

SYNTHESIS, CHARACTERIZATION OF METAL ORGANIC FRAMEWORK FOR ENVIRONMENTAL REMEDIATION USING METHYL ORANGE DYE

Submitted in partial fulfilment of the requirements for the award of

Master of Science in Chemistry

by

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**DEPARTMENT OF CHEMISTRY SCHOOL OF SCIENCE AND
HUMANITIES**

SATHYABAMA

INSTITUTE OF SCIENCE AND TECHNOLOGY

(DEEMED TO BE UNIVERSITY)

Accredited with Grade "A" by NAAC | 12B Status by UGC | Approved by AICTE

JEPPIAAR NAGAR, RAJIV GANDHI SALAI, CHENNAI - 600 119

MAY - 2023



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BONAFIDE CERTIFICATE

This is to certify that this Project Report is the bonafide work of **S. SHIV SHANKAR (41910018)** who carried out the project entitled "**SYNTHESIS, CHARACTERIZATION OF METAL ORGANIC FRAMEWORK FOR ENVIRONMENTAL REMEDIATION USING METHYL ORANGE DYE**" under our supervision from November 2022 to May 2023.

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DECLARATION

I **S. SHIV SHANKAR (41910018)**, hereby declare that the Project Report entitled **"SYNTHESIS, CHARACTERIZATION OF METAL ORGANIC FRAMEWORK FOR ENVIRONMENTAL REMEDIATION USING METHYL ORANGE DYE"** done by me under the guidance of **Dr.S. Supriya, M.Sc., Ph.D.**, Associate professor, Department of Chemistry at **Sathyabama Institute of Science and Technology**, Jeppiaar Nagar, Rajiv Gandhi Salai, Chennai – 600119 is submitted in partial fulfillment of the requirements for the award of Master of Science degree in Chemistry.

DATE: 08/05/23

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DECLARATION

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DATE:

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SIGNATURE OF THE CANDIDATE

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I convey my thanks to **Dr. J KARTHIKEYAN, Head of the Department, Dept. of Chemistry** for providing me necessary support and details at the right time during the progressive reviews.

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

S. SHIV SHANKAR

ABSTRACT

Metal organic frameworks (MOFs) are a class of chemical substances that have shown great potential towards environmental remediation. MOFs are highly customizable and can be used catalysts for the removal of heavy metals and other pollutants from aqueous systems. Metal organic frameworks (MOFs) containing copper and iron are being synthesized and have been used for environmental remediation where degradation of methyl orange dye has been studied . The characterization of pure PVA Cu /PVA Fe films were performed in terms of field emission scanning electron microscopy (FESEM- EDAX), Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) and UV-VIS spectroscopy. Methyl Orange has been found to undergo degradation immediately and also to bring back the normal neutral pH. Incorporation of metals have been to make MOFs an efficient pollutant absorber and can also be reused.

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LIST OF ABBREVIATIONS

XRD - X-Ray Diffraction

- | | |
|--------|---|
| FTIR | - Fourier Transform Infrared Spectroscopy |
| SEM | - Scanning electron Microscope |
| UV-VIS | - Ultraviolet Visible Spectroscopy |

CHAPTER 1

INTRODUCTION

1.1 POLYVINYL ALCOHOL (PVA)

Poly(vinyl alcohol) (PVOH, PVA, or PVAI) is a water-soluble synthetic polymer. It has the idealized formula $[\text{CH}_2\text{CH}(\text{OH})]_n$. It is used in papermaking, textile warp sizing, as a thickener and emulsion stabilizer in polyvinyl acetate (PVAc) adhesive formulations, in a variety of coatings, and 3D printing. It is colourless (white) and odorless. It is commonly supplied as beads or as solutions in water.[3,4] Without an externally added crosslinking agent, PVA solution can be gelled through repeated freezing-thawing, yielding highly strong, ultrapure, biocompatible hydrogels which have been used for a variety of applications such as vascular stents, cartilages, contact lenses, etc.

PVA full form is polyvinyl alcohol. Polyvinyl alcohol is a man-made or synthetic polymer. PVA polymer molecule contains vinyl and alcohol groups. It is a very useful polymer due to its adhesive properties. PVA is water soluble, crystalline and flammable in nature. Presence of alcohol group in it makes it flammable.

1.1.1 PVA Structure or Polyvinyl Alcohol Structure

PVA monomer unit is vinyl acetate. It means, it is formed by the polymerization of vinyl acetate. Vinyl acetate formula is $\text{H}_3\text{C}-\text{CO}_2-\text{CH}=\text{CH}_2$. PVA is not prepared by direct polymerization of vinyl acetate. Instead, it is prepared by hydrolysis of polyvinyl acetate (PVAc) through an alcohol (generally methanol) in presence of an alkaline catalyst.

1.1.2 Properties of PVA

Physical Properties of PVA

1. PVA shows high tensile strength and flexibility.
2. It is soluble in water and has no odour.

3. PVA molecular weight or polyvinyl molecular weight ranges between 26,000-30,000.
4. Its melting point is 185°C.
5. It is insoluble in organic solvents but slightly soluble in ethanol.

Chemical Properties of PVA

1. Polyvinyl alcohol can react with butyraldehyde and formaldehyde.
2. It is atactic type material and resistant to oil and grease.

Polyvinyl Alcohol Uses

PVA polymer is used in many fields. It is used as main component in many drugs. Many of its applications are based on its adhesive property. PVA is a type of synthetic adhesive. PVA is used as PVA glue in many fields. Meaning of PVA glue is a glue or fixative made up of polyvinyl alcohol.

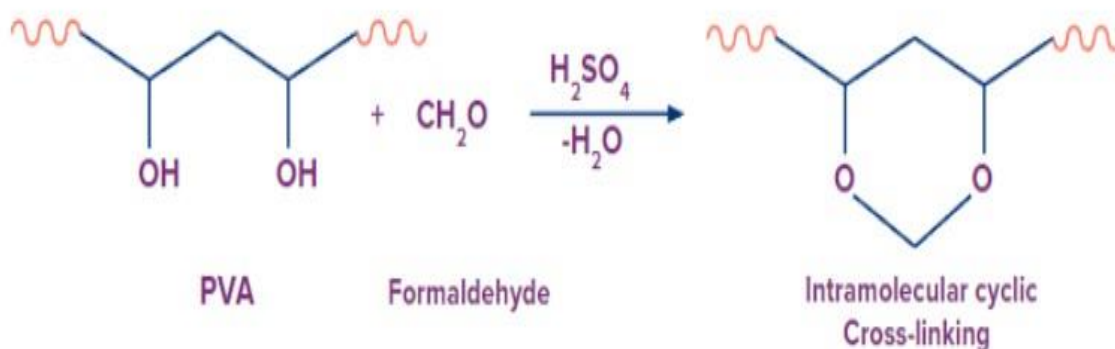


Fig 1.1 Polyvinyl alcohol

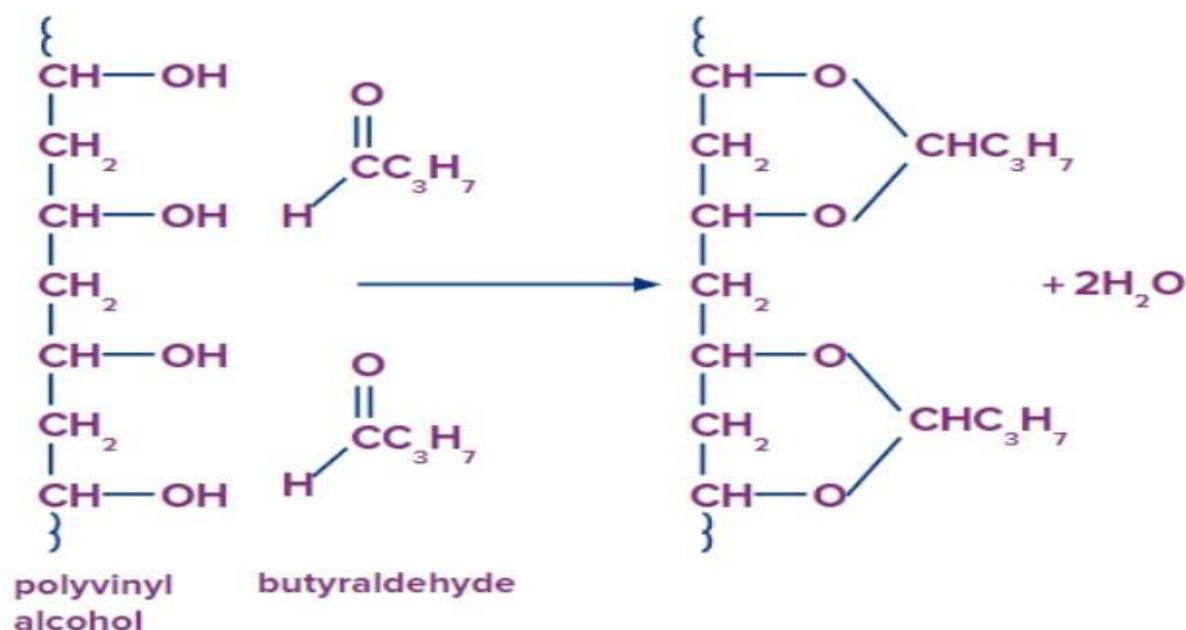


Fig 1.2 Reaction of Polyvinyl Alcohol

1.1.3 FERRIC CHLORIDE : -

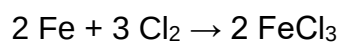
Iron(III) chloride describes the inorganic compounds with the formula $\text{FeCl}_3(\text{H}_2\text{O})_x$. Also called ferric chloride, these compounds are available both in anhydrous and hydrated forms. They are common sources of iron in its +3 oxidation state. The hydrate and the anhydrous derivative have distinct properties.

All forms of ferric chloride are paramagnetic, owing to the presence of five unpaired electrons residing in 3d orbitals. This electronic configuration places electrons in molecular orbitals that are antibonding with respect to ligands. Thus, iron(III) chlorides are labile, undergoing rapid ligand exchange in solution. In contrast to their kinetic lability, iron(III) chlorides are thermodynamically robust, as reflected by the vigorous methods applied to their synthesis.

The anhydrous compound is a crystalline solid with a melting point of 307.6 °C. The colour depends on the viewing angle: by reflected light the crystals appear dark green, but by transmitted light they appear purple-red. Anhydrous iron(III) chloride has the BiI_3 structure, with octahedral Fe(III) centres interconnected by two-coordinate chloride ligands.

Iron(III) chloride has a relatively low melting point and boils at around 315 °C. The vapor consists of the dimer Fe_2Cl_6 (like aluminium chloride) which increasingly dissociates into the monomeric FeCl_3 (with D_{3h} point group molecular symmetry) at higher temperature, in competition with its reversible decomposition to give iron(II) chloride and chlorine gas.

Several hundred thousand kilograms of anhydrous iron(III) chloride are produced annually. The principal method, called direct chlorination, uses scrap iron as a precursor:



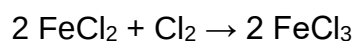
The reaction is conducted at several hundred degrees such that the product is gaseous. Using excess chlorine guarantees that the intermediate ferrous chloride is converted to the ferric state. A similar but laboratory scale process also has been described.

Solutions of iron(III) chloride are produced industrially both from iron and from ore, in a closed-loop process.

Dissolving iron ore in hydrochloric acid



Oxidation of iron(II) chloride with chlorine



Oxidation of iron(II) chloride with oxygen and hydrochloric acid



Heating hydrated iron(III) chloride does not yield anhydrous ferric chloride. Instead, the solid decomposes into hydrochloric acid and iron oxychloride. Hydrated iron(III) chloride can be converted to the anhydrous form by treatment with thionyl chloride. Similarly, dehydration can be effected with trimethylsilyl chloride:

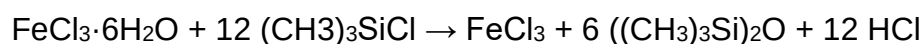


Fig 1.3 FERRIC CHLORIDE(anhydrous)

1.1.4 COPPER BISGLYCINATE

Copper(II) glycinate (IUPAC suggested name: bis(glycinate)copper(II)) refers to the coordination complex of copper(II) with two equivalents of glycinate, with the formula $[\text{Cu}(\text{glycinate})_2(\text{H}_2\text{O})_x]$ where $x = 1$ (monohydrate) or 0 (anhydrous form). The complex was first reported in 1841, and its chemistry has been revisited many times, particularly in relation to the isomerisation reaction between the cis and trans forms which was first reported in 1890.

All forms are blue solids, with varying degrees of water solubility. A practical application of the compound is as a source of dietary copper in animal feeds.

Bis(glycinate)copper(II) is typically prepared from the reaction of copper(II) acetate in aqueous ethanol with glycine.

$\text{Cu}(\text{OAc})_2 + 2 \text{H}_2\text{NCH}_2\text{COOH} + x \text{H}_2\text{O} \rightarrow [\text{Cu}(\text{H}_2\text{NCH}_2\text{COO})_2(\text{H}_2\text{O})_x] + 2 \text{AcOH}$, $x = 0$ or 1

The reaction proceeds through a non-redox dissociative substitution mechanism and usually affords the cis isomer.

Like most amino acid complexes, the glycinate forms a 5-membered chelate ring, with the glycinate ligand serving as a bidentate ($\kappa^2\text{O,N}$) species. The chelating ligands assume a square planar configuration around the copper atom as is common for tetracoordinate d9 complexes, calculated to be much lower in energy than the alternative tetrahedral arrangement.

Cis and trans isomerism

The unsymmetric nature of the ligand and square planar coordination thereof gives rise to two possible geometric isomers: a cis and a trans form.

Multiple ways of differentiating the geometric isomers exist, an easily accessible one being IR spectroscopy with the characteristic number of C–N, C–O, and Cu–N identifying the ligand configuration. Crystal appearance may also be of some value for isomer indication, though the ultimate diagnostic technique is X-ray crystallography.

All forms of the complex have been characterized crystallographically, the most commonly isolated one being the cis monohydrate ($x = 1$).

Isomerisation of the cis to the trans form occurs at high temperatures via a ring-twisting mechanism.

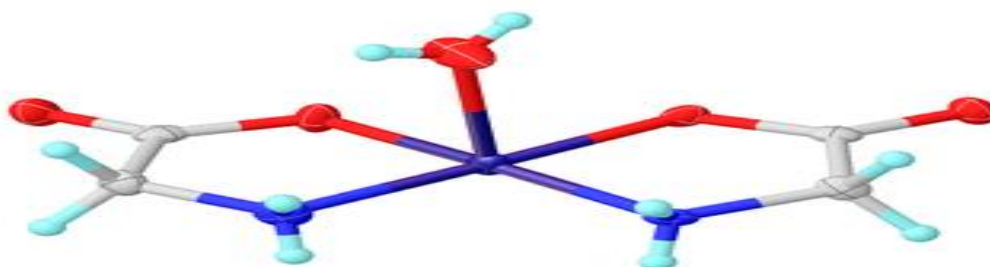


Fig 1.4 STRUCTURE OF COPPER BISGLYCINATE

1.1.5 COPPER SULPHATE : -

Copper(II) sulphate, also known as copper sulphate, is an inorganic compound with the chemical formula CuSO_4 . It forms hydrates $\text{CuSO}_4 \cdot n\text{H}_2\text{O}$, where n can range from 1 to 7. The pentahydrate ($n = 5$), a bright blue crystal, is the most commonly encountered hydrate of copper(II) sulphate. Older names for the pentahydrate include blue vitriol, bluestone, vitriol of copper, and Roman vitriol. It exothermically dissolves in water to give the aquo complex $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$, which has octahedral molecular geometry. The structure of the solid pentahydrate reveals a polymeric structure wherein copper is again octahedral but bound to four water ligands. The $\text{Cu}(\text{II})(\text{H}_2\text{O})_4$ centres are interconnected by sulphate anions to form chains. Anhydrous copper sulphate is a light grey powder.

Copper sulphate is produced industrially by treating copper metal with hot concentrated sulfuric acid or copper oxides with dilute sulfuric acid. For laboratory use, copper sulphate is usually purchased. Copper sulphate can also be produced by slowly leaching low-grade copper ore in air; bacteria may be used to hasten the process.

Commercial copper sulphate is usually about 98% pure copper sulphate, and may contain traces of water. Anhydrous copper sulphate is 39.81% copper and 60.19% sulphate by mass, and in its blue, hydrous form, it is 25.47% copper, 38.47% sulphate (12.82% sulphur) and 36.06% water by mass. Four types of crystal size are provided based on its usage: large crystals (10–40 mm), small crystals (2–10 mm), snow crystals (less than 2 mm), and windswept powder (less than 0.15 mm).



Fig 1.5 COPPER SULPHATE

1.1.6 BIOCATALYST

Some specific chemical reactions are carried outside the living cells by catalysis using natural proteins or nucleic acid is called bio catalysis. From plant, microbes and animal tissues the enzymes are obtained. They are high selectivity, high efficiency and eco- friendly.

1.2 NANOPARTICLES

A nanoparticle is a small particle which have the range between 1 to 100 nanometres in size. Human cannot see it with naked eyes. They exhibit significantly different physical and chemical properties compared to their larger material.

1..2.1 TYPES OF NANOPARTICLES

They are classified into different types based on their size, morphology, physical and chemical properties,

- I. Carbon- based nanoparticles
- II. Ceramic nanoparticles
- III. Metallic-oxide nanoparticles
- IV. Semiconductor nanoparticles
- V. Polymeric nanoparticles
- VI. Lipid-based nanoparticles

1.2.2 CARBON-BASED NANOPARTICLES

They are further classified into two main materials.

- ✦ Carbon nanotubes (CNTs)
- ✦ Fullerenes.

Carbon nanotubes (CNTs) is nothing but graphene sheets rolled into a tube. They are 1000 times stronger than steel.

1.2.3 CERAMIC NANOPARTICLES

These ceramic nanoparticles are made up of oxides, carbides, carbonates and phosphates. They are highly resistance to heat and chemical inertness. They are

crudely used as drug delivery system for a number of diseases like bacterial infections, cancer etc.....

1.2.4 SEMICONDUCTOR NANOPARTICLES

These semiconductor nanoparticles are found in the periodic table in groups 2-6, 2-4. they are used in photocatalysis photo-optics because they have wide bandgap particles.

1.2.5 POLYMERIC NANOPARTICLES: -

These polymeric nanoparticles are based on organic depending of preparation methods, they have structure like nano capsular or nanosphere. Nanosphere particles has a structure like matrix whereas the nano capsular particles have core- shell structure.

1.2.6 LIPID- BASED NANOPARTICLES

Lipid-based nanoparticles are consisting of solid core made of lipid. It is spherical shaped with a diameter of 10 to 100nm. The external surface of these nanoparticle is stabilized by surfactants and emulsifier. They can be used in biomedical field as drug carrier and delivery.

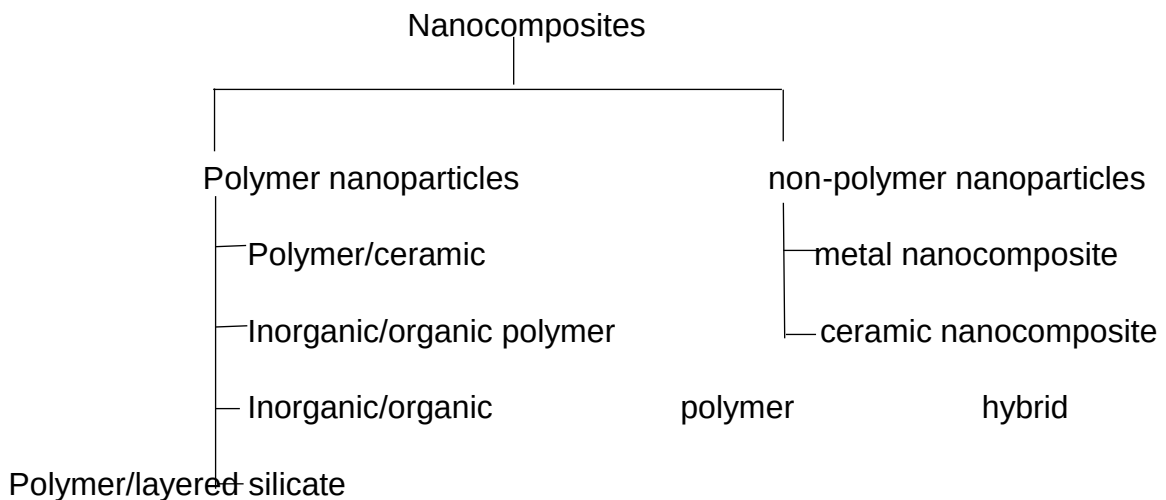
1.2.7 METAL-OXIDES NANOPARTICLES

These nanoparticles can be prepared by chemical, electrochemical or photochemical methods. These nanoparticles have applications in research area, detection and ignoring of biomolecules and in environmental and bioanalytical applications. Metal oxide nanoparticles play vital role in environmental remediation by treating waste water industrial and domestic waste, soil sediments as well as atmospheric pollution.

1.4 NANOCOMPOSITES

General nanocomposites are based on the concept of creativity a very large interface between the nanosized-building blocks and the polymer matrix, the main problems of nanocomposite are usually homogeneous distribution of the particle. Nanocomposites is made up of two or more constituent material with notable different physical or chemical properties after the combination. Its procedure a

material has different characteristics from the individual components. If at least one of the component constituents is nanometric then it is nanocomposite. They are heterogeneous materials thus their properties are determined by the same factors as in traditional composites. Their structure is more complicated than the micro composites.



1.4.1 POLYMERIC NANOCOMPOSITE

Polymeric nanocomposite consists of polymer or co polymer with nanoparticles speared in the polymer phase. They are of different shapes like fibre, platelets and spheroids from those at least one of its one dimension should be in the range of 150nm. They consist of multiphase system. In plastic production polymer nanocomposites cover 95%. They are done by controlled manner of compounding.

1.4.2 NON-POLYMER NANOCOMPOSITES

Nanocomposite which does not consist of any polymer compounds in it is called non polymer nanocomposites.

1.4.3 METALLIC OXIDE NANOCOMPOSITE

Bimetallic nanocomposites are used in the form of alloy or core shell structure because they have vast catalytic properties, they are characterized by,

- ✦ Super plasticity
- ✦ Lower melting point
- ✦ Increased strength and hardness
- ✦ Improved magnetic properties
- ✦ Increased electric resistivity etc...

1.5 PHARMACEUTICAL WASTE

Pharmaceutical waste is used or unused expired drug or medicine pharmaceuticals, home use person care products and medications used or disposed in garage. It can be classified as hazardous or non-hazardous depending on its risk to humans and the environment. There are different methods required for the disposal of hazardous versus non-hazardous pharmaceuticals.

1.5.1 HOW TO DISPOSE OF PHARMACEUTICAL WASTE

Pharmaceutical waste cannot be disposed in the normal way. We should take some special care and precautions must be taken while handling and disposing of pharmaceutical waste due to its dangerous nature. If pharmaceutical waste is not disposed properly, the effect is catastrophic, not only for the peoples for also to the animals and plants.

1.5.2 RISKS OF IMPROPER PHARMACEUTICAL WASTE DISPOSAL

If a drug is disposed incorrectly, dangerous chemicals can leach into the surroundings environments and contaminate ground water, drinking water, plants life and so on. This may cause health problems in the society. Improper disposal methods may include washing drugs down sinks, flushing them down toilets, throwing them away in trash or dumping.

1.6 METHYL ORANGE

Methyl orange is a pH indicator frequently used in titration because of its clear and distinct color variance at different pH values. Methyl orange shows red color in acidic medium and yellow color in basic medium. Because it changes color at the pKa of a mid strength acid, it is usually used in titration of strong acids in weak bases that reach the equivalence point at a pH of 3.1-4.4.[3] Unlike a universal indicator, methyl orange does not have a full spectrum of color change, but it has a sharp end point. In a solution becoming less acidic, methyl orange changes from red to orange and, finally, to yellow—with the reverse process occurring in a solution of increasing acidity.

Methyl orange moves from the color red to to yellow with the opposite occurring for a solution increasing in acidity. This color change from yellow to red occurs because the protons in the acidic solution react with the N=N bond of the molecule, protonating one of them and changing the visible light absorption of the molecule to reflect more red light than orange/yellow.



Fig 1.5 Methyl Orange

General Properties of Methyl Orange

Some general properties of methyl orange are tabulated below.

Chemical formula	$C_{14}H_{14}N_3NaO_3S$
Molar mass	$327.33 \text{ g}\cdot\text{mol}^{-1}$
Appearance	Orange or yellow solid
Density	1.28 g/cm^3

Fig 5.2 PROPERTIES OF METHYL ORANGE

In alkaline solution its colour is yellow, but the colour changes to red on adding a mineral acid. This change of colour is not produced by carbonic or other feeble acids. Hence, this indicator may be used for the titration of the more powerful mineral acids in the presence of carbonic acid and the feebler organic acids. The presence of much water causes the red colour of a faintly acid solution of methyl orange to become yellow, probably due to hydrolytic dissociation.

The indicator solution generally used is prepared by dissolving 0.1gm in 100cc of distilled water. One drop of this solution is used for each 20cc of the solution to be titrated.

A somewhat more sensitive solution, but one in which it requires more experience to detect the colour change, is prepared by dissolving 0.02gm in 100cc of hot water, allowing the solution to cool, and filtering out any deposited m-sulfonic acid. This more dilute indicator is to be preferred for very exact titrations with very dilute acids and alkalis.

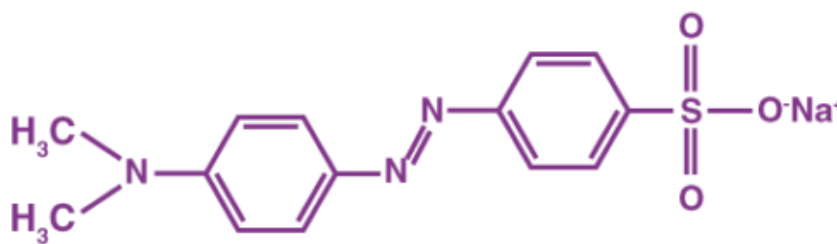


Fig 1.7 Methyl Orange Structure

CHAPTER 2

LITERATURE SURVEY

VI Lozinsky, FM Plieva - Enzyme and microbial technology, - Elsevier

Among them, the cryogens of poly (vinyl alcohol)—cryoPVAGs—have become increasingly

popular as carriers for cell immobilization primarily due to the very high operational stability

MI Baker, SP Walsh, Z Schwart - Journal of Biomedical - Wiley Online Library

A: The structure of vinyl alcohol is shown. B: PVA is synthesized by the hydrolysis of polyvinyl

The extended literature reviewed in this article serves as a good summary of the in vivo

MA Teixeira, MTP Amorim, HP Felgueiras - Polymers,

However, very few are successfully processed using environmentally friendly solvents;

poly (vinyl alcohol) (PVA) is one of those. PVA has been investigated for TE scaffolding production

CH Tsou, ZL Ma, MR De Guzman, L Zhao, J D - Progress in Organic - Elsevier

resistance from this present study were higher than those in the literature (whether graphene

Graphene based poly (vinyl alcohol) nanocomposites prepared by in situ green reduction

L Bian, Y Dong, B Jiang - Journal of Environmental Sciences, - Elsevier

In this present study, a typical water-soluble polymer, polyvinyl alcohol (PVA) as a model

polymer pollutant was degraded using the MIL-53(Fe) solids deposited on polyester (PET)

C Verma, MA Quraishi - Corrosion Engineering, Science and - Taylor & Francis

Further, a literature study suggests that many extracts need a ... vinyl alcohol (monomer) is

more stable than its alcoholic form, PVA is not synthesised by the polymerisation of vinyl alcohol

CHAPTER 3

AIM AND SCOPE

3.1 AIM

The main aim of this project is to synthesize MOFs based on Poly Vinyl Alcohol (PVA) nanoparticle composites. PVA as the organic material which is also a waste product in certain application references. Metals such as Cu and Fe are incorporated into the polymer to enhance degradation of dyes and other pollutants such as methyl orange. Incorporation of Fe make adsorbent magnetic for its efficient removal and reuse. (PVA) nanoparticles were characterized with the help of FTIR, XRD, SEM and UV-VIS Spectroscopy to remove the efficient magnetic adsorbent from methyl orange using as dye.

3.2 Scope

- Synthesizing of MOFs on (PVA) by sol-gel method.
- Characterization of (PVA) by FTIR spectroscopy, XRD, SEM and UV-VIS Spectroscopy.
- Confirmation of product formed by characterization by FTIR.

CHAPTER 4

MATERIALS AND METHODOLOGY

4.1 MATERIALS:

Materials used in this reaction are copper sulphate, sodium hydroxide. copper bisglycinate, glycine and ferric chloride. Distilled water, which were purchased from micro fine chemicals and it can be used without further purification.

4.2. CHARACTERIZATION TECHNIQUES:

4.2.1 Powder X-Ray Diffraction (XRD)

Since most materials have unique diffraction patterns, when an X-ray is incident on the crystal they scattered in accordance with Bragg's law, it diffracts and produces different patterns. Which assumes the diffraction to take place only when the distance travelled by the rays reflected from the successive planes of crystal, by scanning the sample through a range of 2θ angles, plotting the angular positions and intensities of the resultants diffracted peaks produced the pattern. Finally, matching the resultants diffraction peaks to characterize, finally the resultant patterns are also studied for the position of diffraction maxima, peak intensities, and the intensity distribution as a function of the diffraction angle, Here the diffracted pattern is obtained from a powder of the material. Compounds can be determined from its diffracted pattern. Powder diffraction is often easier and more convenient than single crystal diffraction, the purity of a sample can also be determined from its diffracted pattern, Powder X-ray diffraction is a characterization tool that offers a detailed view of the crystallographic structure and chemical composition of the sample. The particle size can be determined by using the Scherrer formula is

$$\text{Scherrer formula} = (D = K\lambda/\beta\cos\theta)$$

Where, $K =$ e Shape factor (0.9) $\lambda =$

wavelength of X-rays, $\beta =$ corrected full

width at half-maximum; θ = angle of peak

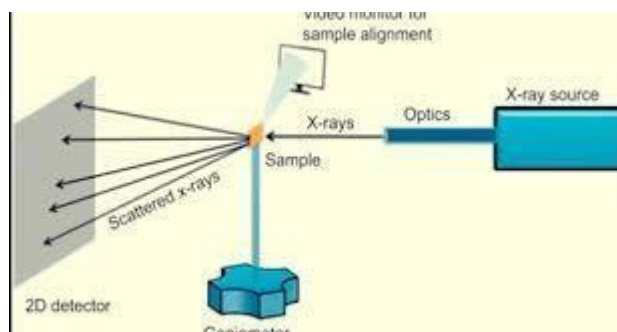


Fig 4.1 X-ray diffractometer

Source: <https://www.14impressions.in/2020/09/principle-instrumentationtypes-and.html>

4.2.2 Fourier Transform Infrared Spectrometer

FTIR stands for Fourier transform infrared, it is a versatile tool for surface characterization of nanoparticle. It involves in various phenomena such as the adoption, reflection, and emission of light using the sample and it is used to identification of organic, inorganic, and polymeric materials using infrared light for scanning the samples. FTIR is useful in identifying and characterizing unknown materials, detection contaminants in a material, finding additives, and identifying decomposition and oxidation. FTIR spectrometer includes a source, sample cell, detector, amplifier, A/D convertor, and a computer. when IR radiation is passed through a sample, some radiation is absorbed by the sample and some passes through (is transmitted), radiation from the source reach the detector after it passes through the interferometer. The signal is amplified and converter to a digital signal by the A/D converter and Amplifier, then the signal is carried to the computer. The resultant signal obtained at the detector is a spectrum generally from the range of $4000\text{-}400\text{ cm}^{-1}$ which represents the fingerprint range of sample. For this purpose, the sample were mixed potassium bromide and made into pellets for analysis.



Fig 4.2 Fourier Transformer Infrared Spectrometer

Source: <https://blogs.getty.edu/iris/conservation-tools-fourier-transforminfrared-spectroscopy-ftir/>

4.2.3 Scanning Electron Microscopy

Scanning electron microscope (SEM) uses a focused beam of high-energy electrons to generate a variety of signals at the surface, the signal comes out from the electron- sample interaction reveal the information about the sample including external morphology, chemical composition, and crystalline structure and orientation of materials making up the sample. it a high-resolution image of the size and surface texture of the particle, SEM equipped with EDX can determine the main atomic composition of pf the particle, particle colours cannot be determined by SEM. SEM/ESEM-EDX. SEM is one of the main testing instruments for in situ analysis of micro areas. It has high magnification, and strong stereoscopic view. Photographs taken by SEM have higher magnification and clearer definitions than those by optical microscopy. SEM can be able to measure only elements with atomic coefficients less than 5. Using SEM we can get the selected point location images of the sample. This approach is especially useful in qualitative determining chemical composition. In SEM examination system the zones territory from around 1cm to 5 microns in width can be imaged in a filtering mode utilizing SEM methods and having amplification run from spatial goals of 50nm to 100nm.

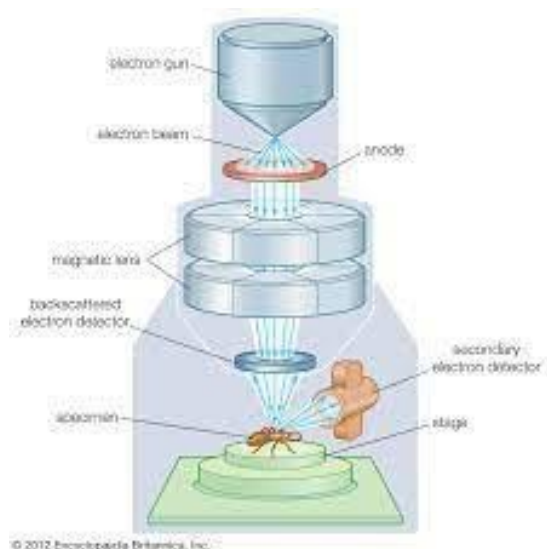


Fig 4.3 Scanning Electron Microscopy

Source: <https://www.britannica.com/technology/scanning-electronmicroscope>

4.2.4 Ultraviolet visible Spectroscopy (UV-VIS)

Ultraviolet-visible spectroscopy or ultraviolet-visible spectrophotometry (UV-Vis or UV/Vis) refers to absorption spectroscopy or reflectance spectroscopy in the ultraviolet-visible spectral region. Ultraviolet-visible (UV-VIS) spectroscopy is an analytical method that can measure the analyte quantity depending on the amount of light received by the analyte. Ultraviolet/Visible area (UV-Vis) measurements span wavelengths from around 200 nm to 800 nm. The absorption by a molecule of ultraviolet or visible radiation results in transitions between the molecule's electrical energy levels. The optical and electronic properties of different materials, such as films, powders, monolithic solids, and liquids, are suitable for characterization.

Generally, the UV and visible spectral bands of substances are large. And may not exhibit a high degree of compound recognition accuracy. Nonetheless, they are sufficient for quantitative assays and are useful as an alternate means of detection for several substances. The radiation from typical hot solids consists of several wavelengths and depends primarily on the temperature of the solid and is predictable from the principle of chance, the energy released at each given wavelength.

A common technique for quantitative analysis of analytes in QA/QC, analytical research, and government regulatory laboratories is UV-Visible spectrophotometry. The fundamentals of the approach are learned in school, such as Beer's Law. UV-Visible Mid-range to Upper-end Spectrophotometers are typically used in research laboratories, including university and industrial laboratories.



Fig 4.5 ULTRAVIOLET VISIBLE SPECTROPHOTOMETER

Source: <https://www.jeol.co.jp/en/products/nmr/basics.html>

UV-vis spectroscopy is a cost-effective, simple, versatile, non-destructive, analytical technique suitable for a large spectrum of organic compounds and some inorganic species. As a function of wavelength, UV-vis spectrophotometers measure the absorption or transmission of light that passes through a medium.

In order to classify and measure the concentration of substances in liquid streams, high performance liquid chromatography and ultra-high performance liquid chromatography incorporate UV-vis detectors. It allows the detection of all animals by integrating these techniques with mass spectrometry.

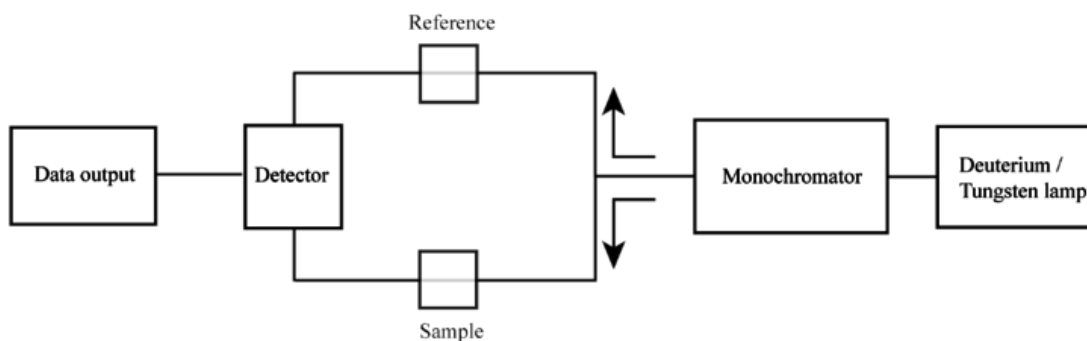


Fig 4.6 WORKING OF UV-VIS SPECTRPHOTOMETER

Source: <https://www.jeol.co.jp/en/products/nmr/basics.html>

In research, ultraviolet/visible spectroscopy is used more commonly than in detection. Through first reacting the sample to bring the metal into solution as an ion, the trace metal content of an alloy, such as manganese in steel, can be determined.

The ion is then complexed or made to react so that it can be measured in a shape, such as manganese as the manganate(VII) ion. When the spectrum is registered, the absorbance is the most valuable bit of information since the concentration of the solution can be determined if the absorption coefficient of the chromophore is known and thus the mass of the metal in the sample.

4.3 METHODOLOGY:

4.3.1 Synthesis of PVA Cu in MOFs nanoparticles

Particles of MOFs in PVA were synthesized via a solvo-thermal method that has been reported previously. First, 2.7 g 1.0 g copper sulphate and 4.8 g NaOH were dissolved in 80mL sodium hydroxide with magnetic stirring for 0.5h. Then the above mixed liquor was transferred to a sealed Teflon-lined stainless-steel which was heated in an autoclave at 60°C for 10h. The resultant PVA-Cu microspheres was collected, washed with acetone several times, and dried at 50°C under vacuum. PVA-Cu particles were prepared follows¹⁸, 0.5 g copper bisglycinate was added to 100mL of acetone solution PVA-Cu under shaking for 24h. The product was collected by an external magnetic field and washed.

4.3.2 Synthesis of PVA Cu / PVA Cu- Fe in MOFs nanoparticles

An aliquant of 0.2 g copper sulphate and microspheres were dispersed in 100mL beaker 1.82 g ferric chloride and for 30min. Then, 100mL of 0.875 g copper bisglycinate was dropped into the above suspension at a constant rate of 1mL min⁻¹ followed by continuous mechanical stirring for 2h. The resulting PVA-Cu / PVA Fe-Cu microspheres were collected from the reaction mixture under an external magnetic field, washed with ethanol several times, and dried at 50 °C under vacuum

4.3.3 Effect of Composite Dosage on Dye Removal

The composite dosage is one of the important factors in the process of the photodegradation of organics because the optimal dosage of composite ensures more active sites and the effective absorption of photons. To investigate the influence of the modified composite dosage (FeCl₃/PVA) on Methyl Orange removal, a series of four dosages (1.5, 2, 3, and 5 g) was carried out, and the results are presented in Table 1. To determine the effect of the amount of composite on the removal efficiency of Methyl Orange, a synthetic solution with an initial concentration of Methyl Orange of $5 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$, at pH of 3.0, was used, with an initial amount of H₂O₂ (6.7 mL) and a contact time of 120 min.

4.3.4 Adsorptive efficiency of adsorption parameters

Reusability of adsorbent.

To assess reusability of the adsorbent, which contributes to reduce the cost of practical application process, methanol, ethanol and acetonitrile were used in desorption and regeneration experiment and acetonitrile shows the best desorption efficiency. Capacity for adsorption of Materials PVA-Cu / PVA Fe-Cu This work composite 20 200 3 Acid modified local clay beads Bamboo based activated polymer – Groundnut shell activated polymer Hierarchically mesostructured Table 2. Comparison of capacities of adsorption of MB on different adsorbents. www.nature.com/scientificreports/ Scientific Report on PVA-Cu / PVA Fe-Cu 2 decreases slowly with increasing cycle number. A 90% removal rate of MB was achieved after five consecutive cycles, indicating the good recycling ability of PVA-Cu / PVA Fe-Cu

CHAPTER 5

RESULT AND DISCUSSION

5.1 CHARACTERIZATION OF CU AND FE OF (PVA) IN MOFs COMPOSITE

5.1.1 FTIR Spectrum of MOFs composites

The FTIR spectrum of PVA in Fe and Fe-Cu particles are shown in Fig.4.1 the IR vibrational frequency obtained at 3332 cm^{-1} 2797 cm^{-1} 1384 cm^{-1} 1028 cm^{-1} 918 cm^{-1} and 738 cm^{-1} correspond to O-H stretching of adsorbable water molecules on magnesium oxide, C=O stretching, water and CO₂ molecule adsorption on PVA in Fe and Fe-Cu surface, O-H in plane bending of carboxyl group adsorbed on Fe and Fe-Cu and metal – oxygen bond Fe/Cu-O stretching respectively. The peak at 738 cm^{-1} is the characteristic peak for PVA in Fe and Fe-Cu particles.

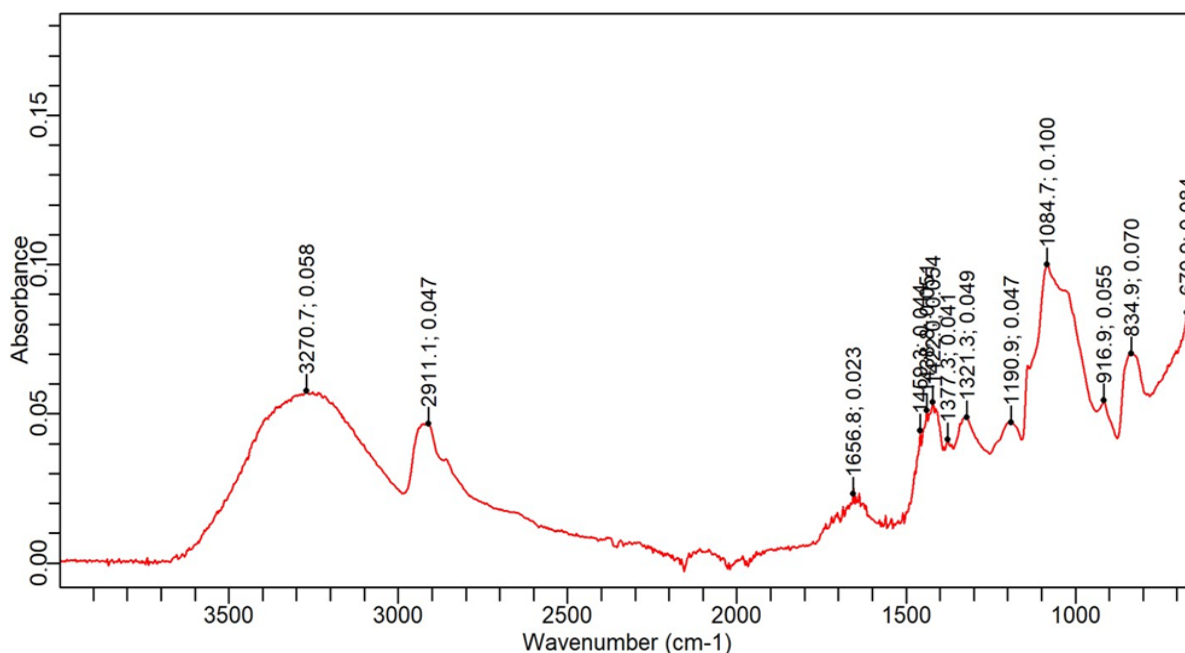
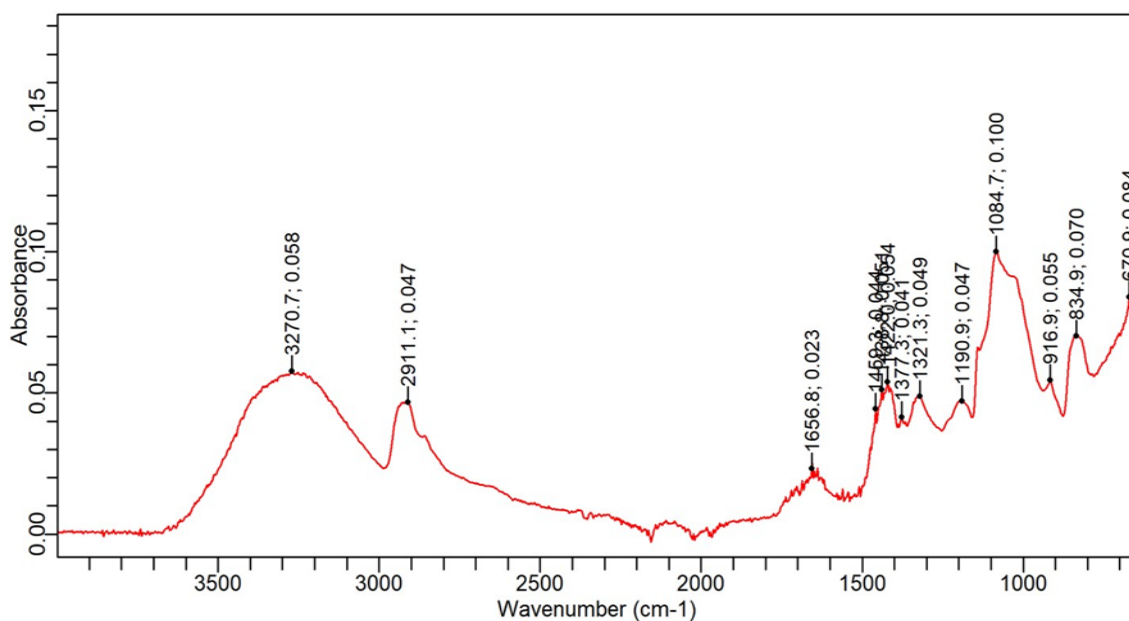


Fig 5.1.1 FTIR spectrum of composite MOFs in PVA-Cu / PVA Fe-Cu



5.1.2 FTIR spectrum of composite MOFs in PVA-Cu / PVA Fe-Cu

The SEM image of Fe and Fe-Cu particle is shown in the Fig. 4.2. the image explains that MOFs in PVA-Cu / PVA Fe-Cu particle obtained have spherical shape. The SEM image also shows the presence of agglomerates of Fe and Fe-Cu nanoparticles.

The EDAX spectra shows the presence of Fe and O in the Fe and Fe-Cu catalyst.

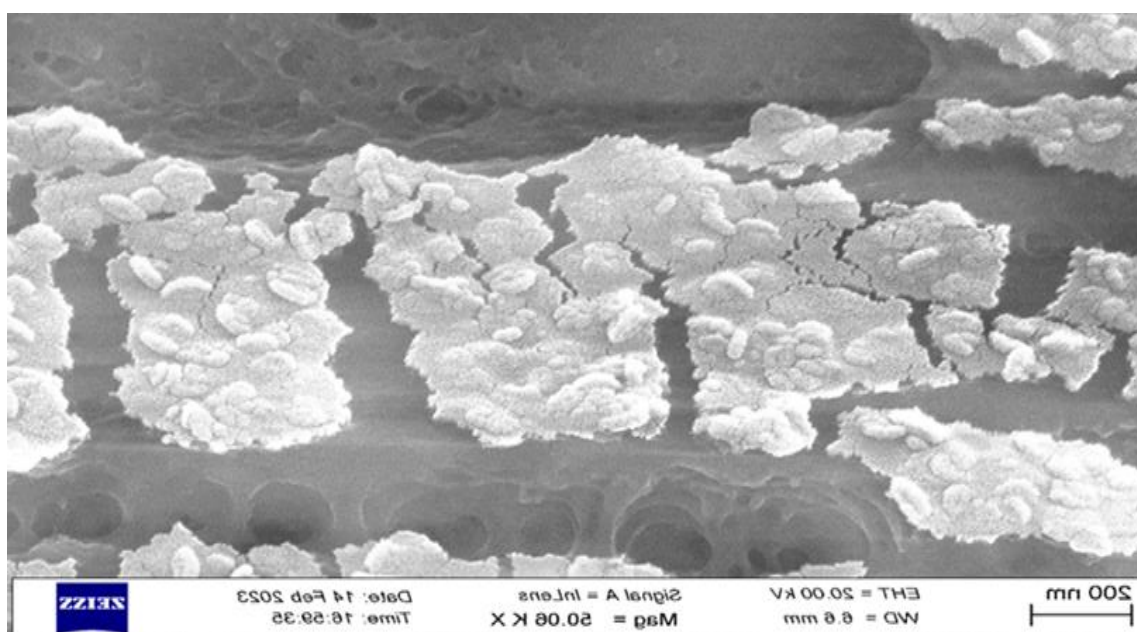


Fig 5.2.1 EDAX image for MOFs in PVA-Cu / PVA Fe-Cu composite

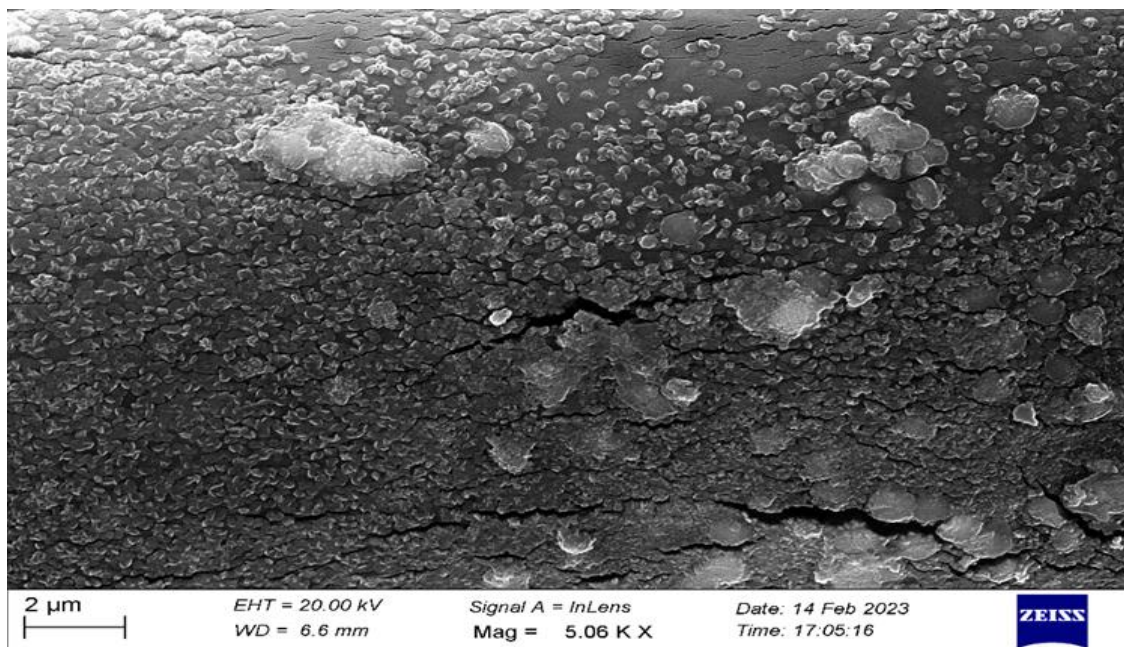


Fig 5.2.2 SEM image of MOFs in PVA-Cu / PVA Fe-Cu composite

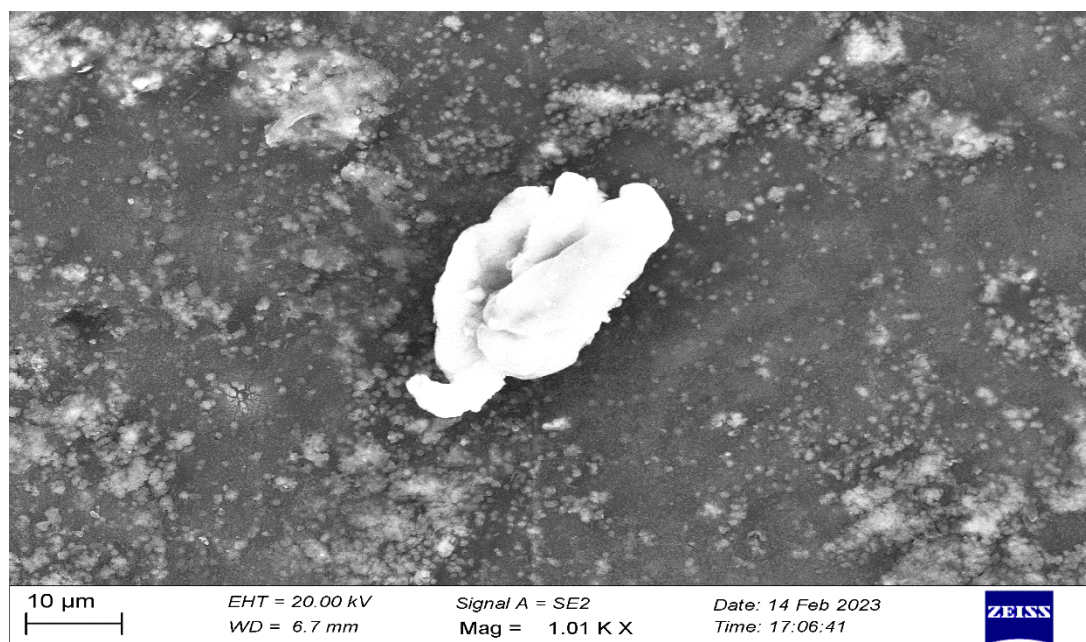


Fig 5.3.2 EDAX image for MOFs in PVA-Cu / PVA Fe-Cu composite

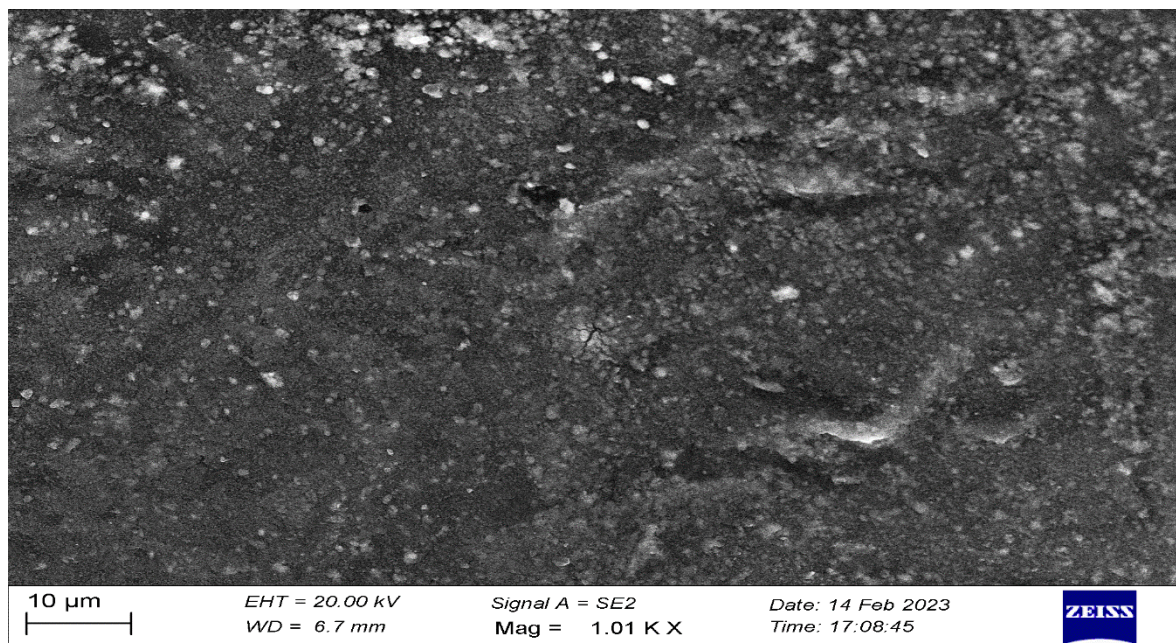


Fig 5.3.1 EDAX image for MOFs in PVA-Cu / PVA Fe-Cu composite

5.1.3 XRD pattern of MOFs in PVA-Cu / PVA Fe-Cu composite

The XRD pattern of MOFs in PVA-Cu / PVA Fe-Cu particle is shown in the Fig 4.4 X-ray diffraction. The peak at the 41 and 61 ascribing to Fe/Fe-Cu were found in MOFs in PVA. And the peak at 29 describes iron and copper.

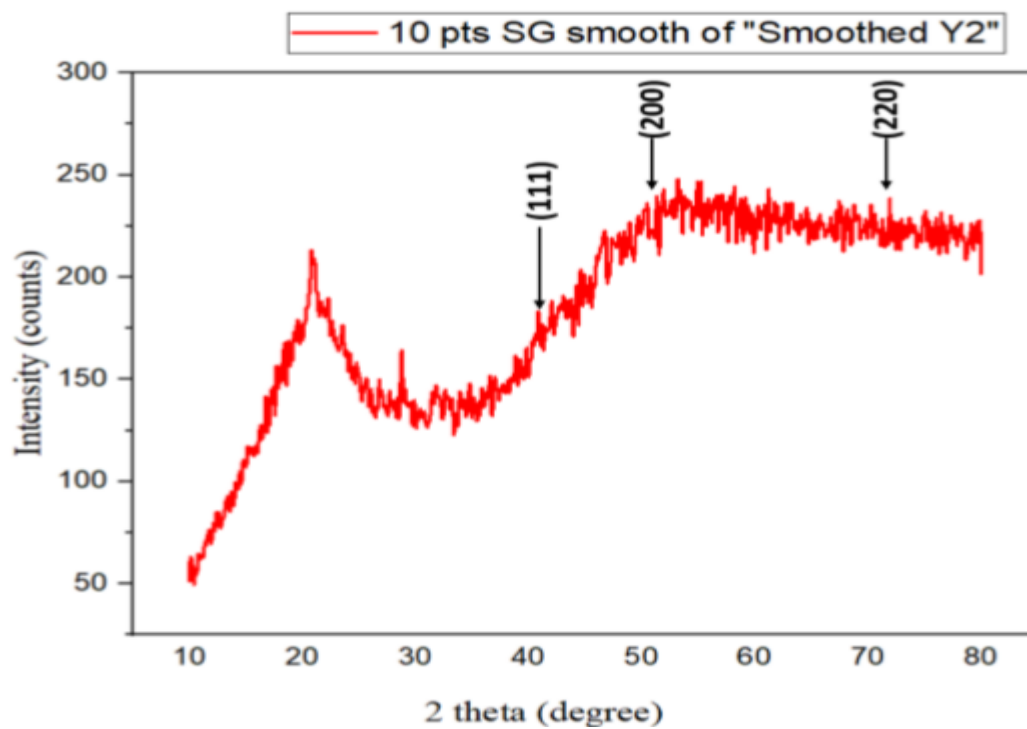


Fig 5.6 XRD pattern for MOFs in PVA-Cu / PVA Fe-Cu composite

5.2 UV-VIS SPECTROSCOPY:

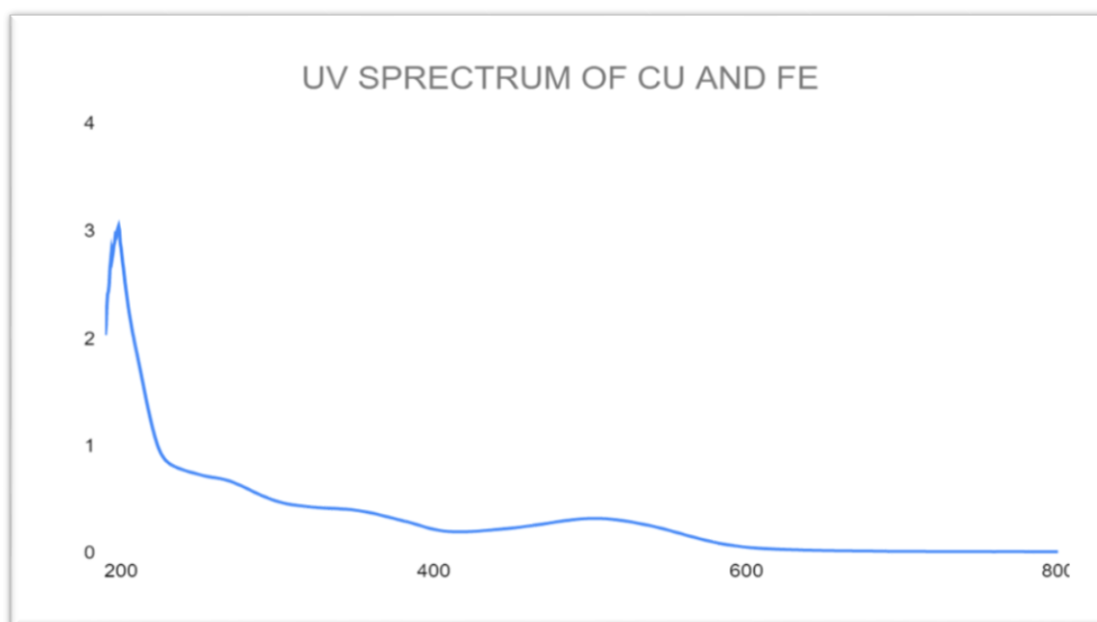


Fig 5.7.2UV VIS Spectrum pattern for MOFs in PVA in Fe and Cu

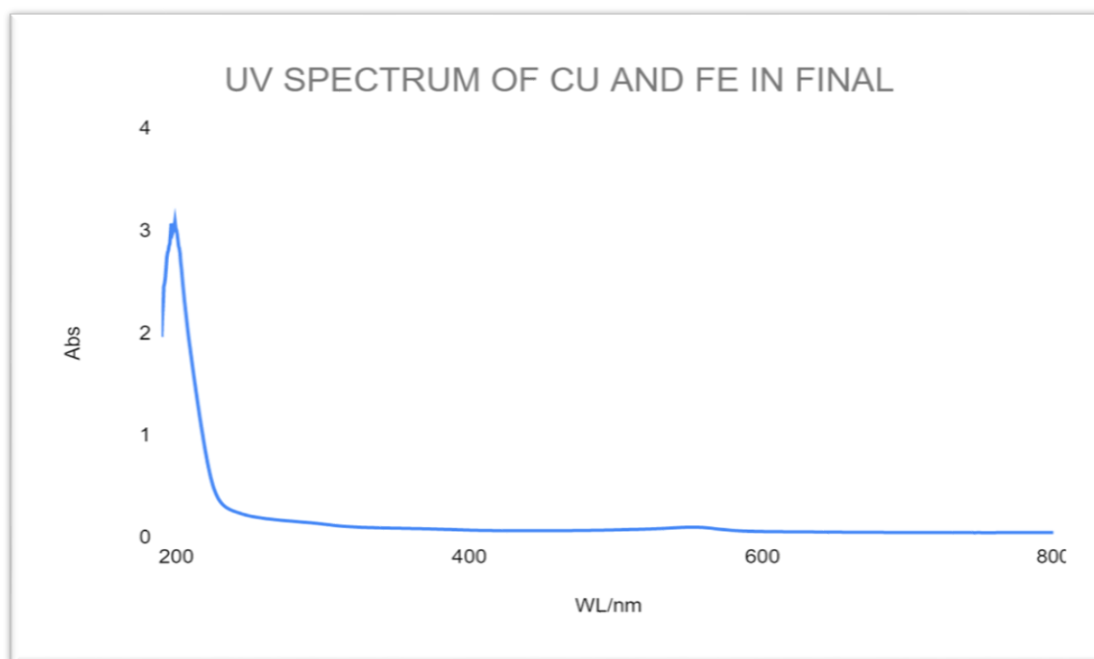


Fig 5.7.1 UV VIS Spectrum pattern for MOFs in PVA in Fe and Cu

CHAPTER 6

RESULT AND CONCLUSION

In this work, we have successfully developed an efficient catalyst for the removal of toxic methyl orange dye from aqueous medium. In many industries Polyvinyl alcohol are generated as waste product utilising it and also using toxic metal which cause heavy metal pollution, we have synthesized an efficient catalyst and characterized using differential analytical techniques. The MOFs will effectively degrade the pollutant methyl orange dye from the industrial waste water pollution. The prepared PVA Cu / PVA Cu-Fe MOFs was regenerated and reused exhibiting an excellent catalytic activity for many consecutive cycles. The prepared catalyst also possesses prominent antibacterial property and recyclability. Thus, from the current work, we can conclude that PVA-Cu/PVA-Cu-Fe catalyst could be a promising candidate for the removal of Methyl Orange from polluted water.

REFERENCES

1. Sun, L. S. & Luo, W. Biochars prepared from anaerobic digestion residue, palm bark, and eucalyptus for adsorption of cationic methylene blue dye: characterization, equilibrium, and kinetic studies. *Bioresour. Technol.* 140, 406–413 (2013).
2. Yao, Y., Xu, F., Chen, M., Xu, Z. & Zhu, Z. Adsorption behavior of methylene blue on carbon nanotubes. *Bioresour. Technol.* 101, (3040–3046 (2010).
3. Auta, M. & Hameed, B. H. Chitosan–clay composite as highly effective and low-cost adsorbent for batch and fixed-bed adsorption of methylene blue. *Chem. Eng. J.* 237, 352–361 (2014).
4. Auta, M. & Hameed, B. H. Acid modified local clay beads as effective low-cost adsorbent for dynamic adsorption of methylene blue. *J. Ind. Eng. Chem.* 19, 1153–1161 (2013).
5. Liu, T. et al. Adsorption of methylene blue from aqueous solution by grapheme. *Colloid. Surface. B.* 90, 197–203 (2012).
6. Rafatullah, M., Sulaiman, O., Hashim, R. & Ahmad, A. Adsorption of methylene blue on low-cost adsorbents: a review. *J. hazard. Mater.* 177, 70–80 (2010).
7. Li, Y. et al. Comparative study of methylene blue dye adsorption onto activated carbon, graphene oxide, and carbon nanotubes. *Chem. Eng. Res. Des.* 91, 361–368 (2013).
8. Wang, L. L. et al. Synthesis of Fe₃O₄@C core-shell nanorings and their enhanced electrochemical performance for lithium-ion batteries. *Nanoscale.* 5, 3627–3631 (2013).
9. Tu, M. & Fischer, R. A. Heteroepitaxial growth of surface mounted metal–organic framework thin films with hybrid adsorption functionality. *J. Mater. Chem. A.* 2, 2018–2022 (2014).
10. Stock, N. & Biswas, S. Synthesis of metal-organic frameworks (MOFs): routes to various MOF topologies, morphologies, and composites. *Chem. Rev.* 112, 933–969 (2012).

11. Talin, A. A. et al. Tunable electrical conductivity in metal-organic framework thin-film devices. *Science*. 343, 66–69 (2014).
12. Zhang, C. F. et al. A novel magnetic recyclable photocatalyst based on a core-shell metal-organic framework Fe₃O₄@MIL100(Fe) for the decolorization of methylene blue dye. *J. Mater. Chem. A*. 1, 14329–14334 (2013).
13. Xuan, W., Zhu, C., Liu, Y. & Cui, Y. Mesoporous metal-organic framework materials. *Chem. Soc. Rev.* 41, 1677–1695 (2012).
14. Ebrahim, A. M. & Bando, T. J. Ce(III) Doped Zr-Based MOFs as Excellent NO₂ Adsorbents at Ambient Conditions. *ACS Appl. Mater. Inter.* 5, 10565–10573 (2013).
15. Xiong, Z. et al. Facile Preparation of Core-Shell Magnetic Metal-Organic Framework Nanospheres for the Selective Enrichment of Endogenous Peptides. *Chem. Eur. J.* 6, 22743–22750 (2014).
16. Ke, F., Qiu, L.G. & Zhu, J. Fe₃O₄@MOF core-shell magnetic microspheres as excellent catalysts for the Claisen-Schmidt condensation reaction. *Nanoscale*. 6, 1596–1601 (2014).
17. Chen, X. et al. Fe₃O₄@MOF core-shell magnetic microspheres for magnetic solid-phase extraction of polychlorinated biphenyls from environmental water samples. *J. Chromatogr. A*. 1304, 241–243 (2013).
18. Ke, F., Qiu, L. G., Yuan, Y. P., Jiang, X. & Zhu, J. F. Fe₃O₄@MOF core-shell magnetic microspheres with a designable metal-organic framework shell. *J. Mater. Chem.* 22, 9497–9450 (2012).
19. Wee, L. H., Lohe, M. R., Janssens, N., Kaskel, S. & Martens, J. A. Fine tuning of the metal-organic framework Cu₃(BTC)₂HKUST-1 crystal size in the 100 nm to 5 micron range. *J. Mater. Chem.* 22, 13742 (2012).
20. Schlichte, K., Kratzke, T. & Kaskel, S. Improved synthesis, thermal stability and catalytic properties of the metal-organic framework compound Cu₃(BTC)₂. *Micropor. Mesopor. Mat.* 73, 81–88 (2004).

21. Ke, F. et al. Facile fabrication of magnetic metal-organic framework nanocomposites for potential targeted drug delivery. *J. Mater. Chem.* 21, 3843–3848(2011).
22. Zeng, T. et al. Assembly of a nanoreactor system with confined magnetite core and shell for enhanced Fenton-like catalysis, *Chem. Eup. J.* 20, 6474–6481 (2014)
23. Zeng, T. et al. In situ growth of gold nanoparticles onto polydopamine-encapsulated magnetic microspheres for catalytic reduction of nitrobenzene. *Appl. Catal. B-Environ.* 134-135, 26–33 (2013).
24. Zeng, T. et al. A functional rattle-type microsphere with a magnetic-carbon double-layered shell for enhanced extraction of organic targets. *Chem. Commun.* 49, 6039–6041(2013).
25. Bandosz, T. J. & Petit, C. MOF/graphite oxide hybrid materials: exploring the new concept of adsorbents and catalysts. *Adsorption.* 17, 5–16 (2010).