

METAL ORGANIC FRAMEWORKS FOR ENVIRONMENTAL REMEDICATION

**Submitted in partial fulfilment of the requirements for the award of
Master of Science in Chemistry**

by

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**SATHYABAMA
INSTITUTE OF SCIENCE AND TECHNOLOGY
(DEEMED TO BE UNIVERSITY)**

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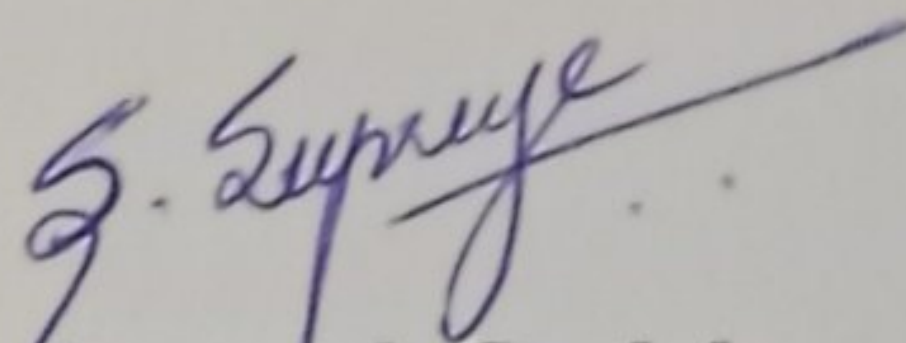
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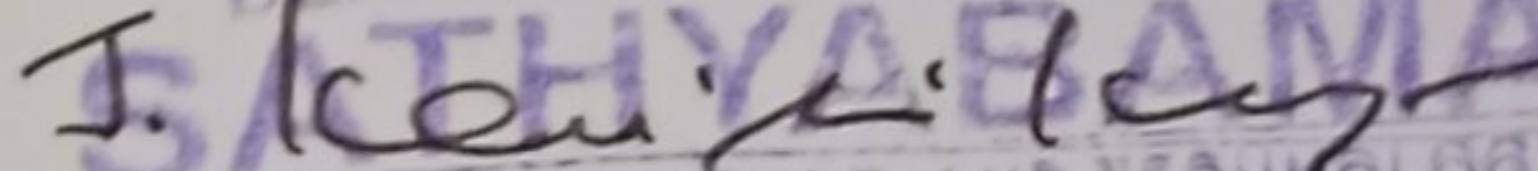
BONAFIDE CERTIFICATE

This is to certify that this Project Report is the bonafide work of **ISWARYA.S** (41910010) who carried out the project entitled "**METAL ORGANIC FRAMEWORKS FOR ENVIRONMENTAL REMEDIATION**" under our supervision from November 2022 to May 2023.


Internal Guide

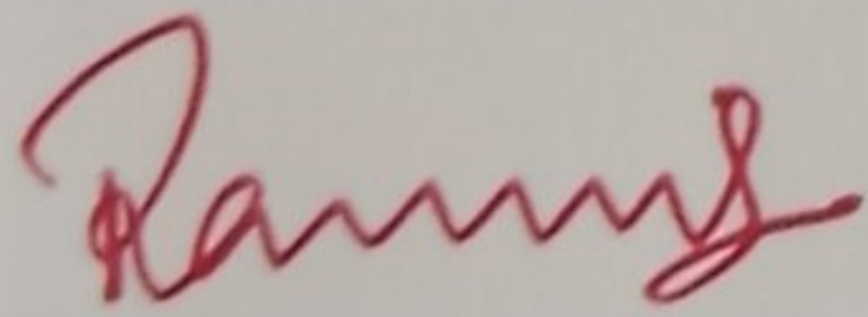
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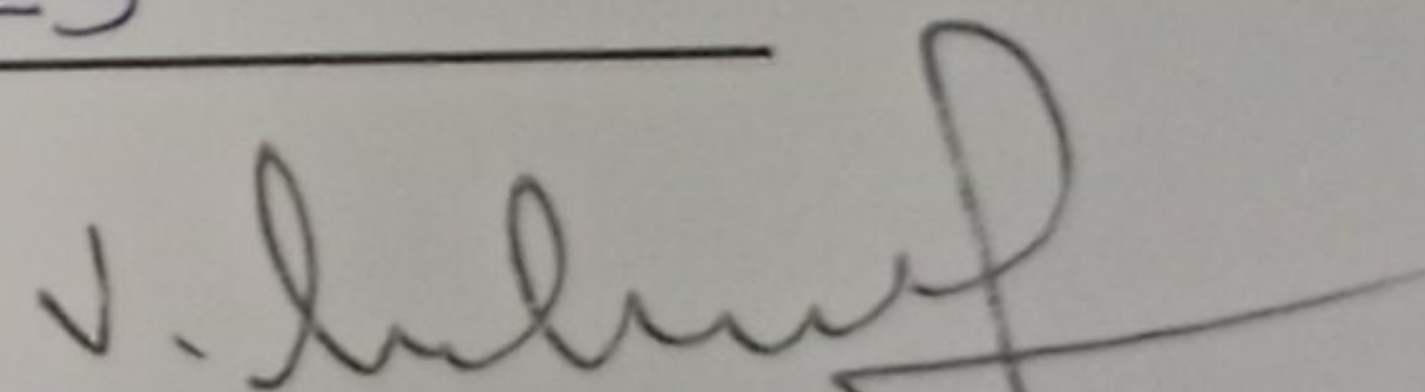

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I ISWARYA.S (41910010), hereby declare that the Project Report entitled "METAL ORGANIC FRAMEWORKS FOR ENVIRONMENTAL REMEDIATION" done by me under the guidance of Dr. S.SUPRIYA, M.Sc., Ph.D., Associate professor, Department of Chemistry at Sathyabama 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.

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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 as 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 Congo red dye has been studied. The characterization of pure PVA/Cu and PVA/Cu/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. Congo red dye has been found to undergo degradation immediately in the presence of MOFs and is used to clean the water bodies from contaminants and also to bring back the normal neutral pH. Incorporation of metals have been found to make MOFs an efficient pollutant absorber and can also be reused.

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LIST OF ABBREVIATIONS

MOF's - Metal Organic Frameworks

PVA - Polyvinyl Alcohol

CRD - Congo Red Dye

Cu - Copper

CuSO₄ - Copper Sulphate

Fe - Iron

HCl - Hydrochloric acid

NaOH - Sodium Hydroxide

g/mL - Gram Per Millilitre

pH - Potential of Hydrogen

mL - Millilitre

UV - Vis Ultraviolet Visible

FTIR - Fourier Transform Infrared

XRD - X-Ray Diffraction

FESEM - Field Emission Scanning Electron Microscope

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CHAPTER 1

INTRODUCTION

1.1 GENERAL:

Metal-organic framework (MOF) is a promising class of materials composed of metal centres or clusters and organic linkers. These are porous crystalline materials in which metal is locked into a position to produce rigid and porous geometry and connected through different organic groups. Due to structural flexibility, large surface area and tailorable pore size, MOFs have wide applications in field of gas adsorption and storage, separation, catalysis, sensing, molecular recognition, drug delivery, non-linear optics, luminescence etc. Due to three dimensional tuneable porous channels, MOFs are useful materials for storage, separation or conversion of molecules on the basis of dimension. However, MOFs are more specific than co-ordination polymers for 2D or 3D crystallized networks with porous structure. Thus these are also termed as porous coordination polymer (PCP). Although, several review articles on metal-organic frameworks have been published previously, however, recent advances including the contributions of some Indian research groups, such as Banerjee et al, Ghosh et al, and Kumar et al (1).

1.1.1 ABOUT PVA:

Poly (vinyl alcohol) (PVA) is a most simple synthetic water-soluble polymer bearing only alcoholic OH groups (2). It is quite interesting that PVA has a property of forming complexes with inorganic ions and compounds and even organic substances in a wide pH ¹⁻⁶; some of the complexes are colloids or gels. PVA which is essentially made from polyvinyl acetate through hydrolysis, is easily degradable by biological organisms and in water is a solubilized crystalline structure polymer. PVA is an artificial polymer that has been used during the first half of the 20th century worldwide. It has been applied in the industrial, commercial, medical, and food sectors and has been used to produce many end products, such as lacquers, resins, surgical threads, and food packaging materials that are often in contact with food. Some man-made polymers, which are made from non-renewable and non-biodegradable sources, such as PVA, are available. Polymers that are biologically decomposable originate from petroleum-based synthetic materials, which decompose naturally under aerobic (composting) or anaerobic (landfill) conditions. PVA is a widely used thermoplastic polymer that is benign to living tissues, harmless, and nontoxic. This polymer is widely investigated because of its use in cross-linked products and nanofillers. PVA is a biodegradable polymer, and its degradability is enhanced through hydrolysis because of the presence of hydroxyl groups on the

carbon atoms. Moreover, it is water-soluble and has a hydrophilic nature . Rates and environmental conditions for degradation may vary for many polymers, such as PVA ; these conditions include composting in the presence of oxygen, underneath soil layers, in aqueous media, and even in anaerobic circumstances.(3)

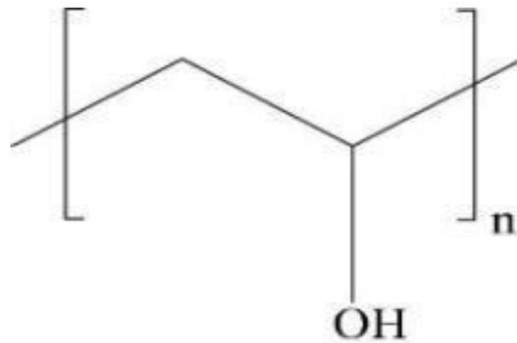


Fig.1.1 The structural formula of PVA

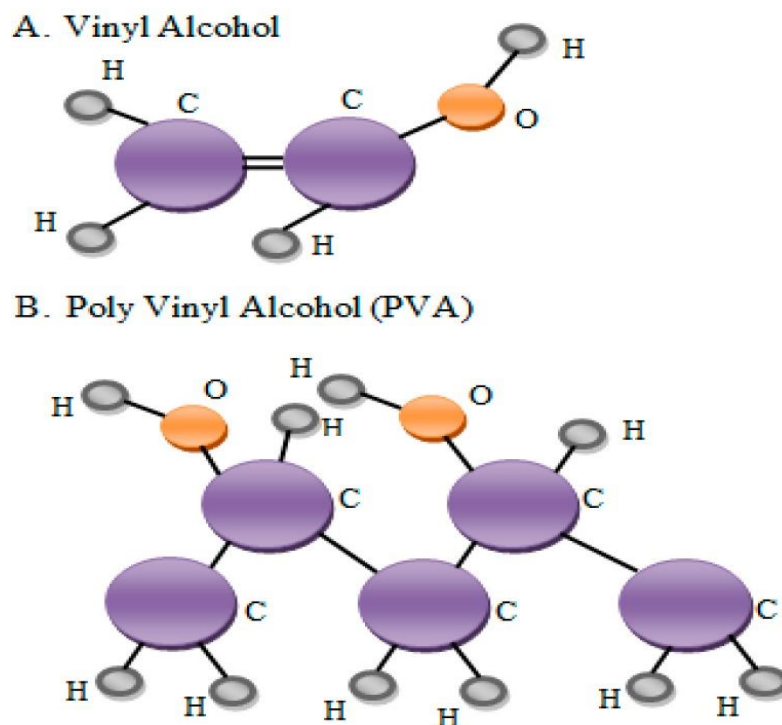


Fig.1.2(a) The structure of vinyl alcohol; (b) PVA is synthesized by the hydrolysis of polyvinyl acetate

1.1.2 CHEMICAL AND PHYSICAL PROPERTIES OF PVA:

The chemical and physical properties of PVA may vary based on the percentage of hydrolysis, which determines the PVA grade and its molecular weight. The surface properties of PVA fillers are fundamentally significant in the selection criteria of PVA fillers. PVA itself has substantial tensile strength, more flexibility, and hardness and gas and aroma barrier characteristics. Compared with any other known polymer, PVA demonstrates remarkably superior features as an oxygen barrier; however, to avoid the degradation of its permeability toward gas, it must be protected from moisture. PVA, like proteins, is a water-soluble polymer. The water solubility and physical properties of PVA, including its film form, are highly (4).

affected by the degree of hydrolysis, molecular weight, and its crystal precipitation. PVA is partially crystalline upon formation and is characterized by properties such as chemical resistance, water solubility, and biodegradability (5). The similarity in physical properties makes it compatible with human tissues. Biocompatible PVA has a structure that can absorb protein molecules and engage with minimal cell adhesion and has no toxic effects, therefore, PVA membranes have been widely developed for biomedical applications. PVA can chemically bound to or physically entangled with a nanoparticle surface. PVAs are very common polymers, widely used as surface materials, which should be retained on water surface, in a huge range of fields as films and glues because of their exceptional chemical and physical properties, biocompatibility, stability to temperature variation, and non-toxicity (4).

1.1.3 NATURE OF POLY(VINYL ALCOHOL) :

PVA is a creamy or whitish, tasteless, odorless, nontoxic, biocompatible, thermostable, granular or powdered semi crystalline or linear synthetic polymer. It possesses astonishing optical properties, large dielectric strength, and excellent charge storage ability. Its mechanical, optical and electrical attributes can readily be tailored by doping with nanofillers. PVA is available on the market in different grades on the basis of viscosity and degree of hydrolysis. PVA is most widely used in the synthesis of poly(vinyl butyral) (PVB) and vinylon fibers. PVB is a low cost flexible thermoplastic, being used as strong adhesive in multiple applications and might be used in shape memory devices. Vinylon is manmade heat and chemical resistant fiber (also called Juche fiber) fabricated from PVA and is widely used in textiles, quilts wadding, ropes, and shoes (6).

Other consumers of PVA include the textile industry, paper making, coatings, adhesives, medicines, optics, 3D printing and so on. The major PVA producers are Europe, Japan, USA, and China. In 2016, worldwide production of plastics and PVA was about 335 million metric tons and 1124 kilo metric tons, respectively. For the same year, contribution in PVA production of Asia pacific and USA was about 580 and 172.8 kilo tons, respectively. (6)

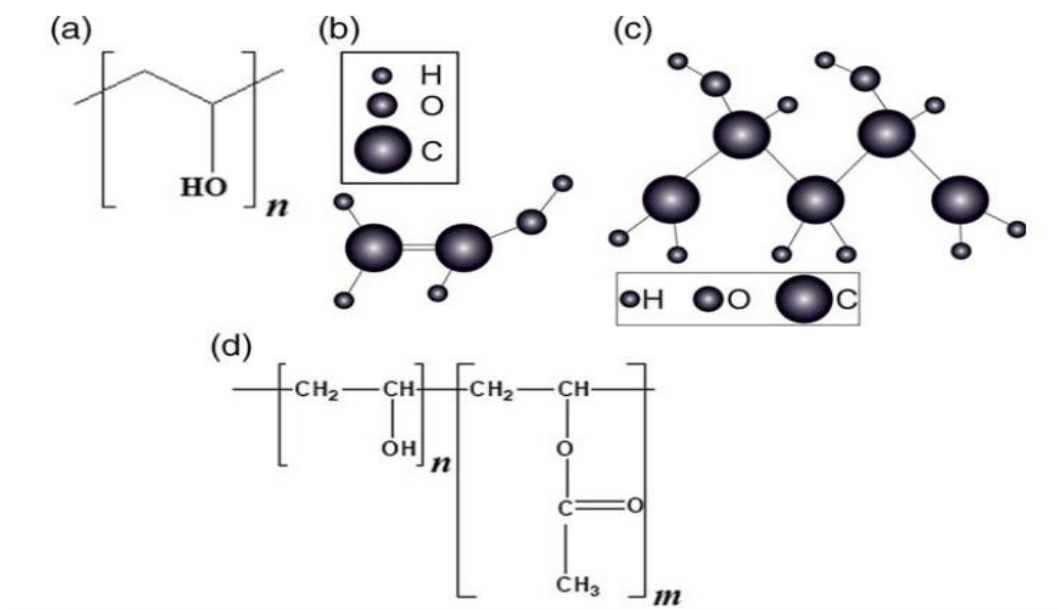


Fig.1.3 Representative (a) PVA monomeric structure/completely hydrolyzed PVA, (b) vinyl alcohol structure, (c) PVA structure, and (d) partially hydrolyzed PVA

1.2 HEAVY METAL POLLUTANTS:

The environment is the surroundings where humans, plants, animals and micro-organisms live or work. It is composed of the land, the Earth's atmosphere and the water. Environmental contaminants, as well as pollutants, are chemicals that are present at higher levels than in any section of the environment. During the last hundred years, industrialisation has grown at a fast rate. It has thus increased the demand for exploitation of the Earth's natural resources at a careless rate, which has exacerbated the world's problem of environmental pollution. The environment has been seriously polluted by several pollutants. (7)

such as inorganic ions, organic pollutants, organometallic compounds, radioactive isotopes, gaseous pollutants and nanoparticles. They are defined as heavy metals either due to their high atomic weight or because of their high density. Nowadays, the word 'heavy metal' has been used to describe metallic chemical elements and metalloids which are toxic to the environment and humans. Some metalloids and also lighter metals such as selenium, arsenic and aluminium are toxic. They have been termed heavy metals while some heavy metals are typically not toxic such as the element gold. A list of heavy metals according to their density of being greater than 5 g/cm³ and which are more common in our everyday life are: Titanium, Vanadium, Chromium, Manganese, Iron, Cobalt, Nickel, Copper, Zinc, Arsenic, Molybdenum, Silver Cadmium, Tin, Platinum, Gold, Mercury and Lead. (7)

1.2.1 SOURCES OF HEAVY METALS:

These heavy metals are found naturally on the Earth's crust since the Earth's formation. Due to the astounding increase of the use of heavy metals, it has resulted in an imminent surge of metallic substances in both the terrestrial environment and the aquatic environment. Heavy metal pollution has emerged due to anthropogenic activity which is the prime cause of pollution, primarily due to mining the metal, smelting, foundries, and other industries that are metal-based, leaching of metals from different sources such as landfills, waste dumps, excretion, livestock and chicken manure, runoffs, automobiles and roadworks.(7) Heavy metal use in the agricultural field has been the secondary source of heavy metal pollution, such as the use of pesticides, insecticides, fertilisers, and more. Natural causes can also increase heavy metal pollution such as volcanic activity, metal corrosion, metal evaporation from soil and water and sediment re-suspension, soil erosion, geological weathering.

1.2.2 COPPER-HEAVY METAL:

Copper is a chemical element its symbol is Cu (It is derived from Latin: cuprum) and atomic number is 29. It is a soft, malleable, and ductile metal and it has very high thermal and electrical conductivity. A freshly exposed surface of the pure copper has a pinkish-orange colour. Copper toxicity (also known as Copperiedus) is a form of metal poisoning caused by a build-up of copper in the body. Copperiedus can be caused by eating acidic meals cooked in uncoated copper cookware, wearing an IUD, being exposed to excessive copper in drinking water and other environmental sources, or

having Wilson's disease, which is a genetic illness. Copper poisoning is possible if you consume too much of it. Ingesting high amounts of copper salts through your skin could cause serious poisoning. Copper can accumulate in your brain, liver, and lungs as it passes through your internal organs. Even persons with a healthy liver can be poisoned by large dosages of copper-containing substances like copper sulphate. However, some persons are more susceptible to copper toxicity than others. Copper is a prevalent suicidal substance in India. Because of its toxicity, copper was no longer used as an emetic in medicine (8).

1.2.3 IRON-HEAVY METAL:

Iron is a chemical element in the periodic table that has the symbol Fe and atomic number 26. Iron is a group 6 and period 4 metal. Iron is notable for being the final element produced by stellar nucleosynthesis, and thus the heaviest element which does not require a supernova or similarly cataclysmic event for its formation. It is, therefore, the most abundant heavy metal in the universe.

Iron is the most abundant metal on Earth and is believed to be the tenth most abundant element in the universe. Iron is also the most abundant element making up the Earth; the concentration of iron in the various layers of the Earth ranges from high at the inner core to about 5% in the outer crust, it is possible the Earth's inner core consists of a single iron crystal although it is more likely to be a mixture of iron and nickel; a large amount of iron in the Earth is thought to contribute to its magnetic field. Iron is a metal extracted to its magnetic field. Iron is a metal extracted from iron ore and is hardly ever found in the free state(7).

Iron is used in the production of steel which is not an element but an alloy, a solution of different metals and some non-metals particularly carbon.

1.3ABOUT CRD:

Worldwide attention has been given to the environmental pollution caused by rapid urbanization, industrial revolution, and increasing population. Wastewater effluent discharged without treatment can negatively affect environmental components like air, water, soil, and food. The most important resource for human survival is water, which must be protected from contamination to maintain environmental sustainability and public health. Dyes are employed extensively in several industries including

pharmaceutical, food, paper, plastic, tannery, printing, and textile. Subsequently, dyes are discharged into the aquatic environment. These dyes contain harmful aromatic structures, which make them highly carcinogenic and mutagenic, and, thus, capable of damaging human and aquatic lives. Therefore, organic-dye pollution is one of the most urgent issues that must be addressed because it poses a long-term danger to human health and environmental ecosystems (9). The water-soluble azo-anionic dye known as Congo red (CR) has a molecular structure containing six benzene rings as depicted. This dye has been widely used because it is inexpensive, stable, and is a pleasant bright colour. However, the presence of CR, even at low concentration, in a water system can diminish the intensity of sub-surface light, preventing the photosynthetic processes carried out by aquatic organisms, and threatening the balance of the ecosystem. CR dye is non-biodegradable and highly toxic as a result of its structural stability structure and persistence. It has an increased level of biotoxicity, which could cause health complications (e.g., difficulty breathing; reproductive disorders; and skin, eye, and gastrointestinal tract diseases) in both humans and animals when it is consumed and bioaccumulated at high concentrations. Hence, the need to completely remove CR dye from wastewater is necessary.

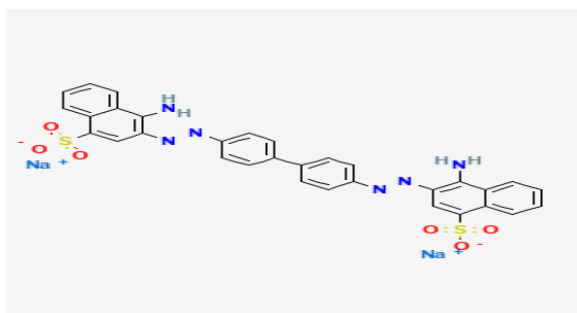


Fig 1.4 Structure of CRD

1.5 ABOUT THE STUDY:

Polyvinyl alcohol (PVA) is an organic material that can be used as an absorbent for the removal of heavy metals and other pollutants from wastewater. Incorporating metals such as Fe and Cu into the PVA polymer can enhance its degradability of dyes and other pollutants, such as Congo Red dye. The incorporation of Fe can also make the absorbent magnetic, which allows for efficient removal and reuse. Studies have shown that incorporating inorganic fillers onto the PVA matrix can improve its adsorption performance against heavy metals.

CHAPTER 2

LITERATURE SURVEY

1.Title: Stabilized nanofibers of polyvinyl alcohol (PVA) crosslinked by unique method for efficient removal of heavy metal ions

Authors: Sana Ullaha, MotahiraHashmia, Nadir Hussaina, AzeemUllaha, Muhammad NaumanSarwara, Yusuke Saitoa, Seong Hun Kimb, Ick Soo Kim

Journal and year: Journal of Water Process Engineering, February 2020

Inference: Removal of heavy metal ions is vital in water purification system. We developed a novel approach for crosslinking polyvinyl alcohol (PVA) nanofibers to improve their adsorption ability against metal ions such as Copper (Cu^{2+}) and Lead (Pb^{2+}) in this paper. By maintaining PVA nanofibers in a crosslinking solution, we were able to successfully crosslink them. Unlike uncrosslinked PVA nanofibers, the morphology of nanofibers did not disintegrate in solution. When vapourcrosslinked PVA nanofibers were compared to solution crosslinked PVA nanofibers, the adsorption capacity of copper and lead ions was significantly improved.

2.Title: An Experimental Study of Photocatalytic Degradation of Congo Red Using Polymer Nanocomposite Films.

Authors: Masha'el Nasser Alshabanat and Murefah M. AL-Anazy.

Journal and year: Polymer, 2 December 2018.

Inference: Biodegradable polymers of chitosan and polyvinyl alcohol as polymeric matrices and carbon black nanoparticles as reinforcement were used to make ecofriendly polymer nanocomposite films. These films were investigated for their suitability for industrial wastewater purification as a photocatalyst for the degradation of Congo red as a target pollutant, as well as the effect of the films' polymeric matrix types on their performance as a semiconductor photocatalyst. The films were characterised using Fourier-transform infrared (FTIR) spectra and X-ray diffraction (XRD).

3.Title: Adsorption of Congo red from solution by iron doped PVA-chitosan composite film.

Authors: Kang Wen, Yi Li, Shuxing Zhang, Xiaoting Zhang, Runping Han.

Journal and year: Desalination and Water Treatment, 18 January 2020.

Inference: Changes in adsorption conditions (temperature, pH, salt) and characterisation were used to explore the adsorption mechanism of Congo red (CR) on composite films (isoelectric point, infrared spectroscopy, photoelectric spectroscopy, scanning electron microscopy). The results showed that the composite film had a 450 mg g⁻¹ adsorption capacity at pH 5.0, and that CR adsorption by high concentration salt had only a minor detrimental effect.

4.Title:Sono catalytic rapid degradation of Congo red dye from aqueous solution using magnetic FeO /polyanilinenanofibers.

Authors:Raghunath Dasa, Madhumita Bhaumik, Somnath Giria ,ArjunMaitya.

Journal and year:UltrasonicsSonochemistry, 16 February 2017.

Inference: For sonocatalytic degradation of organic anionic Congo red (CR) dye, nano-sized magnetic FeO /polyaniline (FeO /PANI) nanofibers were used as an effective material. At room temperature, nano-FeO was reductively deposited onto PANI nanofibers to produce FeO /PANI. HR-TEM, FE-SEM, XRD, and FTIR equipment were used to characterise the catalyst.

5. Title: Efficient removal of Congo red dye from aqueous solution by adsorbent films of polyvinyl alcohol/melamine-formaldehyde composite and bactericidal effects.

Authors:Shahnawaz Ahmad Bhat , Fahmina Zafar, Aftab Hossain Mondal, Azar Ullah Mirza , Qazi Mohd Rizwanul Haq , Nahid Nishat

Journal and year: Journal of Cleaner Production, 10 January 2020.

Inference: One of the highest priorities in both environmental and industrial applications is the removal of hazardous dyes and the inhabitation of bacterial growth. We developed environmentally friendly and sustainable dye adsorbent films in response to rising industrial discharge and fresh water scarcity. The production of melamine-formaldehyde (MF) and cross-linking of polyvinyl alcohol (PVA) with MF were used to create biodegradable composite films in this study. FTIR, XRD, TGA, DSC, and SEM were used to characterise the PVA and PVA/MF composite films. PVA is a water-soluble polymer that has been treated with MF (13 percent, 23 percent, 33 percent, and 43 percent) to increase hydrophobicity, as measured by contact angle (500 to 910).

CHAPTER 3

AIM AND SCOPE

3.1 AIM:

This project's primary goal is to use a metal-incorporated polymer as a catalyst to accelerate the degradation of congo red dye. The synthesis of catalyst using hazardous metals Fe, Cu, and polymer with PVA metal incorporation. The congo red color can be removed with MOFs.

3.2 SCOPE:

Metal such as Cu & Fe are incorporated into the polymer to enhance degradability of dyes and other pollutants such as CRD. Incorporation of Fe makes the absorbent magnetic for its efficient removal and reuse.

CHAPTER 4

MATERIALS AND METHODS

4.1 MATERIALS:

All the chemicals used in this experimental were of analytical grade. Poly vinyl alcohol (PVA), CuSO_4 , FeCl_3 , Acetone, NaOH pellets, HCl. The pH of the solution was measured using pH paper. Congo red (CR) was as a model pollutant dye. Thus, it is prepared using distilled water and used for all the experiments.

4.2 METHODS:

4.2.1 Preparation method:

1g of PVA, CuSO_4 and 0.5g of FeCl_3 are weighed and dissolved in 20mL of distilled water.

PVA and Fe alone are stirred for 24hrs. To this acetone is added drop by drop and the precipitate thus formed is taken and dried in room temperature.

To PVA, CuSO_4 and Fe is added in drop wise and then stirred for 24hrs. To this acetone is added drop by drop and precipitate is taken and dried in room temperature. Then used as a catalyst for degradation of Congo red dye.



Fig.4.1Before drying of PVA-Cu-Fe



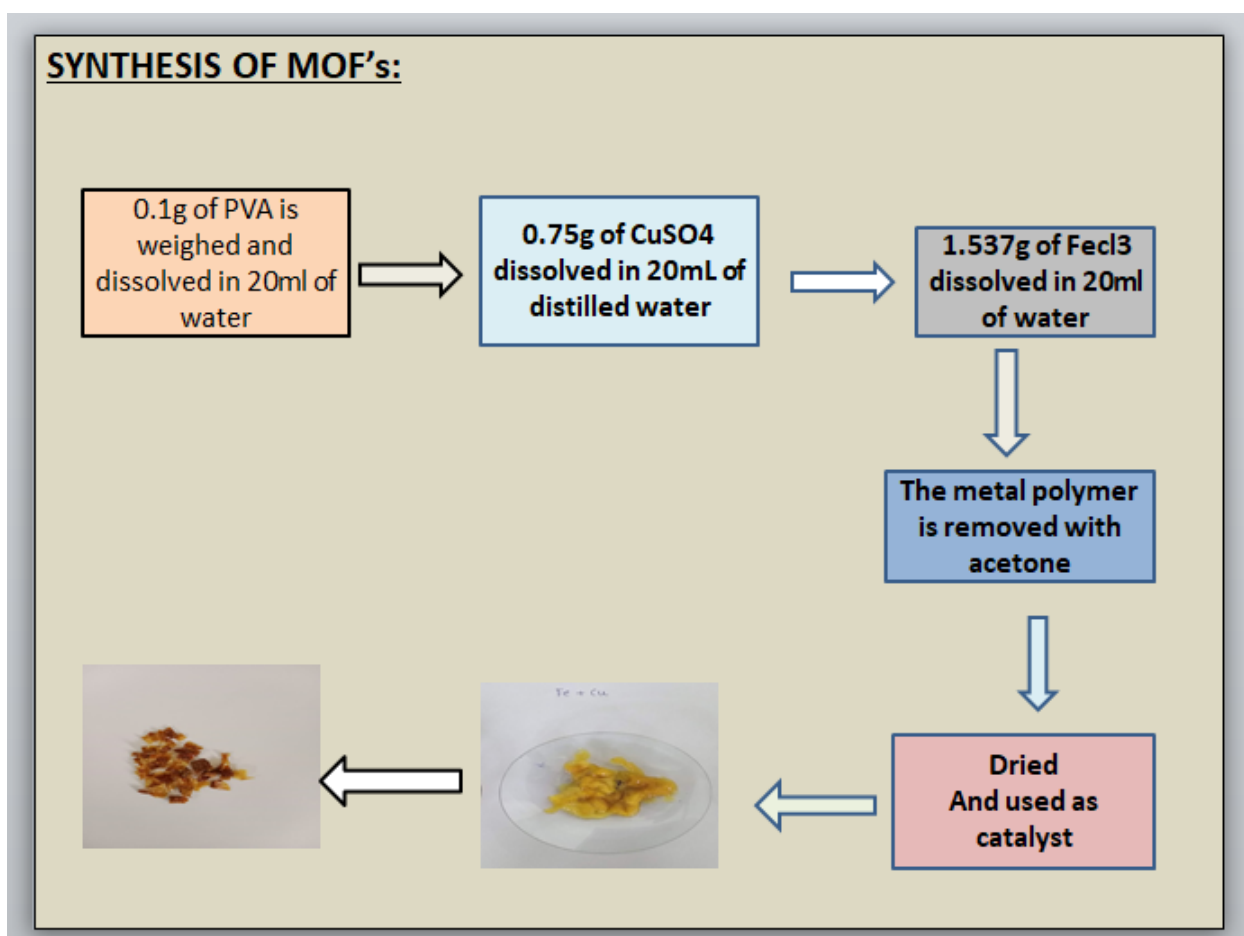
Fig.4.2After drying of PVA-Cu-Fe



Fig.4.3 Before drying of PVA-Cu



Fig.4.4 After drying of PVA-Cu



4.2.2 PREPARATION OF CONGO RED DYE:

0.0501g of CRD is weighed and dissolved in different volume of distilled water to get different concentrations.

1st concentration of CRD solution: 0.0501 of CRD powder is weighed and dissolved in distilled water and made upto 100ml in 100ml of standard flask.

2nd concentration of CRD solution: From this concentration solution, 10ml of CRD and add 40ml of H₂O.

3rd concentration of CRD solution: From this concentration solution, 5ml of CRD and add 15ml of H₂O.

4.2.3 DEGRADATION OF CONGO RED DYE:

COMPARATIVE STUDY OF PVA-Cu and PVA-Cu-Fe:

PVA-Cu:

20mL of CRD solution of 3rd concentration is pipetted out into a clean beaker and 2 drops of NaOH is added into it in order to maintain the pH=9(basic). Then 0.3g of Cu (metal) incorporated polymer is used as a catalyst for degradation which is added into it and stirred for 1 day. Then change the color in dark red and changed colorless after 5hrs .Completely degrade the CRD solution in 1day.

PVA-CU-Fe:

20mL of CRD solution of 3rd concentration is pipetted out into a clean beaker and 2 drops of NaOH is added into it in order to maintain the pH=9(basic). Then 0.3g of Cu-Fe (metal) incorporated polymer is used as a catalyst for degradation which is added into it and stirred for 5 hrs. Then change the colorless and completely degrade the CRD solution.

4.2.4 Comparison of PVA-Cu& PVA-Cu-Fe

Cu-Fe is quickly degraded within a few hours, although Cu takes longer, taking up to a day. Cu-Fe is more efficient than Cu.

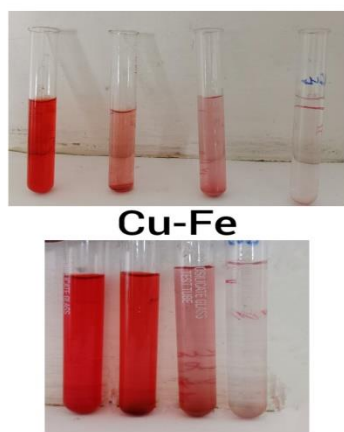
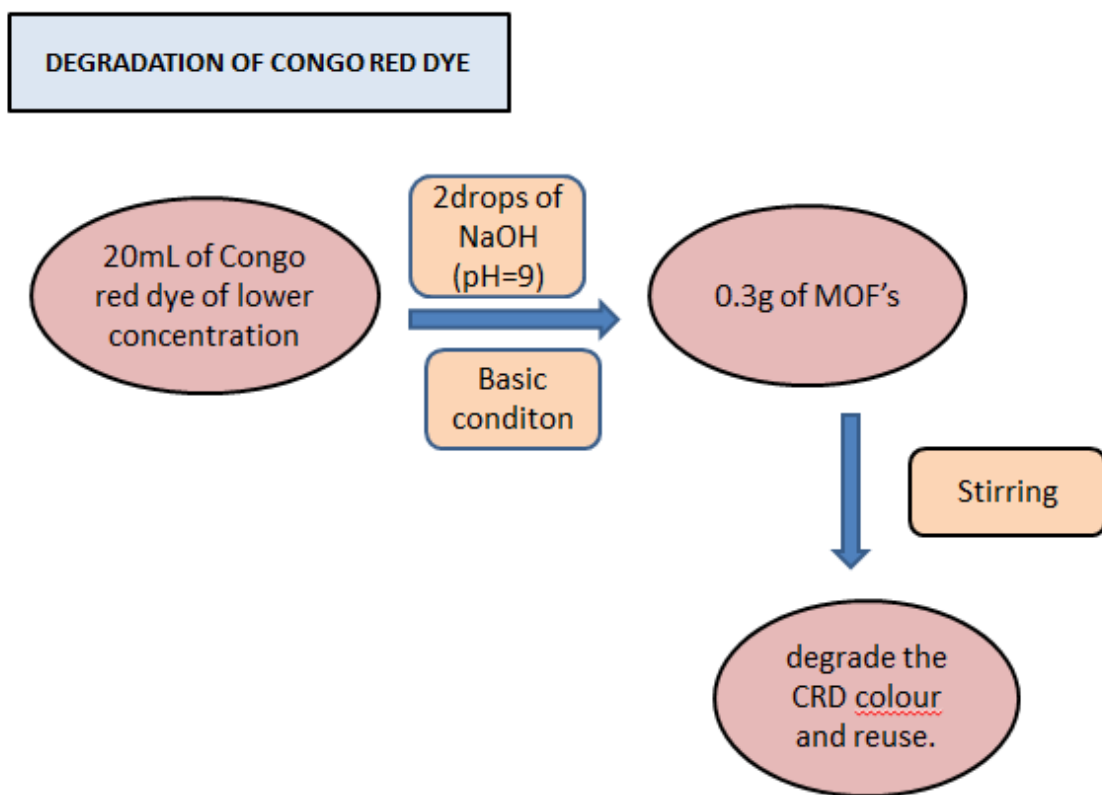


Fig.4.5 DEGRADATION OF CRD in Cu-Fe

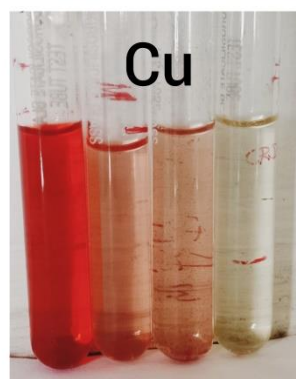


Fig.4.6 DEGRADATION OF CRD in Cu

4.3 CHARECTERISATION TECHNIQUES:

4.3.1 FOURIER TRANSFORM INFRARED SPECTROSCOPY

PRINCIPLE

FTIR (Fourier Transform Infrared) spectroscopy is a technique used to obtain an infrared spectrum of absorption or emission of a solid, liquid, or gas. FTIR spectrophotometers are mainly used to measure light absorption of mid-infrared light, light in the wavenumber range of 4,000 to 400 cm^{-1} (wavelengths 2.5 to 25 μm). The principle of FTIR spectroscopy is based on the fact that when infrared radiation passes through a sample, some of the radiation is absorbed. An FTIR spectrometer simultaneously collects high-resolution spectral data over a wide spectral range. Unlike a monochromator or spectrograph, FTIR spectrometers collect all wavelengths simultaneously.

WORKING

FTIR (Fourier Transform Infrared Spectroscopy) is a widely used analytical technique in various fields such as organic synthesis, polymer science, petrochemical engineering, pharmaceutical industry, and food analysis. FTIR analysis measures the infrared region of the electromagnetic radiation spectrum and provides information about the functional groups present in a sample. An FTIR instrument uses an interferometer to measure the energy of the infrared radiation that passes through a sample. FTIR spectrometers have several advantages, including high signal-to-noise ratio, high accuracy of wavenumber, and the ability to be hyphenated to chromatography.



Fig.4.7 FTIR INSTRUMENT

4.3.2 X-RAY DIFFRACTION (XRD):

X-ray diffraction (XRD) is a technique used to determine the crystal structure, crystallinity, and other properties of a material. It is a non-destructive method that works by analyzing the diffraction pattern produced when X-rays are directed at a crystalline material. XRD is primarily used for phase identification of a crystalline material and can provide information on unit cell dimensions. It is commonly used in materials science to analyze the atomic or molecular structure of materials.

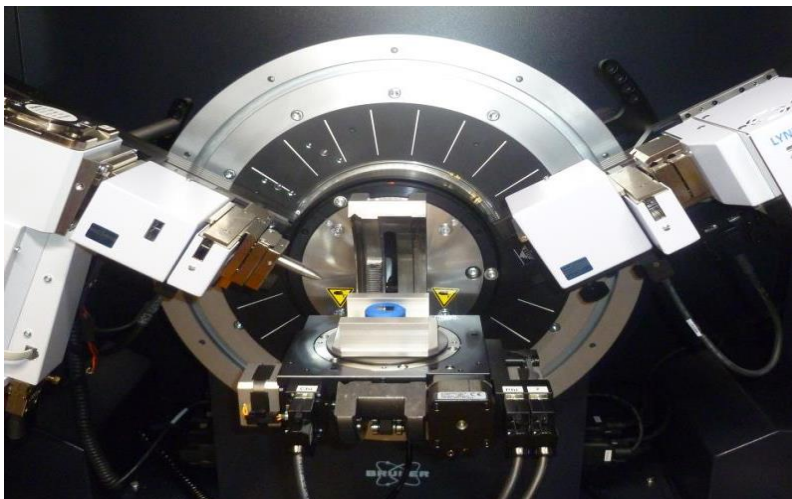


Fig.4.8 XRD Instrumentation

4.3.3 SCANNING ELECTRON MICROSCPE (SEM-EDAX):

PRINCIPLE

The principle of SEM (Scanning Electron Microscope) is based on applying kinetic energy to produce signals on the interaction of electrons with the sample. The SEM produces a magnified image by using electrons instead of light to form an image. A beam of electrons is produced at the top of the microscope by an electron gun. The electron beam follows a vertical path through the microscope, which is held within a vacuum. The electrons interact with atoms in the sample, producing various signals that contain information about the surface topography and abundance of elements in the sample. The resolution of SEM is not limited by the diffraction limit, fineness of lenses or mirrors or detector array resolution.

WORKING:

It is an instrument that produces highly magnified images of a sample by using electrons instead of light to form an image. The SEM works by producing a beam of electrons at the top of the microscope by an electron gun. The electron beam follows a vertical path through the microscope, which is held within a vacuum. The beam is then scanned across the surface of the sample in a raster pattern. As the electrons interact with the sample, they produce signals that are detected and used to create an image of the sample. The resulting image is highly magnified and provides detailed information about the surface of the sample. SEMs are widely used in various fields, including materials science, biology, and nanotechnology, among others.



Fig.4.9 Field Emission Scanning Electron Microscope

4.3.4 UV SPECTROSCOPY:

PRINCIPLE:

The principle of UV spectroscopy is based on the interaction between ultraviolet or visible light and chemical compounds, which results in the production of distinct spectra. When light is absorbed by matter, there will be an increase in the energy of the matter, which can be measured by UV-Vis spectroscopy. This technique is used to determine the absorbency of a substance and map the interaction between light and matter.

WORKING:

UV-Vis spectroscopy is a laboratory technique used to measure the absorbance of light across the ultraviolet and visible regions. In UV spectroscopy, light of the ultraviolet region (200-400 nm) is absorbed by a molecule, which results in the excitation of electrons from the ground state to a higher energy state. UV-Vis spectroscopy can be used to identify molecules in a sample, determine the concentration of a particular molecule, and measure the amount of discrete wavelengths of UV or visible light absorbed by a substance.



Fig.4.10 UV INSTRUMENT

CHAPTER 5

RESULTS AND DISCUSSION

5.1 X-RAY DIFFRACTION (XRD):

X-ray diffraction (XRD) analysis was conducted to identify the crystalline structure of the catalyst.

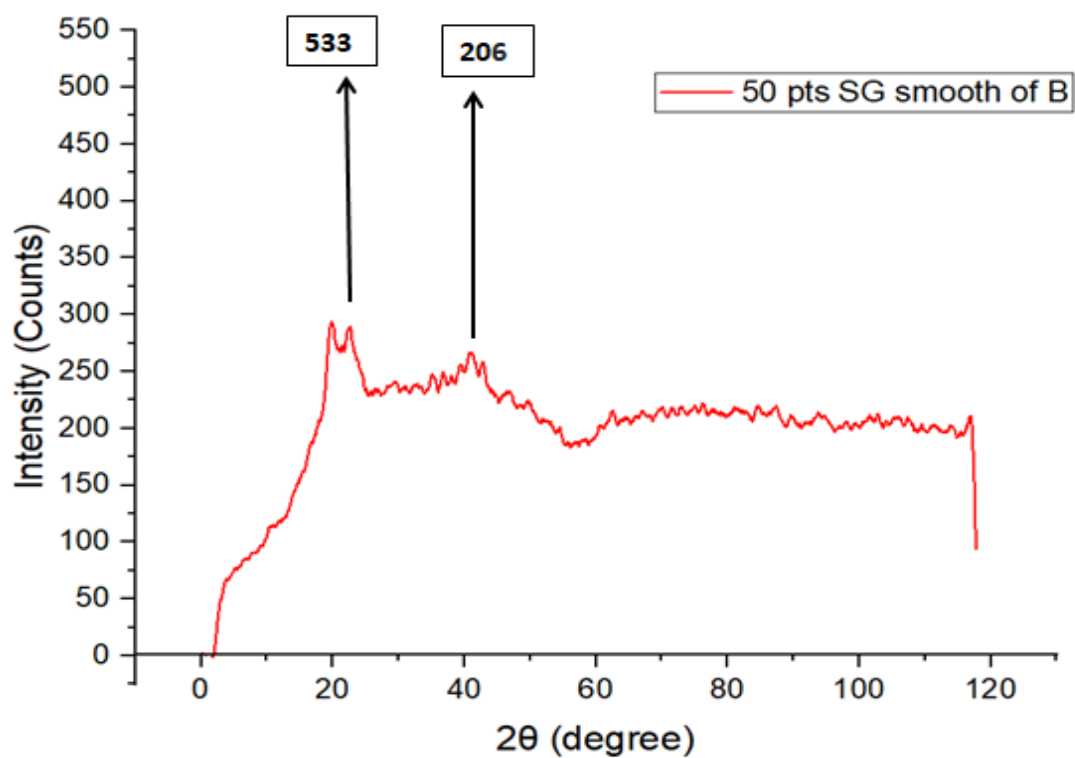


Fig 5.1: Graphical representation of XRD

In the X-ray diffraction patterns of PVA-Cu-Fe nanocomposites the main characteristic peaks of Fe and Cu are clearly visible. XRD patterns have diffraction peaks at $2\theta = 22^\circ$ and 41° which can be indexed to (533) and (206) respectively. These peaks are attributed to the PVA-Cu-Fe catalyst.

5.2 FOURIER-TRANSFORM INFRARED SPECTROSCOPY:

This spectroscopic technique is used to determine the functional groups present in the compound at different frequency levels.

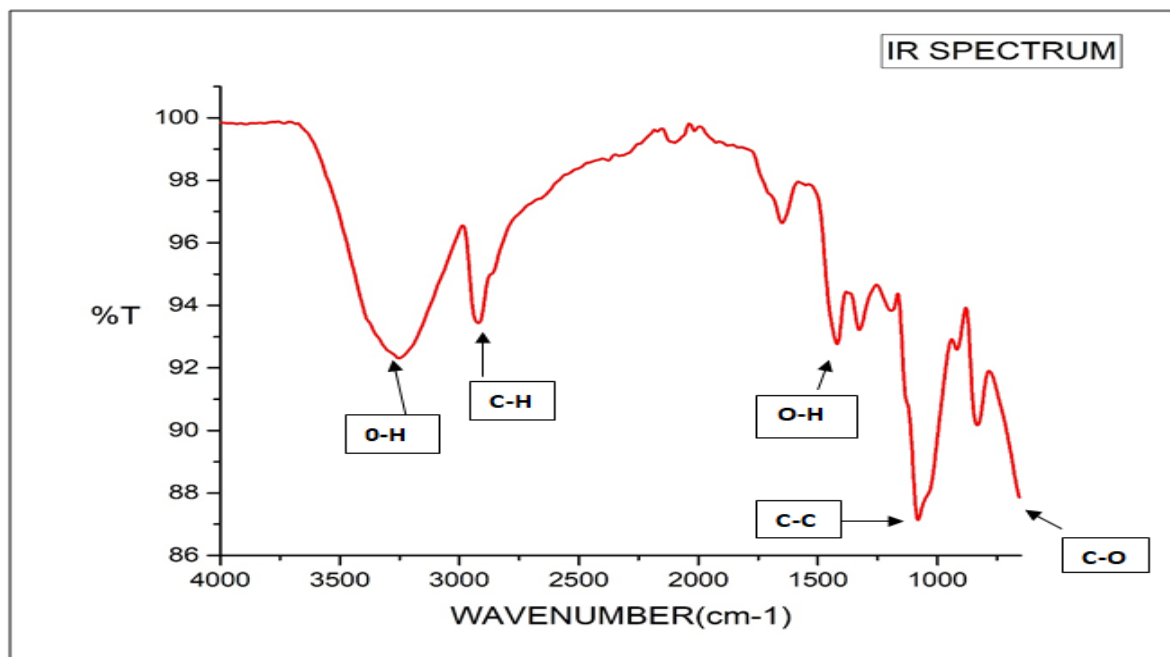


Fig 5.2: Graphical representation of FTIR

S.NO	FUNCTIONAL GROUP	INTERPRETATION	WAVENUMBER (CM-1)
1	O-H	Stretching vibration	3332.24
2	C-H	(aliphatic)Stretching vibration	2797.367
3	O-H	Bending vibration	1384.706
4	C-C	Sharp peak	1028.7452
5	C-O	-	918.7888

TABLE 5.1 Spectral Data of FTIR Spectrum

On the IR spectra of given compound, the major peaks observed were as follows: bands at 3332.24 cm^{-1} are assigned to the stretching vibrations of (O-H) respectively, the vibration bands at 2797.367 cm^{-1} are assigned to (C-H), O-H bending medium carboxylic acid 1384.706 cm^{-1} , a sharp band at 1028.752 cm^{-1} is attributed to the vibration of (C-C), a medium shoulder peak at 918.7888 cm^{-1} is linked to the vibration of (C-O).

5.3 FIELD EMISSION SCANNING ELECTRON MICROSCOPE (FESEM):

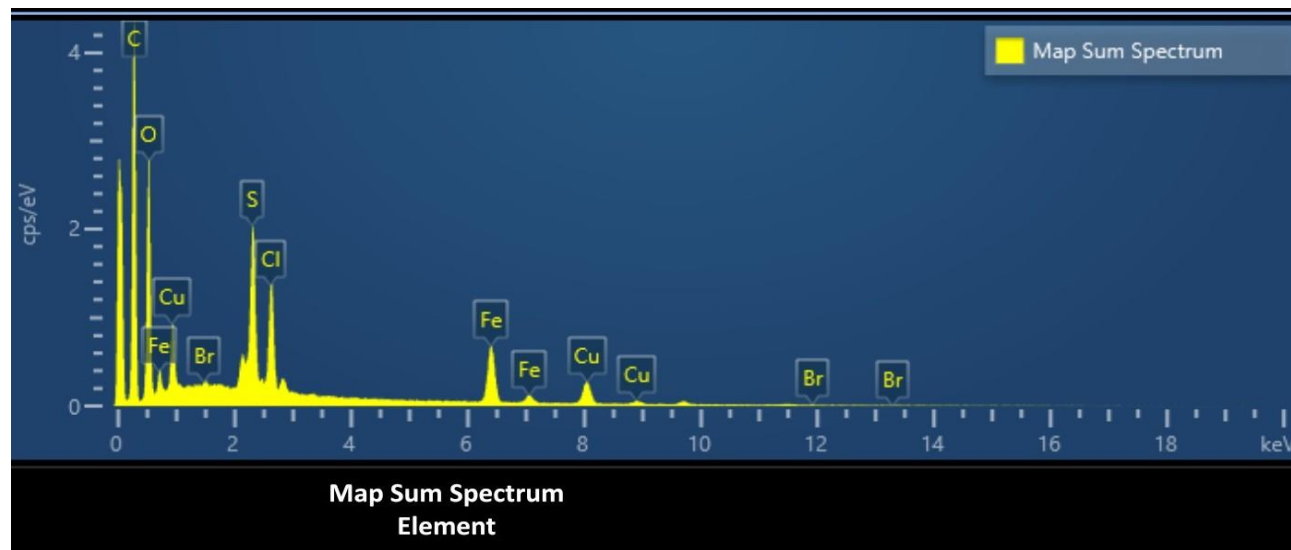
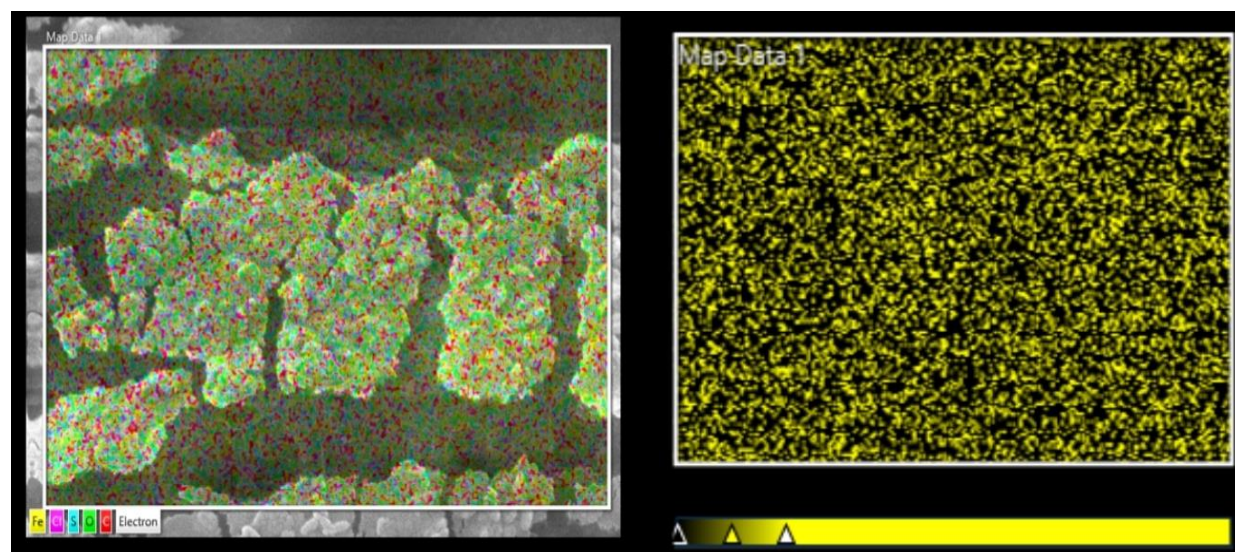
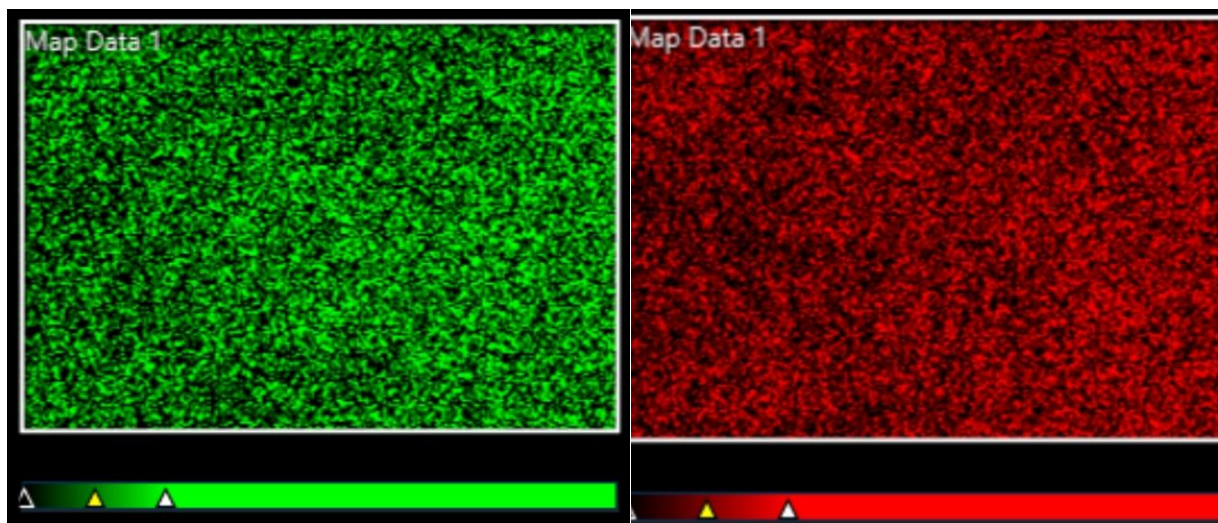


Fig.5.3 spectrum of FESEM & EDAX



A) Mapdata

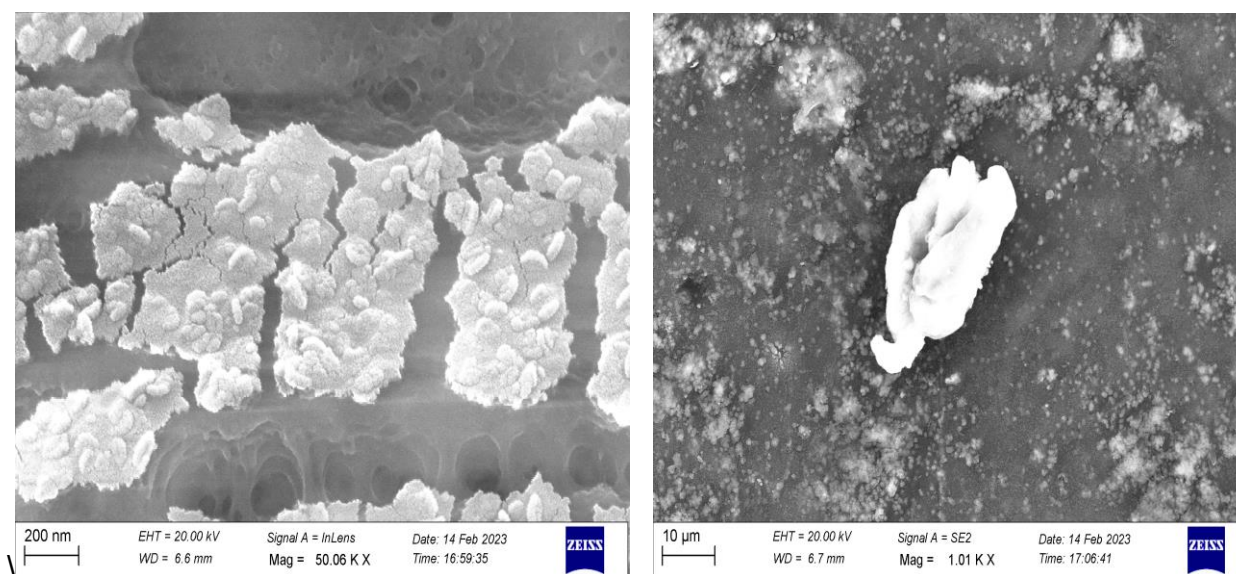
B) Fe



C) Oxygen

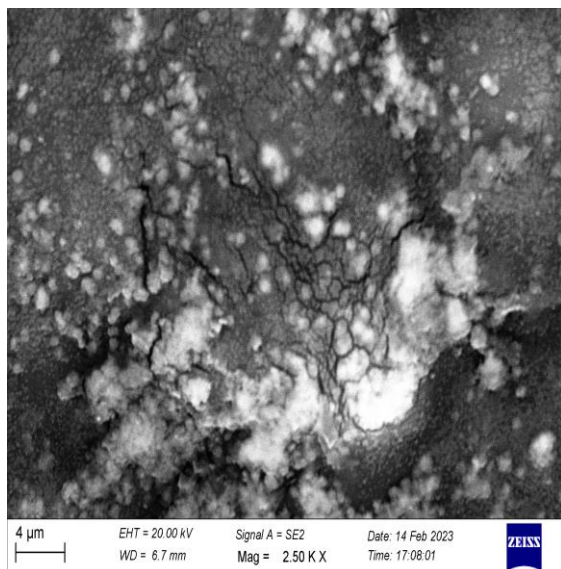
D) Carbon

We used microscopy-imaging techniques for identification of morphology and structure of the catalyst .Figure 5.3(a) and 5.3.1(b) images of the final product. In addition, size distribution of nanoparticles is provided in Figure 5.3.1 (c). The spherical morphology of the PVA-Cu-Fe nanoparticles are clearly shown with an average diameter of ~200 nm in FESEM image.

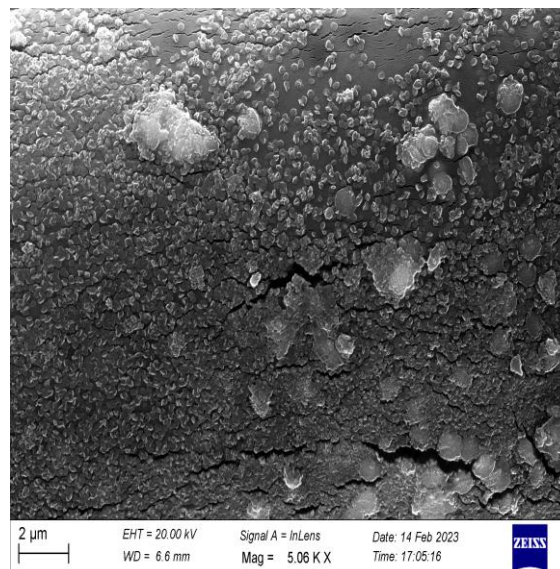


A) Fig 5.4 SEM image of PVA-Cu-Fe

B)



C)



D)

Fig. 5.3.1 (b) shows SEM images of the PVA-Cu-Fe film at 10μm, 4 μm and 2 μm magnifications.

5.4 UV-Vis SPECTROSCOPY:

CR color removal was confirmed by UV-visible analysis (200-800 nm). The UV spectrum of PVA-Cu is depicted in the above figure along with the recorded signal peaks. These peaks were obtained between 200 and 400 nm, but they are not all equally intense. However, one peak showed strong intensity at 375 nm and for this band gap is 3.307 eV, which means this compound shows good electron absorbed substance based on band gap.

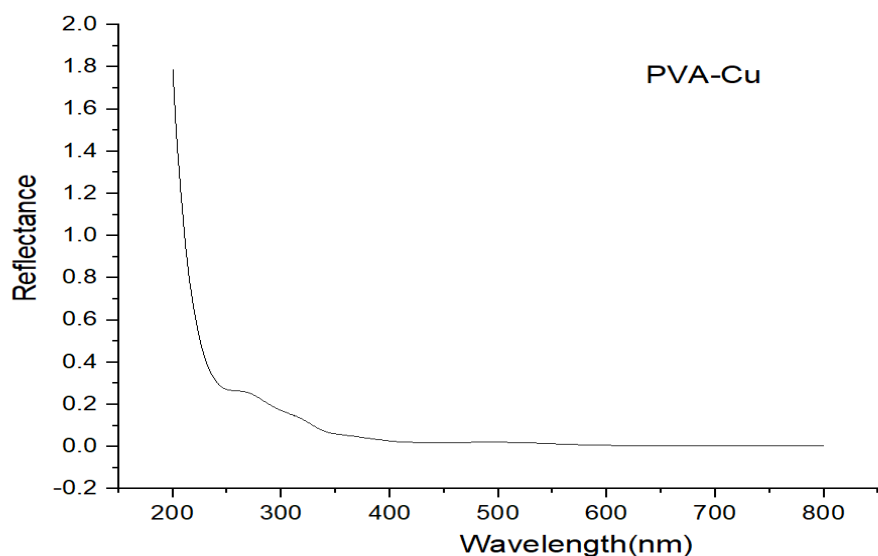


Fig.5.5 Graphical representation of UV

S.NO	WAVENUMBER	REFLECTANCE
1	251	0.738
2	278	0.629
3	322	0.436
4	326	0.43
5	352	0.401
6	375	0.326
7	401	0.217

Table 5.2 Spectral data of UV-PVA/Cu

The UV spectrum of PVA-Cu is depicted in the above figure along with the recorded signal peaks. These peaks were obtained between 200 and 400 nm, but they are not all equally intense. However, one peak showed strong intensity at 375 nm and for this band gap is 3.307 eV, which means this compound shows good electron absorbed substance based on band gap.

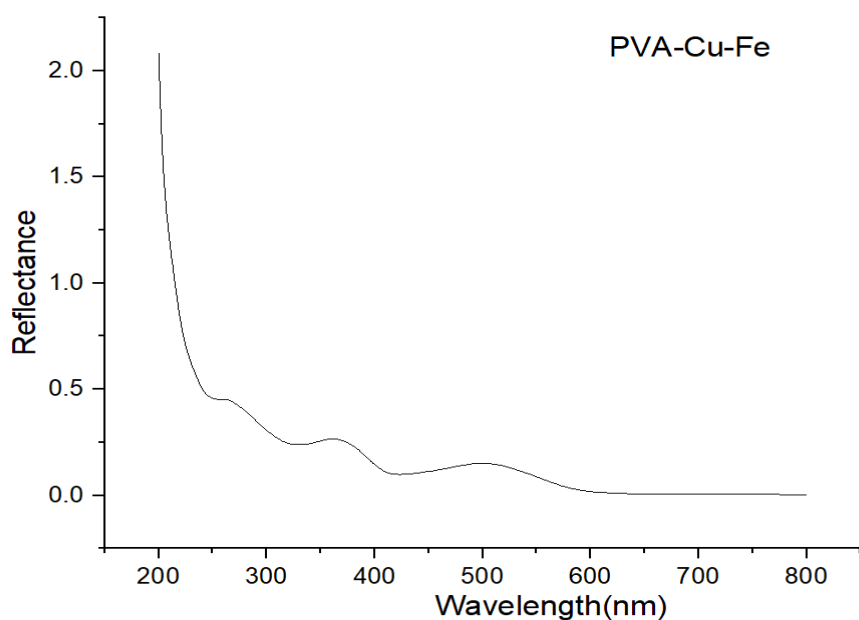


Fig5.6 Graphical representation of UV

S.NO	WAVENUMBER	REFLECTANCE
1	242	0.774
2	252	0.734
3	334	0.424
4	367	0.356
5	429	0.209
6	505	0.328

Table 5.3 Spectral data of UV-PVA/Cu/Fe

The UV spectrum of PVA-Cu-Fe is depicted in the above figure along with the recorded signal peaks. These peaks were obtained between 200 and 600 nm, but they are not all

equally intense. However, one peak showed strong intensity at 367 nm and for this band gap is 3.307 eV, which means this compound shows good electron absorbed substance based on band gap.

5.5 DEGRADATION OF CONGO RED DYE IN COMPARATIVE STUDY:

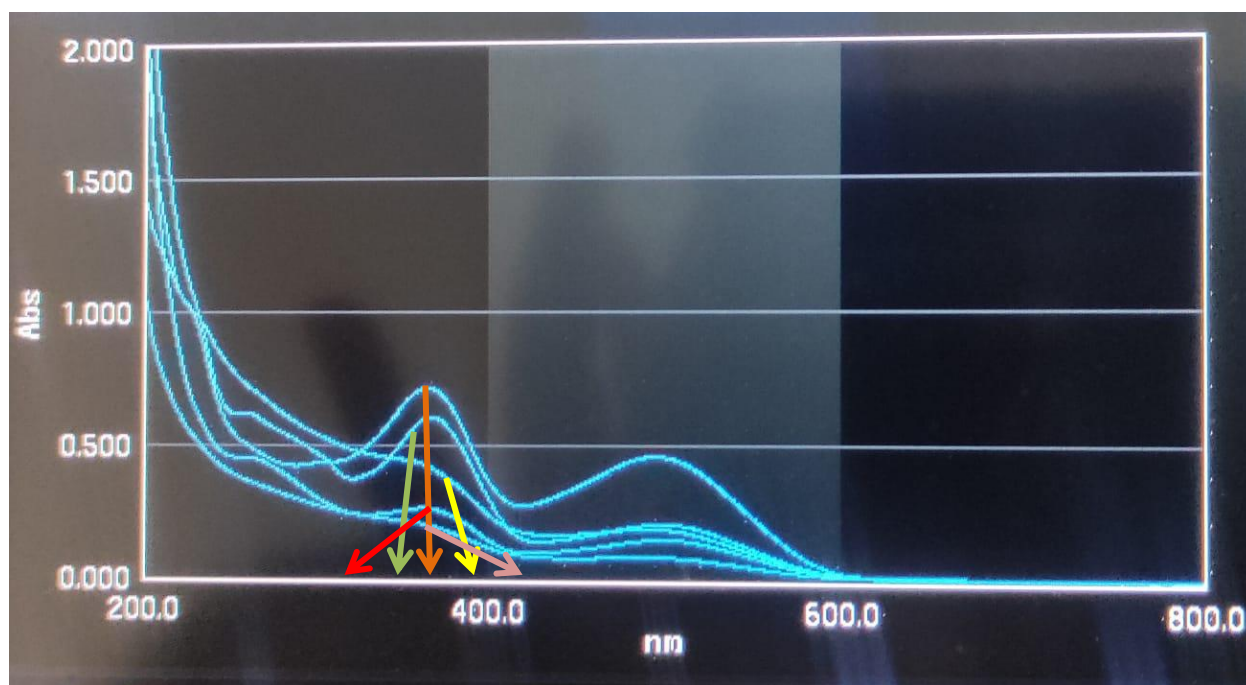


Fig 5.7 Graphical representation of degradation of Congo Red Dye PVA-Cu-Fe

Peak	Absorbance
1	0.453
2	0.27
3	0.115
4	0.017
5	0.006

Table 5.4 Spectral Data of Degradation of CRD

Congo red dye has been kinetically studied under the given conditions, the absorbance of the given dye has been observed at very low absorbance due to its degradation. In this kinetical study 87% of Congo red was degraded is confirmed.

The intensity of the dye quite low and its degradation happens when it is maintained in the basic pH (pH=8) by adding few drops of NaOH with the solution and polymer. This Congo red dye is used for studies in textile industries mostly combinations of metal oxides.

Surface adsorption and intraparticle diffusion occur simultaneously, according to the kinetics data. The adsorption equilibrium matches the Langmuir isotherm well, showing monolayer adsorption on a homogeneous surface. The healing powers of nanocomposite are supported by a desorption investigation.

The kinetic study of degraded Congo red dye has been observed at different wavelengths, the first peak was observed at 776 nm with 0.453 absorbance then second peak was observed at 603 nm with 0.27 absorbance, the absorbance difference between these two peaks are nearly 0.2 absorbance difference.

Then third peak was observed at 452 nm with 0.115 absorbance, after this peak the intensity was decreased gradually, the fourth peak was observed at 310 nm with 0.017 absorbance and the final peak was observed at 776256 nm with 0.006 absorbance.

From the above data we come to know that the Congo red dye has been degraded in continuous time period with different intensity and absorbance, finally we come to know that “on the basis of kinetics” the above dye degrades gradually in 6 hours of duration time with decrease in their intensity.

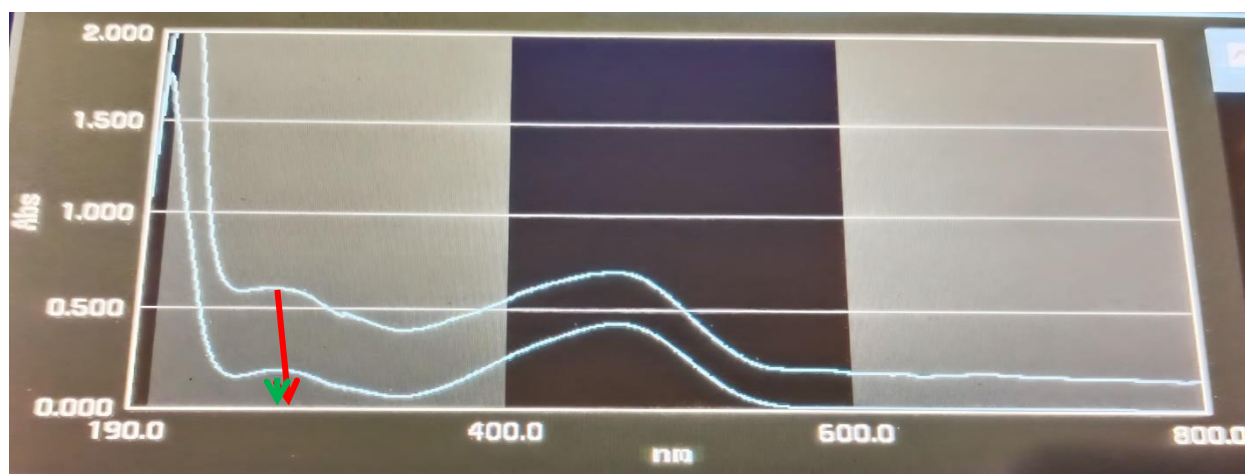


Fig 5.8 Graphical representation of degradation of Congo Red Dye PVA-Cu

Peak	Absorbance
1	3.024
2	0.103

Table 5.5 Spectral Data of Degradation of CRD

The kinetic study of degrade Congo red dye have been observed at different wavelengths, the first peak was observed at 197nm with 3.024 absorbance then second peak was observed at 557 nm with 0.103 absorbance .

From the above data we come to know that the Congo red dye has been degrade in continuous time period with different intensity and absorbance, finally we come to know that “on the basis of kinetics” the above dye degrade gradually in 1 day duration time with decrease in their intensity

By the decrease in the colour intensity of the CRD solution and turning from colored to colorless clear solution we observe the degradation of CRD. And through this spectrum we successfully confirm that the 87% of the Congo red dye got degraded from the solution.

CHAPTER 6

CONCLUSION:

In this work, we have successfully developed an efficient catalyst for the removal of toxic Congo red 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 different analytical techniques. This MOF's will effectively degrade the pollutant Congo red dye from the industrial waste water pollution. The prepared PVA-Cu / PVA-Cu-Fe MOF's 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 Congo red from polluted water.

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