

DEGRADATION OF CONGO RED DYE BY USING A METAL INCORPORATED POLYMER AS A CATALYST

Submitted in partial fulfilment of the requirements for the award of

Master of science Degree in Chemistry

By

K. GIRIDHARAN

Register No:40910013



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

SATHYABAMA

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

Accredited with Grade "A" by NAAC

JEPPIAAR NAGAR, RAJIV GANDHI SALAI, CHENNAI-600119.

MAY 2022



SATHYABAMA

INSTITUTE OF SCIENCE AND TECHNOLOGY

(DEEMED TO BE UNIVERSITY)

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

www.sathyabama.ac.in

DEPARTMENT OF CHEMISTRY

BONAFIDE CERTIFICATE

This is to certify that this Project Report is the bonafide work of **GIRIDHARAN K (40910013)** who carried out the project entitled "**METAL INCORPORATED POLYMER AS CATALYST FOR DEGRADATION OF CONGO RED DYE**" under our supervision from November 2021 to May 2022.

Internal Guide

Dr. S. SUPRIYA, M.Sc., Ph.D.,

Head of the Department

Dr. J. KARTHIKEYAN, M.Sc., Ph.D.

Submitted for Viva voce Examination held on _____

Internal Examiner

External Examiner

DECLARATION

I **GIRIDHARAN K (40910013)**, hereby declare that the Project Report entitled **“METAL INCORPORATED POLYMER AS CATALYST FOR DEGRADATION OF CONGO RED 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:
PLACE:

K. GIRIDARAN
SIGNATURE OF THE CANDIDATE

ACKNOWLEDGEMENT

I am pleased to acknowledge my sincere thanks to Board of Management of **SATHYABAMA** for their kind encouragement in doing this project and for completing it successfully. I am grateful to them.

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.

I would like to express my sincere and deep sense of gratitude to my Project Guide **Dr. S. SUPRIYA**, Department of Chemistry for their valuable guidance, suggestions and constant encouragement paved way for the successful completion of my project work.

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.

GIRIDHARAN K

ABSTRACT

To removal of toxic heavy metal from environment use industrial wastes heavy metal incorporated with polymer make a catalyst and reduce congo red dye from environment this process is low cost and use again and again. Poly vinyl alcohol and heavy metal dissolve incorporated to degrade the Congo red dye. the above dye degrades in 5 minutes of duration time successfully with decrease in their intensity. Its process occurs in pH neutral condition.

TABLES OF CONTENTS

ABSTRACT	
LIST OF ABBREVIATIONS	
LIST OF FIGURES	
LIST OF TABLES	
1.INTRODUCTION	PAGE NO
1.1 POLY VINYL ALCOHOL.....	1
1.2 HEAVY METAL POLLUTANTS.....	2
1.2.1 some heavy metals list.....	3
1.3 REMOVAL OF HEAVY METAL POLLUTANTS.....	4
1.3.1 chemical precipitation.....	4
1.3.2 ion exchange.....	4
1.3.3 membrane separation.....	4
1.3.4 coagulation/flocculation.....	5
1.3.5 adsorption.....	5
1.4 CATALYSIS.....	5
1.4.1 homogeneous catalysis.....	6
1.4.2 heterogeneous catalysts.....	6
1.5 POLYMER.....	7
1.6 Cobalt.....	7
1.6.1 cobalt(ii) sulfate.....	8
1.6.2 preparation.....	8
1.6.3 safety measurement.....	9
1.6.4 cobalt poisoning.....	9
1.6.5 environmental effects of cobalt.....	9

1.7 Congo red dye.....	9
1.7.1 Synthesis.....	9
1.8 CONGO RED DYE POLLUTANT	10
2 LITERATURE SURVEY.....	11
3. AIM AND SCOPE.....	13
3.1. aim.....	13
3.2. scope.....	13
4. MATERIALS AND METHODS.....	14
4.1 MATERIALS.....	14
4.2 CHARACTERIZATION TECHNIQUES	14
4.2.1 fourier transform infrared spectroscopy.....	14
4.2.2 uv spectroscopy.....	16
4.2.3 scanning electron microscopy (sem).....	17
4.2.4 x-ray diffraction spectroscopy (xrd).....	18
4.3 METHADODOLOGY.....	19
4.3.1. 1 st concentration.....	20
4.3.2. 2 nd concentration.....	20
4.3.3. 3 rd concentration.....	20
4.4 DEGRADATION OF CONGO RED DYE.....	20
5. RESULTS & DISCUSSION.....	21
5.1 characterization of metal incorporated polymer.....	21
5.1.1 FTIR spectrum of metal incorporated polymer.....	21
5.1.2 UV / vis spectrum.....	23
5.1.3 SEM image of metal incorporated polymer.....	24

5.1.4 XRD pattern.....	25
5.2 REDUCTION OF CONGO RED DYE.....	26
6.SUMMARY.....	28

LIST OF ABBREVIATION

FTIR	-	Fourier Transform Infrared Spectroscopy.....	21
SEM	-	Scanning Electron Microscopy	23
UV	-	Ultraviolet Visible Spectroscopy.....	24
XRD	-	X-Ray Diffraction Spectroscopy.....	25

LIST OF FIGURES

Fig 1. Structure of PVA.....	2
Fig.2 cobalt (II) sulphate.....	8
Fig.3 FTIR Spectroscopy.....	15
Fig.4 UV spectroscopy.....	16
Fig.5 SEM SCANNING ELECTRON MICROSCOPE.....	17
Fig,6 XRD X-RAY DIFFRACTION SPECTROSCOPY.....	18
Fig.7 SEM IMAGES.....	24
Fig.8 REDUCTION OF CONGO RED DYE.....	26

LIST OF TABELS

1. FTIR SPECTRUM INTERPRETATION	22
2.THE CONGO RED DYE INTERPRETATION.....	27

CHAPTER 1

INTRODUCTION

1.1 POLY VINYL ALCOHOL

Poly (vinyl alcohol) (PVOH, PVA, or PVA I) is a water-soluble synthetic polymer. its molecular formula is $[\text{CH}_2\text{CH}(\text{OH})]_n$.

It is colourless and odourless translucent, white or cream-coloured granular powder it is tasteless, Soluble in water sparingly soluble in ethanol but insoluble in other organic solvents a 5% solution of PVA PH range is 5.0 to 6.5 PH

The average molecular weight of polymer is 120,000 When decomposition it emits acrid smoke and irritating fumes. Decomposes at 228°

Polyvinyl alcohol (PVA) is a water-soluble polymer with a glass transition temperature, TG, of 80°C . Although its name implies a homopolymer structure, the structure of commercial PVA is a copolymer of vinyl alcohol and vinyl acetate.

PVA is prepared hydrolysis of polyvinyl acetate or sometimes vinyl ester-derived polymers with or chloroacetate groups of acetate. The conversion of the polyvinyl esters is usually conducted by base-catalysed transesterification with ethanol.

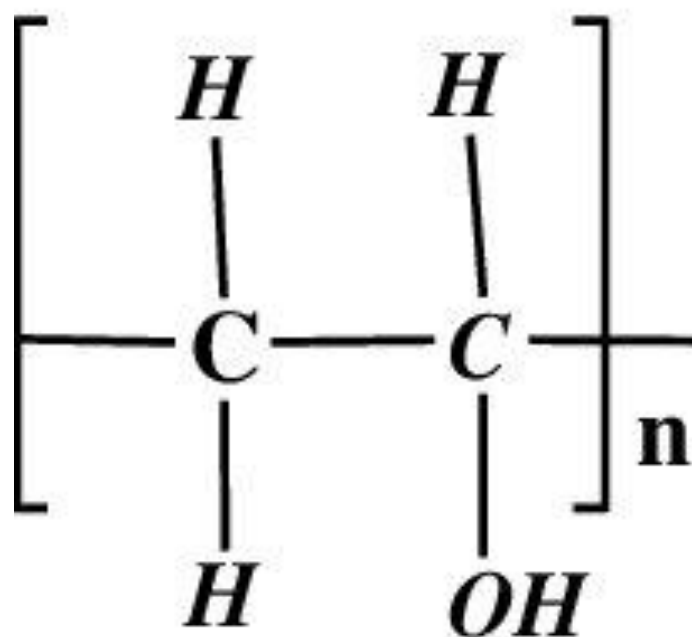


Fig 1. Structure of PVA

1.2 HEAVY METAL POLLUTANTS

Heavy metals normally occur in nature and are essential to life but can become toxic through accumulation in organisms. Some lighter metals and metalloids are toxic and, thus, are termed heavy metals though some heavy metals

Metalloids create covalent bonds they have toxicological characteristics. The ability to bond covalently with organic groups is one among the most important ramifications of this characteristic.

As a result, when they attach to metallic components of cellular macromolecules, they produce lipophilic ions and compounds, which can have harmful effects. Metalloids become lipophilic as a result of being lipophilic.

Cr, Cd, Se, Pb, As, Hg, Cu, Co, Ni, and Zn are some of the heavy metals

Less commonly, metals including iron, copper, zinc, aluminium, beryllium, cobalt, manganese and arsenic may be considered heavy metals. Heavy metals are often assumed to be highly toxic or damaging to the environment.

Heavy metal poisoning is the accumulation of heavy metals, in toxic amounts, are essential to body function in very small amounts in the soft tissues of the body

Many heavy metals, such as zinc, copper, chromium, iron and manganese in metals accumulate in the body in concentrations sufficient to cause poisoning, then serious damage may occur

Due to the discharge of metal-contaminated wastewater, industries bearing heavy metals, such as Cd, Cr, Cu, Ni, , Pb, and Zn, are the most hazardous among the chemical-intensive industries. Because of high solubility in aquatic environment, heavy metals can absorb by living organisms.[7]

1.2.1 SOME HEAVY METALS LIST

- Chromium
- Manganese
- Cobalt
- Nickel
- Copper
- Mercury
- Lead
- Silver

1.3 REMOVAL OF HEAVY METAL POLLUTANTS

There are several methods for heavy metal removal

1. chemical precipitation
2. adsorption
3. ion exchange
4. membrane filtration
5. coagulation-flocculation and floatation.

1.3.1 chemical precipitation

Chemical precipitation is best removal processes for the heavy-metal-containing waste effluent treatment because of its low cost and ease to use. In this technique the metals are precipitated as insoluble hydroxides and sedimentation and filtration. Removed, carbonates, or sulfide Although chemical precipitation is described as the most commonly used technique, it some deficiencies.

1.3.2 Ion exchange

Ion exchange is a technique through which ion is separated from a aqueous suspension and exchange by other ionic group. ion exchange strategy has been applied for heavy metal-containing effluent treatment due to its advantages great removal capacity, higher selectivity for every heavy metal ions and rapid kinetics. the main difficulty of chemical precipitation treatment is less, the disposal of significant amounts of sediments and sludge

1.3.3 Membrane separation

Its decreasing the disposal budgets and material supplies. This method worked for heavy-metal-containing wastewater are ultrafiltration, nanofiltration, reverse osmosis, and electrodialysis, its retain depending on the size of the element. most of heavy metal removal techniques is not the retrieval of metal Nevertheless recovery of heavy metals exhibits higher returns

1.3.4 Coagulation/flocculation

Coagulation and flocculation is one of the best methods for effluent treatment. When a chemical is added to water, a chemical reaction takes place, which is called coagulation. The coagulant boosts the colloidal substances in water to link together into little clusters called “flocs”. Flocculation is a gentle addition of water to stimulate the flocs to form a bigger size that could settle down as a big particle.

1.3.5 Adsorption

Adsorption strategy is one of best method for toxic metal removal in light of the fact that its flexible plan and activity, the higher expulsion rate, and the recovery and reuse of the adsorbent for additional use. The adsorption method can be divided into clump, semi bunch, and nonstop modes. Adsorption happens due to the interfacial attraction between an adsorbed surface and molecules are adsorbed. Activated carbon (AC) is considered as the high amount of evacuation specialist for heavy metal-containing waste effluents. Adsorption could be of two types the attractive intermolecular forces

1.4 CATALYSIS

The process of increasing the rate of a chemical reaction by adding a substance known as a catalyst. Catalysts are not consumed in the reaction and remain unchanged after it. If the reaction is rapid and the catalyst recycles quickly, very small amounts of catalyst often suffice; mixing, surface area, and temperature are important factors in reaction rate. Catalysts generally react with one or more reactants to form intermediates that subsequently give the final reaction product, in the process regenerating the catalyst.

polyacrylamide and they have synthesized its complexes using Cu(II), Ni(II), Zn(II), Co(II) and Hg(II) (9).

Catalysis may be classified

- Homogeneous
- Heterogeneous
- Heterogenized homogeneous catalyst
- Biocatalysts

1.4.1 HOMOGENEOUS CATALYSIS

A homogeneous catalysis is components are dispersed in same phase (gas or liquid) it as reactant's molecules

Homogeneous catalysts in the same phase reactants. Homogeneous catalysts are dissolve in solvent with substrates. One example of homogeneous catalysis involves the influence of H^+ on the esterification of carboxylic acids

In homogenous catalysis, catalysts freely diffuse in the reaction mixture, which typically leads to high reaction rates due to fast and easy access of the active centre

1.4.2 HETEROGENEOUS CATALYSTS

A heterogeneous catalysis is the reaction components are different phase not in same phase.

Heterogeneous catalysts act different phase reactants. Most heterogeneous catalysts are solids that act on substrates in a liquid or gaseous reaction mixture

1.5 POLYMER

Polymers are some of the world's most widely used materials, due to their favourable properties such as high strength, low weight and low cost [1]

Polymer catalysts are used as catalysts of organic synthesis. Cross-linked polymers as polymer support material due to their insolubility [8]

Polymer catalysts are polymers possessing catalytically active moieties. The catalytic moiety is usually attached to the side chain of synthetic polymers such as polystyrene [2]. Insoluble polymer catalysts can separate from the reaction mixture and reused. Some of the catalysts are incorporated in main chain polymer

Most polymerization catalysts are cation complexes. The positive charge increases the Lewis acidity of the complex, while reducing the fraction of any di nuclear alkyl bridged complexes [1]

With low dielectric constants, the solvents typically used are unlikely to separate the cations completely from their anions, even in the case of the most weakly coordinating anions, due to the electrostatic attraction.

1.6 Cobalt

Cobalt is a chemical element with the symbol Co and atomic number 27. As with nickel, cobalt is found in the Earth's crust only in a chemically combined form, save for small deposits found in alloys of natural meteoric iron. The free element, produced by reductive smelting, is a hard, lustrous, silver-metal. [11]

Atomic number - 27

Group -9

Period - 4

Block – d block

Electron configuration – [Ar]3d⁷ 4s²

Melting point – 1768K

1.6.1 Cobalt (II) sulphate

Cobalt (II) sulphate is a red or pink crystalline chemical compound of cobalt. chemical formula of Cobalt (II)sulphate is CoSO_4 . It is commonly encountered in its hydrated form.

1.6.2 Preparation

Cobalt (II) sulphate can be prepared by reacting cobalt metal, or cobalt oxide/hydroxide with aqueous sulfuric acid. Heating the solution to drive off the water will give the hydrated forms of cobalt (II) sulphate



Fig.2 cobalt(II) sulphate

<https://www.google.com/search?q=cobalt+sulfate&sxsrf=ALiCzsZmQLq0QOB U5sghhHn6gO9f5cYx8Q:1652189436036&source=Inms&tbm=isch&sa=X&ved=2ahUKEwiO2r6jhdX3AhWhT2wGHUi DRAQ AUoA3oECAIQBQ&biw=1366&bih=625&dpr=1#imgsrc=wfulKKhrZdT4M>

1.6.3 SAFTEY MEASUREMENT

It causes severe irritation within the skin, and eyes. affects the lungs, kidneys, and heart. anticipated to be a person carcinogen.

1.6.4 COBALT POISONING

Cobalt, employed in making jet engines, may cause nausea, vomiting, lack of appetite (anorexia), ear ringing (tinnitus), nerve damage, respiratory diseases, an oddly large endocrine gland and/or heart and/or kidney damage [12]

1.6.5 Environmental effects of cobalt

Cobalt is a very toxic element affecting the environment. Cobalt is present in the wastewater of nuclear power plants and many other industries such as mining, metallurgical, electroplating, paints, pigments and electronic industries [1]

The standard level of cobalt in drinking water is 2 μ g/L [10]

1.7 Congo red dye

Congo red is an organic compound an azo dye. Congo red is water-soluble, yielding a red colloidal solution; its solubility is greater in organic solvents Congo Red is an indicator dye that is blue-violet at pH 3.0 and red at pH 5.0.

Congo red was first synthesized in 1883 by Paul who had been employed at Friedrich Bayer Company in Elberfeld, Germany.

IUPAC Name of congo red dye- disodium 4-amino-3-[4-[4-(1-amino-4-sulfonato-naphthalen-2-yl) diazanyl phenyl diazenyl-naphthalene-1-sulfonate

1.7.1Synthesis

Congo Red is synthesised by coupling bis-diazotised benzidine with two the blue dye so obtained is converted into its red disodium salt during its salting out with binary compound

1.8 CONGO RED DYE POLLUTANT

CR is a water soluble azo dye with two sulfonic groups. It is one of the most important and widely used colours in the textile industry [3].

Nearly 7 00000 tons of dyes are produced annually throughout the world. Azo dyes are widely used in the textile and paper industries due to their low cost and ease of application. Their extensive use results in large volumes of wastewater being discharged into aquatic ecosystems.[12]

CR is mutagenic and carcinogenic due to the presence of aromatic groups. It is a highly toxic and recalcitrant compound. It is resistant to biological degradation of the environment [13]

That Congo Red is highly toxic to C.. Our results show that this dye produces negative effects at very low concentrations. [11]

Recently nanotechnology has been applied in removal/treatment of several natural and synthetic environmental pollutants and a considerable amount of success has been achieved in environmental clean with the help of nano particles[4]

Different methods have been proposed to remove Congo Red from polluted water, such as adsorption coagulation–flocculation, ultrasound irradiation ion exchange, mineralisation and photocatalysis, etc 5.1Others are flocculation, reverse osmosis and adsorption onto activated carbon.[9].

But these methods are very expensive. At present physical, chemical and biological methods are generally used as a treatment process for removing dyes from textile wastewater [8]

Advanced oxidation process extensively investigate these processes, heterogeneous photocatalysis is found as an emerging destructive technology leading to total mineralization of most of organic pollutants. [9]

That are big differences between the adsorption performances adsorbents towards CR. Therefore, other works should be carried out to investigate CR adsorption by other low-cost sorbents [16].

CHAPTER 2

LITERATURE SURVEY

1.Title: Photocatalytic degradation of Congo red using *Carissa edulis* extract capped zinc oxide nanoparticles.

Authors: J. Fowsiya, G. Madhumitha, Naif Abdullah Al-Dhabi , Mariadhas Valan Arasu

Journal and year: Photochemistry & Photobiology, 11 July 2016.

Inference: The secondary metabolites were extracted using microwave assisted extraction of *Carissa edulis* (*C. edulis*) at 70 °C and 400 W in this study. To make ZnO nanoparticles, the metabolites were utilised as a capping agent and Zn (NO₃)₂ as a metal precursor (ZnO NPs). Nanoparticles were characterised by UV–Vis spectroscopy, FT-IR, XRD, SEM, and HR-TEM

2.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).

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 : Polymer Nanocomposites for Photocatalytic Degradation and Photoinduced Utilizations of Azo-Dyes.

Authors : Emily Z. Wang , Yigui Wang and Dequan Xiao.

Journal and year : Polymer Nanocomposites, 9 April 2021.

Inference : Designed polymer nanocomposites can photo-catalytically destroy azo dyes in wastewater and textile effluents, with TiO₂-based nanocomposites standing out as particularly promising and well-studied.

5.Title: Sono catalytic rapid degradation of Congo red dye from aqueous solution using magnetic Fe₀ /polyaniline nanofibers

Authors: Raghunath Dasa, Madhumita Bhaumik, Somnath Giria , Arjun Maitya.

Journal and year: Ultrasonics Sonochemistry, 16 February 2017.

Inference: For sonocatalytic degradation of organic anionic Congo red (CR) dye, nano-sized magnetic Fe₀ /polyaniline (Fe₀ /PANI) nanofibers were used as an effective material. At room temperature, nano-Fe₀ was reductively deposited onto

PANI nanofibers to produce Fe₀ /PANI. HR-TEM, FE-SEM, XRD, and FTIR equipment were used to characterise the catalyst.

CHAPTER 3

AIM AND SCOPE

3.1. AIM

The main aim of this project is to degradation of cango red dye by using a metal incorporated polymer as a catalyst. The synthesis of catalyst by toxic metal cobalt and poly vinyl alcohol metal incorporated polymer. Use the catalyst to removal of cango red dye

3.2. SCOPE

- Collect heavy metal from environment
- Preparation of Metal with PVA solutions
- synthesis of metal incorporated polymer
- Characterization of synthesized metal incorporated polymer FT-IR, UV, SEM, XRD.
- Confirmation of product formed by characterizing by FT-IR, UV spectroscopy

CHAPTER 4

MATERIALS AND METHODS

4.1 MATERIALS

Materials used in the reaction are Cobalt (II) sulphate poly vinyl alcohol distilled water to make a catalyst and acetone. Congo red dye which were purchased from lab fine chem industry lab equipment and others use in lab chemicals make PVA to powder to use

4.2 CHARACTERIZATION TECHNIQUES

4.2.1 Fourier Transform Infrared Spectroscopy

FTIR is Fourier transform infrared spectroscopy is a technique to obtain infrared spectrum of absorption, emission, and photoconductivity of solid, liquid, and gas. FTIR provide information on the basis of chemical composition and physical state of the whole sample FTIR is a very versatile tool for surface characterization of nanoparticles FTIR spectrum absorption peaks correspond to a frequencies of vibration bonds of atoms in nanoparticle. FTIR analysis is used organic, inorganic, and polymeric materials. FTIR can be used to collect high spectral resolution data over a wide range 10,000 and 4000 cm^{-1} for near-IR region wavelength 5000 and 400 cm^{-1} for mid-IR region wavelength FTIR light of many frequencies can be measured simultaneously this process can be repeated. The spectrum is recorded on a graph wavenumber is

(cm^{-1}) the X-axis and transmittance recorded on the Y-axis. (Wavenumber is $1/\text{wavelength}$ and corresponds to energy of vibration of the molecule bonds.)



Fig.3 FTIR Spectroscopy

Fourier Transform Infrared (FTIR) Spectroscopy

<https://photometrics.net/fourier-transform-infrared-ftir-spectroscopy/>

4.2.2 UV spectroscopy

UV-Visible Spectroscopy is the absorption of ultraviolet light or visible light by chemical compounds results in the production of distinct spectra. Spectroscopy is based on interaction light and matter. This absorption relates excitation of species from a ground state to excited state. less energy is required on this transition, the wavelength of absorption is higher, whereas when more energy is needed, the wavelength is lower single beam all of the light passes through the sample cell. be measured by removing the sample. Its common use in both teaching and industrial labs. Spectrophotometer basic parts light source, a holder for the sample diffraction grating in a monochromator or a prism to separate the different wavelengths of light, and a detector. the ultraviolet region (190–400 nm), Xenon arc lamp The radiation source is often a Tungsten filament (300–2500 nm) 160 to 2,000 nm; or more recently, light emitting diodes (LED) UV/Vis spectroscopy is routinely used in analytical chemistry for the quantitative determination of analytes or sample, transition metal ions, highly conjugated organic compounds biological macromolecules. Spectroscopic analysis is commonly carried out in solutions but solids and gases may also be studied.



Fig.4 UV spectroscopy

https://www.researchgate.net/figure/17-Spectrophotometre-UV-Vis-VARIAN-Cary-100-Scan_fig16_278826646

4.2.3 Scanning Electron Microscopy (SEM)

(SEM) scanning electron microscope is a type of electron microscope that produces images of a sample by scanning the surface with a focused beam of electrons. Is one of the most widely used instrumental methods for the examination and analysis of micro- and nanoparticle image characterization of solid objects. One of the reasons that SEM is preferred for particle size analysis is due to its resolution of 10 nm, that is, 100 Å most applications, Data are collected a selected area of the surface of sample, and a 2-dimensional image is generated. approximately 1 cm to 5 microns in width can be imaged in a scanning mode using conventional SEM techniques. (magnification) ranging from 20X to approximately 30,000X, spatial resolution of 50 to 100 nm) Different modes of SEM exist for characterization of materials (including biomaterials) such as the X-ray mapping, secondary electrons imaging, backscattered electrons imaging, electron Auger electron microscopy.



Fig.5 SEM SCANNING ELECTRON MICROSCOPE

JCM-6000Plus Versatile Benchtop SEM

<https://www.jeol.co.jp/en/products/detail/JCM-6000Plus.html>

4.2.4 X-Ray Diffraction Spectroscopy (XRD)

X-ray diffraction spectroscopy (XRD) techniques used for the analysis of inorganic pigments and extenders by the crystalline structure of the material rather than its elemental content characterization of solid solutions, crystallite size and shape, crystal orientation, internal elastic strains/stresses at different levels, effect of temperature, close surface characterization etc the orientation of a crystal (or grain), stress in crystalline regions, and secondary phases in the sample. It is generally a bulk characterization technique and produces an average diffraction pattern for the area measured. XRD is a destructive technique which can be conducted at room temperature and pressure. X-ray diffraction or XRD is used for phase analysis, crystalline variants, and to study the grain and particle size of nanomaterials. X-ray diffraction spectroscopy as a rapid analysis technique is used to identify the type of material as well as its phase and crystalline properties.



Fig,6 XRD X-RAY DIFFRACTION SPECTROSCOPY

Rigaku MiniFlex 600 (MiniFlex)

<https://scs.illinois.edu/resources/facilities/x-ray-laboratory/instruments/rigaku-miniflex-600-miniflex>

4.3 METHADODOLOGY

First take some toxic heavy metal. Toxic Metal can remove from environment extract heavy metal and separated. Use poly vinyl alcohol to make polymer normal PVA takes time to dissolve the PVA like powder its dissolve easily. Take 75 ml of distilled water in 250 ml beaker. 1.5g of Cobalt (II) sulphate dissolve in 75ml of distilled water and stirred well to completely dissolve in water. After dissolve extract three portions. Each portion 25 ml in 100ml beaker.

This process goes to three different type conditions Acidic, Neutral and Basic conditions. Portion one is acidic use HCL acid and make PH range 3. Second one is neutral condition. Third one use Sodium Hydroxide solution to make base condition PH range is 8 and make 30ml of all portions. 0.5g pf poly vinyl alcohol make powdered and dissolve stirred well by adding PVA. mark to identified the solutions.

Use aluminium foil to close the beaker. Use magnetified stirring to dissolve PVA completely time will be noted. After 24 hours completely dissolved and use acetone to remove polymer. Use measuring tube take 30ml of acetone in three times. This acetone is use to remove polymer from solutions 30 ml of acetone in each portion and add acetone take glass slowly stirred acetone mix complete solutions. Before adding PVA take optical density (OD) value as a initial value and after addition of PVA note a value also OD value only taken in completely dissolved solutions any turbined solutions get incorrect values After removal of polymer acetone solution is increases use water bath to remove acetone and water as vaporisation. Make correct 30 ml to same concentration.

Now OD value is taken as final value. The removed polymer is collected in watch glass make dried and weighted.

Weight will be noted this sample is metal ready to use as catalyst. Balance solution take to uv characterization. compare to acidic and base conditions neutral is good one. Neutral condition polymer used as a catalyst to removal of congo red dye.

Catalyst to use now degradation of congo red dye. Take 0.5g of congo red dye is dissolved in different volume of distilled water to get different concentration of congo red dye.

4.3.1 1st concentration

0.5g of congo red dye powdered and weighted accurately and dissolve in 500ml of distilled water and made up in 500ml clean standard flask

4.3.2 2nd concentration

From first concentration of solution 500ml. 100ml to use second concentration method 100ml measured accurately by measuring tube and transfer into 500ml clean standard flask make 100ml into 500ml solution

4.3.3 3rd concentration

From second concentration of solution take 10ml solution 10 ml pipetted out in to clean 100 ml standard flask use distilled water and make up into 100ml solution 3rd concentration ready transfer in beaker

4.4 DEGRADATION OF CONGO RED DYE

100ml of 3rd concentration congo red dye solution. 20 ml pipetted out in to clean beaker. Add few drops of NaOH solution in to the beaker to maintain the PH level of 3rd concentration solution

The 0.3g of metal (cobalt) incorporated polymer weighted and cut to small pieces used as a catalyst. Add catalyst into the solution and keep it for stirring. This process is completed within 5 minutes the congo red dye solution is degraded

Solutions become decolorised and polymer is removed from the solutions. Precipitations become to brown colour filtrate obtained to clear solution and catalyst has been reused again and again repeating this processes to degradation of congo red dye this reaction is going in normal room temperature.

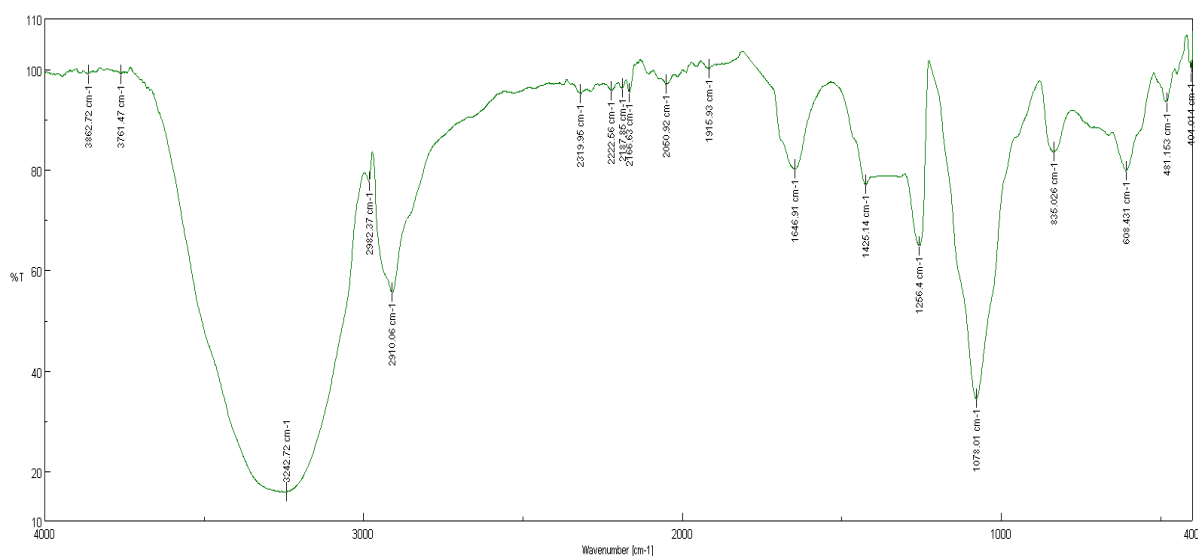
CHAPTER 5

RESULTS & DISCUSSION

5.1 CHARACTERIZATION OF METAL INCOPRATED POLYMER

5.1.1 FTIR SPECTRUM OF METAL INCORPORATED POLYMER

The FTIR spectrum of The IR vibrational frequency obtained at 3242 cm^{-1} O-H stretching strong broad intermolecular bonded 2910 cm^{-1} O-H stretching weak broad intermolecular bonded, 1646 cm^{-1} C=C stretching medium alkene vinylidene, 1425 cm^{-1} O-H bending medium carboxylic acid, 1256 cm^{-1} C-O stretching strong alkyl aryl ether, 1078 cm^{-1} C-O stretching strong primary alcohol in FTIR spectrum in metal incorporated polymer

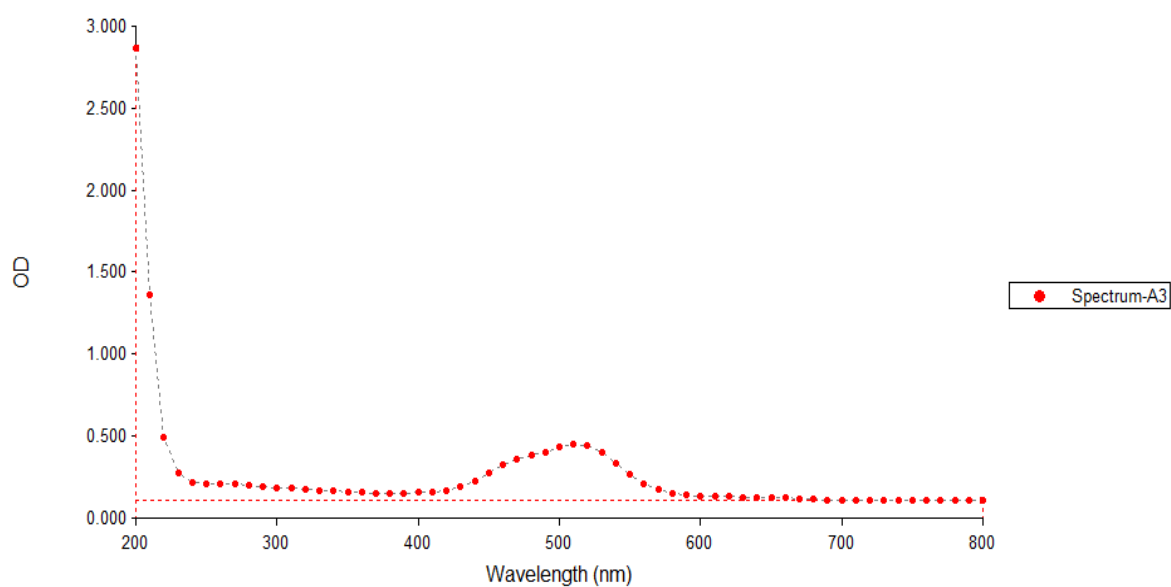


FTIR SPECTRUM VIBRATIONAL FREQUENCY AND FUNCTIONAL GROUP

SI/NO	vibrational frequency	Functional group identification
1	3242	O-H stretching strong broad intermolecular bonded
2	2910	O-H stretching weak broad intermolecular bonded
3	1646	C=C stretching medium alkene vinylidene
4	1425	O-H bending medium carboxylic acid
5	1256	C-O stretching strong alkyl aryl ether
6	1078	C-O stretching strong primary alcohol

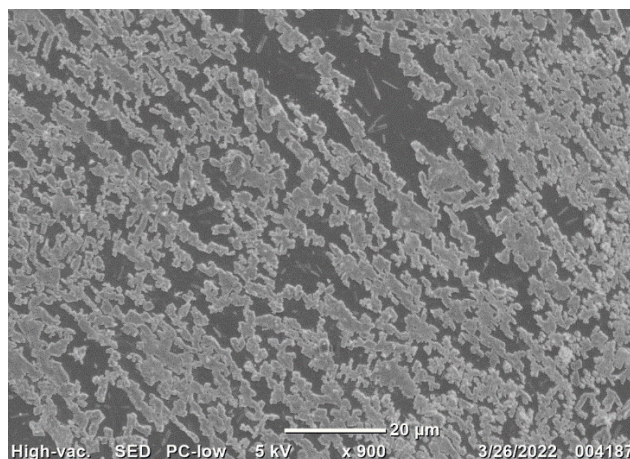
5.1.2 UV / VIS SPECTRUM

The uv / vis spectrum characterized by short wavelengths and high quantum energies as compared to visible light. measures how much chemical absorbed the wavelength obtained from 527(nm) absorption occurs in 2.37 ev in uv / vis spectrum

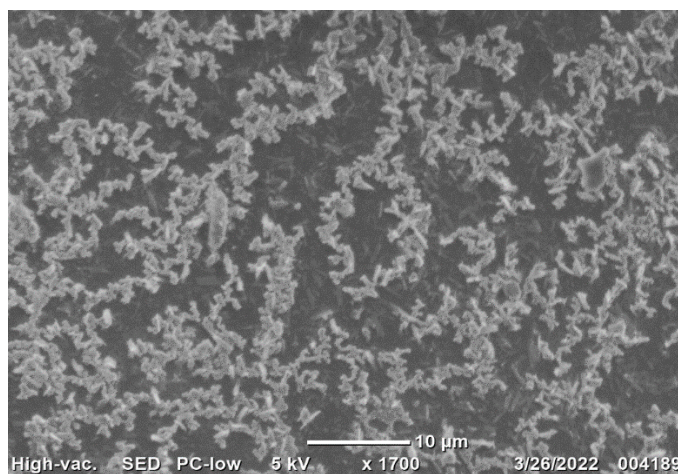


5.1.3 SEM IMAGE OF METAL INCORPORATED POLYMER

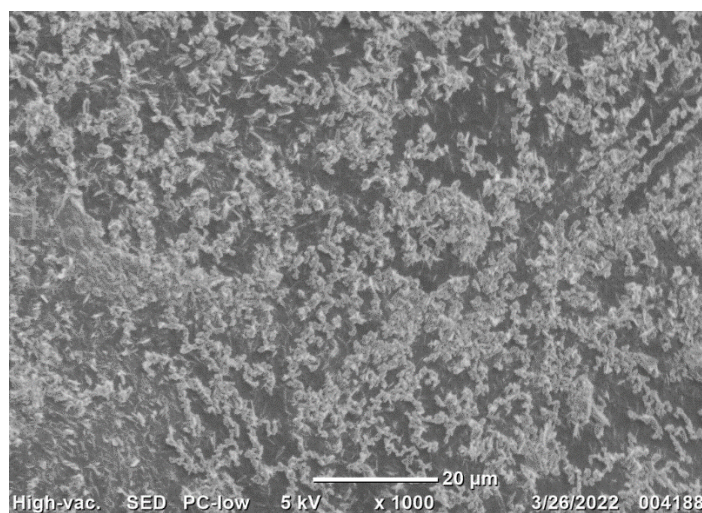
The SEM image of metal incorporated polymer that explains heavy metal cobalt attached polymer the SEM images show presence of heavy metal to absorbed in polymer go catalyst its clearly show in scanning electron microscope



{A}



{B}

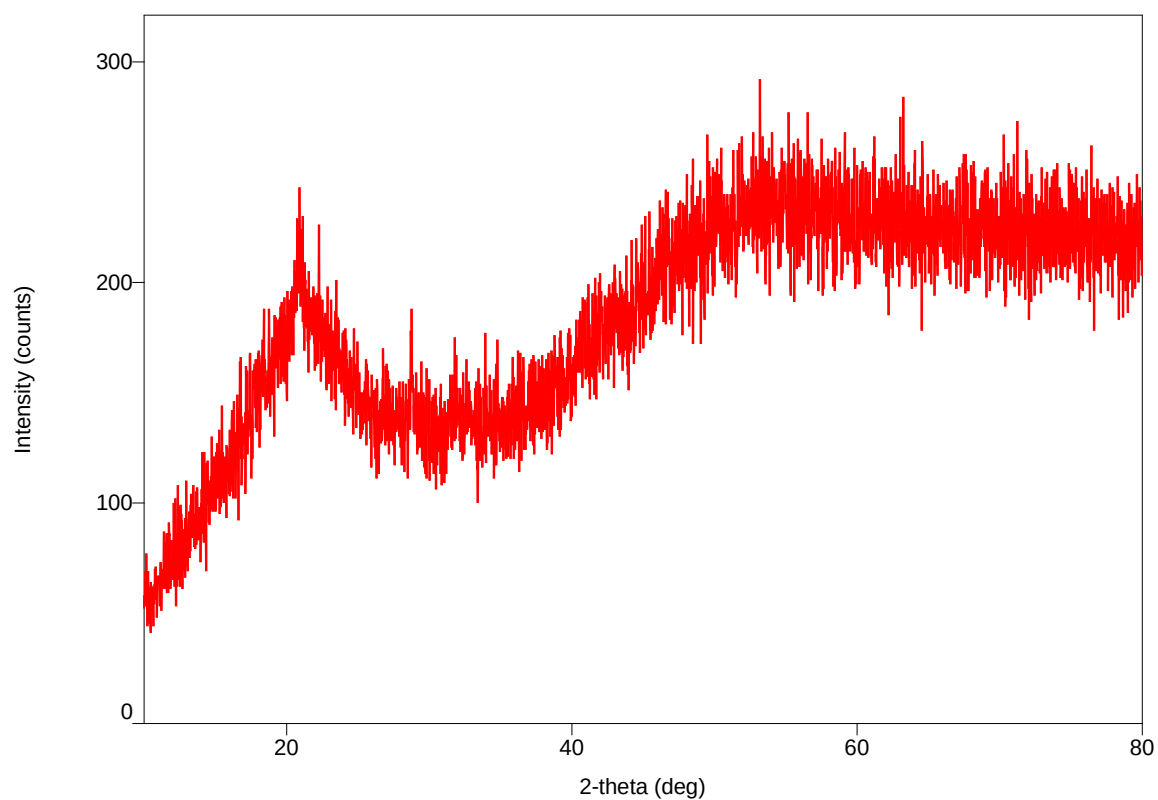


{C}

Fig.7 SEM IMAGES

5.1.4 XRD PATTERN

The XRD pattern of metal incorporated polymer the peaks



Further the sample were taken for XRD analysis to evaluate the cobalt. The characteristic peak represents the cobalt. The given set PVA-Co Nanofibers phase with diffraction peaks at 45.5 and 52.3 corresponding to Miller indices (111) and (220), respectively. These peaks are attributed to the PVA-Co Nanofibers.

No significant peaks corresponding to impurities were detected in the XRD pattern. After mixing PVA and cobalt (II), peaks of PVA-Co nanofibers are detected. In the nanocomposite, some intensities of the peaks changed due to peak interference.

5.2 REDUCTION OF CONGO RED DYE

Congo red is highly toxic and carcinogenic anionic dye. Its removal from aqueous medium by chemical reduction method using sodium borohydride as reducing agent in the presence of various nano-catalytic systems has been widely reported in literature during last ten years

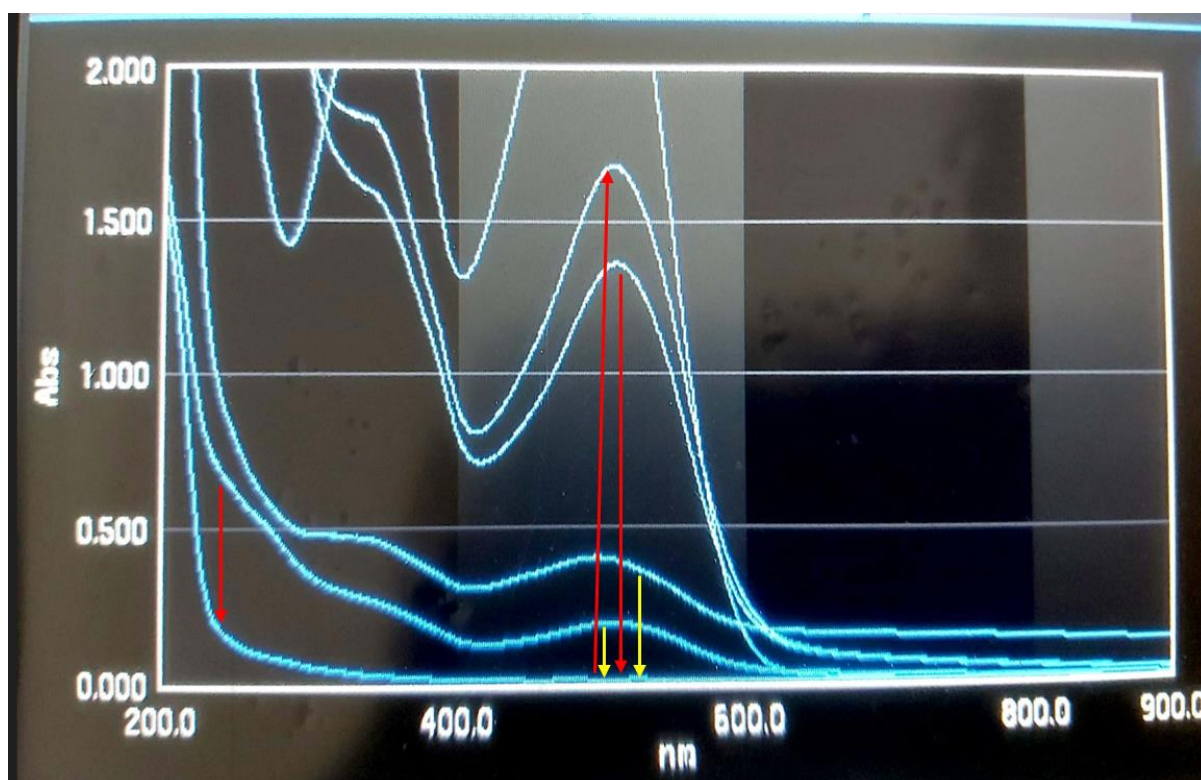


Fig.8 REDUCTION OF CONGO RED DYE

The Congo red dye has been degrading kinetically in 5 minutes duration time with different intensities.

Peak	Wave length	Absorbance
1	507	1.63
2	523	1.41
3	545	0.33
4	511	0.27
5	245	0.22

Congo red dye has been kinetically studied under the given conditions the absorbance the given dye has been observed at very low absorbance due to its degradation.

The intensity of the dye quite low and its degradation happen when dissolved in NaOH with polymer. This Congo red dye is used for studies in textile industries mostly combinations of metal oxides.

The kinetics data revealed that both surface adsorption and intraparticle diffusion take place simultaneously. The adsorption equilibrium is in good agreement with Langmuir adsorption isotherm, indicating monolayer adsorption on homogenous surface. Desorption study corroborates the regenerative abilities of nanocomposite.

The kinetic study of degrade Congo red dye have observed at different wavelength, the first peak was observed at 507 nm with 1.63 absorbance then second peak was observed at 523 nm with 1.41 absorbance the absorbance difference between these two peaks nearly 0.2 absorbance difference.

Then third peak was observed at 545 nm with 0.33 absorbance, after this peak the intensity was decreased gradually, the fourth peak was observed at 511 nm with 0.27 absorbance and the final peak was observed at 245 nm with 0.22 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 degrading in 5 minutes of duration time successfully with decrease in their intensity.

CHAPTER 6

SUMMARY

Toxic Metal can remove from environment extract heavy metal and separated. Use poly vinyl alcohol 1.5g of Cobalt (II) sulphate dissolve in 75ml of distilled water and keep shaken a day after completely dissolve use acetone to remove polymer completely wait for dry and catalyst is ready to use reduce congo red dye. make Congo red dye solution in different concentration add small piece weighted metal incorporated polymer in solution within five minutes the solution become decolourised

REFERENCES

1. Rigved Nagarkar, Department of Pharmaceutics, University of Sciences, Philadelphia, USA. Review Article Received: February 26, 2019; Published: March 12, 2019
2. Anna Khlyustova, Nikolay Sirotkin, Anton Kraev, Alexander Agafonov and Valery Titov. "Effect of metal oxides added onto polyvinyl alcohol via pulsed underwater plasma on their thermal, electrical and dielectric properties". *Journal of Applied Polymer Science*. 13 May 2021.
3. Ashita Sharma, Jatinder Kaur Katnoria, Mandeep Kaur, Avinash Kaur Nagpal. "Heavy Metal Pollution: A Global Pollutant of Rising Concern". January 2015.
4. Buzuayehu Abebe, H. C. Ananda Murthy, and Enyew Amare Zereffa. "Synthesis and Characterization of PVA-Assisted Metal Oxide Nanomaterials: Surface Area, Porosity, and Electrochemical Property Improvement". *Journal of Nanomaterials*. 29 September 2020.
5. CH LINGA RAJU, J L RAO, B C V REDDY and K VEERA BRAHMAM. "Thermal and IR studies on copper doped polyvinyl alcohol". *Bull. Mater. Sci.*, 3 June 2007.
6. Charles Rolsky and Varun Kelkar. "Degradation of Polyvinyl Alcohol in US Wastewater Treatment Plants and Subsequent Nationwide Emission Estimate". *International Journal of Environmental Research and Public Health*. 3 June 2021.
7. Dag G. Ellingsen, Lisbeth Birk Møller, And Jan Aaseth. Copper.
8. Dan Brennan, "What to know about copper toxicity". 03 May 2021.
9. Donald G. Barceloux Topanga, California. "Copper". *Clinical Toxicology*. 1999.
10. Duruibe, J. O., Ogwuegbu, M. O. C. and Egwurugwu, J. N. "Heavy metal pollution and human biotoxic effects". *International Journal of Physical Sciences*. May, 2007.
11. F.M. Ali, I. Ashraf, Sh.M. Alqahtani. "Promising Cu-doped Polyvinyl Alcohol Films for Optical and Photoconductive Applications". *Physica B: Condensed Matter*. December 2017.
12. Faith Mokobi. "Scanning Electron Microscope". 11 November 2021.
13. Fawzy Hamed Abd El-kader, W.H. Osman, H.S. Ragab, A.M. Shehap. "Electrical and Optical Properties of Polyvinyl Alcohol Thin Films Doped with Metal Salts". *Journal of Polymer Materials*. March 2004.

14. Francesca Ferrari, Raffaella Striani, Carola Esposito Corcione and Antonio Greco. "Valorization of Food Industries Wastes for the Production of Poly(vinyl) Alcohol (PVA) Biodegradable Composites". *Original Research*. 25 July 2019.
15. Francesca Ferrari, Raffaella Striani, Carola Esposito Corcione, Paolo Visconti, Antonio Greco. "Bio-Composites Based On Poly (Vinyl) Alcohol (Pva)And Food Wastes". 17 July 2019.
16. Heavy Metal Contamination.
17. J. Fowsiya, G. Madhumitha, Naif Abdullah Al-Dhabi , Mariadhas Valan Arasu. "Photocatalytic degradation of Congo red using Carissa edulis extract capped zinc oxide nanoparticles". *Photochemistry & Photobiology*. 11 July 2016.
18. Jebin Ahmed, Abhijeet Thakur and Arun Goyal. "Industrial Wastewater and its toxic effects". 03 Dec 2021.
19. K. C. Rani, Aduja Naik, Ram Saran Chaurasiya and K. S. M. S. Raghavarao. "Removal of toxic Congo red dye from water employing low-cost coconut residual fiber". *Water Science & Technology*. 2017.
20. Kang Wen, Yi Li, Shuxing Zhang, Xiaoting Zhang, Runping Han. "Adsorption of Congo red from solution by iron doped PVA-chitosan composite film". *Desalination and Water Treatment*. 18 January 2020.
21. M.Rashad. "Tuning optical properties of polyvinyl alcohol doped with different metal oxide nanoparticles". *Optical Materials*. July 2020.
22. Madiha Batool, Muhammad Zahid Qureshi, Farwa Hashmi, Nida Mehboob, and Abdul Salam Shah. "Congo Red Azo Dye Removal and Study of Its Kinetics by Aloe Vera Mediated Copper Oxide Nanoparticles". *Indonesian Journal of Chemistry*. May 2019.