

PROJECT REPORT

On

**Zn AND Fe BASED METAL ORGANIC FRAMEWORK AND THEIR
GRAPHENE HYBRIDS FOR WATER PURIFICATION**

Submitted by
KRISHNENDU L (AM20CHE010)

*In partial fulfillment for the award of the
Master's Degree in Chemistry*



**DEPARTMENT OF CHEMISTRY
AND
CENTRE FOR RESEARCH**

**ST. TERESA'S COLLEGE (AUTONOMOUS)
ERNAKULAM
2021-2022**

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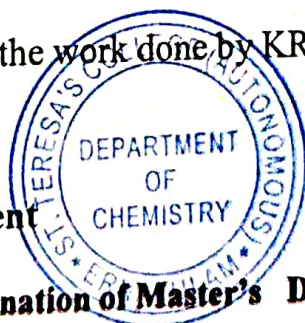


M.Sc. CHEMISTRY PROJECT REPORT

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This is to certify that the project "Zn AND Fe BASED METAL ORGANIC FRAMEWORK AND THEIR GRAPHENEHYBRIDS FOR WATER PURIFICATION" is the work done by KRISHNENDU L.

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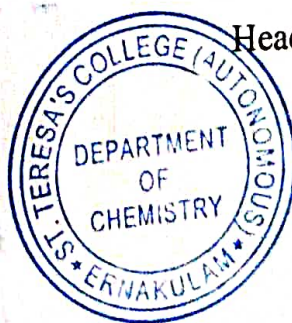


CERTIFICATE

This is to certify that the project work entitled "**Zn AND Fe BASED METAL ORGANIC FRAMEWORK AND THEIR GRAPHENEHYBRIDS FOR WATER PURIFICATION**" is the work done by **KRISHNENDU L** under the guidance of **Dr. NISHA T. P.**, Assistant Professor, Department of **Chemistry and Centre for Research, St. Teresa's College, Ernakulam** in partial fulfillment of the award of the Degree of Master of Science in Chemistry at **St. Teresa's College, Ernakulam** affiliated to **Mahatma Gandhi University, Kottayam.**

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ABSTRACT

In this era of rapid industrialization and urbanization, the world is amidst fresh water scarcity. The improper disposal of waste in water systems has intensified water depletion and extensively impacted developing countries like India. Organic wastes, particularly industrial dyes, are a significant source of polluting lakes and water resources. Most of these dyes are carcinogenic and mutagenic, adversely affecting aquatic life and the ecosystem. Among various sustainable methods employed for water purification, adsorption technology is highly desirable due to its ease of operation and economic compatibility. Among different adsorbents, metal-organic frameworks are materials of broad interest these days, mainly because of their high surface area, tuneable pore size, abundant adsorption sites, favorable adsorption kinetics, reusability, and good thermal stability. MOFs are materials consisting of metal centres that form the inorganic blocks to form a textured structure using organic linkers as binders. Besides, graphene is a promising candidate for dye adsorption due to its high surface area $2630 \text{ m}^2 \text{ g}^{-1}$, and its π - π conjugation with defect centres acts as good adsorption sites.⁴ In this work, we have synthesized graphene hybrids of Zn- and Fe-based MOFs and have studied their dye adsorption properties. While hydrothermal methods were adopted for the synthesis of Fe-MOF and its graphene hybrid, co-precipitation methods were used for Zn-MOF and Zn-MOF/rGO. A modified Hummer's method synthesized the intermediate GO (graphene oxide) for graphene hybrids. XRD, FTIR, and TEM

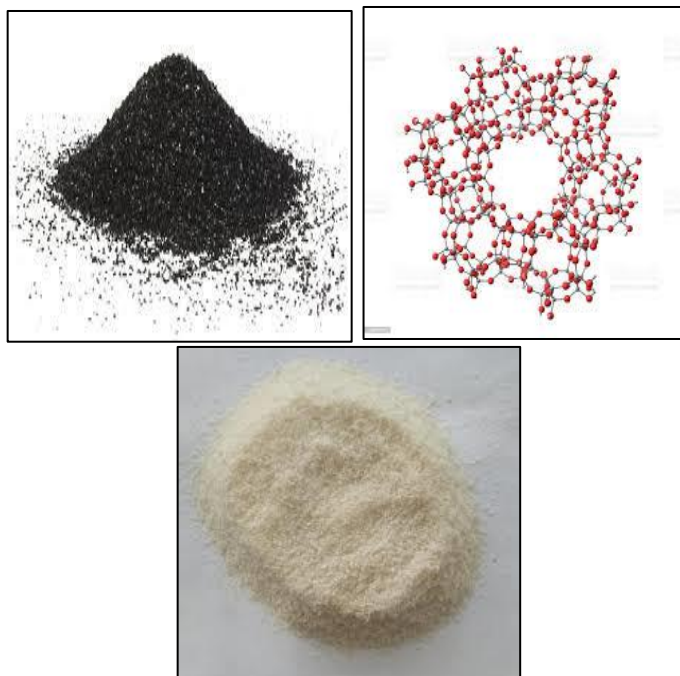
characterized the different synthesized samples. Fe-MOF/rGO and Zn-MOF/rGO, and their parent samples, were finally employed as adsorbents to adsorb organic dyes selected between different cationic, anionic, and carcinogenic dyes such as methylene blue, methyl orange, Congo red, and Rose Bengal. The MOF/rGO hybrids exhibited fairly good adsorption towards dyes than their parent MOFs. Moreover, the kinetic study on adsorption of dye solutions revealed that they follow pseudo-first-order kinetics and that the Fe-MOF/rGO hybrid had a greater adsorption capability among different samples.

Keywords: MOFs, rGO hybrid, dye adsorption, water purification.

CHAPTER 1

INTRODUCTION

The world is in the midst of scarcity of drinking water which is bound to have an impact on developing countries like India.^[1] Now a days population and thereby the demand of water has been increased. The supply of water can be increased with secondary sources of water which mainly comprises of waste water treatment.^[2] Waste water reclamation is advantageous not only in barren fields but also in cities and contaminated areas. Recycled water provides a cost-efficient supply of water that decreases the demand of fresh water and is also good for environment. One of the major pollutants in waste water that mostly discharged from industries are dyes.^[3] Dyes are used in various industrial sectors ranging from pulp and paper industries and textiles to food and pharmaceuticals. Industrial dyes are a major source of pollution of lakes and water resources. Now a days people have been developed many alternatives to prevent the contamination of water by dyes due to their highly visible color and persistence.^[4] Various methods such as physical, chemical, biological have been developed for the removal of dye molecules from industrial effluents. But these methods require sophisticated systems and are not economically practicable. Hence search for low cost and environmentally friendly waste water treatment materials and methods without the generation of hazardous by products has been started. So, such an efficient, cheap, and safe method used for waste water treatment is adsorption. Commonly used adsorbents are activated carbon, zeolites, chitosan, clay minerals etc.



Activated carbon

Zeolites

Chitosan

Figure 1.1: Commonly used adsorbents

The adsorption removal of dyes from waste water is not only important for us but also for the maintenance of ecosystem. A new class of materials which can be also used for adsorption are called metal organic framework.

1.1 METAL ORGANIC FRAMEWORK

Metal organic framework have emerged as a new category of materials that are made up of combining a metal ion or cluster with an organic ligand often called linker to form one-, two- or three-dimensional network structure.^[5] They are

crystalline hybrid with high surface area and tunable pore size. The selectivity of pore size and shape depends upon the nature of linker used.^[6] They show properties similar to that of zeolites. But the unique properties such as large surface area, large pore volume, stability, ability to get functionalized make them more advantageous than commonly used adsorbents such as zeolites, chitosan, silica gel etc.

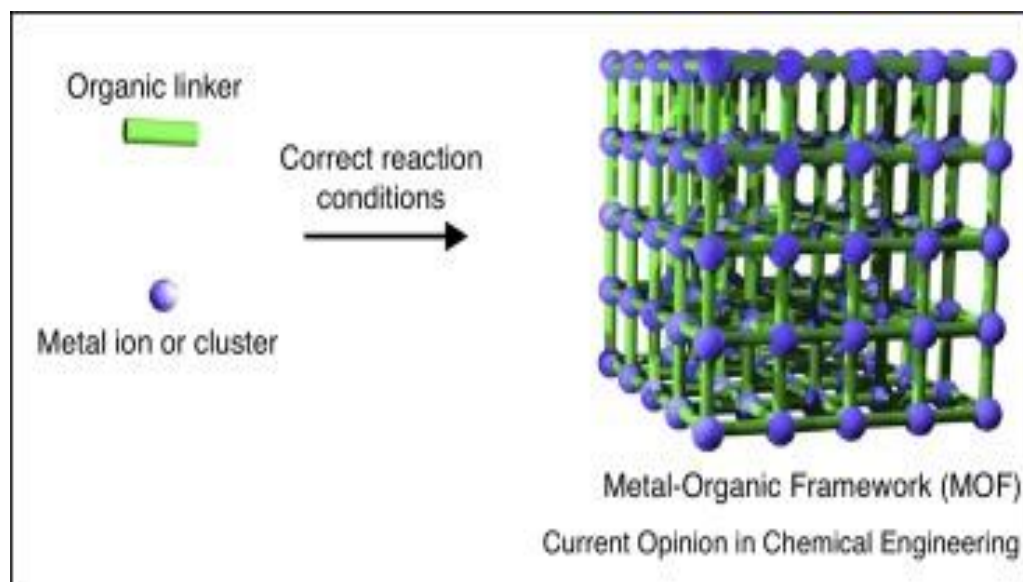


Figure 1.2: diagrammatic sketch of a typical metal organic framework

Eg: MOF-5 : formed from zinc acetate and terephthalic acid through covalent bond



Figure1.3: Structure of Zn MOF(MOF-5)

They can be prepared by different methods such as Hydrothermal, ultrasonic and microwave assisted organic synthesis, electrochemical processing,

mechanochemical processing etc.^[7] They are having wide range of applications such as separation and purification of gases, hydrogen storage, drug delivery, water purification, in catalysis, as supercapacitors, as sensors and also in pharmaceutical field.

1.2 APPLICATIONS OF METAL ORGANIC FRAMEWORK

Metal-organic frameworks (MOFs) are organic-inorganic crystalline hybrid material that consist of a regular array of positively charged metal ions surrounded by organic ligand molecules.^[8]

1.2.1 Separation and purification of gases by metal organic framework

Separation and purification of gases are important for gas production and for processes such as air and water purification, electronics, food industry, and power plants where high purity gases are required. Metal organic frameworks have some unique properties such as high surface area, tunable pore size, high adsorption capacity, favorable adsorption kinetics, regenerability and good thermal stability are that make them suitable for gas separation and purification in a cost effective and environment friendly way. Adsorption is very important in the field of chemical and petrochemical industry especially for processes such as Feedstock separation, Bulk chemical synthesis, Gas purification in loop systems, off-gas cleaning etc. Commonly used adsorbents are activated charcoal, clay minerals, silica gel, zeolites etc. MOF exhibits two main

differences with respect to commonly used adsorbents. First is the framework flexibility and the second one is the fine tunability of pore size. When MOFs are subjected to a feedstock composed of mixture of gases it will adsorb those gases that have high absorptivity and the resultant mixture composed of weakly adsorbed gases. Adsorption capacity depends on nature of adsorbent and relative composition of mixture.

Selective adsorption of CO₂ in particular ambient temperature and pressure from industrial emission is still challenging because it contains other gases such as N₂, CH₄ etc. MOFs can be used for the selective adsorption of CO₂ from CO₂-CH₄ mixture, CO₂-N₂ mixture as they show almost no CH₄ and N₂ uptake because their kinetic diameters are larger than effective channel size of these compounds. One of the most significantly important but energy demanding processes in the petrochemical industry is the separation and purification of light hydrocarbon mixtures.

1.2.2 Metal organic framework in drug delivery

Metal organic framework are widely used in pharmaceutical field. MOFs are materials composed of metal ions/clusters connected with organic linkers to form a network structure. Due to the porous structure MOFs can take up or release substances from their pores. The unique properties of MOFs such as tunable pore size, large surface area, ability to get functionalized etc. make them good for applications in pharmaceutical field, in which we can deliver drugs to a specific area in the body also within a specific period of time.^[9] Moreover MOFs can be used for several other applications such as enzyme

encapsulation, biomedical imaging and sensing. Drugs are incorporated in to MOF by encapsulation or post synthetic modification strategy. Encapsulation is a method suitable for thermostable drugs that help to avoid premature drug release. Post synthetic modification is more complicated and time-consuming strategy helps to avoid destroying of drug molecules.^[10]

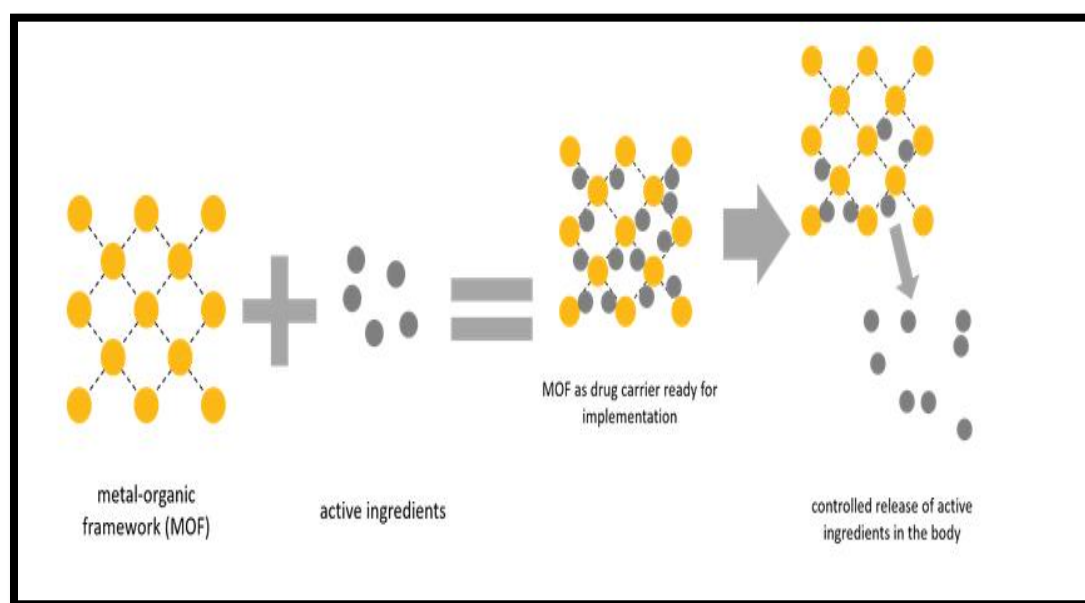


Figure 1.4: Mechanism of drug delivery

The features that MOFs should possess in order to act as drug carriers are the following

1. They should have high loading capacity

2. It could be given to body via intravenous injection
3. Non toxic
4. Be biodegradable
5. They must offer a controllable release of drugs

Drugs can be carried in many ways; by encapsulating them in framework, attaching them in to organic linkers or by using them as linkers of metal organic framework.

1.2.3 Hydrogen storage

MOFs have potential as hydrogen storage materials due to their unique properties such as large surface area, high pore size. Advantage of MOFs over traditional adsorbents such as adsorbents such as Zeolites, porous activated carbon is that their pore size can be tuned from several angstroms to few nm just by controlling the size of organic linker. Because of their crystalline nature, 3D and macromolecular size the properties can be easily studied.^[11] Example is the Hydrogen storage of MOF-5 which showed remarkable uptake of Hydrogen at 77K and 50 bar. Doping MOF with a catalyst increases the hydrogen storage capacity at ambient temperature.^[12]

1.2.4 Water purification by adsorption

One of the greatest challenges that India has been facing nowadays is scarcity of drinking water. Since the population is increased, the demand of water also increased. The supply of water can be increased with secondary sources of

water which mainly comprises of waste water treatment. Recycled water provides a cost-efficient supply of water that decreases the demand of fresh water and is also good for environment. Industrial dyes are a major source of pollution of lakes and water resources. Now a days people have been developed many alternatives to prevent the contamination of water by dyes due to their highly visible colors and persistence. Adsorption is a process where one or more components of a mixture transferred to the surface of a solid material by means of physical or chemical interaction which is particularly useful for compound separation and waste water reclamation.[13] Adsorption removal by Metal organic frameworks represents a low cost and effective alternative. Metal organic framework are good candidates that are used for waste water treatment. They have some unique properties such as high surface area, tunable pore size, high adsorption capacity, favorable adsorption kinetics, regenerability and good thermal stability are properties that make them suitable for water purification in a cost effective and environment friendly way.

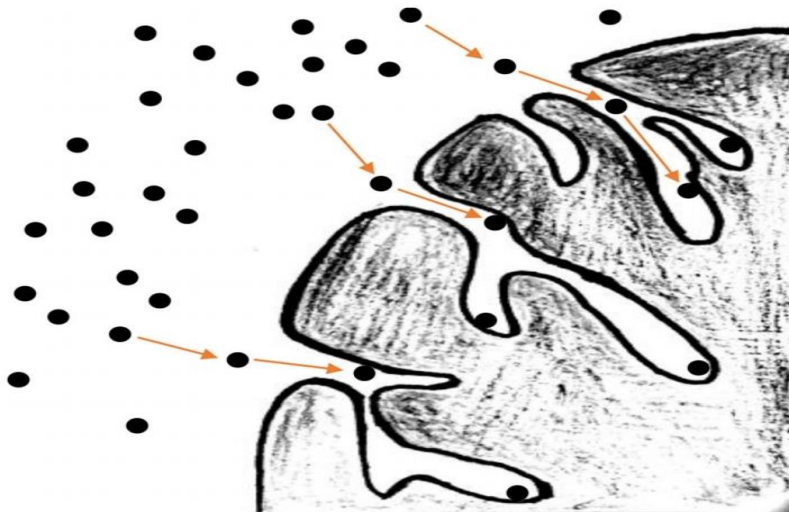


Figure 1. 5: Adsorption Schematization

1.3 Graphene oxide

Graphene is a material made up of carbon atoms bonded together in a hexagonal manner. It is very thin material and two dimensional. Graphene is one of the strongest materials in the world and is a conductor of heat and electricity. It has many applications like electronics, medicine, activation etc. Graphene oxide is an oxidized form of graphene, which leads to increased interlayer spacing and functionalization of the basal planes of graphite.[14] It can be added to other materials to enhance properties like absorptivity, tensile strength, elasticity and conductivity. It can be synthesized by methods like Hofmann, Brodie etc. [15]. Variations of these methods also exist. Here we used modified Hummer's method. Reduced graphene oxide is the form of GO

to reduce oxygen content. Graphene oxide and reduced graphene oxide are useful graphene derivatives. By incorporating reduced Graphene oxide with various compounds, it is possible to enhance the properties of that compound to suit for several applications.

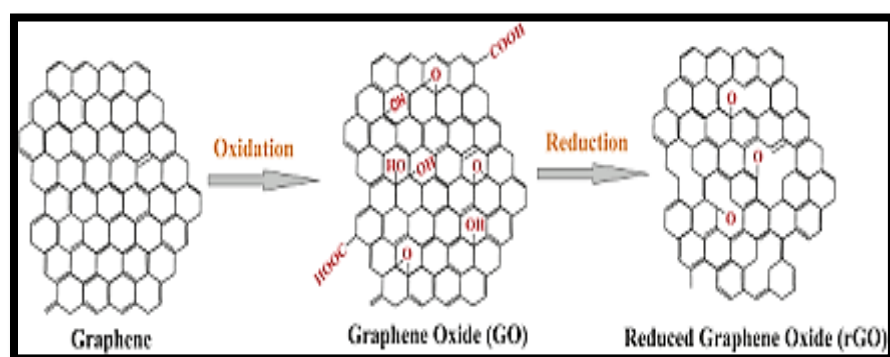


Figure 1.6: Graphene oxide and reduced graphene oxide

CHAPTER 2

MATERIALS AND METHODS

All reagents used were of AR grade.

REQUIREMENTS:

- 1.Zinc acetate
- 2.Ferric chloride
- 3.Terephthalic acid
- 4.Graphene oxide
5. N,N-dimethylformamide
- 6.Methylene Blue
- 7.Methyl orange
- 8.Rose Bengal
- 9.Congo red
- 10.Distilled water

2.1 Synthesis of MOF-5

Terephthalic acid (0.2523g,0.042mmol) was dissolved in 20 ml DMF. $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (0.848g,0.186mmol) was dissolved in 20 ml DMF. The Zinc salt solution was taken in burette and added to the organic solution with stirring over 45 min forming a precipitate. Precipitate washed with DMF centrifuged and dried. Zinc-MOF was obtained.



Figure 2.1: Synthesized MOF-5

2.2 Synthesis of MIL-101(Fe)

Terephthalic acid (0.2532g,1.52mmol) and Iron (III) chloride (0.4866g,3mmol) were separately dissolved in 20 ml DMF. Both the solution was mixed and transferred to a hydrothermal autoclave for 6hr at 150⁰C forming a precipitate. Precipitate washed several times with DMF centrifuged and dried. Fe-MOF was obtained.



Figure 2.2: As-synthesized MIL-121

2.3 Synthesis of Graphene oxide (Modified Hummer's Method)

0.5g Graphite is dissolved in 50 ml Conc H_2SO_4 . The mixture was kept under ice bath and stirred continuously for 12 hrs. 2g KMnO_4 was added to the suspension. It was stirred again for sometimes at ice-cold condition. Ice bath was removed the mixture is stirred for 1hr at room temperature with addition of a definite quantity of water. Reaction is terminated by the when finally treated with 5 ml 30% H_2O_2 . The mixture is washed by rinsing with water several times. It is filtered, dried under vacuum at room temperature. Graphene oxide was obtained as a powder.



Figure2.0.3: Synthesized graphene oxide

2.4 Synthesis of Zn-MOF/ rGO Nanohybrid

5wt % of GO in 20 ml DMF was bath sonicated for 1 hr. It is transferred to a hydrothermal autoclave in for 6hr at 150⁰C and again bath sonicated for 1 hr. It is mixed with (0.186mmol) Zinc acetate. To this mixture Terephthalic acid in 20 ml DMF is added from burette stirred for 45 min. The precipitate is centrifuged, washed using solvent for several times and dried. Zinc MOF/rGO nanohybrid is obtained.



Figure2.4MOF-5/rGO nanohybrid

2.5 Synthesis of Fe-MOF/rGO nanohybrid

5wt% GO in 20 ml DMF was bath sonicated for one hr. It is added to the mixture of (1.52mmol) terephthalic acid in 20 ml DMF and (3mmol) FeCl₃ in 20 ml DMF. Precipitate washed several times with DMF centrifuged and dried. It is transferred to a hydrothermal autoclave, heated at 150^o C for 6hr. Precipitate washed several times with DMF centrifuged and dried. Fe MOF /r GO nanohybrid is obtained.



Figure 2.5: MIL-121/rGO nanohybrid

2.6 Synthetic routes for MOFs and their graphene hybrid

2.6.1 Hydrothermal synthesis

Hydrothermal synthesis is one of the most advantageous processes for the preparation of nanomaterials. There are significant advantages for this method over others. This method can generate nanomaterials which are not stable at elevated temperatures. It is a process in which we are synthesizing single

crystals that depends on the solubility of minerals in hot water under high pressure. The raw materials are mixed and transferred to an apparatus consist of steel pressure vessel called an autoclave. A temperature gradient is maintained between the opposite ends of vessel. At the hotter end the solute dissolves, while at the cooler end it is deposited on a crystal, growing the desired crystal.^[16]

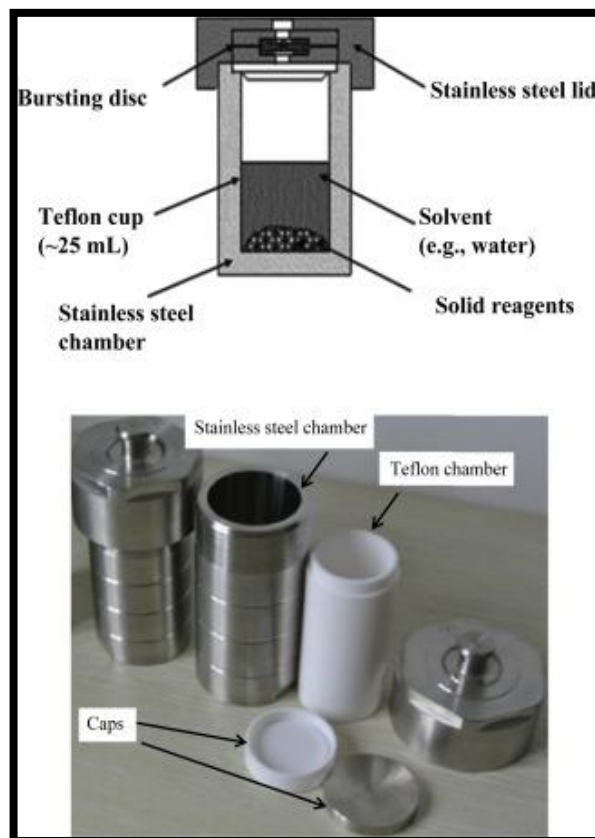


Fig 2.6 Image of Teflon lined stainless steel autoclave

2.6.2 Ultrasonic assisted synthesis

Sonochemistry deals with the use of microwave radiation to undergo chemical reactions. Ultrasound is the part of sonic spectrum, which ranges from 20 to 10 MHz and can be subdivided into three regions including high-power low frequency ultrasound, medium power high frequency ultrasound and low power high frequency ultrasound. Ultrasound have frequencies higher than upper audible limit of human hearing. Ultrasound sonochemistry is more efficient in terms of good yield, low energy requirements, less by product etc. It is also used to disperse the solute uniformly in solvent. This technique has been used in promoting various chemical reactions since the decade 1990-1999. The use of ultrasound in chemical reactions causes specific activation of molecules based on phenomenon called acoustic cavitation. When sound wave propagates through reaction mixture the molecules in it undergo oscillations. During this compression or expansion takes place, as a result of this the distance between molecules is reduced or increased. During expansion the attractive forces between molecules has overcome, leading to the formation of bubbles. This process is called acoustic cavitation. Collapsing of these bubbles produces high temperature and pressure. This initiates chemical reaction.[17]

2.7 DYE ADSORPTION STUDIES

The synthesized MOFs and their graphene hybrids were studied for their efficiency towards dye adsorption. Methylene blue, Methyl orange, Congo red,

Rose bengal etc. were selected because they were commonly found in industrial effluents.

2.7.1. CONGO RED

Congo red is an acid base indicator. Mainly used to stain tissue cells. It is one of the most common dyes used in textile industry. It is an anionic dye and also Carcinogenic.

2.7.2. METHYL ORANGE

It is an anionic dye, pH indicator used in titration. Widely Used in textile, paper, printing and food industries. Mostly discharged in industrial waste water.

2.7.3. METHYLENE BLUE

It is a cationic dye or staining agent used in textile industry. Also used in pharmaceutical field.

2.7.4. ROSE BENGAL

It is an Important xanthene dye widely used in textile and photochemical industry. It is an anionic dye also carcinogenic.

2.8 Synthetic strategy for dye removal from industrial effluents by adsorption

The concentration of each dye solution was 10 ppm. Adsorption was tested by adding 1 mg of synthesized MOFs in 50 mL of dye solution, the solution is

continuously stirred for 1 hr. 5mL aliquots were withdrawn at every 10 min. The absorbance spectra of the dye solution at different time intervals were analyzed after removing the MOF samples from the solution. The % dye adsorption was calculated from change in the absorbance of λ_{max} of a particular dye.

2.9 CHARACTERIZATION TECHNIQUES

2.9.1 X- Ray Diffraction (XRD)

X-Ray diffraction technique is a precise and popular tool for determining the crystal structure of thin films. It yields complete information about the crystal structure, orientation, lattice constants, crystalline size and composition, defects, and stress in the thin film. From the position and shape of the lines, one can obtain information regarding the unit cell parameters and microstructural parameters (grain size, micro strain, etc.), respectively. It requires no sample preparation and is essentially non-destructive. The wave nature of X-Rays means that they are diffracted by the lattice of the crystal to give a unique pattern of peaks of reflections at differing angles and of different intensity, just as light can be diffracted by a grating of suitably spaced lines. The diffracted beam from atoms in successive planes cancels unless they are in phase, and the condition for this is given by Bragg's relationship.

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

Here d is the inter-spacing, Θ is the angle of diffraction, λ is the wavelength of the incident beam and n is the order of diffraction. Diffraction peak position is accurately measured with XRD, which makes it the best method for characterizing homogeneous and inhomogeneous strains. Homogeneous or uniform elastic strain shifts the diffraction peak position. From the shift in peak position, one can calculate the change in d -spacing, which is the result of the change of lattice constants under a strain. In homogeneous strains vary from crystallite to crystallite or within a single crystallite and this cause a broadening of the diffraction peaks that increase with $\cos \Theta$. The crystallite size, D can be determined using Debye- Scherrer formula

$$D = K\lambda / \beta \cos\Theta$$

Where, λ is the X-ray wavelength, K is the Scherrer constant, β is the full width of the height of a diffraction peak, Θ is the diffraction angle. XRD is a non-destructive technique and does not require elaborate sample preparation, which partly explains the wide usage of XRD method in materials characterization. In addition, X-ray diffraction only provides the collective information of the particle sizes and usually requires a sizeable amount of powder. It should be noted that since the estimation would work only for very small particles, this technique is very useful in characterizing nanoparticles.^[18]

2.9.2 UV-Visible spectroscopy

UV spectroscopy or UV-visible spectrophotometry (UV-Vis or UV/Vis) refers to absorption spectroscopy or reflectance spectroscopy in part of the ultraviolet and the full, adjacent visible regions of the electromagnetic spectrum. This

means it uses light in the visible and adjacent ranges. The absorbance or reflectance in the visible range directly affects the perceived color of the chemicals involved. In this region of the electromagnetic spectrum, atoms and molecules undergo electronic transitions. Absorption spectroscopy is complementary to fluorescence spectroscopy. Molecules containing electrons or nonbonding electrons(n) can absorb energy in the form of UV or Visible light to excite these electrons to higher antibonding molecular orbitals. The more easily excite the electrons the longer the wavelength of light it can absorb. This spectroscopy is routinely used in analytical chemistry for the quantitative determination of different analytes such as transition metal ions, highly conjugated organic compounds and biological macromolecules. For instance, solutions of transition metal ions can be coloured because d- electrons within the metal atoms can be excited from one electron state to another. The color of the metal ion solutions is strongly affected by the presence of the ligands. The instrument in the UV-Visible spectroscopy is called UV-Visible spectrophotometer. It measures the intensity of light passing through a sample (I) and compares it to the intensity of light before it passes through the sample (I₀). The ratio I/I₀ are called transmittance and are usually expressed as a percentage (%T). The absorbance A is based on transmittance, $A = -\log(\%T/100\%)$.^[18]

CHAPTER 3

RESULTS AND DISCUSSION

3.1 X-ray diffractograms of synthesized metal organic frameworks

The XRD analysis shown in Fig.3.1 indicated good crystallinity for the as-synthesized Fe-MOFs. 2θ values obtained at 9.02° , 9.91° , 14.87° , 17.85° , 19.35° , 21.18° , 26.39° , 28.72° , and 32.84° corresponds to (200), (220), (420), (511), (440), (711), (731), (751), and (860) reflections, respectively, and can be correlated well with the characteristic peaks of MOF-5.

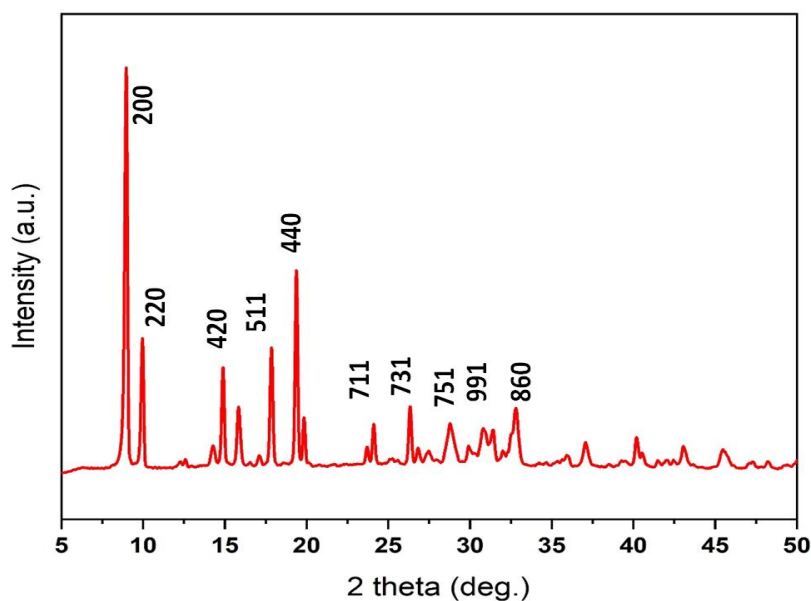


Figure 3.1: X-ray diffractogram of as-synthesized Zn-MOF

Fig.3.2 shows the XRD of Fe-MOF with peaks at $2\theta = 9.03^\circ$, 10.49° , 13.85° , 15.89° , 18.15° , 21.07° , 26.69° , and 32.75° corresponding well with the characteristic peaks (111), (511), (200), (311), (822), (755), (1022), and (1395), respectively of MIL-121. XRD also confirms that the as-synthesized were pure without any impurities or any formation of other phases/oxides of Zn or Fe. Average crystallite size calculated from the Scherrer equation is 76 nm for Zn-MOF (obtained fwhm = 0.186° for (200) reflection) 80 nm for Fe-MOF (fwhm = 0.1756° for (111) reflection).

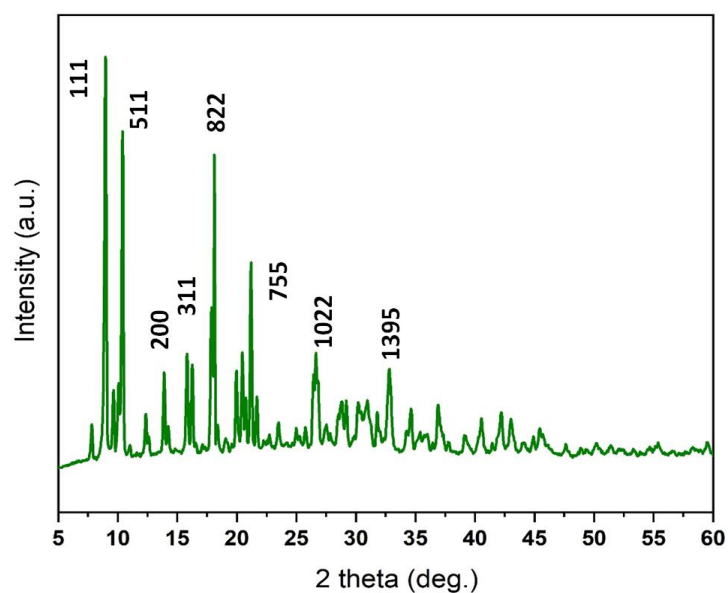


Figure3.2: X-ray diffractogram of as-synthesized Fe-MOF.

3.2 Graphene-oxide synthesized by modified Hummer's method

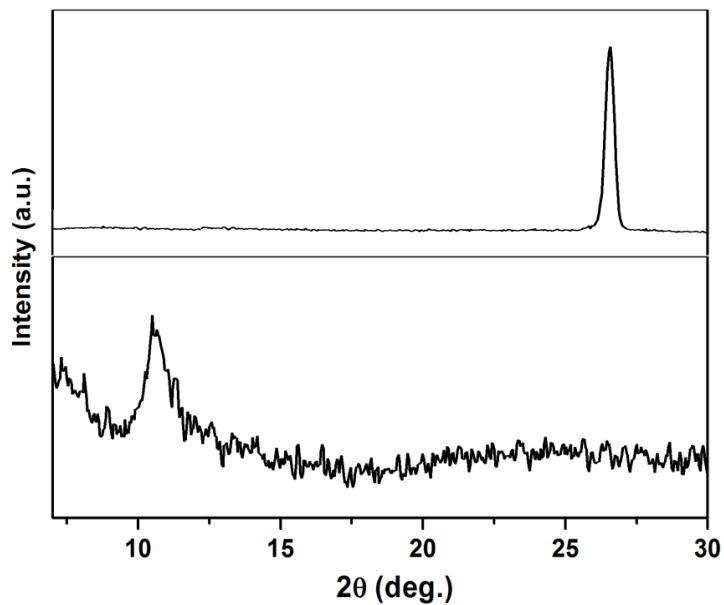


Figure 3.3: XRD of graphite (above) and synthesized GO (below).

Prior to the synthesis of MOF hybrids, we synthesized GO from graphite powder using modified Hummer's method. From the XRD analysis (Fig. 3.3) of both pristine graphite powder and graphene oxide (GO), it is observed that the characteristic (101) plane of graphite is shifted from $2\theta = 26^\circ$ to 10.6° . This is due to increase in the interplanar distance of graphite layers indicating the incorporation of oxygen containing functional groups between them. This incorporation of functional groups is affirmed from FTIR spectra of GO (Fig 3.4). The presence of alkoxy, epoxy and carbonyl and hydroxyl vibrations in

the FTIR confirmed their presence in GO introduced between the layers during the oxidation process.

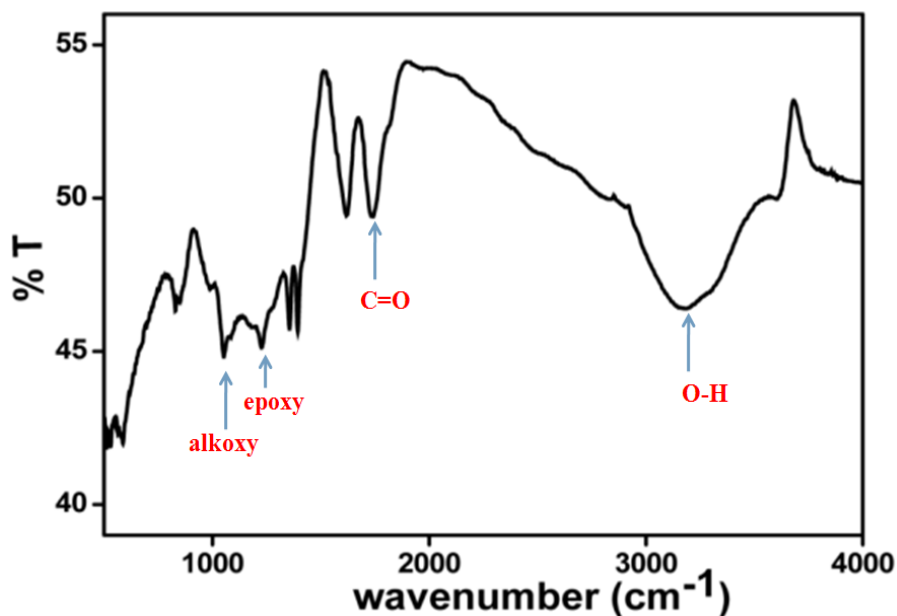


Figure 3.4: FTIR spectra of synthesized GO sample.

3.3 X-ray diffractograms of synthesized MOF/rGO hybrids

Fig. 3.5 and 3.6 shows the XRD of Zn-MOF/rGO and Zn-MOF/rGO respectively. While the prominent peaks of MOF are reproduced in the hybrid samples, the peaks corresponding to GO or rGO is merged with the peaks of MOFs. Particularly, the reflection of $2\theta = 10.6^\circ$ for GO is absent Fe-MOF/rGO hybrid sample, instead a reflection at 26° merged with the peaks of its Fe-MOF

sample. This indicates that GO is reduced to rGO during the hydrothermal process.

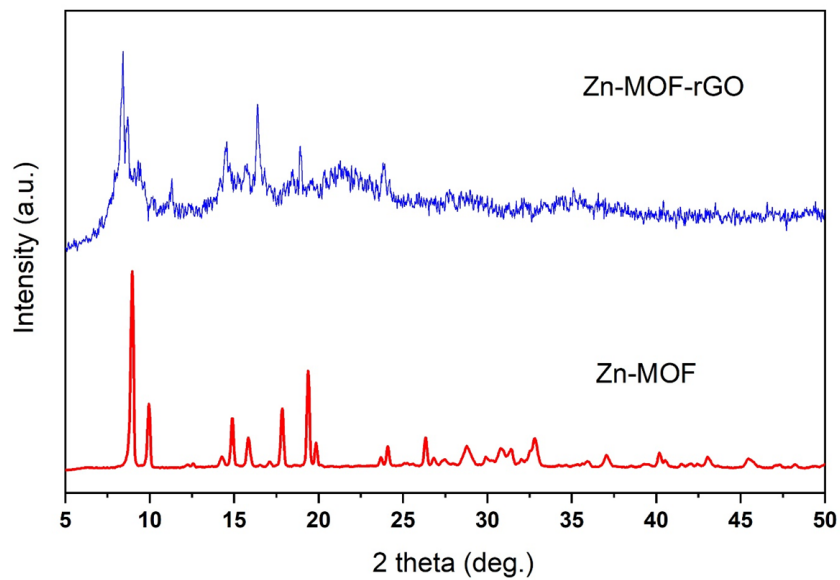


Figure 3.5: XRD of Zn-MOF/rGO compared with its parent MOF sample

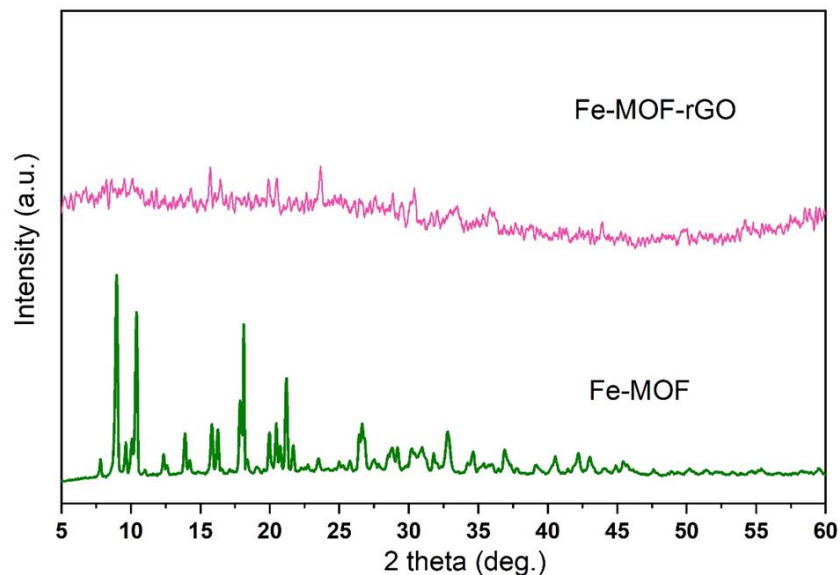


Figure 3. 6: XRD of Fe-MOF/rGO compared with its parent MOF sample.

3.4 Dye adsorption studies using synthesized MOFs and their graphene hybrids

Dye adsorption studies are conducted using different cationic and anionic dyes of which some are carcinogenic too. 10 mg L^{-1} dye solution was administered to the MOFs and their hybrids to a contact time of maximum 1 h. Aliquots at time intervals of 10 min to analyze the extent of adsorption.

The dynamic adsorption of Fe-MOF and its graphene hybrid were first done using Congo-red dye and the adsorption capacities were compared (Fig. 3.7). Adsorption of Congo-red on both the MOF and hybrid samples were carried out at 10 mg L^{-1} Congo-red/water solution for a contact time of 1 h. Fe-

MOF/rGO hybrid adsorbed 99.99% (capacity of 99.99 mg g⁻¹) of Congo-red from the solution while parent Fe-MOF also removed 99% of the dye from the solution with a capacity of 99 mg g⁻¹. After the hybridization of Fe-MOF with graphene, the enhancement in surface area greatly enhanced the adsorption capability in the hybrids. Besides, rGO is synthesized by the reduction of graphene oxide during hydrothermal treatment. This resulted in the re-establishment of π - π conjugation, but with few defect sites on the graphene sheet (hence named reduced graphene oxide /rGO instead of graphene /G). These defect sites also will contribute as active sites during dye adsorption.

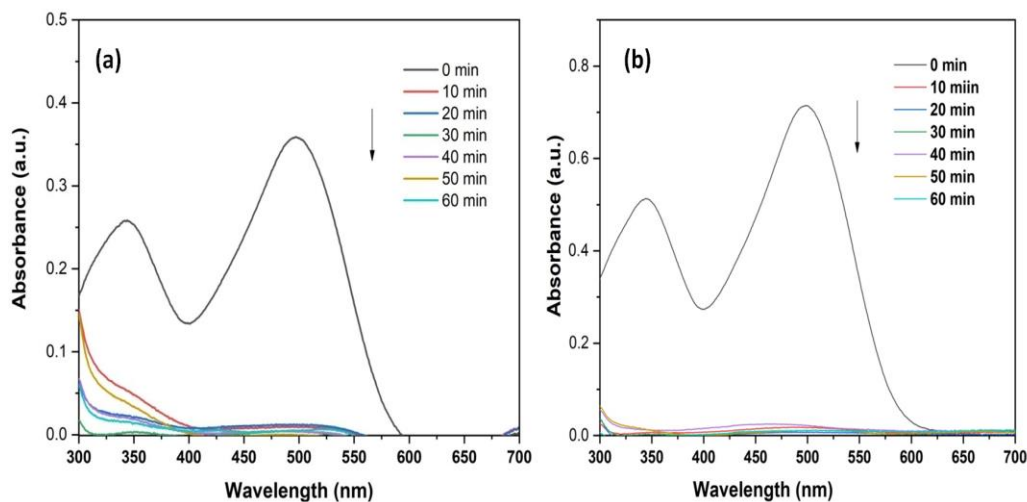


Figure 3.7: UV-Visible spectra of Congo-red/water solution with (a) Fe-MOF and (b) Fe-MOF/rGO, at different contact time (up to 1 h).

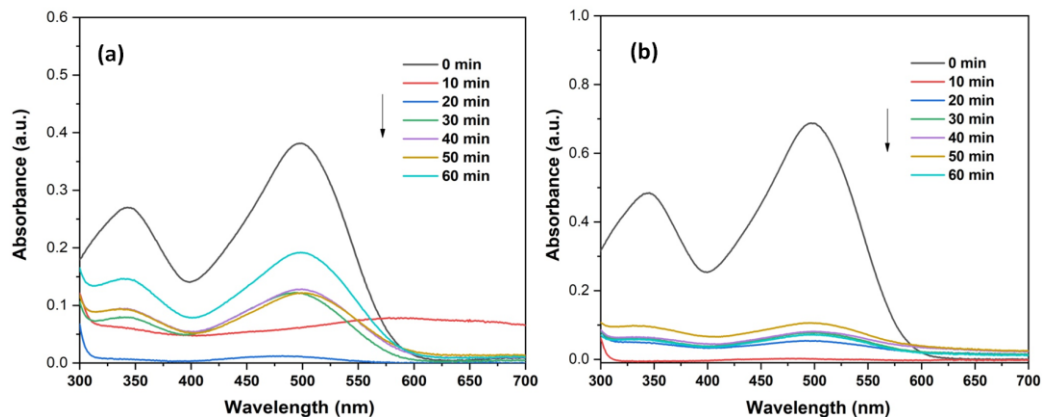


Figure 3.8: UV-Visible spectra of Congo-red/water solution with (a) Zn-MOF and (b) Zn-MOF/rGO, at different contact time (up to 1 h).

The adsorption of Congo-red by Zn-MOF (Fig 3.9a) was slightly lower when compared to that with Fe-MOF and its rGO hybrid. But Zn-MOF/rGO hybrid (Fig. 3.9b) showed fairly good performance as that of Fe-MOF and Fe-MOF/rGO. Zn-MOF showed an absorption capacity of 83 mg g^{-1} while Zn-MOF/rGO showed a capacity of 92 mg g^{-1} .

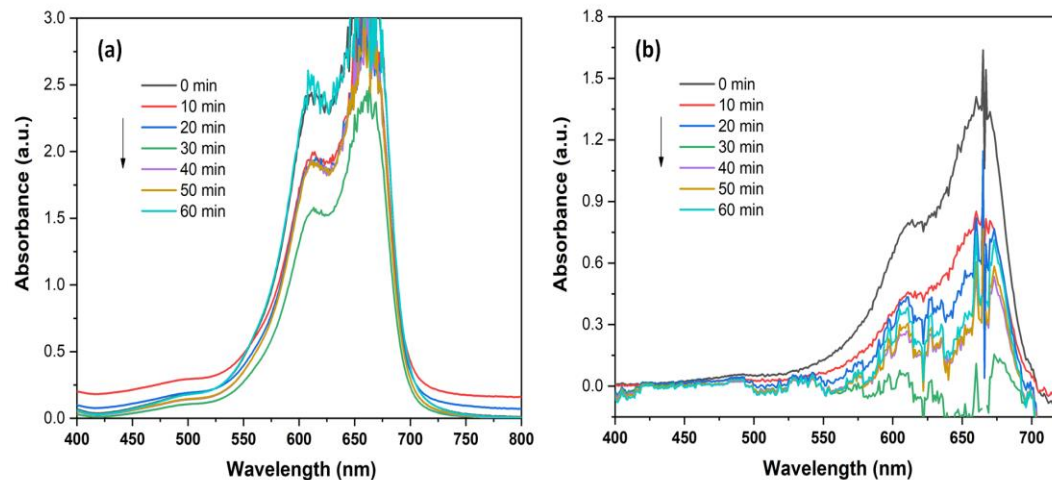


Figure 3.9: UV-Visible spectra of MB/water solution with (a) Zn-MOF and (b) Zn-MOF/rGO, at different contact time intervals.

The adsorption studies were repeated with methylene blue (MB) solution in order to understand the adsorption capabilities of the samples with cationic dyes. While Zn-MOF and its graphene hybrid showed 14% and 79% adsorption (Fig. 3.9) correspondingly with a capacity of 14 mg g⁻¹ and 79 mg g⁻¹, respectively, Fe-MOF and Fe-MOF/rGO showed better adsorption to MB (Fig. 3.10) with an adsorption capacity of 82 mg g⁻¹ and 95 mg g⁻¹, respectively (adsorption rate of 82% and 95%). This infers that the adsorption capacities of the samples were fairly good with the cationic dyes as well.

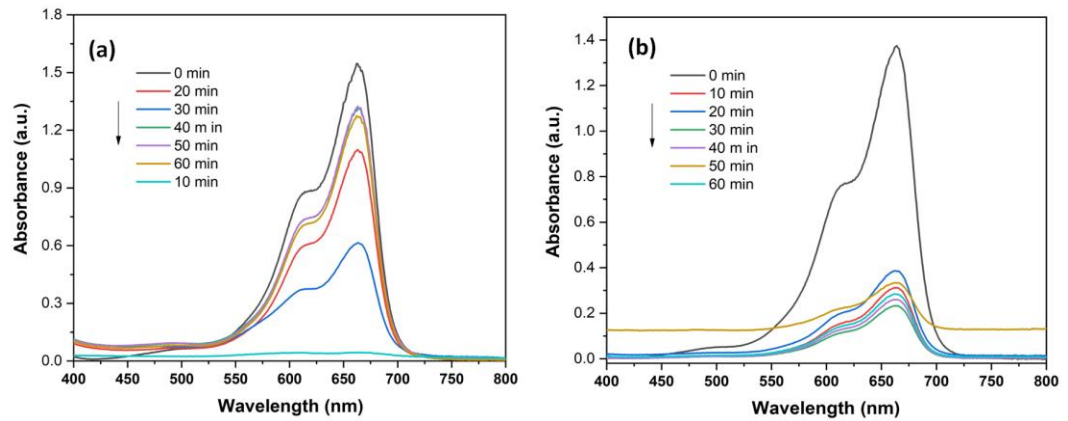


Figure 3.10: UV-Visible spectra of MB/water solution with (a) Fe-MOF and (b) Fe-MOF/rGO, at different contact time intervals.

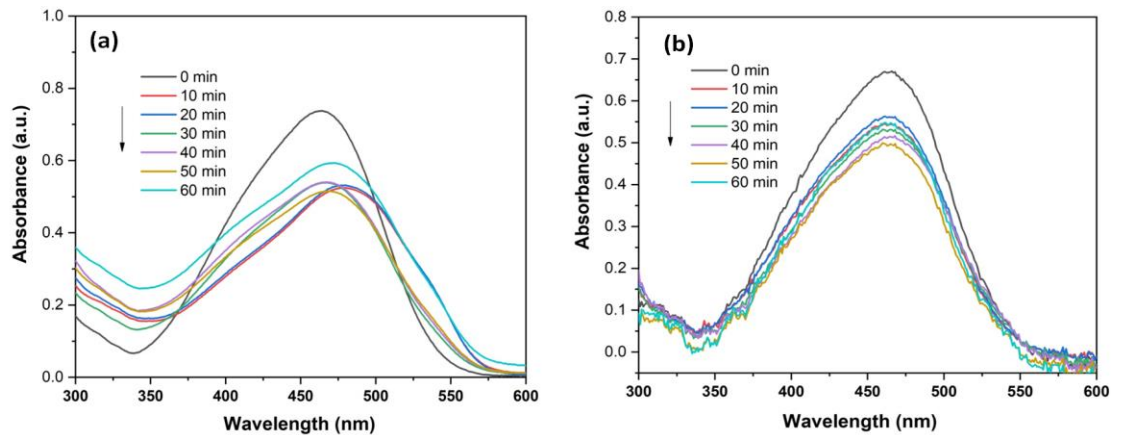


Figure 3.11: UV-Visible spectra of MO/water solution with (a) Fe-MOF/rGO and (b) Zn-MOF/rGO, at different contact time intervals.

Again, to understand the adsorption property of samples to anionic dyes, adsorption studies are repeated with Methyl orange (MO). Adsorption studies

were done with rGO hybrids of Fe-MOF and Zn-MOF as graphene hybrids have comparatively showed enhanced performance relative to their parent MOF samples in the previous cases. The analyses showed that Fe-MOF/rGO (30 mg g^{-1}) showed relatively better adsorption behavior than Zn-MOF/rGO (28 mg g^{-1}).

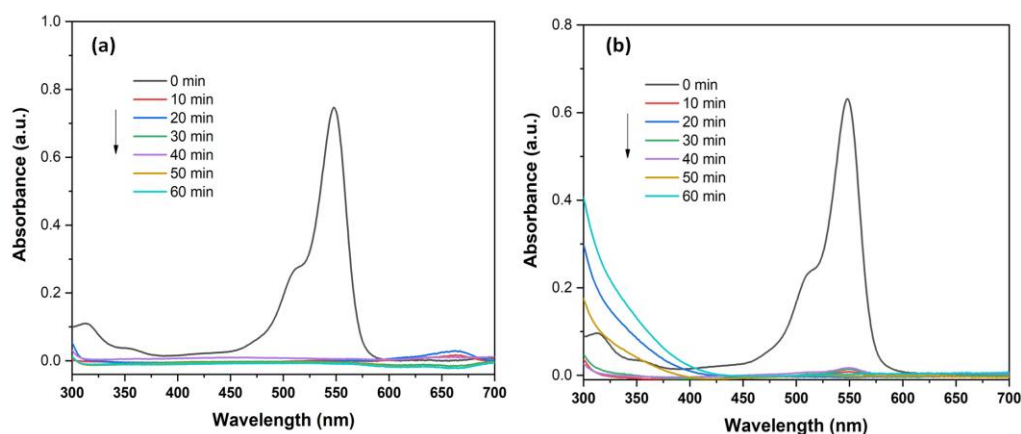


Figure3. 12: UV-Visible spectra of MO/water solution with (a) Fe-MOF/rGO and (b) Zn-MOF/rGO, at different contact time intervals.

Lastly, the adsorption studies were conducted in presence of Rose Bengal which is a carcinogenic anionic dye, most widely used in the dye industry. We further selected Fe-MOF and Fe-MOF/rGO hybrids as they showed superior dye adsorption capabilities in any case aforementioned. Here also, Fe-MOF and its hybrid showed good adsorption properties towards Rose Bengal with an adsorption of 92 mg g^{-1} and 97 mg g^{-1} respectively.

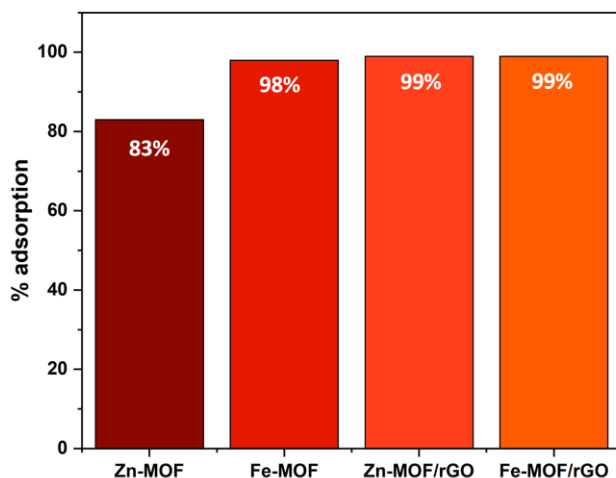


Figure3.13: Percentage adsorption of Congo-red by different MOFs and their graphene hybrids.

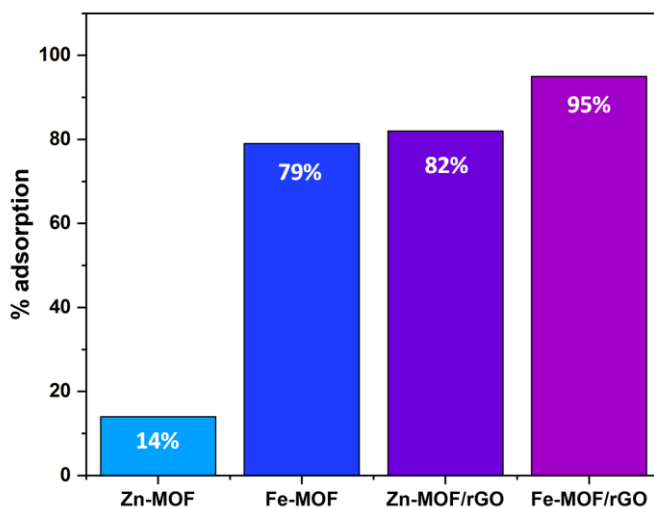


Figure3.14: Percentage adsorption of Methylene blue by different MOFs and their graphene hybrids.

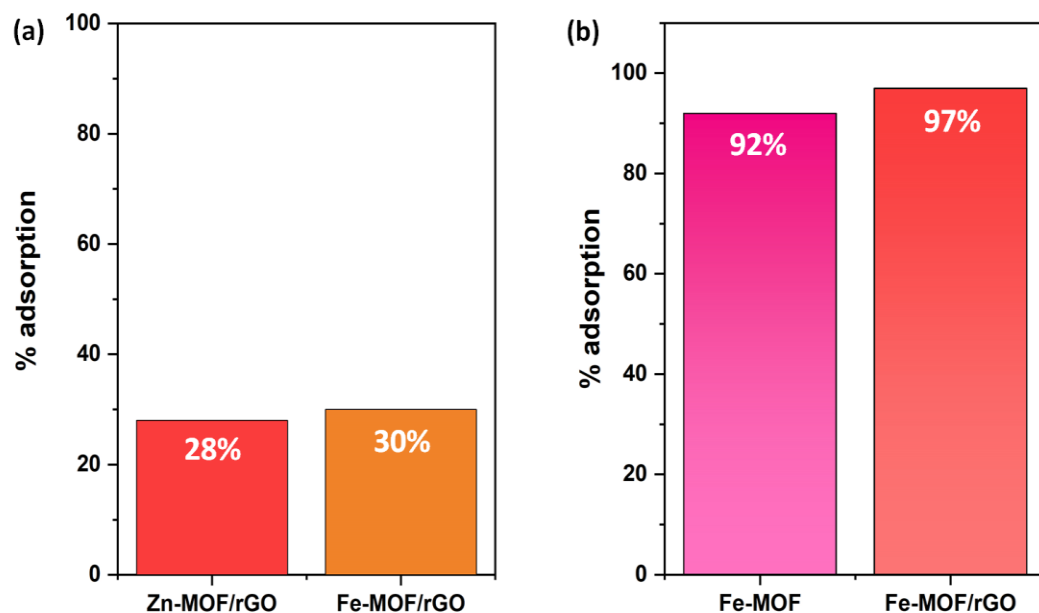


Figure 3.15: Percentage adsorption of (a) Methyl orange by graphene hybrids of Zn-MOF and Fe-MOF, and (b) Rose Bengal by Fe-MOF and its graphene hybrid.

Finally, a comparative study is done to relate the adsorption properties of all samples to different anionic and cationic dyes were done (Fig. 3.11, 3.12 and 3.13). The results showed that Fe-MOF and its graphene hybrid is superior in adsorption to either cationic and anionic dyes. Although, all samples synthesized through the aforementioned cost-effective methodology are effective in dye-adsorption, and can be potential candidates in water purification and treatment of industrial effluents.

CHAPTER 4

CONCLUSION

In this work, we have synthesized graphene hybrids of Zn- and Fe-based MOFs and have studied their dye adsorption properties. While hydrothermal methods were adopted for the synthesis of Fe-MOF and its graphene hybrid, coprecipitation methods were used for Zn-MOF and Zn-MOF/rGO. A modified Hummer's method synthesized the intermediate GO (graphene oxide) for graphene hybrids. XRD and UV-Vis spectra characterized the different synthesized samples. Fe-MOF/rGO and Zn-MOF/rGO, and their parent samples, were finally employed as adsorbents to adsorb organic dyes selected between different cationic, anionic, and carcinogenic dyes such as methylene blue, methyl orange, Congo red, and Rose Bengal. The MOF/rGO hybrids exhibited fairly good adsorption towards dyes than their parent MOFs. These synthesized samples are a cost-effective to deploy them to water purification and wastewater treatment especially effluents from dye industries.

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