

POLLUTANTS- ROLE OF GRAPHENE AS A CATALYST

Submitted in partial fulfilment of the requirements for the award of

Bachelor of Science in Chemistry

by

NANDHINI.R (39030017)

SARANYA.R (39030031)



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

April - 2022



SATHYABAMA

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

Accredited with Grade “A” by NAAC

JEPPIAAR NAGAR, RAJIV GANDHI SALAI, CHENNAI - 600 119

www.sathyabama.ac.in

**DEPARTMENT OF CHEMISTRY
BONAFIDE CERTIFICATE**

This is to certify that this Project Report is the bonafide work of **NANDHINI.R (39030017)** and **SARANYA.R (39030031)** who carried out the project entitled **“POLLUTANTS- ROLE OF GRAPHENE AS A CATALYST”** under our supervision from December 2021 to April 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

We **NANDHINI.R (39030017)** and **SARANYA.R (39030031)** hereby declare that the Project Report entitled **POLLUTANTS- ROLE OF GRAPHENE AS A CATALYST** done by us 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 Bachelor of Science degree in Chemistry.

DATE:

NANDHINI.R

PLACE:

SARANYA.R

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, Associate Professor, Dept. 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.

NANDHINI.R

SARANYA.R

ABSTRACT

The incessant release of pharmaceuticals into the aquatic environment continues to be a subject of increasing concern. This is because of the growing demand for potable water sources and the potential health hazards which these pollutants pose to aquatic animals and humans. Waste water coming from industries it produces major problem to surroundings as well as creates pollution to the environment. The review focuses on advanced oxidation processes that employ graphene-based composites as catalysts for the degradation of pharmaceuticals. These composites have been identified to possess enhanced catalytic activity due to increased surface area and reduced charge carrier recombination. So, we want to recycle the water.

TABLE OF CONTENT

CHAPTER	TITLE	Pg.No.
1	Introduction	1 - 4
1.1	GO catalytic activity	1
1.2	GO+ Cu catalytic activity	1
1.3	Congo Red Dye effluent	2
1.4	PVA catalytic activity	3
1.5	PVA+CuSO ₄ catalytic activity	4
2	Literature Survey	5- 6
3	Aim and Scope	7
4	Materials and Methods	8 – 7
4.1	UV Spectroscopy	8
4.2	IR Spectroscopy	9
4.3	SEM	10
4.4	Preparation of samples and their output	11
4.4.1	Preparation of PVA+CuSO ₄	11

	4.5	Reactions and synthesis of PVA+CuSO ₄ degradation	16
5		Results and Discussion	18 - 20
	5.1	SEM for GO	18
	5.2	UV for (PVA+CuSO ₄)	18
	5.3	IR for (PVA+CuSO ₄)	19
6		Conclusion	21
		Reference	22– 25

LIST OF ABBREVIATION

FTIR	Fourier Transform Infrared Spectroscopy
GO	Graphene Oxide
CRD	Congo Red Dye
PVA	Polyvinyl Alcohol
UV	Ultra Violet Spectroscopy
IR	Infrared Spectroscopy
SEM	Scanning Electron Spectroscopy

LIST OF FIGURES

FIGURE	TITLE	Pg.No
4.1	UV Spectroscopy machine	9
4.2	IR Spectroscopy machine	10
4.3	SEM Spectroscopy machine	6
4.4	Filtered PVA+CuSO ₄ solution sample	12
4.5	PVA+CuSO ₄ precipitate	13
4.6	GO+CRD	14
4.7	GO+CRD filter	15
4.8	GO+CRD filter	15
4.9	CuSO ₄ +CRD and PVA+CRD	16
5.1	SEM for GO	18
5.2	UV spectrum for PVA+CuSO ₄	19
5.3	IR for PVA+CuSO ₄	20

LIST OF TABLES

TABLE	TITLE	Pg.No
4.1	Result of PVA+CuSO ₄	13

CHAPTER 1

INTRODUCTION

Graphene Oxide is an oxidized form of graphene, laced with Oxygen-containing groups. Graphene Oxide is not a good character but processes exist to augment its properties.

PVA is a major artificial polymer that has been available for more than nine decades. PVA, a colourless, water-soluble synthetic resin employed principally in the treating of textiles and paper.

1.1 GO CATALYTIC ACTIVITY

Graphene Oxide (GO), a two-dimensional nanomaterial with various oxygen functionalized groups, has shown very good activity as catalysts in organic transformations such as oxidation, hydration, alkylation reaction. Although graphene was known to exist within graphite materials, it was assumed to be thermodynamically unstable in distinct 2D structures at finite temperatures. The use of graphene-based nanomaterials as catalyst support was hampered by the high price associated with the laborious synthesis and processing (e.g., sublimation of silicon from silicon carbide wafers, chemical vapor deposition, oxidation/reduction protocols etc. However, the process for liquid phase exfoliation through oxidation of graphite in presence of strong oxidizing agents generating the graphene analogue with oxygenated functionalities on their surface has brought tremendous excitement in the nano catalyst research community. These materials termed as “graphene oxide” can be obtained in sufficient quantities from commercially available graphite through reliable, now well-established preparation procedures. Further potential chemical modifications of the graphene surface introduce different newer catalytically active site important for specific catalytic reactions.

1.2 GO+Cu CATALYTIC ACTIVITY

Catalysts play deterministic roles in the hydrogenation of nitroaromatics to amino aromatics. Graphene has been extensively employed as a stable and excellent

nano catalysts support for synthesizing efficient heterogeneous catalysts; its exceptional conductivity can facilitate the electron transfer during the transformations. Consequently, metal nano catalysts supported on the graphene may potentially promote the reductants' electrons donation in the reaction media enhancing the reduction efficiency. Indeed, the synergetic effect between less-reactive nano catalysts and graphene leads to highly active hybrid nanocomposite catalysts. Motivated by the aforementioned advantages, we synthesized an efficient nanocomposite catalyst consist of graphene oxide (GO) supported copper oxide NPs (CuO–GO) via a facile hydrothermal self-assembly process for the reduction of nitroaromatics. The CuO– GO nanocomposite catalyst exhibited high yields for the reduction of various nitroaromatics using aqueous sodium borohydride (NaBH₄) at room temperature.

1.3 CONGO RED DYE EFFLUENT

The dye of Congo red (CR) is known as typically anionic diazo dye having four different color-assisted functional groups and has various molecular structures in the aqueous solutions that differ in their PH. It is highly soluble in water and stable in air and light. CR dye is used in laboratories as a pH indicator, histological dye, amyloidosis diagnosis, and for testing the contents of HCl in gastric. This dye is also used in various industries like industry of textile due to its significant affinity to fibers of cellulose, papermaking, and industry of plastic, cosmetics, and pharmaceuticals. CR is a member of benzene compounds and contains in its structure aromatic amines; therefore, it will be converted to carcinogenic materials in the environment. Moreover, benzidine produced from metabolizing of CR poses hazard effects on human health such as irritation of gastrointestinal, eye, and skin. Benzidine also causes clotting of blood, somnolence, and breathing problems.

Consequently, it is necessary to remove CR from sewage of those laboratories and industries before their discharge to the aquatic system. Thus, conventional biological methods have been established for decolorization of CR from the sewages of laboratories and industries, e.g., fungi of white rot, and foams of polyurethane and polypropylene were applied for biodegradation of CR. It was reported that the biodegradation efficiency of CR is insufficient due to different aromatic structures and

synthetic origin of this dye. Despite the effectiveness of the photocatalytic degradation techniques towards CR, the harmfulness of this dye may be less than that of its degradation products. Hence, several low or uncostly materials were applied as effective adsorbents for CR elimination from waters. The outcomes of these studies indicate that there are big differences between the adsorption performances of these cheap adsorbents towards CR. Therefore, other works should be carried out to investigate CR adsorption by other low-cost sorbents.

1.4 PVA CATALYTIC ACTIVITY

Polyvinyl alcohol (PVA) is a biodegradable, water-soluble, and environmentally benign polymeric material with unique emulsifying, adhesive, and film-forming properties. It can be used in the synthesis of organic-inorganic hybrid membrane for biodiesel production and has been regarded as appropriate matrix in microbial fuel cell applications. PVA has also been used in production of biomedical hydrogels with high ability to swell. Moreover, diversity of industrial applications of PVA has been reported such as optical and humidity sensors, food packaging, surgical devices, manufacture of polarizing sheet, and production of thin film transistors. Recently, many industrial applications of aluminum oxide (Al_2O_3) nanoparticles have been disseminated such as; drilling fluids agent, separators for lithium batteries, and biosensors for vitamin E. Recently, metal oxide nanoparticles embedded within the polymer matrix have attracted growing interest due to the unique properties that displayed by the hybrid nanocomposites.

The properties of the created nanocomposites depend on many factors like the method of preparation, the morphological structure of the prepared nanocomposite, nature of metal oxide nanoparticles that incorporated in, the structural features of the polymer used, and the chemical properties of both metal oxide and polymer molecules. The physicochemical properties of the nanosized particles within the hybrid material differ markedly from those of molecular and bulk materials.

1.5 PVA + CuSO₄ CATALYTIC ACTIVITY

The present investigation reports, the complex formation of Cu (II) with polyvinyl alcohol (PVA) and the synthesis of PVA-stabilized Cu₂O particles. This PVA-Cu₂O composite has been prepared via chemical reduction method using PVA-Cu (II) complex as precursor. At first, Cu (II) ions were stabilized in PVA-Cu (II) macromolecular complex as precursor reacted with ascorbic acid as reducing agent at pH=12 to prepare PVA-Cu₂O composite. The products were characterized by FTIR, XRD, FE-SEM, HRTEM, Visible Spectroscopy and atomic absorption. In the following, the antibacterial properties of as-prepared composites were examined against Gram-positive (*Bacillus thuringiensis*) and Gram-negative bacteria (*Escherichia coli*), and the results showed excellent antibacterial activity of these materials.

CHAPTER 2

LITERATURE SURVEY

1. TITLE: Adsorption of Congo red solution by iron doped PVA- chitosan composite film

AUTHOR: Kang Wen, Yi Li, Shuxing Zhang, Xiaoting Zhang, Runping Han

JOURNAL AND YEAR: Desalination and Water Treatment. 2020

INFERENCE: Chitosan-polyvinyl alcohol-iron (CS-PVA-Fe) composite films with acid resistance and largenadsorption capacity were prepared by doping trivalent iron, chitosan, and polyvinyl alcohol. The adsorption mechanism of Congo red (CR) on the composite films was investigated by changing the adsorption conditions (temperature, pH, salt) and characterization (isoelectric point, infrared spectroscopy, photoelectric spectroscopy, scanning electron microscopy). The results showed that the adsorption capacity of the composite film was 450 mg g⁻¹ at pH 5.0, and the adsorption of CR by high concentration salt had only a slight negative effect. The adsorption was following Langmuir, pseudo-first-order kinetics and pseudo-second-order kinetics model, which showed that the adsorption process was based on the single-layer heterogeneous adsorption, and there were both physical and chemical adsorption processes. Thermodynamic analysis shows that adsorption was spontaneous, endothermic and entropy increasing process. According to the characterization analysis, the adsorption mechanism of CR was mainly hydrogen bonding, ion exchange, and complexation. Also, the desorption of CR-loaded film can be performed using 75% alcohol at pH 12. The results showed that CS-PVA-Fe composite films are promising as a suitable candidate for the efficient removal of CR from solution.

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

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

JOURNAL AND YEAR: Journal of Cleaner Production. 2020

INFERENCE: Removal of harmful dyes and inhabitation of bacterial growth is one of the outstanding priorities in both environmental and industrial applications. The recognition of the alarming industrial discharge and insufficiency of fresh water has prompted us to develop eco-friendly and sustainable dye adsorbent films. The present investigation reports the synthesis of melamine-formaldehyde (MF) and cross-linking of polyvinyl alcohol (PVA) with MF to develop biodegradable composite films. The PVA and PVA/MF composite films were characterized by FTIR, XRD, TGA, DSC and SEM.

3. TITLE: Removal of anionic dye Congo red from aqueous environment using polyvinyl alcohol/sodium alginate/ ZSM-5 zeolite membrane

AUTHOR: Sabarish Radoor, Jasila Karayil, Jyotishkumar P arameswaranpillai & Suchart Siengchin

JOURNAL AND YEAR: 2017

INFERENCE: In this study, a novel PVA/SA/ZSM-5 zeolite membrane with good regeneration capacity was successfully prepared by solvent casting technique. The properties of the membranes were assessed by employing different characterization techniques such as X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FT-IR), scanning electron microscope (SEM), optical microscopy (OP), thermogravimetric analysis (TGA), contact angle and universal testing machine (UTM). XRD, TGA and UTM results revealed that the crystallinity and thermo-mechanical performance of the membrane could be tuned with zeolite content. The successful incorporation of zeolite into the polymer matrix was confirmed by FT-IR, SEM and OP analysis.

CHAPTER 3

AIM AND SCOPE

- To prepare an efficient catalyst by using heavy metals.
- To degrade Congo Red Dye
- Treating CRD by using GO as catalyst
- Treating CRD with the help of PVA+CuSO₄ as catalyst

CHAPTER 4

MATERIALS AND METHODS

4.1 UV SPECTROSCOPY

The principle of UV Visible spectroscopy is based on the absorption of ultraviolet or visible light by a compound, which produces a variety of spectra.

Basically, spectroscopy is related to the interaction of light and matter. When light is absorbed by a substance, the energy content of the atom or molecule increases. When ultraviolet light is absorbed, electronic excitation occurs from the ground state to the high-energy state. Molecules containing π or nonbonding electrons (n electrons) can absorb energy in the form of ultraviolet light and excite those electrons into higher antibonding molecular orbitals. The more electrons are excited, the longer the wavelength of light that can be absorbed. There are four types of transitions, ($\pi-\pi^*$, $n-\pi^*$, $\sigma-\sigma^*$, $n-\sigma^*$), which can be rearranged as follows: $\sigma-\sigma^* > n-\sigma^* > \pi-\pi^* > n-\pi^*$. The absorption of UV light by a compound produces a clear spectrum that helps identify the compound.

This is one of the best ways to measure impurities in organic molecules. Additional peaks are observed due to impurities in the sample and can be compared to the peaks of standard raw materials. Impurities can also be detected by measuring the absorbance at a specific wavelength.

This is useful for elucidating the structure of organic molecules, such as the presence or absence of unsaturated atoms and the detection of the presence of heteroatoms. UV absorption spectroscopy can be used to quantitatively measure UV-absorbing compounds. UV absorption spectroscopy can be used for qualitative measurements of compounds because it can characterize the type of compound that absorbs UV radiation. This is identified by comparing the absorption spectrum with the spectrum of known compounds. This technique is used to detect the presence or absence of functional groups in a compound. The absence of a band at a particular wavelength is considered evidence of the absence of a particular group. Reaction kinetics can also be studied using UV spectroscopy. Ultraviolet light passes through the reaction cell and its absorption can be observed. Many medicines are either in the form of raw

materials or in the form of formulations. They can be tested by making a suitable solution of the drug in the solvent and measuring the absorbance at a particular wavelength. The molecular weight of compounds can be measured spectrophotometrically by preparing appropriate derivatives of those compounds. The UV spectrophotometer can be used as an HPLC detector.

Using UV Spectroscopy analyzed the sample PVA + CuSO₄

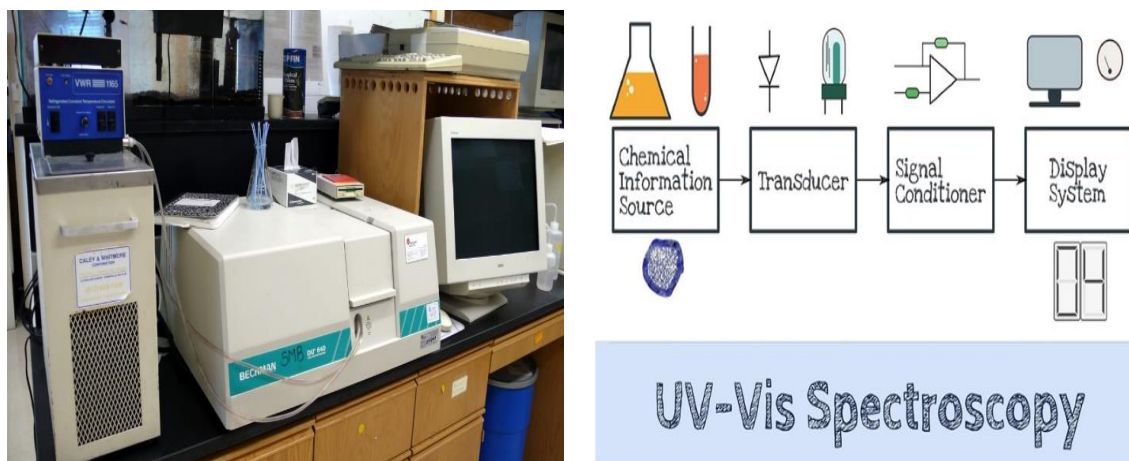


Fig.4.1. UV Spectroscopy machine

4.2 IR SPECTROSCOPY

Infrared spectroscopy (IR spectroscopy) is a spectroscopy that deals with the infrared region of the electromagnetic spectrum, that is, light with a wavelength longer and a lower frequency than visible light. It mainly covers the range of techniques based on absorption spectroscopy. Like all spectroscopic techniques, it can be used to identify and study chemicals. A common laboratory instrument that uses this technique is a Fourier transform infrared (FTIR) spectrometer. The infrared part of the electromagnetic spectrum is usually divided into three areas; near-infrared, mid-infrared, and far-infrared. Named after its relationship with the visible spectrum. The higher energy near IR, approximately 144 cm⁻¹ (.825 μm wavelength) can excite overtone or harmonic vibrations. The midinfrared, approximately 44 cm⁻¹ (2.525 μm) may be used to study the fundamental vibrations and associated rotational vibrational structure. The far infrared, approximately 41 cm⁻¹ (251 μm), lying adjacent to the

microwave region, has low energy and may be used for rotational spectroscopy. The names and classifications of these subregions are conventions, and are only loosely based on the relative molecular or electromagnetic properties.

Using IR Spectroscopy analysed the sample PVA + CuSO₄

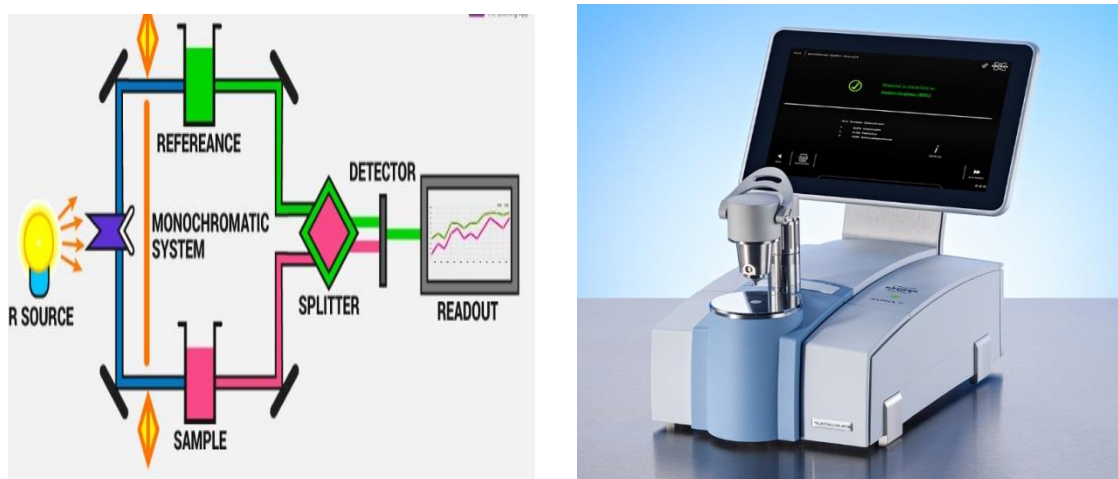


Fig 4.2. IR Spectroscopy machine

4.3 SEM

Scanning Electron Microscope (SEM) is a type of electron microscope that scans surfaces of microorganisms that uses a beam of electrons moving at low energy to focus and scan specimens. The development of electron microscopes was due to the inefficiency of the wavelength of light microscopes. Electron microscopes have very short wavelengths in comparison to the light microscope which enables better resolution power.

The Scanning electron microscope works on the principle of applying kinetic energy to produce signals on the interaction of the electrons. These electrons are secondary electrons, backscattered electrons, and diffracted backscattered electrons which are used to view crystallized elements and photons. Secondary and backscattered electrons are used to produce an image. The secondary electrons are emitted from the specimen play the primary role of detecting the morphology and topography of the specimen while the backscattered electrons show contrast in the composition of the elements of the specimen.

The major components of the Scanning Electron Microscope include; Electron Source – This is where electrons are produced under thermal heat at a voltage of 1-40kV. the electrons condense into a beam that is used for the creation of an image and analysis. There are three types of electron sources that can be used. i.e Tungsten filament, Lanthanum hexaboride, and Field emission gun (FEG) Lenses – it has several condenser lenses that focus the beam of electrons from the source through the column forming a narrow beam of electrons that form a spot called a spot size. Scanning Coil – they are used to deflect the beam over the specimen surface. Detector – It's made up of several detectors that are able to differentiate the secondary electrons, backscattered electrons, and diffracted backscattered electrons. The functioning of the detectors highly depends on the voltage speed, the density of the specimen. The display device (data output devices), Power supply, Vacuum system. Using SEM analysed the sample PVA + CuSO₄

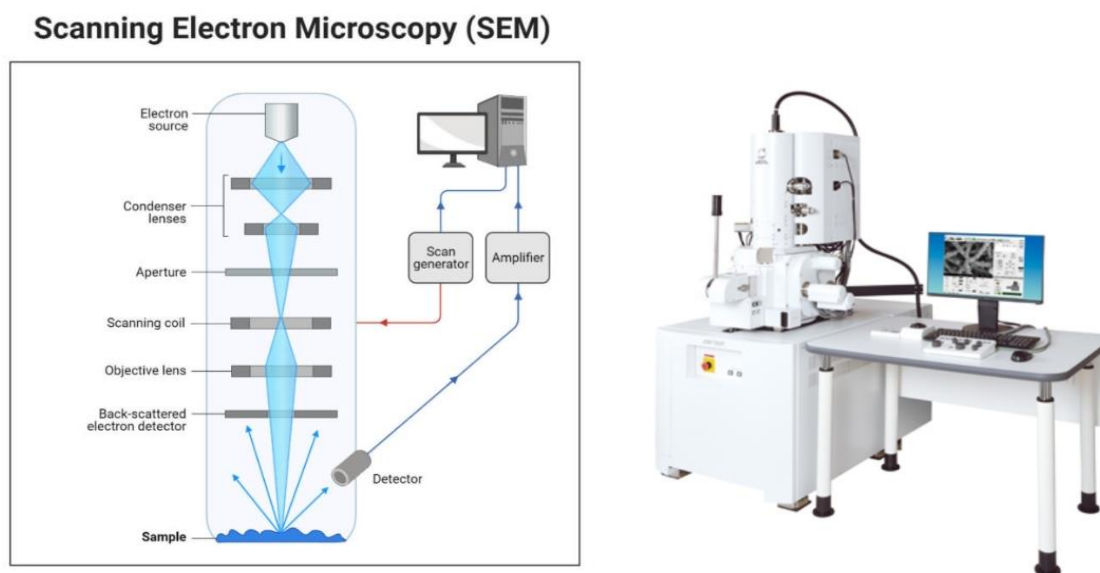


Fig 4.3. SEM Spectroscopy Machine

4.4 PREPARATION OF SAMPLES AND THEIR OUTPUT

4.4.1 Preparation of PVA+ CuSO₄

Weighted PVA (2.0056) g and CuSO₄ (1.0025) g. Took 50 ml water + NaOH, pH adjusted to 9. Added CuSO₄ and dissolve, then added PVA. Kept for stirring for 45 mins at temperature 65 Degree Celsius. Temperature set at 65 Degree Celsius at

(knob at 60 on the instrument) for 45 mins, colour is blue green precipitate formed. After adding NaOH + CuSO₄ --- finally the solution was greenish blue in colour.

Dissolved 1.0038 and 1.0051 g of CuSO₄ in 100 ml distilled water maintained at pH 9 using NaOH. Added 2.0053 g of PVA to 50 ml CuSO₄ solution and 2.0053 g of PVA to another 50 ml CuSO₄ solution (pH =9). Stirred the solutions for 45 mins keeping the temperature of 1 solution at 40 Degree Celsius and another at 55 Degree Celsius.

1. I st solution, 65degree Celsius (knob at 60 for 65 Degree Celsius) — Polymer dissolved, greenish blue deposit with pale blue solution.
2. II nd solution, 40degree Celsius (knob at 30 for 40 Degree Celsius).
3. III rd solution, 55degree Celsius (knob at 40 for 55 Degree Celsius)— blue colour deposit with greenish blue coloured solution.

Filtered the solution next day



Fig 4.4 Filtered PVA + CuSO₄ Solution Sample

Using PVA + CuSO₄ analysed the samples in various methods:

Here, NO means we didn't get the result

YES means we got the result

And then, PVA (0.5 g) + CuSO₄ (0.5 g)

Acidic = white PVA

Neutral = pale green/ yellow PVA

Basic = 1. PVA (0.5 g) + CuSO₄ (0.5 g) = light green ppt (1.6509 g)

2. PVA (0.5 g) + CuSO₄ (1 g) = dark green ppt (1.9075 g)¹⁴

PVA (0.5 g) + CuSO₄ (0.5 g) = contact time immediate = Dark green Precipitate.



Fig 4.5 PVA + CuSO₄ precipitate

Various methods	Solution	I	II	III
Acidic, basic, neutral	PVA 2g + CuSO ₄ 1g	NO	NO	YES
Using temperature	PVA 2g + CuSO ₄ 1g (pH = 9)	40 Degree Celsius [YES]	55 Degree Celsius [NO]	60 Degree Celsius [NO]
Change the CuSO ₄ weight	PVA 2g + CuSO ₄	0.5g [NO]	1g [YES]	1.5g [NO]
Extend the time period	PVA 2g + CuSO ₄	4 hours	1 day	2 days

Table 4.1 Result of PVA + CuSO₄

Using CRD (CONGO RED DYE):

Took a 100 ml of CRD and make it into 500ml (add 400 ml of distilled water).

In this 500 ml took 10 ml and make it into 100 ml (add 90 ml of distilled water).

100 ml CRD solution (OD = 1.37) --- make up in 500 ml (OD = 1.33) --- make up into 100 ml (OD = 1.08).

Using final CRD for preparation:

1. 20 ml of CRD + 0.01 g of GO - stirring
2. 20 ml of CRD + (GO + Cu) - stirring
3. PVA + GO + CRD - stirring
4. PVA + M + CRD - stirring
5. PVA + GO - stirring = No result, Remain in solution red colour.

With CRD, [final dilution]

GO – Neutral --- It take more time (24 hours) = got the result.

GO + Cu – Neutral --- Faster = didn't got the result

GO + PVA – Neutral --- GO leached out = didn't got the result

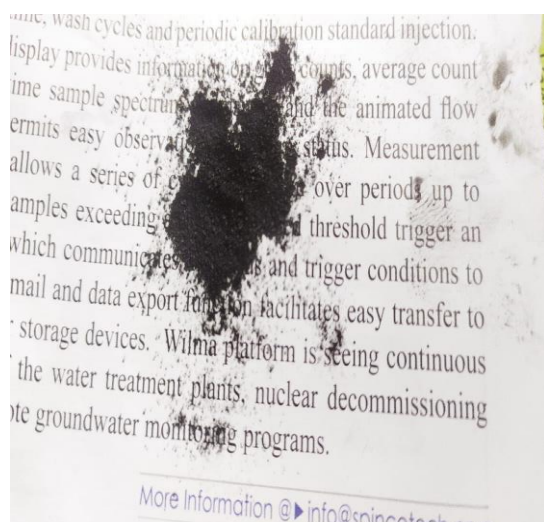


Fig 4.5 GO



Fig 4.6 GO + CRD

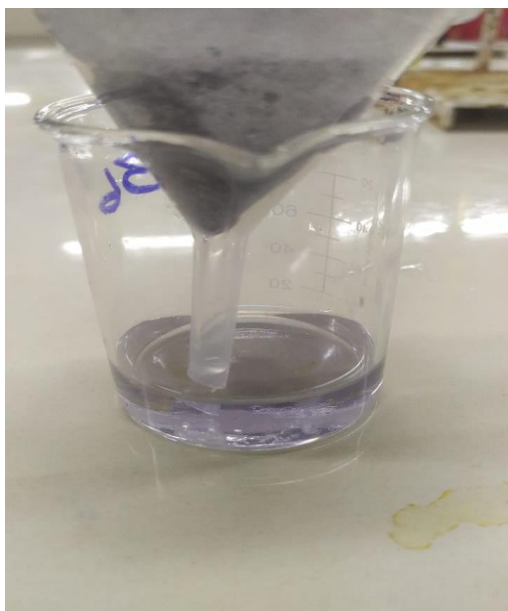


Fig 4.7 GO + CRD Filter



Fig 4.8 GO + CRD filter

PVA + M – Neutral - 4-5 hours

PVA + M – Acidic - Colour changed to blue

PVA + M – Basic - immediate colour change= got the result.

CRD + acidic - colour changed to blue

CRD + Basic - no colour change

CRD + CuSO_4 - immediate colour change

CRD + PVA - NO change.

GO, PVA + CuSO_4 - got the result suddenly

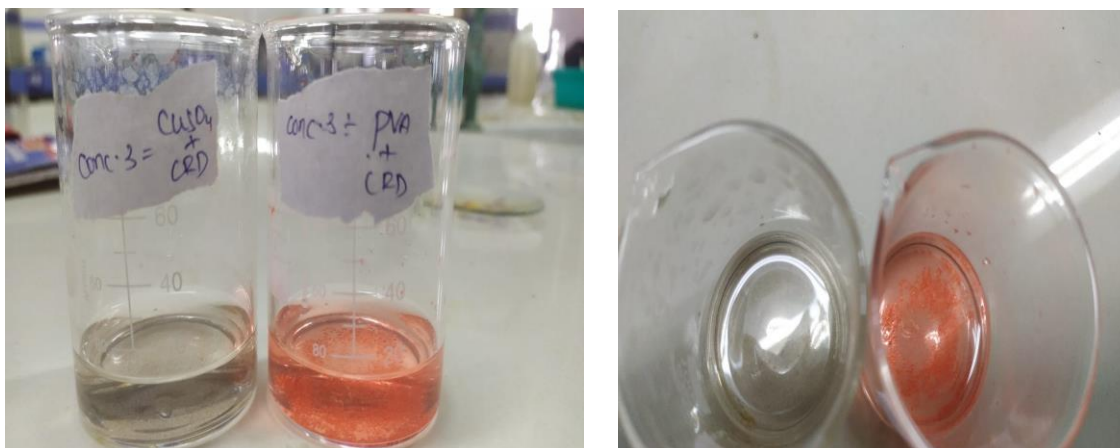


Fig 4.9 CuSO_4 + CRD and PVA + CRD

4.5 REACTIONS AND SYNTHESIS OF PVA+ CuSO_4 DEGRADATION

Weighted PVA (2.0056) g and CuSO_4 (1.0025) g. Abstract Advanced oxidation processes (AOPs) constitute a promising technology to treat wastewater containing organic pollutants that are not easily biodegradable. They have received increasing attention in the research and development of wastewater treatment technologies in recent decades for their removal or degradation of recalcitrant pollutants or as pretreatments to convert pollutants into smaller compounds, which can be treated using conventional biological methods. Polyvinyl alcohol (PVA) is a typical refractory organic pollutant. It is of particular interest because of its low biodegradability and the discharge of large amounts of PVA-containing wastewater from textile and paper mills. This review focuses on PVA removal and PVA wastewater pretreatment with AOP, including ozone treatment, Fenton oxidation, persulfate hydrochloride, ultrasonic cavitation, ionizing radiation, photocatalytic oxidation, wet air oxidation, and PVA degradation by AOP. In addition, a new classification of AOP for the treatment of PVA applies.

Weighted PVA (2.0056) g and CuSO_4 (1.0025) g . Took 50 ml water + NaOH, pH adjusted to 9. Added CuSO_4 and dissolve, then added PVA. Kept for stirring for 45 mins at temperature 65 degree Celsius. Temperature set at 65degree Celsius at (knob at 60 on the instrument) for 45 mins, colour is blue green precipitate formed. After adding NaOH + CuSO_4 --- finally the solution was greenish blue in

colour. Dissolved 1.0038 and 1.0051 g of CuSO_4 in 100 ml distilled water maintained at pH 9 using NaOH. Added 2.0053 g of PVA to 50 ml CuSO_4 solution and 2.0053 g of PVA to another 50 ml CuSO_4 solution (pH =9). Stirred the solutions for 45 mins keeping the temperature of 1 solution at 40degree Celsius and another at 55degree Celsius.

1. I st solution, 65degree Celsius (knob at 60 for 65degree Celsius) - Polymer dissolved, greenish blue deposit with pale blue solution.
2. II nd solution, 40degree Celsius (knob at 30 for 40degree Celsius).
3. III rd solution, 55degree Celsius (knob at 40 for 55degree Celsius - blue colour deposit with greenish blue coloured solution.

Filtered the solution next day.

CHAPTER 5

RESULTS AND DISCUSSION

5.1 SEM FOR GO:

Scanning Electron Microscope (SEM) is a type of electron microscope that scans surfaces of microorganisms that uses a beam of electrons moving at low energy to focus and scan specimens. The development of electron microscopes was due to the inefficiency of the wavelength of light microscopes. Electron microscopes have very short wavelengths in comparison to the light microscope which enables better resolution power. SEM is taken for GO.

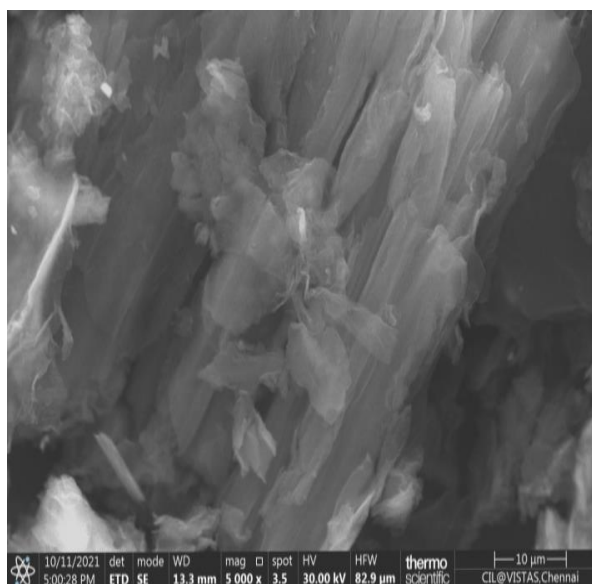
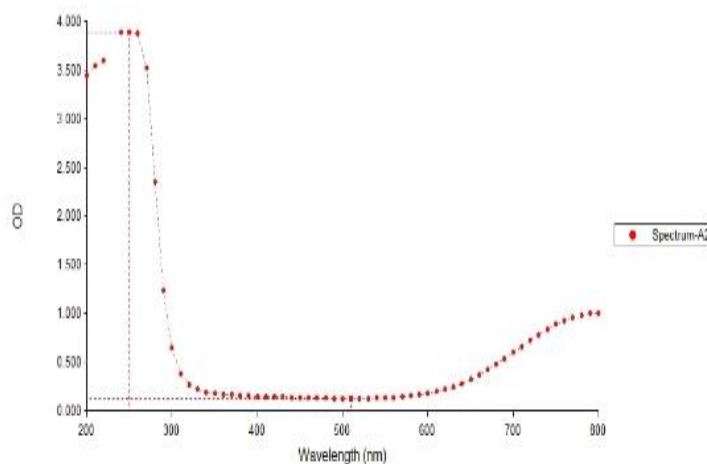


Fig 5.1 SEM for GO

5.2 UV FOR (PVA+CUSO4)

The principle of UV Visible spectroscopy is based on the absorption of ultraviolet or visible light by a compound, which produces a variety of spectra.

UV absorption spectroscopy can be used for qualitative measurements of compounds because it can characterize the type of compound that absorbs UV radiation. This is identified by comparing the absorption spectrum with the spectrum of known compounds. UV is taken for (PVA + CuSO₄).



UV-spectrum for PVA-Cu

Fig 5.2 UV Spectrum for PVA + CuSO₄

5.3 IR FOR (PVA+CuSO₄):

Infrared spectroscopy (IR spectroscopy) is a spectroscopy that deals with the infrared region of the electromagnetic spectrum, that is, light with a wavelength longer and a lower frequency than visible light. It mainly covers the range of techniques based on absorption spectroscopy. Like all spectroscopic techniques, it can be used to identify and study chemicals. A common laboratory instrument that uses this technique is a Fourier transform infrared (FTIR) spectrometer. IR is taken for PVA + CuSO₄.

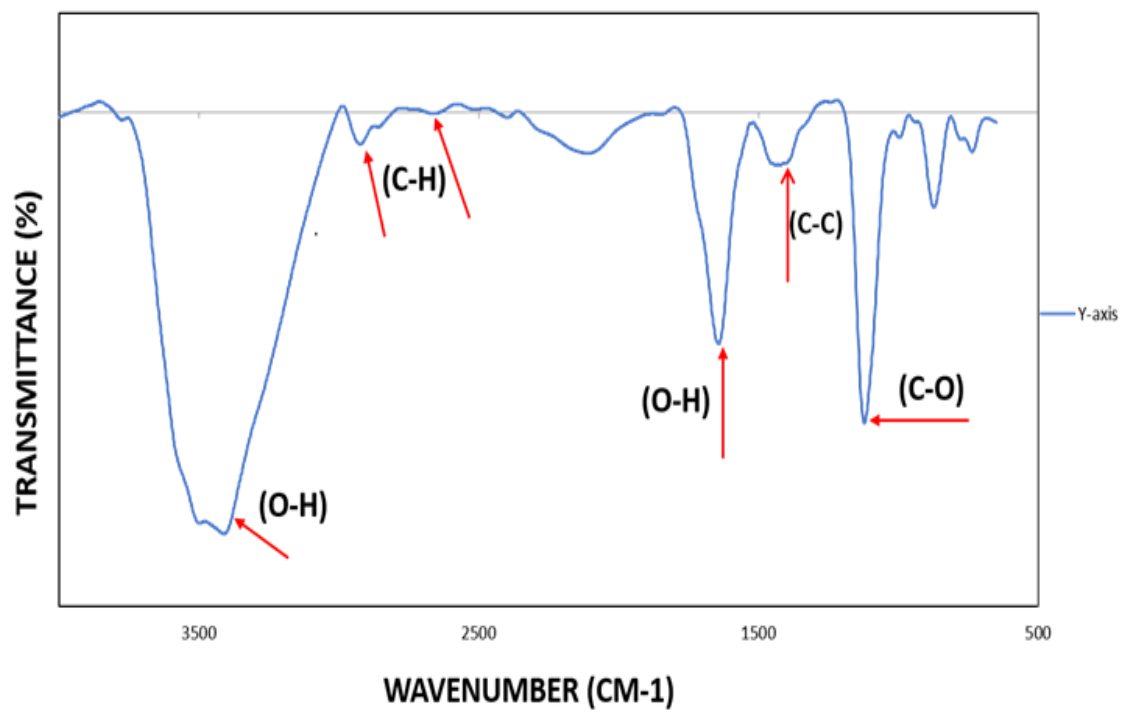


Fig 5.3 IR for PVA + CuSO₄

CHAPTER 6

CONCLUSION

Pollutants in the environment is a growing problem of global concern. Drugs taken by humans and animals find their way into rivers, lakes and even drinking water and can have devastating effects on both aquatic and human health. For that we want to recycle the waste. Using (PVA + CuSO₄, GO) these materials we can recycle the waste water.

A review of process employing Graphene based composites, and PVA + CuSO₄ as catalyst for degradation of pollutants have been identified in the explored literatures. Each of the process showed high degradation efficiencies, with the generation of reactive radical species being responsible for the activity of each process. In corporation of graphene/graphene derivatives, PVA + CuSO₄ was observed to enhance the degradation efficiency by improving on the generation of radical species, through improved surface area, light absorption and reduce recombination of generated charge carriers. A key factor in enhancing the activity of the composite is the determination of the optimal weight percentage of graphene required for improving the catalytic activity. Comparative analysis of these techniques showed that while they exhibit similar degradation efficiency.

REFERENCES

1. Alenizi M.A., Kumar R., Aslam M., Alseroury F.A., Barakat M.A. Construction of a ternary g-C₃N₄/TiO₂@polyaniline nanocomposite for the enhanced photocatalytic activity under solar light. *Sci. Rep.* 2019; 9: 12091. doi: 10.1038/s41598-019-48516-3. [PMC free article] [PubMed] [CrossRef] [Google Scholar]
2. Ali I., Gupta V.K. Advances in water treatment by adsorption technology. *Nat. Protoc.* 2006; 1: 2661. doi: 10.1038/nprot.2006.370. [PubMed] [CrossRef] [Google Scholar]
3. Araña J., Tello Rendón E., Doña Rodríguez J.M., Herrera Melián J.A., González Díaz O., Pérez Peña J. Highly concentrated phenolic wastewater treatment by the Photo-Fenton reaction, mechanism study by FTIR-ATR. *Chemosphere.* 2001; 44: 1017–1023. doi: 10.1016/S0045-6535(00)00359-3. [PubMed] [CrossRef] [Google Scholar]
4. Bhatia V., Malekshoar G., Dhir A., Ray A.K. Enhanced photocatalytic degradation of atenolol using graphene TiO₂ composite. *J. Photochem. Photobiol. A Chem.* 2017; 332:182–187. doi: 10.1016/j.jphotochem.2016.08.029. [CrossRef] [Google Scholar]
5. Boppana V.B.R., Doren D.J., Lobo R.F. A Spinel Oxynitride with Visible-Light Photocatalytic Activity. *ChemSusChem.* 2010; 3:814–817. doi: 10.1002/cssc.201000036. [PubMed] [CrossRef] [Google Scholar]
6. Brooks B.W., Huggett D.B., Boxall A.B. Pharmaceuticals and personal care products: Research needs for the next decade. *Environ. Toxicol. Chem.* 2009; 28:2469. doi: 10.1897/09-325.1. [PubMed] [CrossRef] [Google scholar]
7. Daughton C.G. Cradle-to-cradle stewardship of drugs for minimizing their environmental disposition while promoting human health. I. Rationale for and avenues toward a green pharmacy. *Environ. Health Perspect.* 2003; 111:757–774. doi: 10.1289/ehp.5947. [PMC free article] [PubMed] [CrossRef] [Google Scholar]
8. Du B., Haddad S.P., Luek A., Scott W.C., Saari G.N., Kristofco L.A., Connors K.A., Rash C., Rasmussen J.B., Chambliss C.K., et al. Bioaccumulation and

- trophic dilution of human pharmaceuticals across trophic positions of an effluent-dependent wadeable stream. *Philos. Trans. R. Soc. B Biol. Sci.* 2014; 369:20140058. doi: 10.1098/rstb.2014.0058. [PMC free article] [PubMed] [CrossRef] [Google Scholar]
9. Fent K., Weston A.A., Caminada D. Ecotoxicology of human pharmaceuticals. *Aquat. Toxicol.* 2006; 76:122–159. doi: 10.1016/j.aquatox.2005.09.009. [PubMed] [CrossRef] [Google Scholar]
 10. Franzellitti S., Fabbri E. Response to Commentary on “Are some invertebrates exquisitely sensitive to the human pharmaceutical fluoxetine?” *Aquat. Toxicol.* 2014; 146:264–265. doi: 10.1016/j.aquatox.2013.11.019. [PubMed] [CrossRef] [Google Scholar]
 11. Gomez C.F., Constantine L., Moen M., Vaz A., Wang W., Huggett D.B. Ibuprofen Metabolism in the Liver and Gill of Rainbow Trout, *Oncorhynchus mykiss*. *Bull. Environ. Contam. Toxicol.* 2011; 86:247–251. doi: 10.1007/s00128-011-0200-8. [PubMed] [CrossRef] [Google Scholar]
 12. Hai F.I., Yang S., Asif M.B., Sencadas V., Shawkat S., Sanderson-Smith M., Gorman J., Xu Z.-Q., Yamamoto K. Carbamazepine as a Possible Anthropogenic Marker in Water: Occurrences, Toxicological Effects, Regulations and Removal by Wastewater Treatment Technologies. *Water.* 2018; 10:107. doi: 10.3390/w10020107. [CrossRef] [Google scholar]
 13. Khan H.K., Rehman M.Y.A., Malik R.N. Fate and toxicity of pharmaceuticals in water environment: An insight on their occurrence in South Asia. *J. Environ. Manag.* 2020; 271:111030. doi: 10.1016/j.jenvman.2020.111030. [PubMed] [CrossRef] [Google Scholar]
 14. Khataee A.R., Kasiri M.B. Artificial neural networks modeling of contaminated water treatment processes by homogeneous and heterogeneous nanocatalysis. *J. Mol. Catal. A Chem.* 2010; 331:86–100. doi: 10.1016/j.molcata.2010.07.016. [CrossRef] [Google Scholar]
 15. Kümmerer K. Pharmaceuticals in the Environment—Scope of the Book and Introduction. In: Kümmerer K., editor. *Pharmaceuticals in the Environment:*

- Sources, Fate, Effects and Risks. Springer; Berlin/Heidelberg, Germany: 2004. pp. 3–11. [Google Scholar]
16. Larsen T.A., Lienert J., Joss A., Siegrist H. How to avoid pharmaceuticals in the aquatic environment. *J. Biotechnol.* 2004; 113:295–304. doi: 10.1016/j.jbiotec.2004.03.033. [PubMed] [CrossRef] [Google Scholar]
 17. Larsson D.J., de Pedro C., Paxeus N.J. Effluent from drug manufactures contains extremely high levels of pharmaceuticals. *J. Hazard. Mater.* 2007; 148:751–755. doi: 10.1016/j.jhazmat.2007.07.008. [PubMed] [CrossRef] [Google Scholar]
 18. Lin L., Wang H., Xu P. Immobilized TiO₂-reduced graphene oxide nanocomposites on optical fibers as high performance photocatalysts for degradation of pharmaceuticals. *Chem. Eng. J.* 2017; 310:389–398. doi: 10.1016/j.cej.2016.04.024. [CrossRef] [Google Scholar]
 19. Magureanu M., Mandache N.B., Parvulescu V.I. Degradation of pharmaceutical compounds in water by non-thermal plasma treatment. *Water Res.* 2015; 81:124–136. doi: 10.1016/j.watres.2015.05.037. [PubMed] [CrossRef] [Google Scholar]
 20. Memmert U., Peither A., Burri R., Weber K., Schmidt T., Sumpter J.P., Hartmann A. Diclofenac: New data on chronic toxicity and bioconcentration in fish. *Environ. Toxicol. Chem.* 2013; 32:442–452. doi: 10.1002/etc.2085. [PMC free article] [PubMed] [CrossRef] [Google Scholar]
 21. Mompelat S., Le Bot B., Thomas O. Occurrence and fate of pharmaceutical products and by-products, from resource to drinking water. *Environ. Int.* 2009; 35:803–814. doi: 10.1016/j.envint.2008.10.008. [PubMed] [CrossRef] [Google Scholar]
 22. Nassour C., Barton S.J., Nabhani-Gebara S., Saab Y., Barker J. Occurrence of anticancer drugs in the aquatic environment: A systematic review. *Environ. Sci. Pollut. Res.* 2020; 27:1339–1347. doi: 10.1007/s11356-019-07045-2. [PMC free article] [PubMed] [CrossRef] [Google Scholar]
 23. Nikolai L.N., McClure E.L., MacLeod S.L., Wong C.S. Stereoisomer quantification of the β -blocker drugs atenolol, metoprolol, and propranolol in

- wastewaters by chiral high-performance liquid chromatography–tandem mass spectrometry. *J. Chromatogr. A.* 2006; 1131:103–109. doi: 10.1016/j.chroma.2006.07.033. [PubMed] [CrossRef] [Google Scholar]
25. Patel M., Kumar R., Kushor K., Msna T., Pittman C.U., Mohan D. Pharmaceuticals of emerging concern in Aquatic Systems: Chemistry, Occurrence, Effects and Removal Methods. *Chem. Rev.* 2019; 119:3510–3673. doi: 10.1021/acs.chemrev.8b00299. [PubMed] [CrossRef] [Google Scholar]
 26. Radjenovic J., Petrovic M., Barcelo D. Fate and distribution of pharmaceuticals in wastewater and sewage sludge of the conventional activated sludge (CAS) and advanced membrane bioreactor (MBR) treatment. *Water Res.* 2009; 43:831–841. doi: 10.1016/j.watres.2008.11.043. [PubMed] [CrossRef] [Google Scholar]
 27. Vieno N., Sillanpää M. Fate of diclofenac in municipal wastewater treatment plant—A review. *Environ. Int.* 2014; 69:28–39. doi: 10.1016/j.envint.2014.03.021. [PubMed] [CrossRef] [Google Scholar]
 28. Wongso V., Chung H.K., Sambudi N.S., Sufian S., Abdullah B., Wirzal M.D.H., Ang W.L. Silica–carbon quantum dots decorated titanium dioxide as sunlight-driven photocatalyst to diminish acetaminophen from aquatic environment. *J. Photochem. Photobiol. A Chem.* 2020; 394:112436. doi: 10.1016/j.jphotochem.2020.112436. [CrossRef] [Google Scholar]
 29. Zur J., Michalska J., Pinski A., Mrozik A., Nowak A. Effects of Low Concentration of Selected Analgesics and Successive Bioaugmentation of the Activated Sludge on its Activity and Metabolic Diversity. *Water.* 2020; 12:4113. doi: 10.3390/w12041133. [CrossRef] [Google Scholar]