste PET material in the reaction.

2.9 Yong Liu et.al., (2018) have prepared Fe@Cu-BDC catalysts by adsorbing various contents of Fe ions on the surface and into the channels of Cu-BDC support through a in situ method under ultrasonication. The reaction, the catalyst could be easily separated from the reaction mixture by centrifugation and reused for five times without significant decrease in activity.

2.10 P.K. Bajpai et.al., (2020) examined Cobalt doping, the adsorption efficiency of Fe -Benzene dicarboxylic acid metal organic system for the removal of methylene blue dye from waste waters was improved in this research. Effect of various parameters such as pH, amount of adsorbent, dye concentration, temperature, and contact time on dye removal has been studied. It has been observed that extent of adsorption increases in acidic medium and dye removal decreases on increasing pH of dye solution.

2.11 Guoliang Zhang et.al., (2016) have investigated on manganese, cobalt, and nickel which used for partially isomorphism iron in the Fe(BDC)(DMF,F) metal organic system for the first time. During the solvothermal crystallisation process, different amounts of Mn, Co, and Ni were incorporated into the Fe-based structure. The stability and reusability of these catalysts under mild conditions were also

demonstrated in this study. This work illustrates the potential of bimetallic MOF structures in developing active heterogeneous catalysts for toxic compounds degradation process.

2.12 Xoliswa Dyosiba et.al., (2016) have examined economic value to produce high-value PET-based MOF materials by the veritable elimination of waste PET, and provide sufficient MOF materials for hydrogen storage applications. Consequently, this work demonstrates the use of waste PET bottles as direct source of BDC acid linker during the synthesis of Cr-MOF. The PET-derived Cr-MOF materials showed even better textural and hydrogen storage properties than that from commercial BDC.

2.13 Arunachalam Ramanani., (2013) have analysed the purity requirement of terephthalic acid (TPA) for synthesis of metal organic frameworks (MOFs) is very stringent. In this paper, a simple and economically viable microwave-assisted process to convert poly(ethylene terephthalate) (PET) waste into high purity TPA which in turn has been used for the synthesis of two archetypal MOFs. The efficiency of this process was compared with conventional heating route, and characteristic parameters like conversion and TPA purity were quantified. The time required for alkalotic depolymerization could be significantly reduced (5 min) by using a microwave as an energy source, as compared to the conventional thermal process, which requires a minimum of 3 h to reach the same level.

2.14 Shadpour Mallakpour , Vajiheh Behranvand , 2016 have investigated the possibility of utilizing recycled PET bottle waste as matrix of novel composites. The effect of various MWCNT-ZnO quantum dot (QD) loadings (1, 2 and 4 by weight) on the morphology, thermal, electrical conductivity properties and water treatment of PET was studied. Results showed that the incorporation of MWCNT-ZnO QDs into the PET matrix causes that the pure polymer undergoes transition from electrically insulated to conductive at room temperature.

2.15 Ana C. et.al., (2020) Fernandes have worked to describes the efficient and selective reductive depolymerization of PET, PBT, PCL, PLA and PDO plastic waste into value-added compounds and fuels, including 1,6-hexanediol, xylene and propane, catalyzed by the eco-friendly, cheap and air-stable dioxomolybdenum complex $\text{MoO}_2\text{Cl}_2(\text{H}_2\text{O})_2$ using silanes as reducing agents. The catalyst $\text{MoO}_2\text{Cl}_2(\text{H}_2\text{O})_2$ can be used in at least 8 catalytic cycles in the reductive depolymerization of PCL with excellent activity and the catalytic system PMHS/ $\text{MoO}_2\text{Cl}_2(\text{H}_2\text{O})_2$ was successfully applied in the production of propane from the reductive depolymerization of PLA on gram scale. Moreover, this method was also efficiently applied in the selective reduction of a PCL, PLA and PET mixture.

2.16 Kevin Van Geemet.al., (2016) have studied a comprehensive description of the current pathways for recycling of polymers, via both mechanical and chemical recycling. The principles of these recycling pathways are framed against current-day industrial reality, by discussing predominant industrial technologies, design strategies and recycling examples of specific waste streams. It also includes some industrial examples such as polyethylene terephthalate (PET) recycling, and SPW from post-consumer packaging, end-of-life vehicles or electronic devices.. A separate section is dedicated to the relationship between design and recycling, emphasizing the role of concepts such as Design from Recycling. The section on chemical recycling collects a state of-the-art on techniques such as chemolysis, pyrolysis, fluid catalytic cracking, hydrogen techniques and gasification.

2.17 Jonggeon Jegal et.al.,(2020) reprocessing of waste plastic has been extensively studied. Herein, a facile and efficient method for solving the plastic recycling crisis was developed using microwave assisted hydrolysis of poly(ethylene terephthalate) (PET) into terephthalic acid (TPA).The reaction kinetics and activation energy of the PET hydrolysis reaction in the presence of the developed catalyst were studied and compared with catalyst-free conditions. Based on this investigation, the correlation between Brønsted and Lewis acidic sites in ZSM-5-based catalysts and PET depolymerization yield was identified.

2.18 Joseph T. Hupp et.al., 2009 have discussed about (a) opportunistic catalysis with metal nodes, (b) designed catalysis with framework nodes, (c) catalysis by homogeneous catalysts incorporated as framework struts, (d) catalysis by MOF-encapsulated molecular species, (e) catalysis by metal-free organic struts or cavity modifiers, and (f) catalysis by MOF-encapsulated clusters.

2.19 Marina knynazeva et.al., (2018) metal–organic framework, Fe–BDC, was synthesized by solvothermal method from iron salt and terephthalic acid using N,N-dimethylformamide as the solvent.

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 ferric chloride and from waste material like (scrap iron and PETs).

3.2 OBJECTIVES :

The environmental challenges were addressed, and a low-cost, long-term method for creating hybrid content from PET bottles and surface-grown metal-organic frameworks was created.

Main objective of the study

- Recycle of plastic bottles.
- 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 analyser (EDX).

CHAPTER 4

MATERIALS AND METHODS

4.1 MATERIAL AND CHEMICAL REQUIRED

All chemicals and solvent were used from commercial suppliers without further purification. Distilled water was used throughout the experiment.

4.2 METHODS

4.2.1 COLLECTION OF PLASTIC BOTTLES

The PET bottles collected were washed with water. The bottles were dried in direct sunlight for 20 days. Then PET bottles were cut into small pieces and collected in a box.

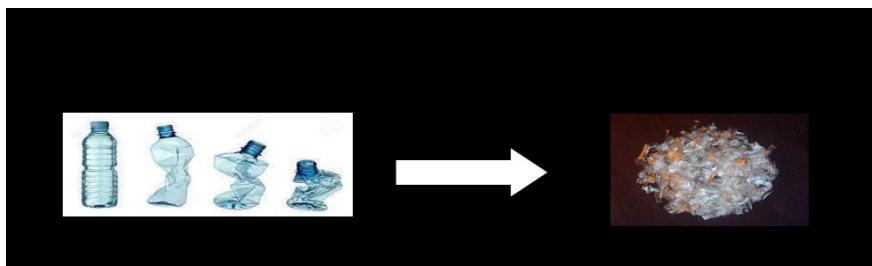


FIG 4.1 Collection of PET bottles and Grinding

4.2.2 PREPARATION OF BENZENE DICARBOXYLIC ACID

A 250 mL beaker was filled with a weighted 6.5 gram of and 100 mL of sodium hydroxide, which was stirred for 1 hour at 180 degrees celsius in a magnetic stirrer. The mixture is then added 100 mL of distilled water and held at 180°C for another hour. Finally, 100 mL sodium hydroxide is added to the beaker and stirred in a magnetic stirrer for 1 hour at the same temperature. After obtaining the white, curdy precipitate, it is cooled for half an hour before adding 5 mL sulphuric acid. Benzene dicarboxylic acid is the end product. In a magnetic stirrer, benzene dicarboxylic acid was prepared in different normalities of sodium hydroxide at the

same temperature. Throughout the entire process of making benzene dicarboxylic acid, distilled water was used.

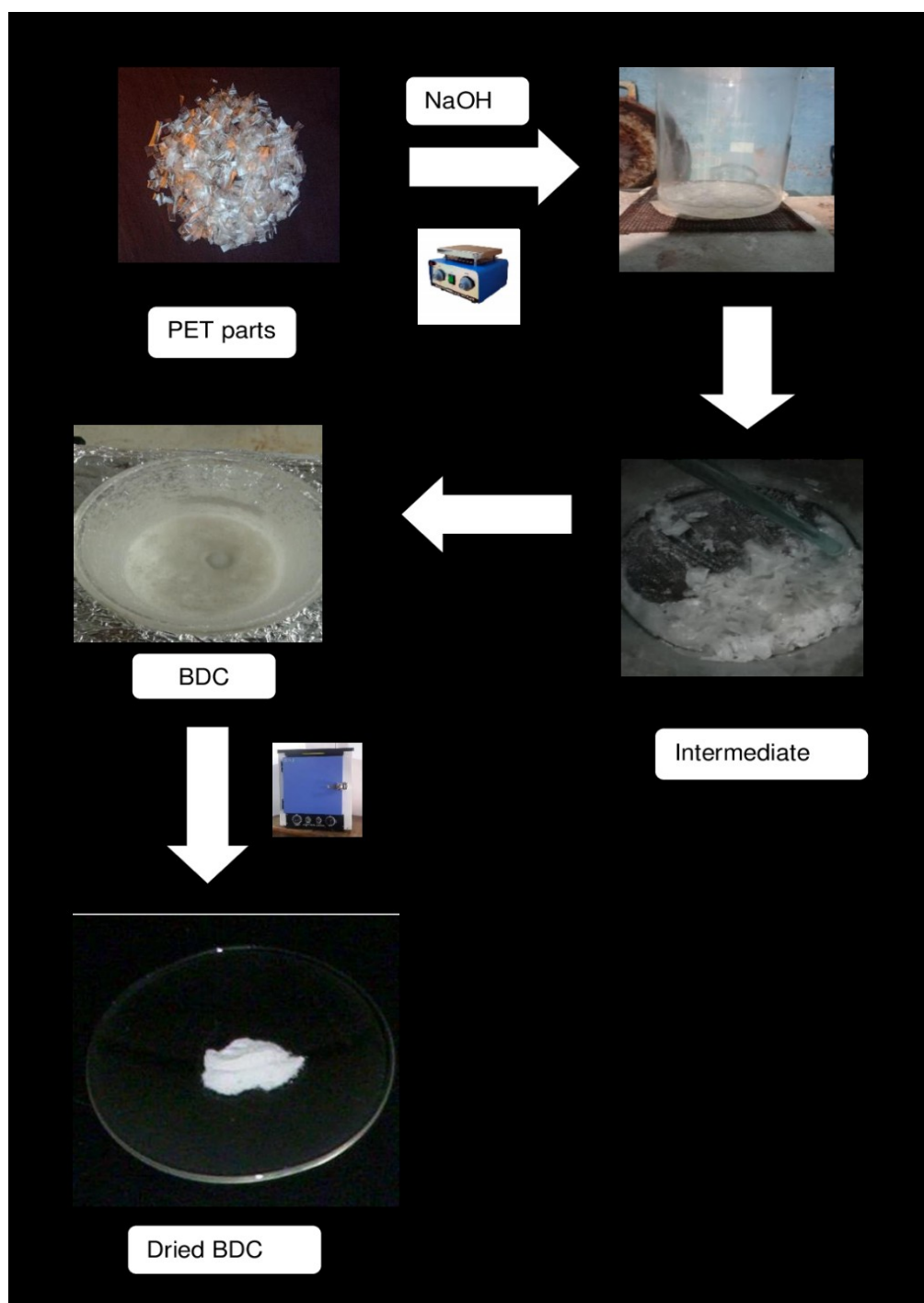


Fig.4.1 Preparation of BDC

4.2.3 PREPARATION OF IRON - BENZENE DICARBOXYLIC ACID

(Fe -BDC) FROM SCRAP IRON

0.2 grams BDC is weighed and placed in a 250 mL beaker. 15 mL N,N dimethylformamide is added to this and stirred for 5 minutes with a magnetic stirrer. After that, a weighted volume of 0.4 grams of scrap iron was applied to the solution, along with 5 mL of sulphuric acid, and the mixture was set aside for one hour. This solution is placed in a magnetic stirrer for 6 hours after one hour. The dull orange solid powder was centrifuged and purified with dimethylformamide ethanol before being dried for two hours at 180 degrees Celsius.

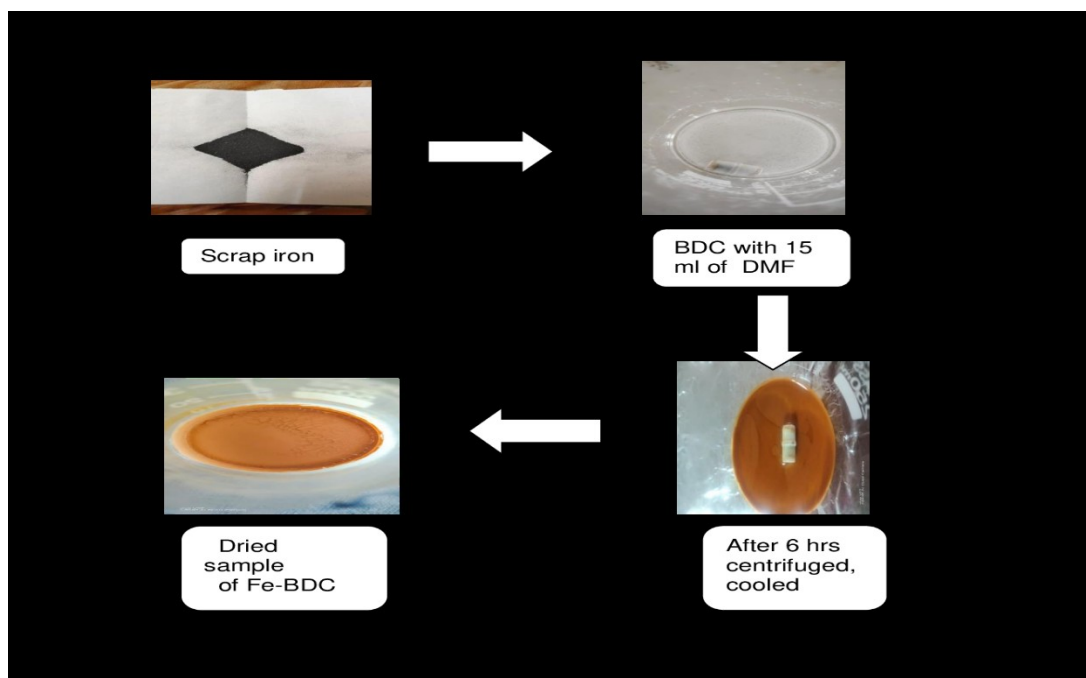


Fig 4.2 Preparation of Fe-BDC from Scrap iron

4.3 CHARACTERIZATION TECHNIQUES

4.3.1 (FTIR) Fourier Transform - Infrared Spectrometer

The infrared spectrum of absorption, emission, and photoconductivity of solids, liquids, and gases is obtained using the Fourier transform infrared spectroscopy (FTIR) technique. Between 4000 and 400 cm^{-1} , the FTIR spectrum is registered. The mathematical method (Fourier transform) is used in Fourier transform infrared

spectroscopy (FTIR) to convert the raw data (interferogram) into the real spectrum. FTIR can be used to analyse a broad range of chemical compounds, especially polymers and organic compounds.



Fig 4.3 FTIR Instrument

4.3.2 (XRD) X - ray Powder Diffraction

X-ray diffraction is a powerful nondestructive technique for characterizing crystalline materials. It provides information on structures, phases, preferred crystal orientations (texture), and other structural parameters, such as average grain size, crystallinity, strain, and crystal defects. XRD peaks are produced by constructive interference of a monochromatic beam of X-rays scattered at specific angles from each set of lattice planes in a sample. The peak intensities are determined by the atomic positions within the lattice planes. The XRD analysis is done with an X-ray source of Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). Consequently, the XRD pattern is the fingerprint of periodic atomic arrangements in a given material.

X-rays are scattered by atoms when they strike the surface of a crystal and follows Bragg's law, is given by

$$n \lambda = 2d \sin \theta$$

where, n is an integer. λ is the wavelength of x-rays.
 d is the spacing between the planes.

θ is an angle between the incident ray and the scattering planes

The technique of X-ray line broadening used to give information on the particle sizes in a catalyst sample. This method uses the Debye Scherrer equation:

$$B(2\theta) = K \lambda / L \cos \theta$$

Where,

B is the peak width

2θ is the diffraction angle,

λ is the X-ray wavelength

L is the crystallite size

K is a constant as a function of the crystallite shape.



Fig 4.3 XRD Instrument

4.3.3 Scanning Electron Microscope (SEM)

The scanning electron microscope (SEM) is a type of electron microscope that uses a centred beam of electrons to scan the surface of a sample to create images. As electrons communicate with atoms in a sample, they produce a variety

of signals that reveal details about the sample's surface topography and composition. A raster scan pattern is used to scan the electron beam, and the location of the beam is combined with the strength of the detected signal to create an image. Secondary electrons released by atoms excited by the electron beam are detected using a secondary electron detector in the most common SEM mode.



Fig 4.3 SEM Instrument

4.3.4 Energy Dispersive X-ray(EDX)

Energy Dispersive X-Ray Analysis with Scanning Electron Microscopy (SEM) (EDX) By rastering a focused electron beam across the surface and detecting secondary or backscattered electron signals, SEM provides detailed high resolution images of the sample.



Fig 4.3 EDX Instrument

CHAPTER 5

RESULTS AND DISCUSSION

Experiments were conducted to synthesize BDC and Fe-BDC from waste materials using PET bottles and iron granules as described in the section 3.5. The BDC is prepared from PET bottles by varying the amount of hydrolysing agent, NaOH from 2N to 6N. The as-synthesized samples are named as BDC 2; BDC4; BDC 6 which represents the BDC prepared using 2N, 4N and 6N respectively along with Fe-BDC. The synthesized samples were characterized by FTIR, XRD and SEM. Characterization of BDC and iron-BDC.

5.1 Fourier Transform Infrared (FT-IR)

The 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 5.1. The peak at 1673 cm^{-1} , 1530 cm^{-1} , 1542 cm^{-1} was due to C-O bond stretching of COOH group in BDC. The sharp peaks at 1378 cm^{-1} represent 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. A characteristic peak at 1121cm^{-1} represents the bending O-H peaks in BDC. The low intensity sharp peak in the fingerprint region at 734 cm^{-1} indicates the C-H bending vibration of benzene in BDC. The emergence of a new peak in the fingerprint 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.

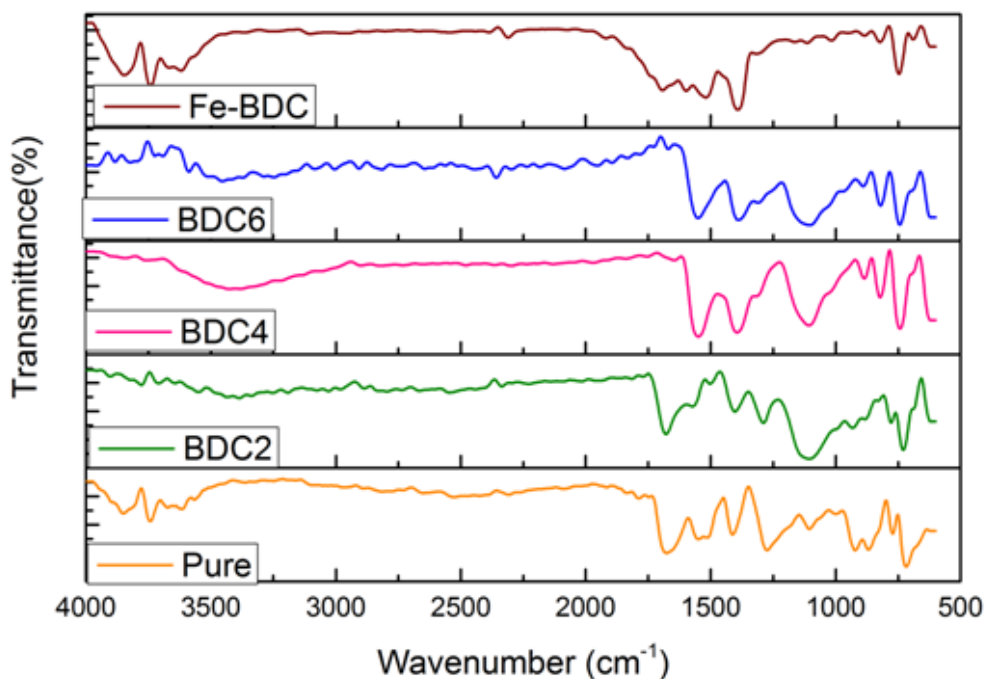


FIG 5.1 FT-IR spectrum for pure, 2N, 4N, 6N-BDC, Fe-BDC

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 BDC and Fe-BDC synthesized from its PET and iron granules is shown in the Fig 5.2. The XRD pattern is obtained by scanning from 5 to 60° with a scan rate of 0.001°/sec. The peaks of pure BDC are at 16.75° ; 25.02° ; 27.77° ; which are entirely the same as that of BDC2, BDC4 and BDC6. In the synthesized BDC (2,4,6) new peaks are at 23.54°, 25.12°, 31.63°, 33.94° which represents the peaks of sodium terephthalate which is formed during the synthesis of BDC from PET. 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 (Matériaux de L'Institut Lavoisier).

The observed peaks in Fe-BDC at lower than 10° (9.74°) indicate the crystalline nature of the Fe-BDC.

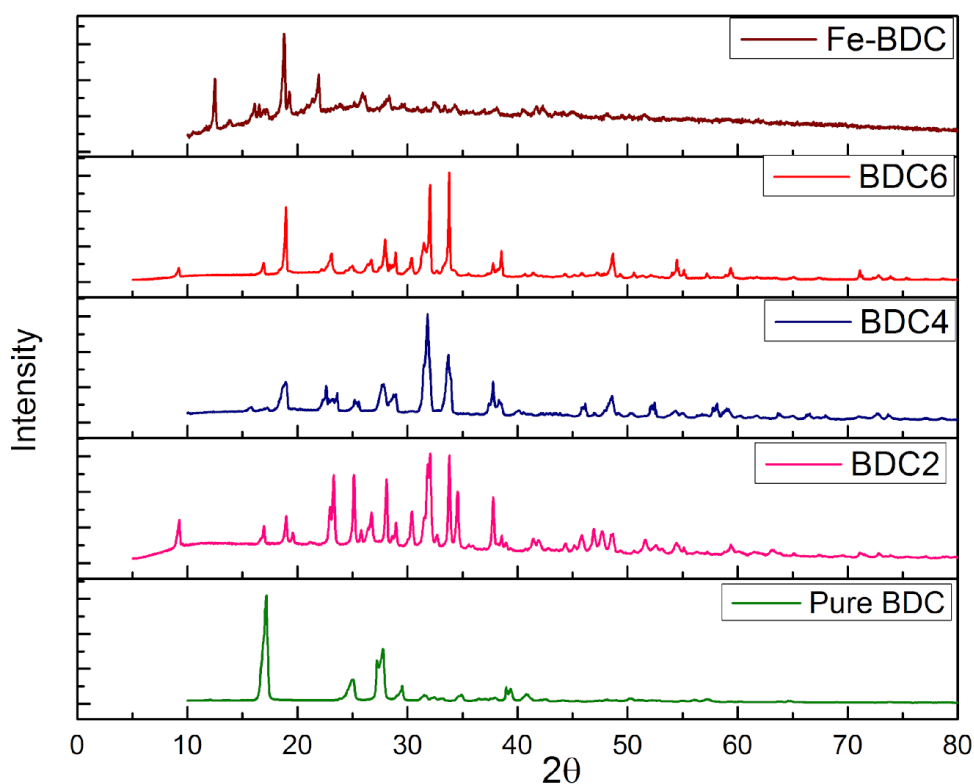


FIG 5.2 XRD graph for pure, 2N, 4N, 6N-BDC and Fe-BDC

The average crystallite size for synthesized Fe-BDC by Scherer was found to be 366nm indicating the crystalline nature of Fe-BDC and the crystalline size found from Williamson-Hall plot for Fe-BDC is presented in Table

Table 5.1 Crystalline size for Fe-BDC

Sample	Crystallite size (nm)	Lattice strain	Crystallinity (nm)
Fe-BDC	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,

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

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 that 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 is plotted and is depicted in the Fig 5.2.1. The linear graph is plotted by taking into consideration the major XRD peaks of Fe-BDC. 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.

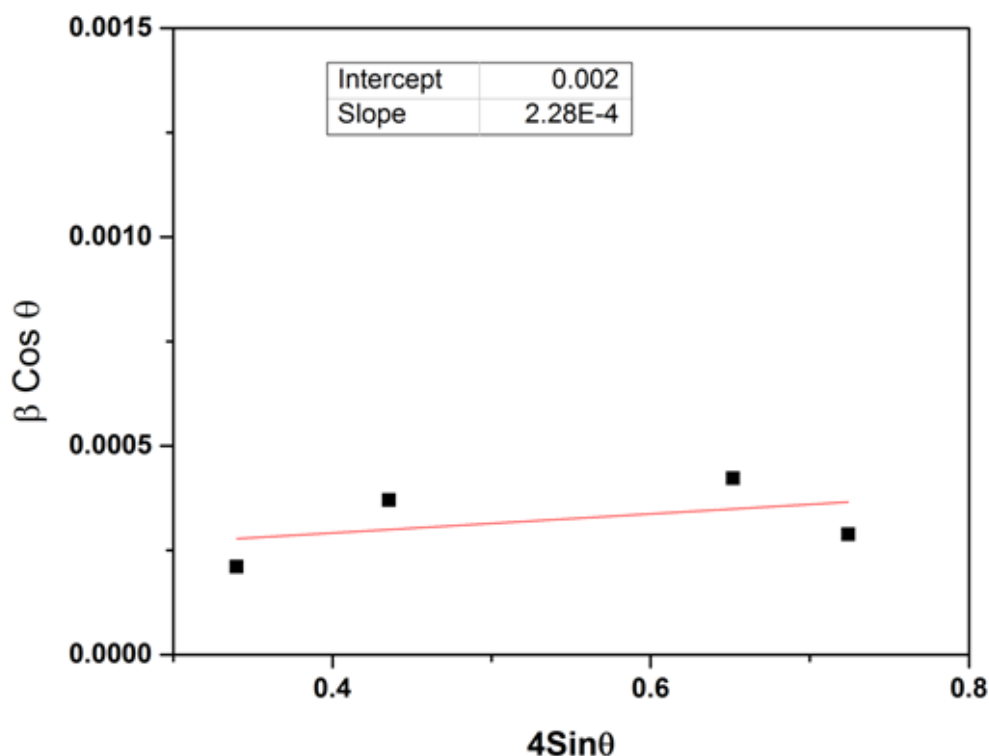


FIG 5.2.1 Williamson-Hall Plot of Fe-BDC

5.3 Scanning Electron Microscope (SEM)

The structural morphology of the Fe-BDC crystal along with the crystal size is deduced. The SEM images for Fe-BDC and BDC-4 is presented in the Fig 5.3. The morphology of BDC-4 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 5.3.1. As seen from the Fig, the frequency of crystal size is in the range of $0.7\mu\text{m}$ i.e 700nm.

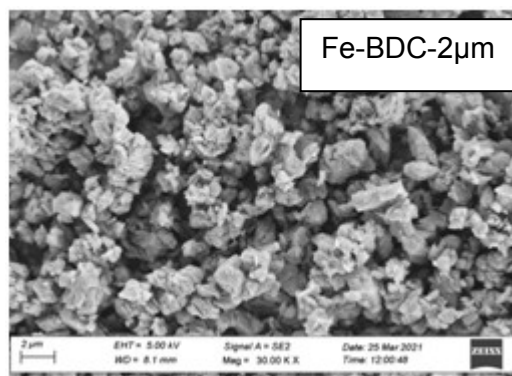
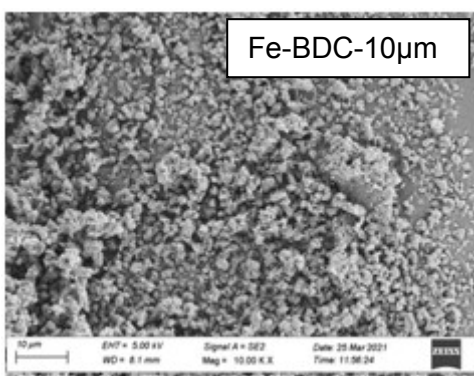
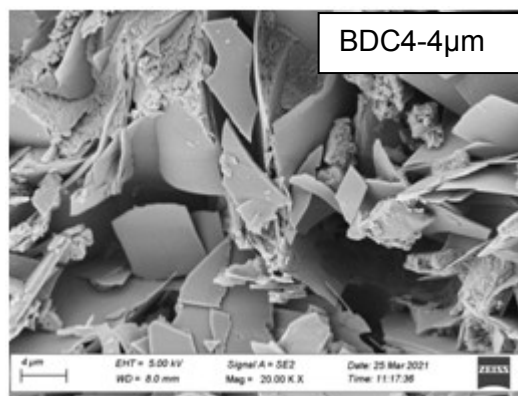
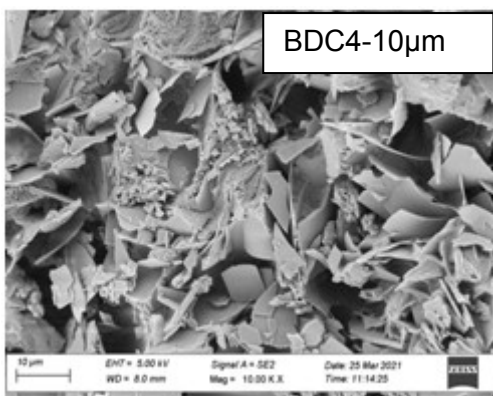


Fig 5.3 SEM Images of BDC and Fe-BDC

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.

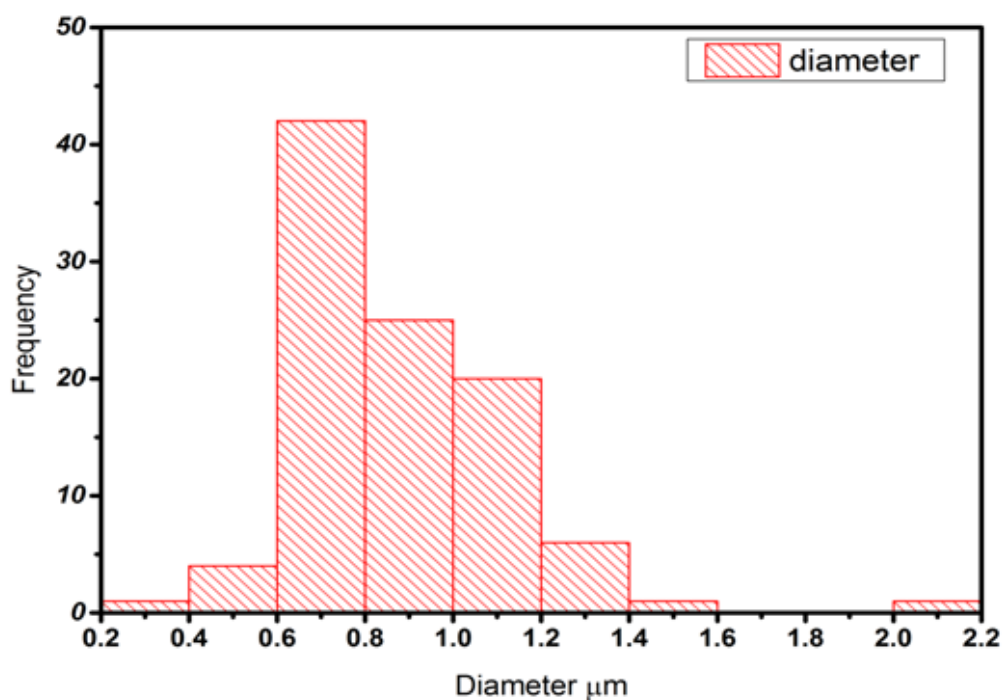


FIG 5.3.2 Histogram Graph for Fe-BDC

5.4 Electron Dispersive X-ray (EDX)

The elemental composition of the synthesized Fe-BDC is monitored by EDX and is presented in the fig 5.4.1. 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.

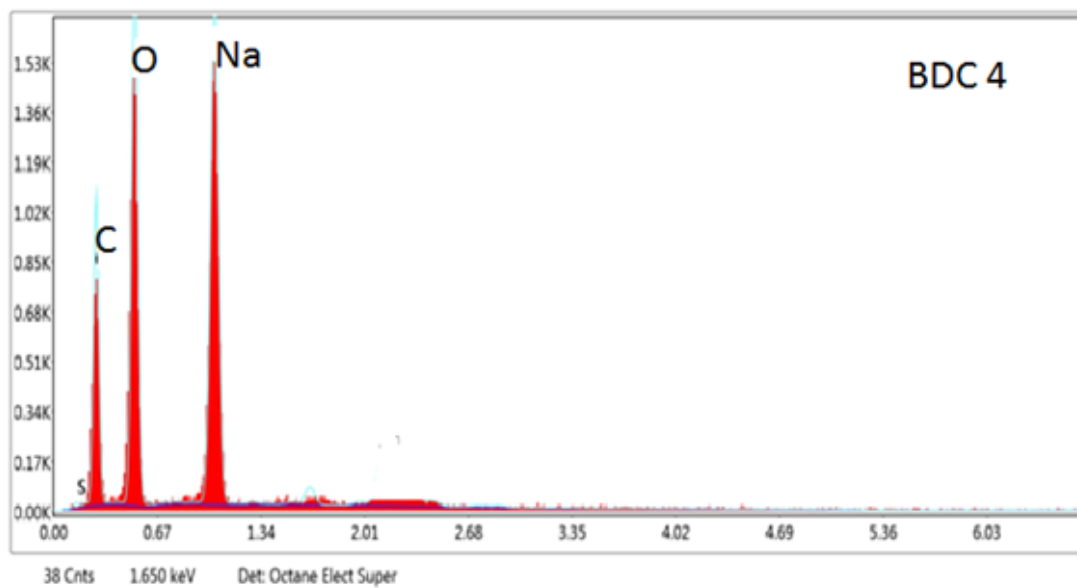


FIG 5.4 EDX for 4 N-BDC

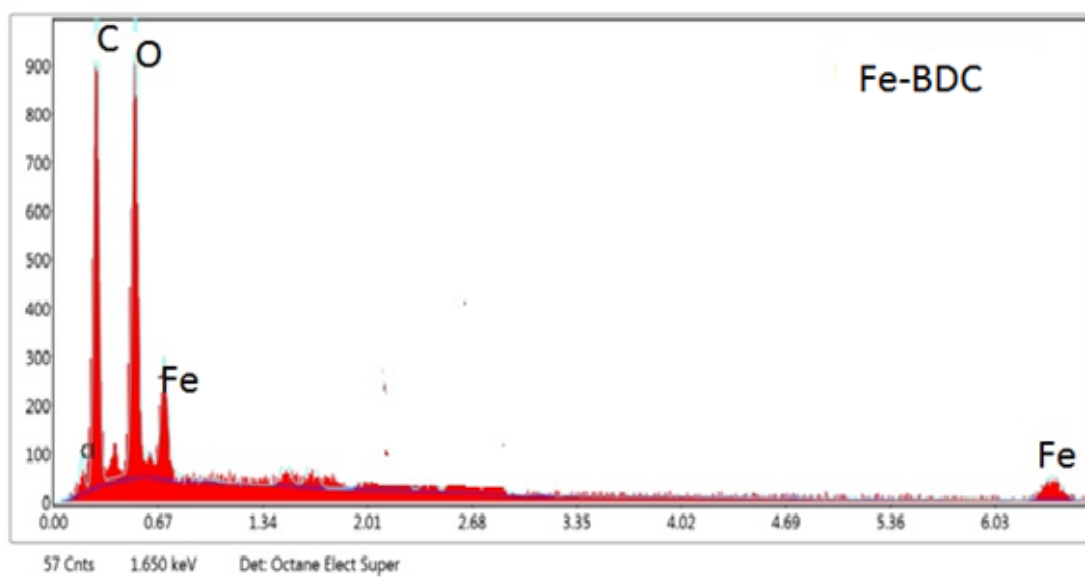


FIG 5.4.1 EDX Fe-BDC

CHAPTER 6

SUMMARY AND CONCLUSIONS

- We are able to synthesis Fe – BDC from waste material.
- The FT-IR characterization for BDC show the peak in the fingerprint region at 677cm^{-1} in the Fe-BDC spectrum indicate the presence of Fe-O bond where the iron is linked to the organic linker BDC through oxygen site.
- The XRD characterization of BDC 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 (Matériaux de L'Institut Lavoisier).
- The SEM images for Fe-BDC , BDC-4 is in the form of flakes while the Fe-BDC assumes the form of bulky triangular rod shape of Fe-BDC.
- The EDX of BDC have atomic weight % of Fe was determined as 2.58% which corresponds to 4Fe atoms in the crystal structure of Fe-BDC.

REFERENCES

1. Aldykiewicz A J, Davenport A J, Isaacs H S, Studies of the formation of cerium rich protective films using x-ray absorption near-edge spectroscopy and rotating disk electrode methods, J. Electrochem. vol 143, 1996pg no 147–154.
2. Baes C F, Mesmer R E, , A compilation of corrosion potentials reported for intermetallic phases in aluminium alloys, J. Electrochem. Soc. 142 (1995) 3994–3996. Galvele J R, De Michel S M D, Mechanism of intergranular corrosion of Al-Cu alloys, Corros. Sci. 10 (1990).
3. Hoepfner D W, “Estimation of component life by application of fatigue crack growth threshold knowledge,” in Fatigue, Creep and Pressure Vessels for Elevated Temperature Service, C. W. Lawton and R. R. Seeley, Eds., pp. The American Society of Mechanical Engineers, New York, NY, USA, 1981 Jone D, Principle, and Prevention of Corrosion, Macmillan Publishing, New York, NY, USA, 1992
4. Kendig M, Jeanjaquet S, Addison R, Waldrop J, Role of hexavalent chromium in the inhibition of corrosion of aluminium alloys, Surf. Coat. Technol. vol 140, 2001pg no 58– 66.
5. Koteswara Rao S R, Madhusudhan Reddy G, Srinivasa Rao K, Kamaraj M, Prasad Rao K, Reasons for superior mechanical and corrosion properties of 2219 aluminium alloy electron beam welds, Mater. Charact. 55 (2005) 345–354.
6. Mishra A K, Balasubramanian R, Corrosion inhibition of aluminium alloy AA 2014 by rare earth chlorides, Corros. Sci. 49 2007pg no 1027–1044.
7. Muster T H *et al.*, An investigation of rare earth chloride mixtures: combinatorial optimisation for AA2024-T3 corrosion inhibition, Surf. Interf. Analysis, vol 42, 2010pg no 170–174

8. Neil W, Garrard C, The corrosion behaviour of aluminium-silicon carbide composites in aerated 3.5% sodium chloride, *Corros. Sci.* 36 (1994) 837–851. Pinner W R, Sheardy P G, The surface treatment of aluminium and its alloys, Finishing publications, (1987), p.194.

9. Scully J R, Knight T O, Buchheit R G Peebles D E, Electrochemical characteristics of the Al_2Cu , Al_3Ta and Al_3Zr intermetallic phases and their relevance to the localized corrosion of Al alloys, *Corros. Sci.* 35 1993 pg no 185–195.

10. Venkata Narayana G, Sharma V M J, Diwakar V, Sree Kumar K, Prasad R C, Fracture behaviour of aluminium alloy 2219-T87 welded plates, *Sci. Technol. Weld. Joi.* vol 9, 2004 pg no 121–130.

11. Yasakau K A, Zheludkevich M L, Lamaka S V, Mario, Ferreira VG S, Mechanism of Corrosion Inhibition of AA2024 by Rare-Earth Compounds, *J. Phys. Chem. B*, vol 110, (11) 2006 pg no 5515–5528.

12. Geyer, R., J. Jambeck, and K. L. Law. "Producción, uso y destino de todos los plásticos jamás fabricados." *Science Advances* 3.7 2017 pg no 1207-1221

13. Kobielska, Paulina A., et al. "Metal–organic frameworks for heavy metal removal from water." *Coordination Chemistry Reviews* 358 2018) pg no 92-107

14. Kumar, Pawan, Vasudha Bansal, Ki-Hyun Kim, and Eilhann E. Kwon. "Metal-organic frameworks (MOFs) as futuristic options for wastewater treatment." *Journal of industrial and engineering chemistry* 62 2018) pg no 130-145

15. Feng, Mingbao, et al. "Water-stable metal-organic frameworks for aqueous removal of heavy metals and radionuclides: A review." *Chemosphere* 209 2018 pg no 783-800.

16. Kang, Myung Jong, Hye Jin Yu, Jonggeon Jegal, Hyun Sung Kim, and Hyun Gil Cha. "Depolymerization of PET into terephthalic acid in neutral media catalyzed by the ZSM-5 acidic catalyst." *Chemical Engineering Journal* vol 398, 2020 pg no 125655.

17. Mallakpour, Shadpour, and Vajiheh Behranvand. "Water sanitization by the elimination of Cd^{2+} using recycled PET/MWNT/LDH composite: morphology, thermal, kinetic, and isotherm studies." *ACS Sustainable Chemistry & Engineering* 5.7 2017pg no 5746-5757.

18. Deleu WP, Stassen I, Jonckheere D, Ameloot R, De Vos DE. Waste PET (bottles) as a resource or substrate for MOF synthesis. *Journal of Materials Chemistry A*. 2016;pg no 9519-25.

19. Dhakshinamoorthy, Amarajothi, Zhaohui Li, and Hermenegildo Garcia. "Catalysis and photocatalysis by metal organic frameworks." *Chemical Society Reviews* 47.22(2018 pg no 8134-8172.

20. Roy, Prasun Kumar, Arunachalam Ramanan, and Chitra Rajagopal. "Post consumer PETwaste as potential feedstock for metal organic frameworks." *Materials Letters* vol106, 2013pg no:390-392.

21. Chenot, Cécile, Raphaël Robiette, and Sonia Collin. "First evidence of the cysteine and glutathione conjugates of 3-sulfanyl pentan-1-ol in hop (*Humulus lupulus* L.)." *Journal of agricultural and food chemistry* 67.14 2019

22. Dhakshinamoorthy, Amarajothi, Zhaohui Li, and Hermenegildo Garcia. "Catalysis and photocatalysis by metal organic frameworks." *Chemical Society Reviews* 47.22 2018pg no: 8134-8172.

23. Zhang, F., Yao, H., Chu, T., Zhang, G., Wang, Y. and Yang, Y., 2017. Lanthanide MOF Thin-Film Fixed with Co₃O₄ Nano-Anchors as a Highly Efficient Luminescent Sensor for Nitrofurantoin Antibiotics. *Chemistry–A European Journal*, 23(43), pp.10293-10300.

24. Zheng, Kai, et al. "Hybrid membrane of agarose and lanthanide coordination polymer: a selective and sensitive Fe³⁺ sensor." *Photochemistry and photobiology* 91.4 2015pg no: 814-818

25. Lee, J.; Farha, O.K.; Roberts, J.; Scheidt, K.A.; Nguyen, S.T.; Hupp, J.T. Metal–organic framework materials as Author Contributions: Conceptualization Feng Zhang; Methodology, Shuyi Chen.; Formal Analysis, catalysts. *Chem. Soc. Rev.* 2009, pg no 1450–1459