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UV-Irradiation-Assisted Synthesis, Characterization and Biological Activities of zinc oxide Nanoparticle Embedded Metal Based Organic Framework

Hifsa Nawaz [1]

[1] MPhil. Scholar Department of Chemistry, Abdul Wali Khan University Mardan, Pakistan
ORCID ID: 0009-0009-8855-8204 Email: hifsa923937@gmail.com

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Abstract

The composite of metal organic framework have gained much attention in the biological field due to their porous nature and enhance biological activity. In the first step of the current study zinc oxide nanoparticles was prepared and in the second step zinc based carboxylic acid metal organic framework (Zn-BTC) was prepared using precipitation method. At the last step the zinc oxide nanoparticles have been incorporated into zinc based carboxylic acid metal organic framework (Zn-BTC) using UV irradiation method. The synthesised samples was characterized using Scanning electron microscopy and energy dispersive x-ray and then the samples were used for the inhibition of alpha amylase and alpha glucosidase enzymes. The IC_{50} values for ZnO, Zn-BTC and zinc oxide incorporated Zn-BTC for alpha amylase was found to be **7.01 ±0.064, 8.06± 0.054 and 5.89± 0.083, respectively. Further** the IC_{50} values for ZnO, Zn-BTC and zinc oxide incorporated Zn-BTC for alpha glucosidase was found to be **11.06 ±0.053, 8.02± 0.045 and 10.87± 0.087 respectively.**

Key Words: MOFs, Synthesis,ZnO, Zn-BTC, UV Irradiation, Organic Ligands, Enzymes

Introduction

MOFs is comprise of metal center and organic ligands. These include octahedrons, trigonal prisms, square paddle-wheels, and triangles. In theory, a metal ion with several labile sites reacts with a bridging ligand, which can be ditopic, tritopic, tetratopic, or multitopic. The final topology of MOF frameworks is controlled by organic ligand linkers and SBU connections. It is possible for infinite-extended polymeric to form, depending on the system in question (Erxleben, 2003). Metal is locked into a position to create rigid and porous geometry in these porous crystalline materials, which are linked by distinct organic groups. Luminescence, gas adsorption and storage, separation, catalysis, molecular recognition, drug delivery, non-linear optics, and structural flexibility make MOFs ideal for a broad range of applications (Kitagawa, 2014). Additionally, MOFs are useful materials for storing, separating, or modifying molecules depending on the dimension because of their three-dimensional tunable porous networks (Furukawa et al., 2013).

Types of Metal organic framework

The following are the classification of MOFs

Rigid frameworks: Whether guest molecules are adsorbed or desorption, these porous frameworks remain stable and strong. Molecular sieving is one area where these MOFs can be used (Soni et al., 2020).

Flexible/dynamic frameworks: When external variables like pressure and temperature are introduced, as well as when guest particles are inserted or removed, flexible frameworks exhibit a remarkable degree of shape variation. While dynamic MOFs undergo a framework change upon solvent molecule removal. Several MOFs have a breathing effect when adsorbed or desorption. The effect of guest molecule adsorption and desorption on the unit cell volume (pore volume) of breathing MOFs is dramatic. Various forms of flexibility modes are outlined and examined as shown in the Figure 1 (Soni et al., 2020).

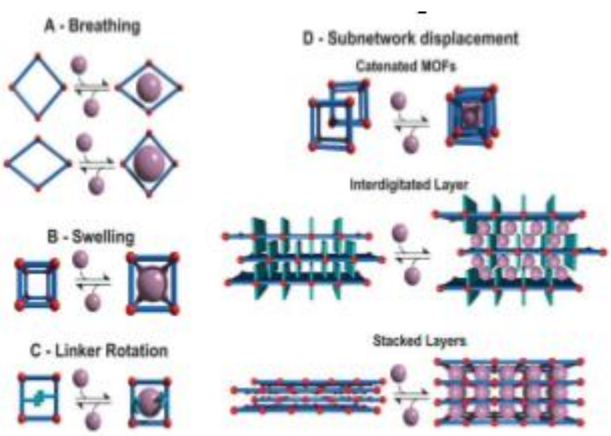

Figure 1.1Flexibility in the MOFs. Adapted from (Soni et al., 2020).

Open metal site: The presence of an exposed metal site can increase the performance of metal organic frameworks. Water improves the CO_2 collection capability of open metal site MOFs. A compound with an open metal site structure and paddlewheel units $Cu^2(COO)^-$ coupled through $(BTC)^3$ ligands shows a notable increase in CO_2 adsorption when 4.0% water by weight is added, as an example. This compound is HKUST-1$[(Cu)_3(btc)]$ (Liang et al., 2009).

Porous nature of the metal organic framework

In addition to a virtually infinite variety of possible configurations of ligands, MOFs offer an unprecedented degree of freedom in isoreticular manipulation while preserving structural design and topology invariant. The vast array of structural and functional changes can be easily retrieved either during or after synthesis (Eddaoudi et al., 2002).The high porosity of MOFs is one of its most notable qualities; it has led to their use in gas storage, catalysis, sensing, encapsulating biomolecules, drug administration, conductivity, and magnetism, among other applications. However, in the 1980s and 1990s, researchers began to think about the possibility of porosity in metal-organic materials with long structures. Kitagawa demonstrated that metal-organic polymers could absorb gas phase guest molecules and provided a description of gas adsorption isotherms at moderate temperature and high pressure (Kitagawa, 2014).

Yaghi reported the first metal-organic framework (MOF) with persistent porosity in 1998. The isotherms for nitrogen adsorption and desorption were measured at 77 K and low pressure. This method has been used previously to determine the initial values of the apparent surface area and pore volume in a MOF, as well as to probe the long-term porosity of other porous materials such zeolites, porous silica, in addition to porous carbon. Achieving increased porosity and stability in MOFs relies heavily on both the design and synthesis of MOFs and the development of better activation methods, which are essential for accessing their porosity (Senkovska and Kaskel, 2014). Not only do mesoporous MOFs have the highest known specific surface area and show off large adsorption volumes for tiny molecules, but they are also crucial solids for chromatography and liquid phase separation. Mesoporous MOFs are incredibly porous, but they also have a lot of cool stuff going for them, like crystallinity, elasticity, and the placement of functional groups is crystallographically well-defined. All of this makes it possible to tailor these materials to fulfill certain jobs. Despite the fact that organic linker solubility and synthesis are common constraints on large pore MOF synthesis, the process is notoriously difficult, time-consuming, expensive (noble metals like palladium are needed as catalysts), and yields modest reactions. Scaling up these MOFs is thus not an easy task. More investigation into "green" synthetic conditions is required, as the solvents normally employed in MOF synthesis are not user-friendly. The pores found in many MOFs allow them to accommodate a wide range of guest molecules, including gases and liquids. The mechanical behavior (e.g., compressibility) of the corresponding MOF can be significantly impacted by these guests, even if they are not part of the extended framework skeleton (Chapman et al., 2008, Bennett et al., 2010, Graham et al., 2012).

Methods for Production of MOFs

Diffusion Method

Slowly introducing new species into an existing community is the gold standard of the diffusion method: I One approach is the solvent liquid diffusion. The first step is to make a two-layer structure with different densities; one layer will hold the solvent that will precipitate, while the other will contain the product that will be dissolved. Keep in mind that a solvent layer separates them. At the contact, crystals form as the precipitant liquid slowly diffuses into the isolated sheet. (ii) The second method involves the use of physical barriers, specifically two vials of different sizes, to progressively diffuse the reactants. To prevent bulk material precipitation and slow diffusion, gels are also utilised as diffusion and crystallisation media. If the goods in question are not particularly soluble, the diffusion approach can be used to create single crystals thus replacing non- or poly-crystalline products (Abazari et al., 2019, Gao et al., 2019).

Electrochemical Method

The high temperatures needed and the high investment costs are the main drawbacks of solvothermal and microwave-assisted synthesis techniques. The production of MOF nanoparticles at room temperature utilising a changeable solvent is very desirable as a means to eliminate or at least reduce these difficulties. One such approach that uses electrical energy to create MOF micro crystals endlessly in 10–30 minutes is electrochemical synthesis, which does not involve metal ions. This process is fast, clean, and safe for the environment since water is a simple byproduct. Organic ligands and electrolytes are dissolved anodically in the electrochemical synthesis process (Boldrin et al., 2021). The electrochemical cell is prepared by inserting conducting salt and placing organic linkers at the cathode. A 5 mm thick copper plate and an organic linker, 1,3,5-benzenetricarboxylate (BTC), were used as anodes in an electrolytic cell to create Cu-based MOF composites. A bias voltage of 12-19 V was applied to induce an electric field across the electrodes. The formation of greenish blue MOFs was achieved via the reaction of Cu ions with BTC in the solvent, which released electrons to form Cu^{2+} cations due to the generated electric field. This possibility could be pursued in order to use MOF in gas processing for potential industrial uses in the future (Wang et al., 2020). An electrochemical method is used to manufacture MOF powders on a large scale in industry. In comparison to solvothermal synthesis, this approach has several benefits, such as a significantly shorter synthesis time, lower reaction temperatures, and the absence of anions such nitrates from metal salts. The bulk step crystallisation is limited by metal ion generation near the support surface, which is expected to decrease the accumulation of unfavorable crystals during membrane formation. The lower temperatures also seem to help with thermally-induced cracking during cooling (rather than solvothermal synthesis), which means it must be less noticeable (Boström et al., 2022, Asgari et al., 2021).

Mechanochemical Method

Mechanical disruption of intramolecular bonds precedes chemical change in mechanochemical synthesis. Mechanically triggered MOF synthesis is intriguing for a number of reasons. Consequently, the surroundings is a crucial factor. Particularly helpful when organic solvents are not an option is the ability to conduct reactions at room temperature without the use of solvents. Reaction times range from 10 to 16 minutes, and small component products can be made with quantitative yields (Safaei et al., 2019, D'Amato et al., 2021). In addition, metal oxides, when utilized as a starting material, produce water as a single byproduct; this water can then be used in place of metal salts in certain cases. However, because of their poor solubility, metal oxides are seldom utilized in processes that rely on solvents. Chemical reactants that have low melting points and hydrated metal salts, especially those that contain important anions, seem to be appropriate. Consequently, compounds with good crystallinity were obtained by means of metal acetates or carbonates. Thus, acetic acid is known to be a pore byproduct, but it may be readily removed by heat activation (Štrukil et al., 2010). One method that has proven to be quite beneficial is liquid-assisted grinding (LAG), which involves adding small volumes of solvents. This method may enhance the molecular mobility of the reactants, which in turn accelerates mechanochemical reactions. Concurrently, the liquid can exhibit features that direct the structure. We have now shown that ions and solvents have a structure-directing influence by expanding the technology to ion- and liquid-assisted grinding (ILAG) for the selective manufacture of pillared-layered MOFs (Safaei et al., 2019). We additionally employed green synthesis in the mechanochemical approach. In industrialized chemical manufacturing, MOFs are most notably needed for green synthesis. Therefore, mechanochemical grinding could supplant conventional solvent-intensive procedures, which normally involve grinding solid reagents at ambient temperature in an environment with no or very little solvent. An additional goal of the modern MOF building era is to lessen the impact on the environment in terms of energy usage, pollution, and safety. When compared to conventional solvent-based approaches, mechanochemical synthesis offers a more straightforward and competitive approach to the large-scale production of MOFs.

Microwave assisted Synthesis

MOFs, which are crystalline solids composed of metal ions and bridging organic ligands ("linkers"), have lately attracted a lot of interest due to their high and modifiable inner surface. Research on MOFs has focused on their possible use in catalysis.,(Maurin et al., 2017) sensing, gas separation, and storage, drug delivery, cyclic adsorption processes,(Lustig et al., 2017), and many other fields. The characteristics of metal-organic frameworks (MOFs) can be tuned by adjusting the metal and linker used to create them (Adil et al., 2017). Nevertheless, MOF preparedness still faces a number of significant obstacles: more efficient and environmentally friendly purification and activation processes as well as speedier, larger-scale synthesis (Waitschat et al., 2018). Reinsch has said that the availability of MOFs will always be constrained by the sustainability of the synthesis process. Hydrofluoric acid (HF) and other acidic modulators, as well as solvo-hydrothermal conditions, seem to be energy and time hogs. In contrast to mechanochemical, supercritical, and continuous-flow approaches are well-established in MOF synthesis, but there is still a lot of room for improvement in terms of improving synthetic techniques. To address energy-related concerns and further decrease environmental impacts, we opted for dry-gel conversion (DGC) as a solvent-saving synthesis method for MOFs. This approach allowed us to generate materials with optimized performance and reduced negative consequences. Despite their widespread use in synthetic chemistry, microwave-assisted syntheses are still in their infancy when it comes to MOF syntheses, but they have the potential to significantly reduce energy and time requirements. (Tan and Souza, 2020) The reaction mixture absorbs the microwave energy, which causes it to heat up instead of the vessel, as happens with conductive heating. This is in contrast to microwave radiation. The outcome is localised superheating that can achieve the targeted temperatures in a matter of seconds thanks to its incredibly effective heating rates according to Tannert et al. (2018). Although the idea originated from zeolite synthesis, as far as we are aware, no report has been published on the microwave-assisted DGC manufacture of MOFs (Lee et al., 2017).

Post synthetic charge in already formed MOFs

In a 2019 study, Zimmerle et al. had shows that in the previous ten years, Fe-MOFs have been mass-produced once their industrial significance was identified. Since its inception, the solvothermal synthesis process has been the go-to for synthesizing Fe-MOFs because of its convenience of use, rapid effects, and straightforward operation, as reported in the literature.

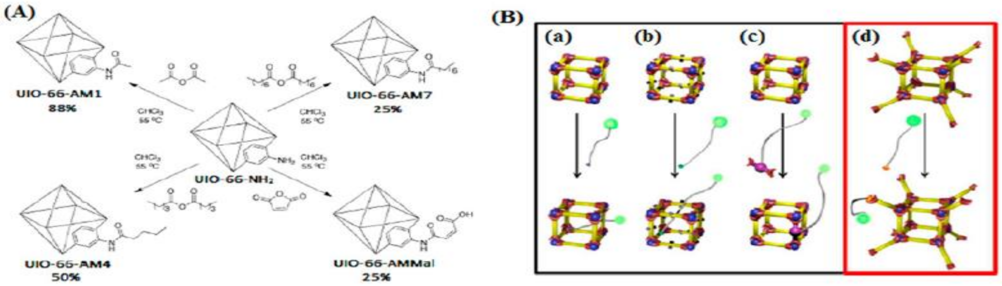

Figure 1.2 Different types of MOFs. Adapted from(Zhang et al., 2021)

Solvo thermal method

One common way to produce MOFs is through solvothermal synthesis. Research by Dadashi et al. (2022) and Li et al. (2020a) Here, the solvents, metal salts, and ligands are combined in a precise proportion before being placed in an autoclave to undergo a self-assembly reaction. Synthetic reactions and crystal formation are both aided by the acceleration of the reaction rate and the increase in solubility of insoluble or poorly soluble reactants at high temperatures and pressures. The 80 to 250 °C temperature range is utilized in solvothermal synthesis due of the MOF crystals' modest temperature sensitivity. When building MOFs, the synthesis conditions are crucial. Isoreticular Fe-MOFs were synthesized by Bauer et al. using a high-throughput approach. Source: Dadashi et al., 2022. The development of MOF structures is heavily influenced by the reaction solvent Iron trimer is also more stable in dimethylformamide (DMF) than in acetonitrile, methanol, or water. Nevertheless, there are a few downsides to this process. The synthesis period is quite extensive, and there are tight requirements for high temperature and pressure. Additionally, there is a risk of auxiliary reagent toxicity. Since the metal nodes are notoriously difficult to manipulate during synthesis, manipulating the MOF's structure is an even bigger challenge. Organic solvents show strong interactions that impact product structure assembly due to their diverse functional groups, polarity, and characteristics. The source is Zhang et al. (2021). Although During synthesis, it is important to think about the reactants' and solvents' thermal stability and the products' decomposition temperature.

Sonochemical method

Applying high-energy ultrasound to a reaction mixture is what sonochemistry is all about. Ultrasound uses mechanical vibrations at a frequency of 10 MHz, which falls between 20 kHz and the highest audible frequency for humans. Cavitation can be enhanced by deploying micro jets that can activate, clean, and corrode any solid surfaces in the vicinity. The dispersal of aggregates of smaller particles is another phenomenon. Under extreme circumstances, chemical reactions in a homogeneous liquid can occur in the cavity; under intermediate conditions, at the interface; and under strong shear forces, in the bulk medium. Intense shear pressures and harsh environments can set molecules in an excited state, break bonds, and produce radicals (for more on this, see mechanochemistry). At the same time, ultrasonication can help the first compounds dissolve better. A variety of sonochemistry techniques are employed in the production of organic and nano materials. Creating a process that is fast, safe for the environment, efficient with energy, easy to use, and can be done at room temperature is the primary objective of sonochemical synthesis in MOF research. Since scaling up happens through rapid reactions, MOFs are being used with special interest for the future (Safaei et al., 2019, Wang et al., 2019b). A wide range of methods, a multitude of components, and adjustable process settings have all contributed to the creation of thousands of MOF materials.

Applications of metal organic framework

Drug delivery system

By incorporating around 36.4% by weight of the anticancer medication 5-Fu into the activated functionalized MOF, promising drug delivery results were achieved, resulting in the regulated and gradual release of the drug in phosphate buffer saline at two different pH levels. Here, we demonstrate that 5-Fu@1a exhibited clear anticancer activity by demonstrating cytotoxicity towards human liver cancer cells HCC using the MTT assay (Sun et al., 2019b).An extremely durable and water-resistant microporous metal-organic framework (1), $[Zn_8(O)_2(CDDB)_6(DMF)_4(H_2O)]$ An open N-H site (Fig. 2) was used to synthesis CDDB, which stands for 4,4'-(9-H carbazole-3,6-diyl)dibenzoic acid. Curiously, it showed a remarkable loading capacity (about 53.3 wt%) and adequate release capability (64.9% and 81.9% for 5fluorouracil), resulting in absolutely no cytotoxicity (Bag et al., 2016). Guo et al. created a porous metal-organic framework (MOF) based on Dy(III) using solvothermal synthesis. The structure is $[Dy(HABA)(ABA)](DMA)_4]$ (1, H_2ABA = 4,4'-azanediyldibenzoic acid, DMA = N,Ndimethylacetamide) and it has open N donor sites. A bent polycarboxylic acid linker made the fabrication process possible. The anticancer agent 5-Fu was loaded into functionalized 1D channels with the correct window size using the activated 1. It exhibited a high drug loading and drug-release behavior that was dependent on pH . The MTT experiment further verified that this drug/MOF combo exhibited anticancer efficacy against the MG63 human osteosarcoma cell lines (Guo et al., 2019). The 2D tunnels and empty face centered cubic cubes of Cu-MOF porous were loaded with ibuprofen by Javanbakht et al. through immersion in the drug solution. They introduce the Cu-Based metal organic framework/ibuprofen nanohybrid (CuMOF/IBU), which is pH-sensitive and protected by biopolymeric gelatin microspheres. Furthermore, gelatin was used to encase the Cu-MOF/IBU microsphere (CuMOF/IBU@GM). The Cu-MOF/IBU@GM showed minimal toxicity to $CaCO^{-2}$ cells in the MTT assay (Javanbakht et al., 2019).

Adsorption in aqua solutions

Due to its simplicity, lack of complexity, practicality, and low cost, as well as the utilization of a wide range of recoverable adsorbents, adsorption is an intriguing technique. Various living and non-living pollutants can be removed from water systems using this technology. Organic ligands and metal ions come together in MOFs, a novel hybrid crystal material. Porous, adaptable, structurally flexible, and photonic, MOFs also possess features with an extraordinarily high bearing capacity. Because of these characteristics, MOFs have several potential uses and a leg up in the field of molecular identification and separation. The large specific surface area and high adsorption capacity of MOF have drawn the attention of researchers. The effects of MOFs and other chemicals on people and the environment are outside the scope of this essay (Bag et al., 2020).

Biological compounds

A composite of magnetic metal and biological frameworks was made by Pan et al. using the self-assembly method. The adsorbent made of the produced material demonstrated remarkable improvement potential for glufosinate, bialaphos, and glyphosate. Based on these features, we devised a technology that combines high resolution, extremely high efficiency liquid chromatography with magnetic solid-phase extraction for processing and identifying five target mixes in environmental fluids. All three primary glyphosate metabolites aminomethylphosphonic acid, 3-methylphosphinicopropionic acid, and bialaphos were precisely and concurrently detected in natural water samples, with recovery rates ranging from 86.2% to 104.6% and relative standard deviations below 10%. We achieved the desired linearity, and five of the target analytes were within the range of 1.0-100.0 mg/L (Pan et al., 2019).

Following the suggestion of Wang et al., five isomorphic MOFs were successfully synthesized by functionally altering UMCM-151. These MOFs belong to diverse application groups and are displayed in Figure 1.3.

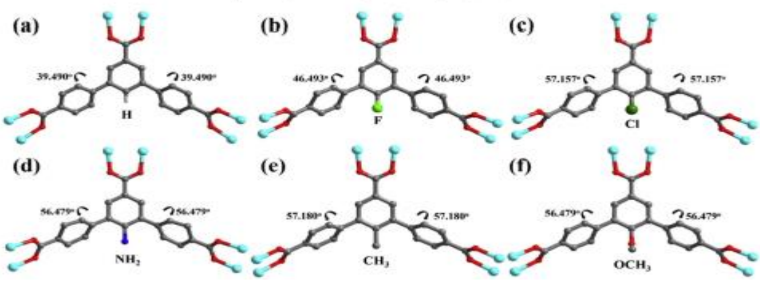

Figure 1.3. Isomorphic MOFs. Adapted from(Wang et al., 2019).

X. He and his colleagues created MG@MIL-100-B nanoparticles by adding polymeric mesopores to MOFs using the straightforward MLFC method. A team of specialists utilized MG@MIL100-B composites to isolate adrenaline, dopamine, and non-adrenaline from rat plasma. The circumstances for removal were improved by the analyzed extraction of the characteristics of the solid phase. The adrenaline and dopamine identification thresholds (S/N = 3) were predicted .On a daily basis, the accuracy ranged from 2.84 to 6.63% and from 5.70 to 11.44% (N = 6). The results of the confounding tests were positive, ranging from 94.40% to 109.51%. This approach is a novel sample pre-treatment procedure for both academic research and therapeutic therapy (He et al., 2018).

Antibiotics

Zeolite Imidazole Framework-8 (ZIF-8) was tested by Li et al. to determine its capacity to extract oxytetracycline hydrochloride and tetracycline, two widely used medications. Using ZIF-8 simultaneously eliminated 83% of OTC and 91% of TC according to their findings. The most effective adsorbents were tetracycline (312.5 mg g1) and oxytetracycline hydrochloride (303.0 mg g1). At 303 K, the Langmuir adsorption model was optimal for tetracycline (R2=0.963) and oxytetracycline hydrochloride (R2=0.981), two drugs with persistent pseudo-second-order kinetics(Li et al., 2018).

Toxic pollution

For their investigation, forgan et al. synthesized graphene oxide (GO)-MIL-53(Al) nanoparticles and tested their ability to remove arsenic (As(III)), a commonly found pollutant in groundwater. Batch testing was used to assess the kinetics and isotherm behavior of MIL-53(Al)-GO nanocomposites as they adsorbed As (III) in a water solution under different environmental conditions. Various factors were examined in relation to As (III) adsorption, including temperature (298-318 K), starting concentrations (10-110 mg/L), pH of the solution (2-11), and adsorbent dosage (0.2-3.0 g/L). Improved As (III) removal was achieved in MIL-53(Al)-GO nanoparticles with a 3% GO ratio and a retention capability of 65 mg/g (Forgan, 2020). Tian et al. suggested a complicated case with channels of carboxylic O^2 porous structure for the effective extraction of uranium (VI) from water. Using adeninate and 4, 40-biphenyldicarboxylate (BPDC2) ligands, a three-dimensional JXNU-4 zinc-MOF was used to collect U (VI). One thing to keep in mind is that JXNU-4 acts like the U (VI) sorption model described by Langmuir (Tian et al., 2020). A water-stable Zr-CAU-24 was used to achieve sensitive aflatoxin B1 recognition, as suggested by Li et al. Eight carboxylate groups form a cluster with a concentrated orthorhombic structure ([Zr6 (œ3-O)4(μ3- OH)4] 12+). The clusters enhance the SCU architecture by increasing the number of bridging TCPB-4 linkers, which creates rhombic channels with diameters of approximately 5.3 × 10.5 Å and 2.4 × 3.5 Å. With this porous nanomaterial, aflatoxin B1 can be detected down to 64 nm. Aflatoxin B1 was directly applied to spiked almond and walnut beverages using the manufactured waters table LMOF. The high recovery rates (91-108%), achieved in just five minutes (Li et al., 2018).

Scientists Ullah et al. used a Zr (BTC), a highly porous MOF, to adsorb benzothiophene from fuel liquids. Recent reports on adsorbents show that Zr(BTC) has a maximum anticipated adsorption capacity of 238 mg.g1 and HPW (1.5)/Zr(BTC) has a capacity of 290 mg.g1. Further confirmation of the adsorption results was provided by density-functional theory (DFT) calculations, which showed that benzothiophene could be successfully adsorbed After the adsorbents were renewed, a large number of adsorption sites were recorded (Ullah et al., 2019).

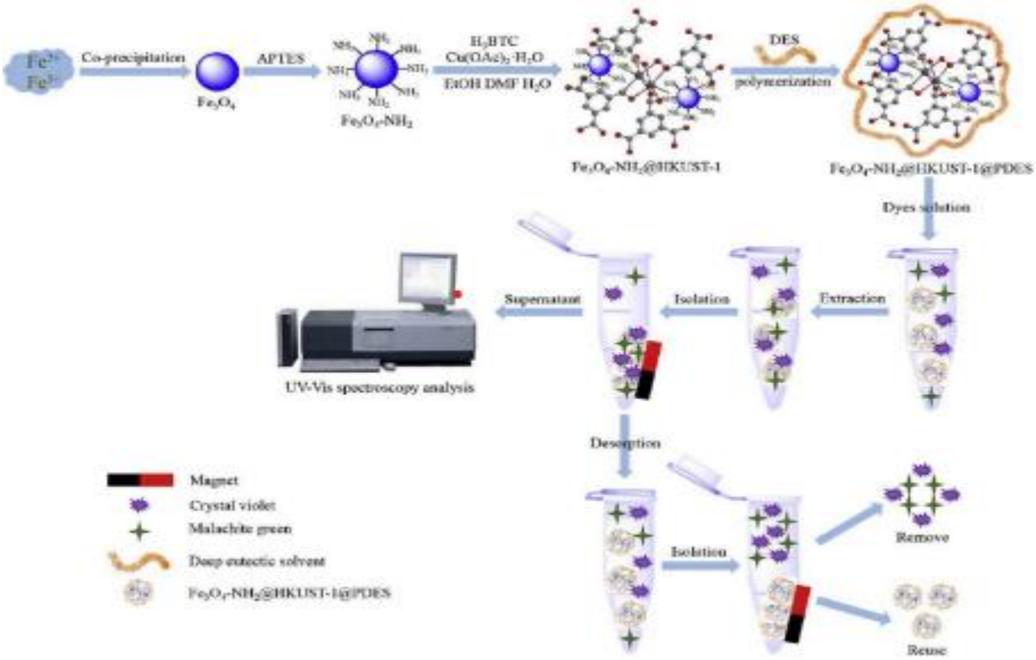

Figure 1.4 Fabrication of Fe_3O_4-NH_2@HKUST-1@PDES composites and its application (Figure was reproduced from (Van Tran et al., 2019)

The Dowson-type polyoxometalate@MIL-101(Cr) metal-organic framework (P2W18@MIL-101(Cr)) nanohybrid, with a surface area of 1167.4 m2 g-1, was created by Jarrah and Farhadi. A novel adsorbent called P2W18@MIL-101(Cr) was used to remove organic dyes from water-based solutions. This compound was effective in treating harmful organic pollutants found in the colored wastewater (Jarrah and Farhadi, 2019). The three-dimensional anionic metal-organic framework: [(CH_3)2NH2][Zn_6 (m3-OH) (m4-O) (NSBPDC) 5(H_2O) 2] developed by Cui and colleagues. DMF.12H_2O_n (Zn^{-1}), A, 6-nitro-2,20-sulfone-4,40-dicarboxylic acid etc. Even cationic dyes can be efficiently and selectively absorbed. Studying the kinetics of the methylene blue adsorption process reveals how closely it follows the pseudo second-order model. Furthermore, in a saturated DMF/ethanol solution of LiNO3, not only was the Zn-1 material recoverable, but the deposited color methylene blue could be liberated as well(Cui et al., 2019)(Li et al., 2020). A metal-organic framework (MOF) based on manganese (II), selectively absorbs Congo red from water. Furthermore, it was found that 1 has a maximum adsorption capacity of 1393 mg g1 and can be adequately increased(Tian et al., 2020).

Objective of the study

1. To synthesize zinc oxide nanoparticles
2. To synthesize composite of zinc oxide with zinc based MOF
3. To evaluate the enzyme inhibition of synthesized MOF composite

Experimental work

chemicals used in the study

All the chemicals used in the study were of analytical grade and used without further purification. The zinc acetate was purchased from Merck, Germany. The Benzene tricarboxylic acid (BTC), sodium hydroxide (NaOH), dimethylformamide (DMF),and ethanol was purchased from sigma Aldrich. The distilled water was buyed from local chemical laboratory. The glass wares was provided by the department of chemistry Abdul Wali Khan University Mardan.

Synthesis of zinc oxide nanoparticles

The co-precipitation approach has been used to generate ZnO NPs. Two 0.1 molar solutions of zinc (ac_2) were first produced. ($2H_2O$) and 0.2 molar of NaOH by dissolving them in deionized water. We proceeded to combine the two solutions in a single beaker and stirred them at 750 rpm for two hours at 60 ºC. The formerly clear fluid turned white and milky after 2 hours. After 2 minutes of centrifugation at 4500 rpm, a white precipitate was obtained. After that, the precipitate was rinsed with acetone and de-ionized water. The product was dried in a laboratory conventional oven at 75 ºC for 6 hours to obtain ZnO NPs in powder form (Adam et al., 2018).

Synthesis of Zn-BTC metal organic framework

In a beaker, 25 mL of DMF was used to dissolve 2.5 mmol of zinc nitrate and 2.5 mmol of TMA. After that, a watch glass was placed over the beaker and placed it in the middle of the plate of the microwave oven. A power level of 80 W was chosen for the microwave. Synthesis took place at the hour mark. We then let the beaker cool down at ambient temperature for 30 minutes, washed the precipitate multiple times with DMF, and set it aside in the dissector for further examination (da Silva et al., 2016).

Synthesis of zinc incorporated zinc based metal organic framework

In order to create ZnO-MOF nanoparticles, a 70 KW Uv lamp was used for a reaction duration of 60 minutes. The first step was to make a solution of MOF dissolved in twenty milliliters of ethanol, and the other solution was of ZnO (50 mg) dissolved in twenty milliliters of deionized water. The resulting mixtures were then subjected to sonication for 60 minutes at room temperature. The mixes were allowed to sit for 12 hours after the Uv light step in order to get brown precipitates. After 24 hours in an oven set at 35 °C, the precipitates were removed (Firouzjaei et al., 2018).

Alpha-Amylase Inhibition Assay

An alpha-amylase inhibition methodology outlined in the literature was used to evaluate the produced complexes (Palmer and Bonner, 2007). I pre-incubated a 96-well plate with 10µL of Alpha-amylase, 20µL of the test chemical mixtures in varying concentrations, and 100 mM of phosphate buffer (pH = 6.8) for 20 minutes at 37°C. As a foundation, 20µL of a solution containing 1% soluble starch in 100 mM phosphate buffer was introduced. A 30-minute incubation period was thereafter repeated at 37°C. Following a 10-minute heating, 100µL of the DNS color reagent was added. The absorbance of the final combination was measured at 540 nanometers. A variety of concentrations of acarbose were utilized as standards.

Alpha-Glucosidase inhibition Assay

According to Rouzbehan et al. (2017), a methodology that was modified was utilized to determine the inhibitory activity of alpha-glucosidase. Each of the 96 wells in this experiment retained 210µL of total volume. In each well, there was 210µL of reaction media, which consisted of 20µL of sample mixture that had been diluted with DMSO, 20µL of Alpha-glucosidase solution, 130µL of PBS, and 40µL of the substrate, p-Nitrophenyl alpha D glucopyranoside. Each sample is diluted 5 times in DMSO by 20µL in a serial fashion. Afterwards, the alpha-glucosidase enzyme and 130µL of phosphate buffer (pH 6.8) were introduced. The mixture was left to incubate at 37°C for 15 minutes. Using an Elx 800 Reader, the absorption was measured at 405 nm.

Statistics of the data

Results were expressed as the alpha-glucosidase inhibitory assay's IC50 value. Using a non-regression methodology that took into account both the average inhibitory value and a graph showing percent inhibition against log inhibitor concentration, we were able to calculate the IC50 value. Acarbose was the reference that was used. Three repetitions of each test were performed.

Result and Discussion

SEM Images of ZnO and Zinc incorporated MOFs

The SEM images of ZnO and Zinc incorporated MOFs are offered in Figure 4.1 (a and b). The image of ZnO displayed that the surface is irregular, round and agglomerated. The size of the ZnO particles was determined using image j software and found to be in the range of 60 to 80 nm. The image of Zinc incorporated MOFs (Figure 4.1a) showed that the surface is irregular, porous, and round. The size of the Zinc incorporated MOFs Figure 4.1b) particles was determined using image j software and found to be in the range of 90 to 110 nm.

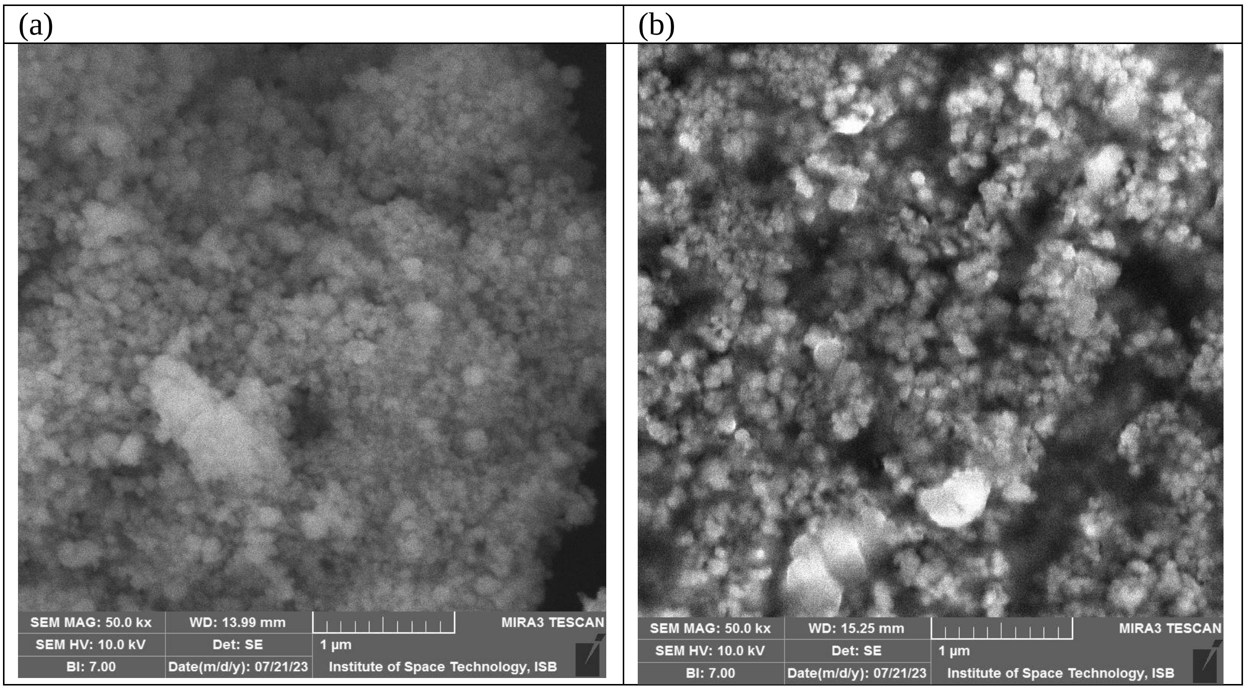

Figure 4.1. SEM images of synthesized zinc oxide nanoparticles and zinc based MOFs

EDX Spectrum of Zinc incorporated MOFs

The elemental composition of the synthesized ZnO and Zinc incorporated MOFs was established by EDX. In Figure 4.2, the EDX is showed. The existence of oxygen and carbon shows that organic ligands is present. The EDX spectrum clearly showed that ZnO are encapsulated in the MOF. Table 4.1 EDX spectrum of zinc incorporated metal organic framework.

Table : 4.1 EDX spectrum of Zinc incorporated MOFs

Element	Weight%	Atomic%
C K	40.91	58.84
O K	30.03	32.43

Al K	1.11	0.71
Si K	1.82	1.12
Zn L	26.12	6.90

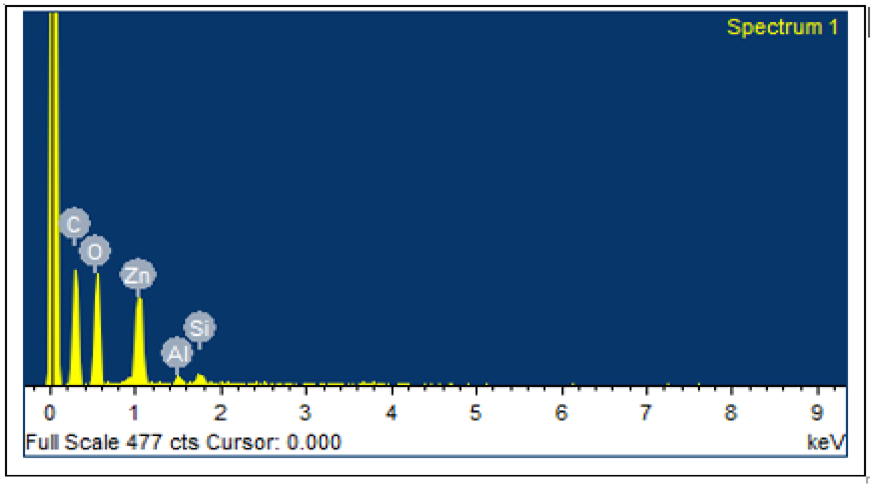

Figure 4.2 EDX of the synthesize zinc based metal organic framework

Enzyme inhibition activity of synthesized composite

Alpha-Amylase inhibition activity

At various doses, Figure 4.3 shows how effective the ZnO and Zinc incorporated MOFs are at inhibiting alpha-amylase. Table 4.2 provides the IC50 values. The results show that as the concentrations of the samples increases, so does their ability to block alpha-amylase increases.

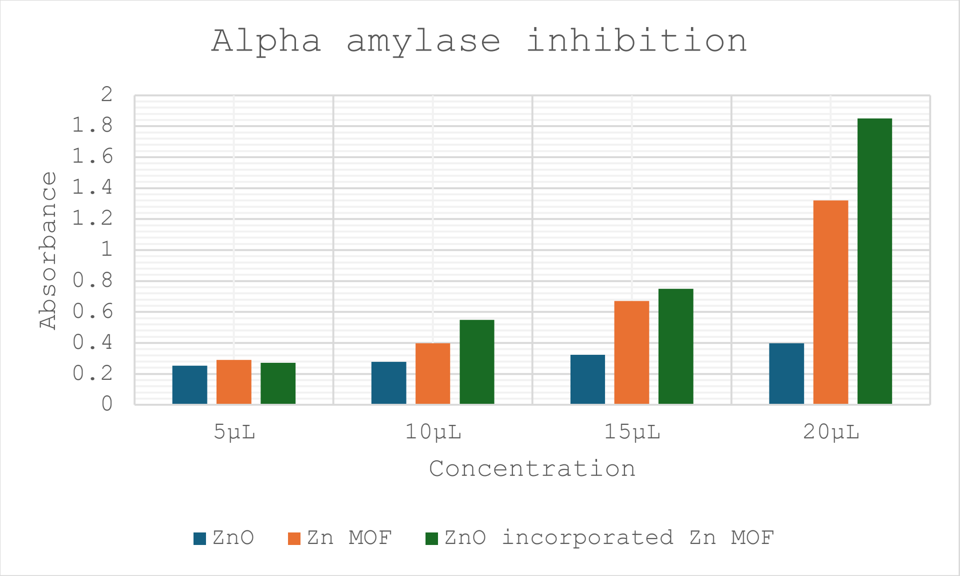

Figure 4.3: Alpha-Amylase inhibition activity

Table 4.2 IC_{50} values of ZnO, Zn MOF and ZnO incorporated Zn MOF

Materials	IC_{50} ± SEM
ZnO	7.01 ±0.064

Zn MOF	8.06± 0.054
ZnO incorporated Zn MOF	5.89± 0.083

Alpha-Glucosidase inhibition activity

Various concentrations (5-20 uL) were used to assess the efficacy of the produced ZnO, Zn MOF and ZnO based Zn MOF in inhibiting alpha glucosidase. Inhibitory activity of materials increases with increasing sample concentration, according to the results. Table 4.3 contains the IC50 values, and Figure 4.4 shows the activity of samples in inhibiting Alpha-Glucosidase.

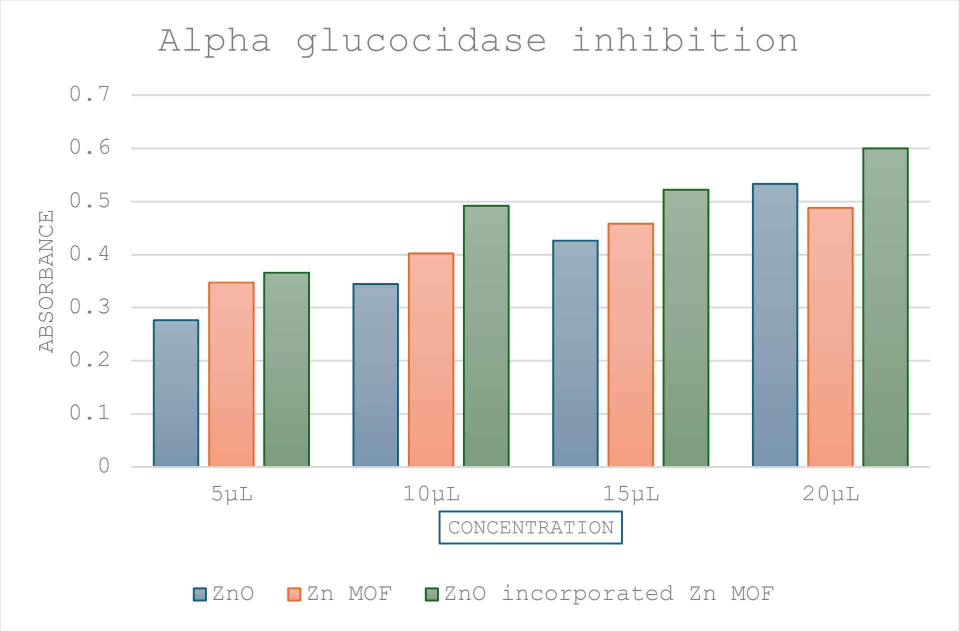

Figure 4.4: Alpha-Glucosidase inhibition activity.

Table 4.3 IC_{50} values of ZnO, Zn MOF and ZnO incorporated Zn MOF

Materials	IC_{50} ± SEM
ZnO	11.06 ±0.053
Zn MOF	8.02± 0.045
ZnO incorporated Zn MOF	10.87± 0.087

Conclusion

The composite of metal organic framework have gained much attention in the biological field due to their porous nature and enhance biological activity, In the first step of the current study, zinc oxide nanoparticles was prepared and in the second step zinc based carboxylic acid metal organic framework (Zn-BTC) was prepared using precipitation method successfully. At the last step the zinc oxide nanoparticles have been incorporated into zinc based carboxylic acid metal organic framework (Zn-BTC) using UV irradiation method. The synthesized samples was characterized using Scanning electron microscopy and elemental dispersive x-ray and then the samples was used for the inhibition of alpha amylase and alpha glucosidase enzymes and compared the samples activity and it was found **that for both alpha amylase and alpha glucosidase enzymes the zinc oxide incorporated Zn-BTC showed better activity than ZnO, Zn-BTC.**

The IC_{50} values for ZnO, Zn-BTC and zinc oxide incorporated Zn-BTC for alpha amylase was found to be 7.01 ±0.064, 8.06± 0.054 and 5.89± 0.083, respectively. Further **The IC_{50} values for ZnO, Zn-BTC and zinc oxide incorporated Zn-BTC for alpha glucosidase was found to be**11.06 ±0.053, 8.02± 0.045 and 10.87± 0.087, respectively.

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