

SYNTHESIS AND CHARACTERIZATION OF MONOMETALLIC AND BIMETALLIC METAL ORGANIC FRAMEWORK (MOFs) AND THE STUDY OF THEIR PHOTOCATALYTIC ACTIVITY

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1. INTRODUCTION

MOFs, or metal-organic frameworks, are an intriguing class of porous materials that have a wide range of uses, including drug delivery, gas storage, separation, catalysis, and sensing. Because of their huge surface areas, adaptable functions, and adjustable structures, MOFs have attracted a lot of interest from researchers all around the world since they were discovered. By combining organic linkers with inorganic nodes, MOF characteristics can be customized to almost any desired extent for a wide range of applications. Because of the modular nature of their synthesis, MOFs provide an extremely varied range of structures and characteristics. It is possible to adjust their properties by combining different metal ions and organic ligands, allowing for customization to fit specific applications in a variety of domains. MOFs are highly porous, with huge surface areas and variable pore sizes, making them ideal for gas storage, separation, catalysis, and drug delivery. The ability to accurately adjust the porosity of MOFs allows researchers to build materials with better gas adsorption capabilities and selectivity. Many MOF applications address major global concerns such as energy sustainability, environmental pollution, and healthcare.¹ MOFs have demonstrated potential in carbon capture and storage, renewable energy storage, pollutant removal from water and air, and targeted medicine delivery, making them viable instruments for addressing these concerns.

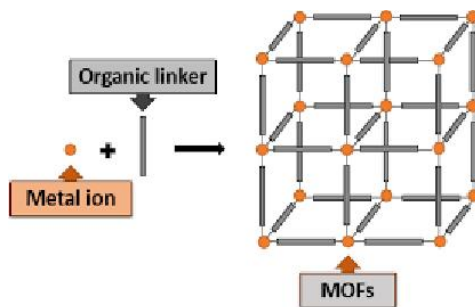


Fig 1: Basic methodology of synthesis of MOFs

MOFs have catalytic activity because they include metal cores and accessible active sites inside their porous architectures.

Investigations are ongoing on using MOFs as catalysts for a variety of chemical reactions, such as hydrogenation, oxidation, and photocatalysis, with the goal of producing more efficient and sustainable chemical transformation processes. Metal-organic frameworks (MOFs) can be synthesized using various techniques, such as solvothermal / hydrothermal, coprecipitation, grinding (ball milling), ultrasonication, microwave synthesis and many more. Solvothermal method is a popular method for synthesizing MOFs. It entails heating a combination of metal ions, organic ligands, and a solvent in a sealed autoclave to high temperatures and pressures. The size, shape, and crystallinity of the MOF crystals produced can be influenced by the solvent and reaction conditions used. Mechanochemical synthesis is the application of mechanical force to cause chemical reactions between solid reactants. Metal salts and organic ligands are combined in a milling jar with grinding balls. The mechanical energy produced by milling promotes the production of MOF crystals via solid-state processes. Ball milling has several advantages, including quicker reaction times, lower solvent usage, and scalability. Coprecipitation is a typical approach for producing MOFs, notably nanoparticles and nanocrystals. To produce the MOF material, metal ions and organic ligands must be precipitated from a solution at the same time.

Ultrasonication is the use of high-frequency sound waves (ultrasound) to create cavitation and promote mixing, dispersion, and chemical reactions in liquid medium. It is frequently used as a supplemental technique with other synthesis methods to increase reaction kinetics and material qualities.

Various types of MOFs are synthesized by using any of the above suitable methods. The efficiency in the performance of the MOF depends on the type of metal as well as the ligand that is used. Various metals such as Fe, Co, Ni, Cu, Zn are being used vastly in the preparation of MOFs. Copper-based MOFs particularly draw greater attention because they can be synthesized with commercially available reagents and possess the high surface area. Copper (Cu) was selected as a classical transition metal which is one of the most attractive elements for use in the preparation of MOFs due to its abundance of resources, low cost, non-toxic properties, and most importantly high complexation strength. The high and excellent stability of Cu based MOFs is related to the strong interaction between Cu (II) from metal and-O- from organic ligands which make these materials stable in aqueous solution and over a wide pH range. Terephthalic acid (BDC) is used as a common ligand which has very low toxicity and is easily available, was applied in which the COOH groups can strongly interact with Cu²⁺ cations via coordination interaction. Also, molecules with aromatic rings tend to interact with MOFs due to the p-p interactions.^{1,2} In this project, we have synthesized Cu-BDC and Cu-Zn-BDC through two methods possible in our laboratory i.e. through co-precipitation and ultrasonication. Zinc is known to exhibit good photocatalytic properties due to which it has been used in conjugation with copper to study the dye degradation ability of the prepared MOFs.³ The prepared MOFs were characterized, and their dye degradation study was conducted which is discussed in the following sections.

2. EXPERIMENTAL SECTION

2.1 MATERIALS AND METHODS:

All the chemicals and reagents were provided from the laboratory having AR grade. Copper acetate (Cu(CH₃COO)₂), benzene dicarboxylic acid (BDC), N, Ndimethylformamide (DMF), acetonitrile, crystal violet dye (5ppm).

All the glassware were cleaned properly, washed with acetone and water and dried. Glassware such as beakers, pipettes, standard measuring flasks, test tubes, magnetic stirrer etc. were used with proper care.

2.2 SYNTHESIS OF METAL ORGANIC FRAMEWORK

Synthesis of metal organic framework can be carried out by a variety of methods which include solvothermal/hydrothermal, co-precipitation, ultrasonication, grinding method etc. The merits and demerits of each of these techniques have been mentioned in the introduction section. Herein, the major methods used for synthesis of MOFs was co-precipitation and ultrasonication method. Monometallic Cu-BDC MOF and bimetallic Cu-Zn-BDC MOFs were prepared using both these methods.

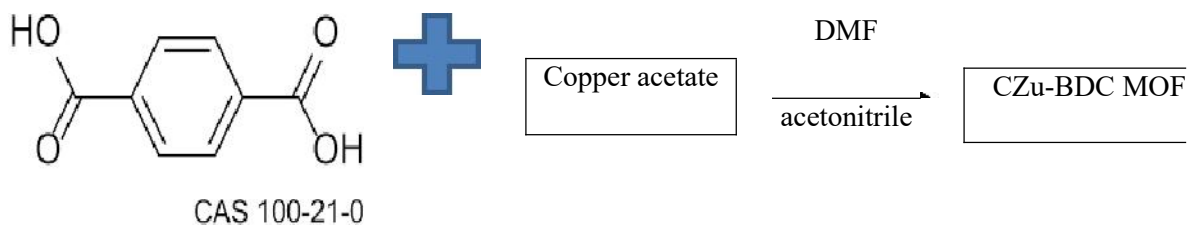


Fig 2.2.1: Methodology for synthesis of Cu-BDC MOF by both co-precipitation and ultrasonication

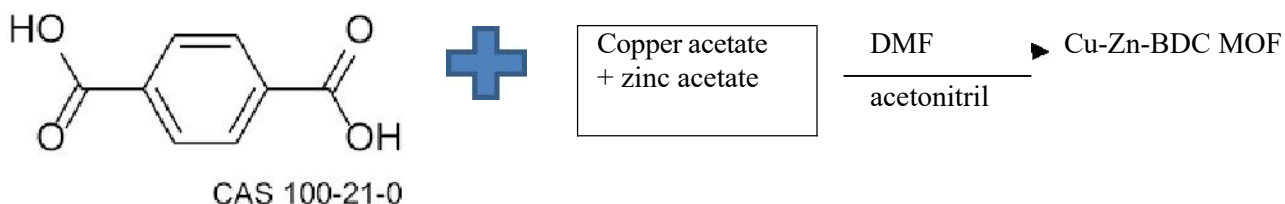


Fig: 2.2.2: Methodology for synthesis of Cu-Zn-BDC MOF by both co-precipitation and ultrasonication

2.2.1 Co-precipitation method:

Metal-Organic Frameworks (MOFs) are flexible porous materials with a wide range of uses. The co-precipitation method is frequently used to synthesize MOFs. By precipitating metal ions and organic ligands from a solution simultaneously, this technique makes it easier for MOF crystals to form. Based on the intended MOF composition, the first stage entails the meticulous selection of metal precursors, often transition metals like zinc, copper, or nickel. The selection of organic ligands, which work in tandem with the metal ions to define the MOF structure, is equally important. The size, form, and functionality of these ligands differ greatly, which affects the final MOF product's characteristics. Precursor solutions are made when the metal salts and organic ligands are individually dissolved in appropriate solvents. Selecting solvents that are compatible with both metal ions and ligands is crucial. The properties of the resultant MOF are largely determined by the concentrations of these solutions. The precursor solutions are then combined under carefully monitored circumstances, which usually include temperature and pH. It is important to mix materials carefully and gradually in order to guarantee that MOF crystals nucleate and develop uniformly.

Insoluble MOF crystals start to form and separate from the solution as a result of the reaction between the metal ions and organic ligands. The precipitation and crystallization stage is critical, because variables like temperature, pH, and stirring rate can have a big impact on the final MOF particle's size, shape, and crystallinity. Once the co-precipitation reaction is finished, the resulting MOF crystals are cleaned using an appropriate solvent to get rid of any leftover precursors or impurities. The MOF crystals are usually dried after the washing process, resulting in a finished product that is prepared for additional characterization and use in a variety of industries, including gas storage and catalysis.⁴

Preparation of samples:

For preparing **Cu-BDC MOF**, 1:1 ratio of copper acetate and BDC was weighed (500mg) in two separate beakers and dissolved in 75cm³ DMF + 25 cm³ acetonitrile solution. Both the solutions were subjected to sonication for a few minutes to ensure complete dissolution. The metal solution was mixed into the ligand solution and was stirred using magnetic stirrer for about 30 minutes. As soon as precipitate formation is observed to be even, we stop the stirring and keep the solution to undergo ageing for 24 hours. After 24 hours, centrifugate the solution, and the filtrate is collected in a petri dish and then kept in the oven for evaporating the remaining solvent for up to 30 mins at 160°C. The prepared material is then scrapped and collected in vials for further characterization. Yield of the product obtained is 0.646g .

Preparation of **Cu-Zn-BDC MOF** was conducted in a similar manner, For preparing Cu-Zn-BDC MOF, 1:1 ratio of copper acetate + zinc acetate and BDC was weighed (250mg) in two separate beakers and dissolved in 25cm³ DMF+ 16.6 cm³ acetonitrile solution. Both the solutions were subjected to sonication for few minutes to ensure complete dissolution. The solution containing metal ions was mixed into the ligand solution and was stirred using magnetic stirrer for about 30 minutes. As soon as precipitate formation is observed to be even, we stop the stirring and keep the solution to undergo ageing for 24 hours. After 24 hours, centrifugate the solution , and the filtrate is then collected in a petri dish and then kept in the oven for evaporating the remaining solvent for up to 30 mins at 160°C. The prepared material is then scrapped and collected in vials for further characterization. Yield of the product obtained is 0.444g.

2.2.2 Ultrasonication Method:

Ultrasonication, also known as sonication, is a powerful technique used in the synthesis of Metal-Organic Frameworks (MOFs). It includes exposing a reaction mixture to high-frequency sound waves (ultrasound), which causes MOF crystals to form. First, the organic ligands and metal precursors are individually dissolved in the proper solvents. The organic ligand solution is made up of organic molecules that will serve as linkers in the MOF structure, whereas the metal precursor solution often contains metal salts or metal-organic complexes. The solutions are combined in a reaction vessel after they have been prepared. Next, an ultrasonic bath or probe sonicator is used to apply ultrasonic waves to the reaction mixture. Little bubbles in the liquid form and burst due to cavitation, which is caused by these high-frequency sound waves. These bubbles burst, creating concentrated hot areas and high pressures that speed up mass transfer, chemical reactions, and mixing in the fluid.

By quickening the chemical kinetics, the ultrasonication procedure promotes the nucleation and development of MOF crystals. It improves reactant dispersion, expands the surface area accessible for interaction, and aids in getting past kinetic obstacles that would prevent the creation of MOFs under standard synthesis circumstances. The particular MOF system and the intended qualities of the finished product can be taken into consideration while adjusting the ultrasonication time and intensity. To separate the solid MOF crystals, the ultrasonicated MOF slurry is usually filtered or centrifuged after the required reaction time. To get rid of any contaminants or unreacted precursors, the separated crystals are further cleaned in an appropriate solvent.⁵

For MOF synthesis, ultrasonication has a number of benefits overall, such as reduced reaction times, increased crystallinity, and better control over particle size and shape. It is a flexible and effective technique that has been effectively used for a number of applications on a variety of MOF systems. The preparation of the solutions for ultrasonication as well as coprecipitation of the same, just the distinction is that in ultrasonication we use the energy in the form of sound waves for the efficient reaction to occur.

Preparation of samples:

For preparing **Cu-BDC MOF**, copper acetate (0.525g) and BDC (0.25g) was weighed in two separate beakers and dissolved in 25 cm³ DMF+ 16.6 cm³ acetonitrile solution. Both the solutions were subjected to sonication for few minutes to ensure complete dissolution. The metal solution was mixed into the ligand solution and was kept for ultrasonication at around 160-170 kHz for 20 minutes. The solution was then removed and kept for ageing for 24 hours. After 24 hours, centrifugate the solution, and the filtrate is then collected in a petri dish and then kept in the oven for evaporating the remaining solvent for up to 30 mins at 160°C. The prepared material is then scrapped and collected in vials for further characterization. Yield of the product obtained is 0.361g

Preparation of **Cu-Zn-BDC MOF** was conducted in a similar manner, For preparing Cu-Zn-BDC MOF, copper acetate + zinc acetate (0.25g each) and BDC (0.25g) were weighed in two separate beakers and dissolved in 25ml DMF+ 16.6ml acetonitrile solution. Both the solutions were subjected to sonication for few minutes to ensure complete dissolution. The solution containing metal ions was mixed into the ligand solution and was kept for ultrasonication at around 160-170 kHz for 20 minutes. The solution was then removed and kept for ageing for 24 hours. After 24 hours, centrifugation of the solution is conducted, and the filtrate is then placed in a petri dish and then kept in the oven for evaporating the remaining solvent for up to 30 mins at 160°C. The prepared material is then scrapped and collected in vials for further characterization. Yield of the product obtained is 0.376g.

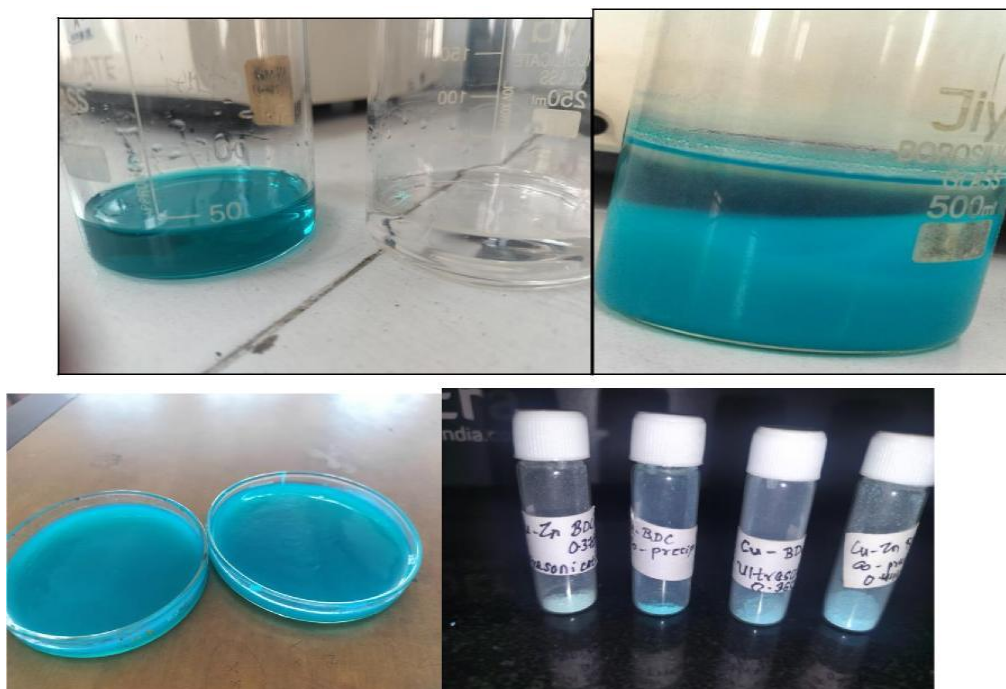


Fig 2.2.3: Course of synthesis of Cu-BDC and Cu-Zn-BDC MOF.

3. CHARACTERISATION TECHNIQUES:

3.1. X-RAY DIFFRACTION

The major characterization techniques used for the determining the structures were namely X-Ray Diffraction and UV-Vis spectroscopy. X-Ray diffraction of the above prepared samples were conducted and the results are presented below.

Cu-BDC- Co-precipitation

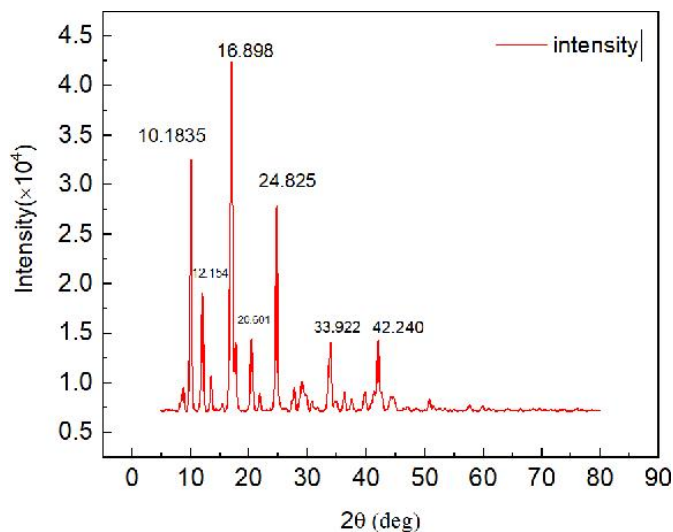


Fig 3.1.1: XRD spectra of Cu-BDC MOF prepared by co-precipitation method

Cu-BDC- Ultrasonication

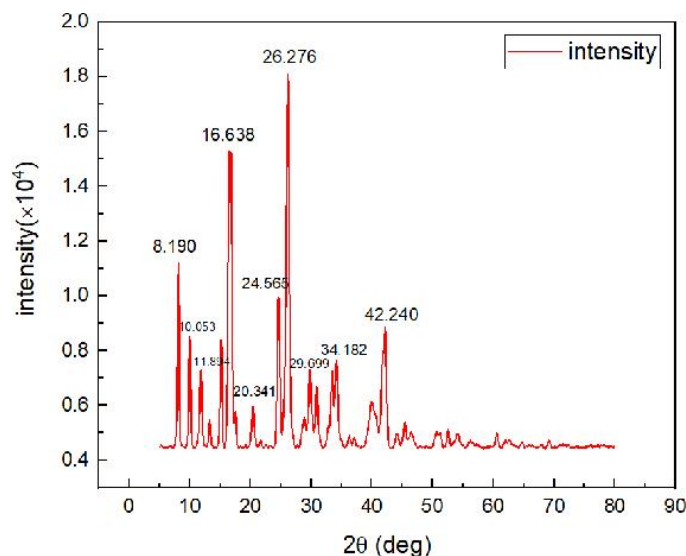


Fig 3.1.2: XRD spectra of Cu-BDC MOF prepared by ultrasonication method

The XRD pattern of Cu-BDC in previous reported literature (Cambridge crystallographic information data with deposit number of 112954) depicts that the peaks at 2θ of 7.0 ,13.8 ,15.7 ,19.6 ,30.0 ,37.0, 42.5 are related to (220), (222), (333), (420), (422), (773) and (882) crystal planes.⁶ The XRD pattern obtained by us through the synthesis of Cu-BDC MOF has been found to almost match the actual values of the Cu-BDC MOF according to the values of the reported literature.

Cu-Zn-BDC- Co-precipitation

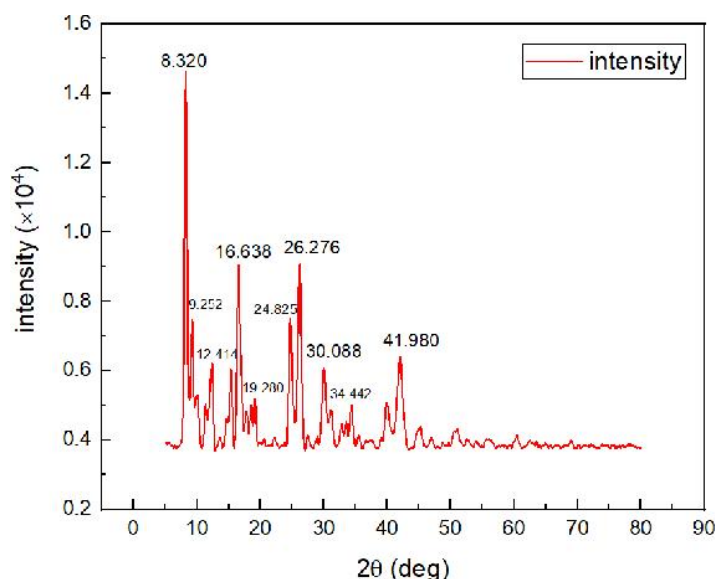


Fig 3.1.3: XRD spectra of Cu-Zn-BDC MOF prepared by co-precipitation method.

Cu-Zn-BDC- Ultrasonication

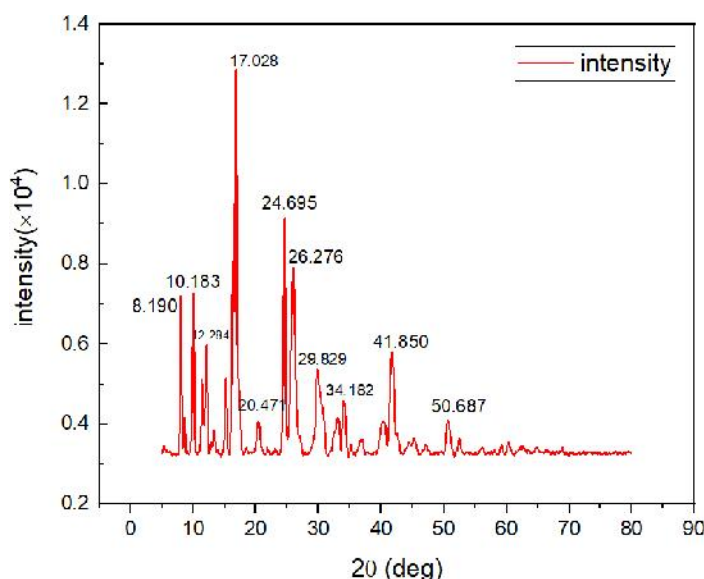


Fig 3.1.4: XRD spectra of Cu-Zn-BDC prepared by ultrasonication method

The XRD pattern observed for Cu-BDC would also be present in Cu-Zn-BDC along with the peaks observed for Zn-BDC. The strong XRD intensity of the peak at 10.1° demonstrates that many of the crystal faces at (220) were formed in the Zn (BDC) MOF. The weak XRD intensity of the three theta peaks at 15.5°, 16.8°, and 20.8° reveals a few crystal faces at (400), (420), and (531), respectively, in Zn (BDC) MOF. The XRD pattern of Cu-BDC in previous reported literature (Cambridge crystallographic information data with deposit number of 112954) in which the peaks at 2θ of 7.0°, 13.8°, 15.7°, 19.6°, 30.0°, 37.0°, 42.5° are related to (220), (222), (333), (420), (422), (773) and (882) crystal planes⁷ are also observed in the XRD spectra and is found to match with the values observed for Cu-BDC.

3.2. UV VIS SPECTROSCOPY

The dye degradation study of the prepared MOFs was conducted by using UV-Vis spectrophotometry. The dye chosen for the study was crystal violet which shows its maximum absorbance between 585-590nm. 5ppm solution of crystal violet was prepared (5cm³ of 500ppm solution dissolved in 100cm³).

Mechanism for photocatalytic dye degradation:

The basic mechanism for dye degradation is shown in Fig 3.2.1. When a photocatalyst is irradiated with a light of suitable wavelength, an electron is excited to the conduction band (CB), leaving behind a positive hole in the valence band (VB).⁸

The electron in the CB can be utilized to reduce any substrate, whereas the hole in the VB can be used for oxidizing some compounds. The photocatalyst used in this work is the synthesized metal organic framework that works on the similar principle. There are three basic processes that take place during photocatalytic degradation namely, oxidation, electron injection and reduction.⁹

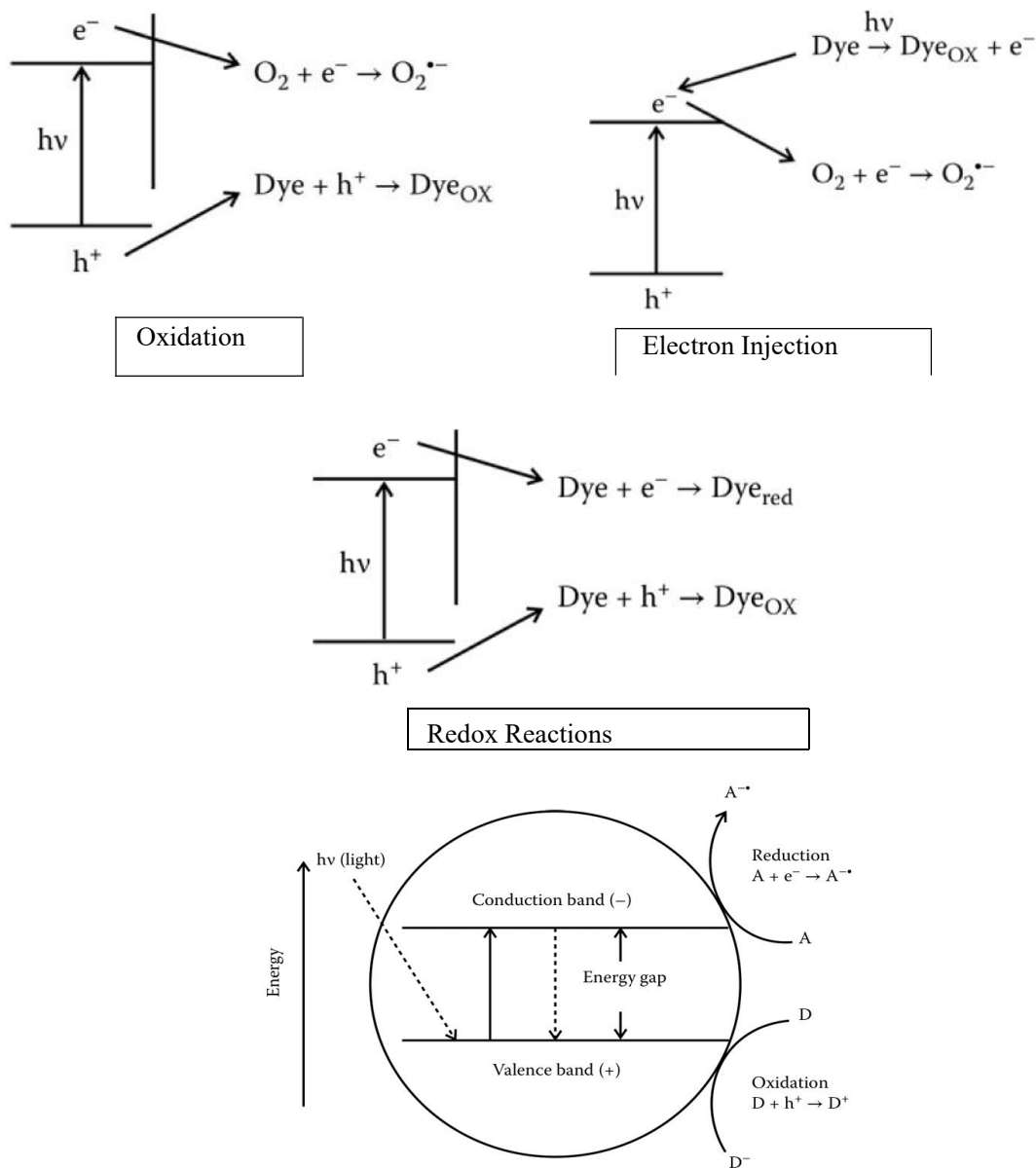


Fig 3.2.1. Mechanism for photocatalytic dye degradation

Procedure for the dye degradation study: **Cu-BDC**

20mg of Cu-BDC sample (co-precipitation) was weighed in a 100cm³ beaker and 25 cm³ of 5ppm crystal violet solution was mixed in it. The solution was equilibrated for almost 15 mins for efficient mixing of the MOF with the dye and then at regular intervals of time, the readings were taken. The procedure was similar for Cu-BDC (ultrasonication).

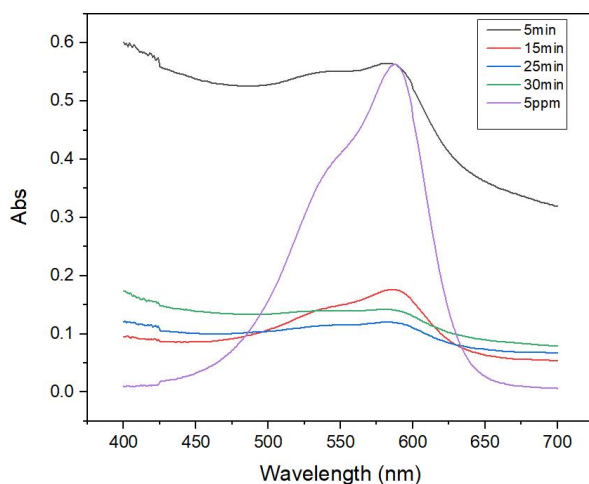


Fig 3.2.2: UV Vis spectra showing degradation of CV dye by Cu-BDC MOF.

Cu-Zn-BDC

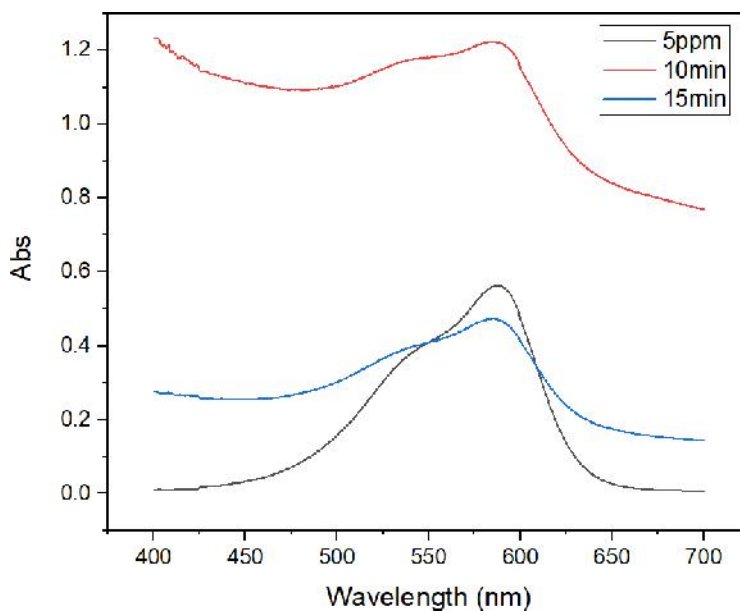


Fig 3.2.3: UV Vis spectra showing degradation of CV dye by Cu-Zn-BDC MOF (co-precipitation).

20mg of Cu-Zn-BDC sample (co-precipitation) was weighed in a 100cm³ beaker and 25 cm³ of 5ppm crystal violet solution was mixed in it. The solution was equilibrated for almost 15 mins for efficient mixing of the MOF with the dye and then at regular intervals of time, the readings were taken. Similar procedure was conducted for CuZn-BDC (ultrasonication).

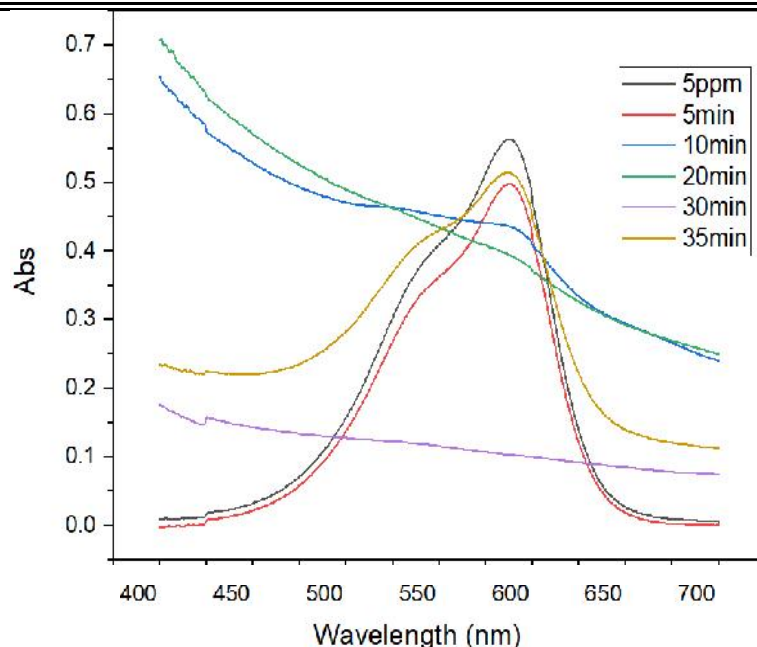


Fig 3.2.4: UV Vis spectra showing degradation of CV dye by Cu-Zn-BDC MOF (ultrasonication).

4. RESULTS:

XRD analysis of the MOFs shows that the values of the peaks found in Cu-BDC are almost similar to the actual 2θ values of the peaks as per the JCPDS file. The XRD analysis of Cu-Zn-BDC MOF provides an insight onto the peaks that are shown by Zn-BDC as well as Cu-BDC MOFs. Zn-BDC shows the presence of one intense peak and three weak intense peaks that are readily observed in the XRD pattern of the synthesized Cu-Zn-BDC MOF and the actual values of 2θ for Cu-BDC also almost matches to that of the synthesized Cu-BDC. The molecular structure of the Cu-BDC MOF as well as Cu-Zn-BDC has been interpreted to be cubical as per the obtained results.

As per Fig 3.2.2, the UV spectra observed for the Cu-BDC MOF, during the first 5 mins, no dye degradation has been observed under normal light conditions. As and when the time of interaction between the dye and the MOF increases, it has been observed that there is slight lowering of the absorbance peak of the crystal violet dye which interprets that the dye degradation has taken place. In case of dye degradation study done for Cu-Zn-BDC through co-precipitation (Fig 3.2.3), the reading at first 10 minutes do not show any type of dye degradation under normal light conditions whereas again after interacting for more 5 minutes, we observe the slight lowering of the absorbance peak of the crystal violet dye. The dye degradation study of CuZn-BDC MOF through ultrasonication (Fig 3.2.4) has been observed to possess no dye degradation in the first 10 mins but later after the 10th minute, it has been observed that the dye degradation has slightly happened which is observed by the slight decrease in the absorbance peak of crystal violet dye. In all these cases, the efficiency or the percentage of dye degradation is calculated by using the formula: Efficiency (%) = $((C_o - C_e)/C_o) \times 100$

Where C_o and C_e is the concentration of the dye before and after photoirradiation.

5. CONCLUSION:

We have successfully synthesized Cu-BDC and Cu-Zn BDC MOF by both the co-precipitation as well as the ultrasonication method. The products were obtained in excellent yields within short reaction times. Results from XRD and UV Vis Spectroscopy concluded that the synthesis for formation of MOF has undergone completion and the values of the XRD peaks almost match to the values of the XRD that are obtained by synthesizing the MOFs. It has been observed that the dye degradation has certainly occurred well when the interaction between the MOF and the dye is kept for a longer period of time. The efficiency /percentage of dye degradation that occurred in each of the MOFs has been calculated as per the formula: Efficiency (%) = $((C_o - C_e)/C_o) \times 100$

The calculated efficiency for each of the MOF is depicted in the table below:

Name of the MOF	Time taken for dye degradation	Efficiency of dye degradation
Cu-BDC- Co-precipitation	30 minutes	78.68%
Cu-BDC- Ultrasonication	30 minutes	78.68%
Cu-Zn-BDC- Co-precipitation	15 minutes	68.2%
Cu-Zn-BDC- Ultrasonication	30 minutes	82.46%

The above table shows that the efficiency is maximum when the interaction between the MOF and the dye is for a longer period and Cu-Zn-BDC shows better efficiency than all of them due to the presence of Zn which has good photocatalytic properties.

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