

UTILIZING ACTIVATED CARBON DERIVED FROM CORN HUSK INCORPORATED WITH BIMETALLIC NANOPARTICLE TO ELIMINATE OFLOXACIN FROM PHARMACEUTICAL WASTE

Submitted in partial fulfillment of the requirements of the award of

Master of Technology Degree in Biotechnology

by

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DEPARTMENT OF BIOTECHNOLOGY
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SATHYABAMA

INSTITUTE OF SCIENCE AND TECHNOLOGY

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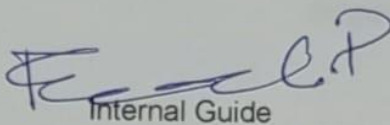
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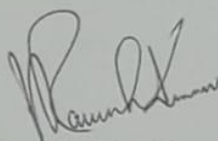
BONAFIDE CERTIFICATE

This is to certify that this Project Report is the bonafide work of **KOWSALYA DEVI V (42810004)** who carried out the Project Report entitled "**UTILIZING ACTIVATED CARBON DERIVED FROM CORN HUSK INCORPORATED WITH BIMETALLIC NANOPARTICLE TO ELIMINATE OFLOXACIN FROM PHARMACEUTICAL WASTE**" under my supervision from November 2023 to April 2024.



Internal Guide

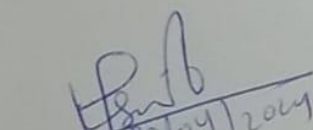
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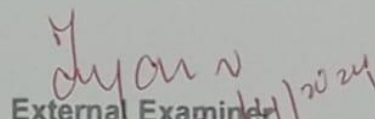
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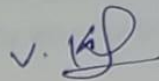
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DECLARATION

I, **Kowsalya devi. V (42810004)** hereby declare that the Project report entitled **"UTILIZING ACTIVATED CARBON DERIVED FROM CORN HUSK INCORPORATED WITH BIMETALLIC NANOPARTICLE TO ELIMINATE OFLOXACIN FROM PHARMACEUTICAL WASTE"** done by me under the guidance of **Dr. P. PRAKASH**, at **Department of Biotechnology, Sathyabama Institute of Science and Technology** is submitted in partial fulfilment of the requirements for the award of Master of Technology degree in Biotechnology.

Date: 20.04.2024

Place: Chennai


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ABSTRACT

The escalating presence of pharmaceuticals in the environment has sparked interest in effective removal methods. This study focuses on the removal of Ofloxacin, a commonly used antibiotic, from pharmaceutical waste using a novel composite material. The composite consists of bimetallic nanoparticles (MgO NPs- Fe₃O₄ NPs) incorporated with activated carbon derived from corn husk. Adsorption studies were conducted using UV-visible spectroscopy at 295 nm to monitor the adsorption process. The activated carbon (AC), MgO nanoparticles, and Fe₃O₄ nanoparticles were characterized using SEM and FTIR spectroscopy to understand their morphological and chemical properties. Additionally, the initial and final adsorption of Ofloxacin using the AC-MgO-Fe₃O₄ composite was studied to determine its effectiveness in removing the antibiotic from solution. The results indicated that the maximum adsorption of Ofloxacin occurred at 5 hours using a concentration of 500 ppm, with 1 g of activated carbon, 50 mg of MgO nanoparticles, and 50 mg of Fe₃O₄ nanoparticles. Isotherm studies were conducted to analyze the adsorption behaviour of the composite material. The Freundlich isotherm model was found to be the best fitting isotherm for describing the adsorption process. Overall, the study demonstrates the potential of the bimetallic nanoparticle incorporated with activated carbon for the removal of Ofloxacin from pharmaceutical waste.

Keywords: *Ofloxacin, pharmaceutical waste, bimetallic nanoparticles, activated carbon, corn husk, adsorption, isotherm studies*

TABLE OF CONTENTS

CHAPTER NO.	TITLE	PAGE NO.
	LIST OF ABBREVIATION	V
	LIST OF FIGURES	Vi
	LIST OF TABLES	viii
1	INTRODUCTION	1
2	LITERATURE SURVEY	6
	2.1 OVERVIEW OF PHARMACEUTICAL WASTE	6
	2.2 OFLOXACIN	7
	2.3 ENVIRONMENTAL CONCERNS OF OFLOXACIN	8
	2.3.1 Persistence and prevalence	8
	2.3.2 Disruption of microbial communities	8
	2.3.3 Antibiotic resistance	8
	2.3.4 Toxicity to aquatic life	9
	2.4 CURRENT METHOD FOR PHARMACEUTICAL WASTE TREATMENT	9
	2.5 ADSORPTION TECHNIQUES FOR REMOVING OFLOXACIN	11
	2.5.1 Effectiveness of activated carbon for ofloxacin removal	12
	2.5.2 Mechanism of ofloxacin adsorption on activated carbon	12
	2.6 NANOPARTICLES IN PHARMACEUTICAL WASTE TREATMENT	13
	2.7 STUDIES ON OFX REMOVAL USING BIMETALLIC NPS INCORPORATED WITH ACTIVATED CARBON	14

3	AIM AND OBJECTIVES	17
	3.1 AIM	17
	3.2 OBJECTIVES	17
4	MATERIALS AND METHOD	18
	4.1 COLLECTION OF ADSORBENT AND ADSORBATE	18
	4.1.1 Standard graph of ofloxacin	18
	4.2 SYNTHESIS OF MAGNESIUM OXIDE NANOPARTICLE	18
	4.2.1 Preparation of <i>Tecoma stans</i> flower extract	18
	4.2.2 Synthesis of MgO NPs from <i>Tecoma stans</i> flower extract	19
	4.2.3 Characterization of MgO NPs	19
	4.2.3.1 SEM	19
	4.3 SYNTHESIS OF MAGNETITE NANOPARTICLE (Fe ₃ O ₄)	20
	4.3.1 Characterization of Fe ₃ O ₄ NPs	20
	4.3.1.1 SEM	20
	4.4 PREPARATION OF ACTIVATED CARBON FROM CORN HUSK	21
	4.4.1 Property analysis of activated carbon	21
	4.4.1.1 Pore volume	21
	4.4.1.2 Moisture content determination	22
	4.4.2 Characterization of Activated carbon	22
	4.4.2.1 SEM	22
	4.4.2.2 FTIR	22
	4.5 ADSORPTION STUDIES	22
	4.5.1 Adsorption using Activated carbon	23
	4.5.2 Adsorption using AC-MgO NPs	23
	4.5.3 Adsorption using AC- Fe ₃ O ₄ NPs	24
	4.5.4 Adsorption using AC-MgO NPs- Fe ₃ O ₄ NPs	25
	4.5.5 Characterization of adsorbent	26

	4.5.5.1 SEM	26
	4.5.5.2 FTIR	26
	4.6 ISOTHERM STUDIES	26
	4.6.1 Langmuir isotherm	26
	4.6.2 Freundlich isotherm	27
	4.6.3 Temkin isotherm	28
5	RESULT AND DISCUSSION	29
	5.1 STANDARD GRAPH OF OFLOXACIN	29
	5.2 SYNTHESIS OF MAGNESIUM OXIDE NANOPARTICLE	30
	5.2.1 Preparation of <i>Tecoma stans</i> (F) extract	30
	5.2.2 Synthesis of MgO NPs from <i>Tecoma stans</i> flower extract	31
	5.2.3 Characterization of MgO NPs	32
	5.2.3.1 SEM	32
	5.3 SYNTHESIS OF MAGNETITE NANOPARTICLE (Fe ₃ O ₄)	34
	5.3.1 Characterization of Fe ₃ O ₄ NPs	35
	5.3.1.1 SEM	35
	5.4 PREPARATION OF ACTIVATED CARBON FROM CORN HUSK	36
	5.4.1 Property analysis of Activated carbon	37
	5.4.1.1 Pore volume	37
	5.4.1.2 Moisture content determination	39
	5.4.2 Characterization of Activated carbon	40
	5.4.2.1 SEM	40
	5.4.2.2 FTIR	41
	5.5 ADSORPTION STUDIES	42
	5.5.1 Adsorption using Activated carbon	42
	5.5.2 Adsorption using MgO NPs	43
	5.5.3 Adsorption using Fe ₃ O ₄ NPs	44

	5.5.4 Adsorption using AC-MgO NPs- Fe_3O_4 NPs	45
	5.5.5 CHARACTERIZATION OF ADSORBENT	48
	5.5.5.1 SEM	48
	5.5.5.2 FTIR	50
	5.6 ISOTHERM STUDIES	53
6	SUMMARY AND CONCLUSION	56
	REFERENCES	58
	ANNEXURE	72

LIST OF ABBREVIATION

ABBREVIATIONS	DESCRIPTION
AC	Activated carbon.
AMX	Amoxicillin
API	Active Pharmaceutical Ingredients.
APO	Advanced Oxidation Process
ARG	Antibiotic Resistance Gene
CH ₃	Methyl group
CHAC	Corn Husk Activated Carbon.
COOH	Carboxylic acid
Fe ₃ O ₄ NPs	Magnetite Nanoparticles
FTIR	Fourier-Transform Infrared Spectroscopy
HNO ₃	Nitric acid
MgO NPs	Magnesium Oxide Nanoparticle
NaOH	Sodium Hydroxide
NH ₄ OH	Ammonium Hydroxide
OFL	Ofloxacin
SEM	Scanning Electron Microscope

LIST OF FIGURES

FIGURE NO.	DESCRIPTION	PAGE NO.
1.1	Antibiotic waste main streams to aquatic environment	2
1.2	Chemical structure of Ofloxacin	3
2.1	Research work on removing antibiotic component from wastewater	7
4.1	Grinding of <i>Tecoma stans</i> flower	19
4.2	a) corn husk b) dried corn husk	21
5.1	Standard graph of ofloxacin	30
5.2	Extract of <i>Tecoma stans</i> flower	31
5.3	Magnesium Oxide Nanoparticle (MgO NPs)	32
5.4	SEM images of synthesized MgO NPs using <i>Tecoma stans</i> flower extract, a) 5µm, b)10µm. C)20µm, d)30µm.	33
5.5	Magnetite Nanoparticle (Fe ₃ O ₄ NPs)	34
5.6	SEM images of Fe ₃ O ₄ NPs	35
5.7	Activated carbon from corn husk	37
5.8	a) Initial volume b) volume after boiling and filtration	38
5.9	FTIR result of Activated carbon	40

5.10	SEM image of Activated carbon from corn husk	41
5.11	Ofloxacin Concentration for adsorption using AC-MgO- Fe ₃ O ₄	46
5.12	SEM image of initial adsorption of 500ppm at 0 th hour	48
5.13	SEM images of final adsorption of 500ppm at 5 th hour	49
5.14	FTIR results of initial adsorption of 500ppm at 0 th hour	50
5.15	FTIR results of final adsorption of 500ppm at 5 th hour	51
5.16	Isotherm model (Freundlich)	54

LIST OF TABLES

TABLE NO.	DESCRIPTION	PAGE NO.
5.1	concentration and OD values of Ofloxacin	29
5.2	FTIR result of peak obtained	40
5.3	Adsorption of ofloxacin using Activated carbon	43
5.4	Adsorption of ofloxacin using MgO NPs	44
5.5	Adsorption of ofloxacin using Fe ₃ O ₄ NPs	45
5.6	Adsorption of ofloxacin using AC-MgO-Fe ₃ O ₄	47
5.7	FTIR initial adsorption result peak obtained	50
5.8	FTIR final adsorption result peak obtained	52
5.9	Isotherm study	53
5.10	Freundlich isotherm	54

CHAPTER 1

INTRODUCTION

The presence of drug and pharmaceutical residues, also known as emerging pollutants, in aquatic systems is a rapidly growing environmental concern (Husein *et al.*, 2019; Guedidi *et al.*, 2013). This issue has attracted significant interest from environmental researchers, as evidenced by numerous publications in prestigious scientific journals (Mahouachi *et al.*, 2020; Noutsopoulos *et al.*, 2015; Rivera-Utrilla *et al.*, 2013; Neha *et al.*, 2021). Pharmaceuticals encompass a wide range of chemicals used as medications for humans, animals, and even plants. While historically valued for their role in treating and preventing diseases, they are now increasingly recognized as significant emerging environmental contaminants (McBride and Wyckoff 2002, Fawell and Ong 2012, Bu *et al.*, 2013). Several factors contribute to the increasing presence of pharmaceuticals in water. Population growth, coupled with a rise in medical complications and health issues, has led to a surge in demand, production, and consumption of these drugs (Attia and Hu, 2013; Ferrer-Polonio *et al.*, 2020). This can threaten soil health, aquatic life, and ecological balance.

Due to regular medication use, damage, and expiration, pharmaceutical waste is released into the environment at low concentrations by households, farms, healthcare facilities, and the pharmaceutical industry. It is unknown how active pharmaceutical ingredients (API) affect environmental non-target species. Over time, traces of medications like ibuprofen and diclofenac have been found in both surface and groundwater systems as well as public water systems (Nyaga *et al.*, 2020). Many different types of pharmaceuticals have been found in fresh and marine water across the globe (Benotti *et al.*, 2009).

Antibiotics and pharmaceuticals play a crucial role in enhancing the quality of life globally and in public health. However, the pharmaceutical industry's wastewater, which often contains high concentrations of antibiotics, can be discharged into the environment, posing a significant concern. Larsson *et al.* (2007) identified a high level

of ciprofloxacin, 31 mg/L, in the wastewater from 90 pharmaceutical manufacturers in India, which is treated at the pharmaceutical wastewater treatment plant (WWTP). Studies by Guo et al. (2018) and Phoon et al. (2020) have shown that antibiotic resistance genes (ARG) are notably more prevalent in pharmaceutical industry effluent receiving wastewater (2.36×10^7 copies/mL) compared to municipal wastewater (9.50×10^5 copies/mL). Over the past decade, global antibiotic consumption has significantly increased. Antibiotics end up in wastewater because of their use in treating both humans and animals, eventually being excreted in urine and feces. Aside from water, antibiotics are also commonly found in other environments such as sludge and soil, which hastens the development of antibiotic resistance in the environment and its subsequent spread. This poses a heightened risk to the prevention and control of human diseases (Phoon *et al.*, 2020; Hou *et al.*, 2019).

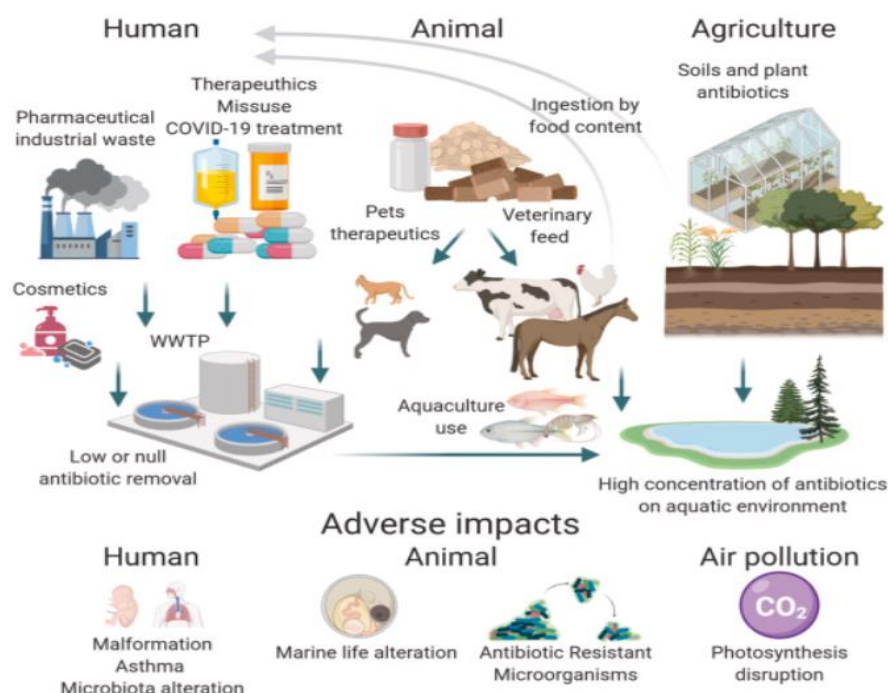


Figure:1.1: Antibiotic waste main streams to aquatic environment.

(Hernández et al., 2021)

The fluoroquinolone ofloxacin (OFL), a third-generation antibiotic, possesses broad-spectrum antimicrobial properties. Widely used in both human and veterinary

medicine, OFL is often excreted through feces or urine post-administration, eventually entering the environment (Amorim *et al.*, 2014; Zhu *et al.*, 2020). Fluoroquinolones (FQs) like OFL have been detected in various environmental compartments such as soils, natural surface waters, ground water, and municipal wastewater influent and effluent, indicating the necessity for further investigations into their environmental fate and transport (Vieno *et al.*, 2007; Wieren *et al.*, 2012).

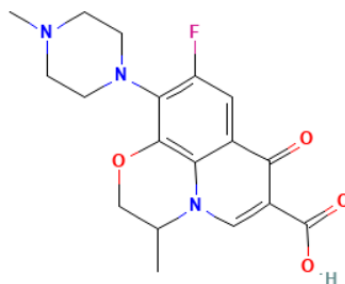


Figure:1.2: Chemical structure of Ofloxacin.

(Morrissey *et al.*, 1996)

The complex structure of Ofloxacin, characterized by multiple rings and functional groups, is illustrated in the two-dimensional image in Figure 1.2. Notable features include a fluorine atom (F) attached to one ring, a methyl group (CH₃) attached to another ring, and a six-membered ring with two nitrogen atoms known as a piperazine ring. Additionally, there is an acid carboxylic group (COOH).

Due to its widespread use and the limited effectiveness of traditional wastewater treatment plants in removing it, Ofloxacin is often found in environmental settings (Yang *et al.*, 2020). Various techniques, such as adsorption, oxidation, photocatalysis, and biodegradation, are currently employed to remove fluoroquinolones (FQs) from water (Ma *et al.*, 2022). Among these, adsorption is particularly favored for its simplicity, cost-effectiveness, and lack of harmful byproducts that could further contaminate the environment (Barquilha and Braga, 2021; Akhtar *et al.*, 2021). However, other methods also exist. Adsorbents like activated carbon, carbon nanotubes, clay minerals, ion exchange resins, and biochar have been utilized for this purpose, with biochar standing out due to its widespread availability and affordability (Ashiq *et al.*, 2021).

Conventional techniques, including biological processes, sand filtration, ultraviolet (UV) radiation, membrane filtration, and sedimentation, have been employed to eliminate fluoroquinolones from water (Sharma *et al.*, 2017; Naushad *et al.*, 2019). Among these, adsorption and biodegradation have gained prominence in recent times.

The excellent adsorption capacity of activated carbon (AC) is due to its highly porous structure and large specific surface area. Consequently, it is commonly used as an adsorbent in the treatment of domestic and industrial wastewater (Aksu and Tunç, 2005). However, the cost remains a major obstacle to its widespread application in wastewater treatment (Putra *et al.*, 2009). Recent studies have explored the use of plant materials, which are inexpensive and environmentally friendly, to develop new carbon materials with unique structural properties (Li *et al.*, 2014; Kong *et al.*, 2017). There are two distinct methods used to prepare activated carbon: physical activation and chemical activation. Among the various dehydrating agents, zinc chloride and nitric acid are widely utilized in the chemical activation process (Khodaie *et al.*, 2013).

Bimetallic nanoparticles, as compared to single-metal nanoparticles, may perform better because they combine the qualities of two different metals. Ofloxacin adsorption or degradation may benefit from this. Studies have explored using metal oxides like Fe₃O₄ and MgO NPs for ofloxacin removal.

Magnesium oxide (MgO) is an effective catalyst for decomposing pollutants due to several advantages, including its non-toxic nature, ease of production, small particle size with high potential energy, and buffering properties in acidic environments (Yue *et al.*, 2019). However, the accumulation of MgO particles in the working solution can be problematic, but this can be mitigated by fixing MgO on a stand. Various materials, such as activated carbon, have been used as stands to construct MgO-based catalysts (Haidari *et al.*, 2016; Jalali *et al.*, 2021).

The use of plant extracts for synthesizing MgO nanoparticles (NPs) is strongly advocated for its notable advantages (Jeevanandam *et al.*, 2017). These green

methods predominantly employ biodegradable materials, leading to minimal release of harmful substances into the water (Jeevanandam *et al.*, 2018). Furthermore, MgO NPs synthesized biogenically are typically biocompatible and sustainable, rendering them more appropriate for a wide range of applications (Pugazhendhi *et al.*, 2019).

Fenton degradation is a process in which Fe_3O_4 , also known as magnetite, efficiently eliminates the antibiotic ofloxacin from water. This method generates highly reactive hydroxyl radicals ($\text{OH}\cdot$) by combining hydrogen peroxide (H_2O_2) with a catalyst like Fe_3O_4 . These hydroxyl radicals are extremely effective in breaking down organic contaminants, including ofloxacin. Fe_3O_4 can be utilized for various wastewater treatment applications, such as adsorbing arsenite, arsenate, chromium, cadmium, and nickel (Zaitsev *et al.*, 1999). Additionally, Fe_3O_4 is employed for alkalinity and hardness removal, desalination, decolorization of pulp mill effluent, and the elimination of natural organic compounds. Studies have synthesized Fe_3O_4 using co-precipitation methods and evaluated its ability to remove ofloxacin (Fuertes and Tartaj, 2006). Furthermore, research has investigated the use of Fe_3O_4 in combination with Ammonium Hydroxide (NH_4OH) for thermal activation to degrade ofloxacin, achieving an impressive degradation efficiency of up to 88% (Velayos *et al.*, 2023).

By exploring the potential of bimetallic nanoparticles and sustainable activated carbon, this project contributes to developing a novel and efficient method for ofloxacin removal from pharmaceutical wastewater. This research holds promise for mitigating the environmental and health impacts of pharmaceutical contaminants. This thesis investigates the efficacy of bimetallic $\text{MgO-Fe}_3\text{O}_4$ nanoparticles incorporated with activated carbon derived from corn husk for the removal of ofloxacin from pharmaceutical wastewater. By combining the unique properties of bimetallic nanoparticles and activated carbon from a renewable source, this research aims to propose a novel and sustainable solution for ofloxacin remediation in pharmaceutical waste.

CHAPTER 2

LITERATURE SURVEY

2.1 OVERVIEW OF PHARMACEUTICAL WASTE

Pharmaceutical waste comprises medications that are contaminated, unwanted, or discontinued, including expired products. When medications are prescribed for preventive purposes or to treat acute or chronic illnesses, the active ingredients are only partially metabolized. When these drugs and their metabolites enter water bodies through waste discharges, they can contaminate recreational lakes and even the intakes of drinking water treatment plants.

Pharmaceutical compounds are designed to exhibit biochemical activity at low concentrations within target organisms (Fram and Belitz, 2011; Kadam *et al.*, 2016). After absorption and metabolism within the body, these compounds are excreted as waste, eventually entering wastewater treatment plants and then the drainage system. Antibiotics, including OFL, enter the aquatic ecosystem through incomplete metabolism, agricultural runoff, and wastewater effluent. Given their persistence and potential genotoxic and mutagenic effects, significant research has been conducted over the past decade (Huang *et al.*, 2011; Baquero *et al.*, 2008).

OFL is considered an emerging environmental pollutant due to its widespread use in humans and animals, with less than 10% of the substance being absorbed by the body and the remaining 90% being released in urine and feces. This leads to substantial amounts of OFL entering water bodies globally, either as metabolites or in its original chemical form (Georgin *et al.*, 2023).

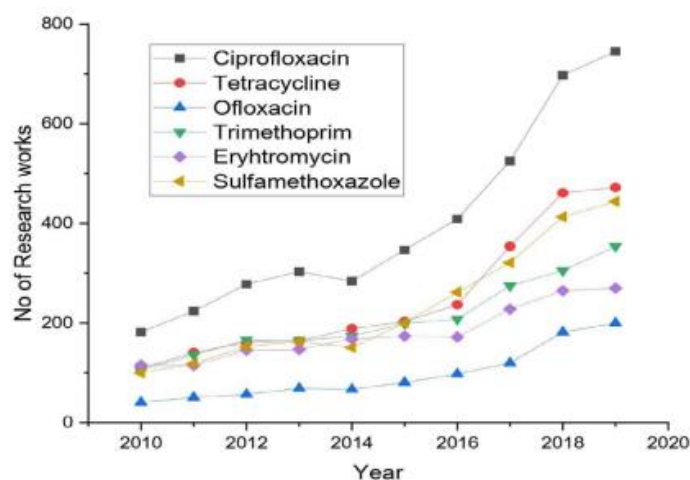


Figure:2.1: Research work on removing Antibiotic component from wastewater.

(Georgin *et al.*, 2023)

2.2 OFLOXACIN

Ofloxacin is a derivative of nalidixic acid, belonging to the pyridone-carboxylic acid class, with distinct structural modifications. It differs from nalidixic acid through the addition of a fluorine atom, an N-methylpiperazine moiety, and an additional oxazine ring, rendering it a tricyclic quinolone. Its chemical name is 9-fluoro-2,3-dihydro-3-methyl-10-(4-methyl-1-piperazinyl)-7-oxo-7H-pyrido[1,2,3-de]-1,4-benzoxazine-6-carboxylic acid. The fluorine atom at position 6 enhances its binding to DNA gyrase and cellular penetration. The C-7 methyl piperazinyl group improves its oral absorption and enhances its *in vitro* activity against the Enterobacteriaceae family. The fused ring connection between C-8 and N-1 contributes to improved gram-positive and anti-anaerobic activity, while also reducing the metabolic susceptibility associated with the 4-methyl piperazinyl group at C-7. Furthermore, ofloxacin exists as a mixture of two isomers.

The methyl group attached to the oxazine ring can be in either the R(+) or S(-) configuration. The S(-) isomer demonstrates significantly higher potency, being approximately 8 to 128 times more effective against both gram-positive and gram-

negative bacteria compared to the R(+) isomer. Moreover, the S(-) isomer is twice as active as the original compound. Ofloxacin has shown remarkable clinical and bacteriological efficacy in treating urinary tract infections, achieving an overall cure rate of approximately 90%. Studies by Ball (1990) indicate that the drug concentrations in sputum, lung tissue, and bronchial mucosa are comparable to or even higher than the minimum inhibitory concentrations (MIC90s) required to inhibit these pathogens.

2.3 ENVIRONMENTAL CONCERNS OF OFLOXACIN

Ofloxacin, an antibiotic belonging to the fluoroquinolone class, finds extensive use in both human and veterinary medicine. Nonetheless, its environmental presence gives rise to concerns regarding potential adverse effects (Janecko *et al.*, 2016).

2.3.1 Persistence and prevalence

As per Kovalakova *et al.* (2020), Ofloxacin exhibits resistance to degradation in the environment. Its incomplete elimination during wastewater treatment leads to its entry into and persistence within aquatic environments, such as rivers and streams.

2.3.2 Disruption of microbial communities

According to Deng *et al.* (2022), research indicates that the use of ofloxacin may impede the proliferation of unintended microorganisms such as algae and certain bacteria that play pivotal roles in maintaining ecological equilibrium. This disruption can have repercussions on nutrient circulation within ecosystems.

2.3.3 Antibiotic resistance

The existence of ofloxacin in the environment may foster the emergence of antibiotic-resistant bacteria. Even minimal exposure to antibiotics can favor the selection of resistant strains, posing a long-term risk to both human and animal health.

2.3.4 Toxicity to aquatic life

Studies have indicated that at low concentrations, ofloxacin can exhibit toxicity towards certain aquatic organisms. Such toxicity poses a threat to populations of fish, invertebrates, and other forms of aquatic life (Harrower *et al.*, 2021).

2.4 CURRENT METHOD FOR PHARMACEUTICAL WASTE TREATMENT

Various methods have been developed to treat pharmaceutical wastewater, combining physical, chemical, and biological treatments (Hube and Wu, 2021). Autoclaving involves treating the waste at high temperatures to break down harmful chemicals and microbes. Antibiotic residues, which often have high organic loads, can be effectively treated with autoclaves. Despite its high efficiency (>98%), autoclaving or supercritical fluid carbon dioxide sterilization requires subsequent treatments and is currently considered costly (Hossain *et al.*, 2011).

Physico-chemical methods, including ion exchange, adsorption, coagulation-flocculation, frothing, precipitation, chemical reduction, and electrochemical processes (Cheng *et al.*, 2007), as well as combinations of these processes, are used to treat wastewater at various stages, from initial production to handling their cumulative toxic concentrations in different sewage streams (Torres *et al.*, 1997).

Advanced Oxidation Processes (AOPs) encompass a range of treatments such as heterogeneous and homogenous photocatalysis based on near ultraviolet or solar visible irradiation, electrolysis, ozonation, ultrasonication, wet air oxidation, and Fenton's treatment. Emerging processes include ionizing radiation, microwave treatment, and pulsed plasma treatment. AOPs exploit specific characteristics of oxidizing agents to degrade pharmaceuticals and personal care products (PhACs). Some studies (Gupta *et al.*, 2009) have shown that AOPs can be highly effective, especially in treating persistent pollutants or drugs like carbamazepine. The mechanisms of degradation can vary depending on the treatment method.

Adsorption is an effective method for removing persistent pharmaceutical and personal care products (PhACs) from wastewater. By using adsorbents, undesirable substances can be extracted from treated pharmaceutical wastewater before it is discharged into streams. Adsorbents derived from plant-based sources are particularly advantageous due to their ease of fabrication and environmental friendliness (Ternes *et al.*, 2003).

There has been a notable increase in research focused on using zeolites to remove specific compounds and micropollutants that are not efficiently eliminated by traditional activated carbon-based adsorbents (Ridder *et al.*, 2012). Activated sludge and similar processes often utilize similar designs, and the final effluent quality can be enhanced through tertiary treatments such as activated carbon adsorption and additional nutrient removal. Activated sludge demonstrates significant removal efficiencies against certain pharmaceuticals, such as 68% for tetracycline, 78% for chlortetracycline, and 67% for doxycycline (Karthikeyan and Meyer, 2006; Yang *et al.*, 2005). However, for activated sludge to be economically viable in real-life applications, it must effectively remove at least one specific class of drugs. This is crucial because most unused medicines disposed of in garbage eventually enter sewers in their unmetabolized form, posing a direct risk to the environment (Ruhoy and Daughton, 2008).

Vermicomposting is a promising method for managing solid waste, offering benefits such as improved soil aeration, decomposition of chemical compounds, and conversion of organic waste into biofertilizer. Earthworms play a crucial role in vermicomposting, as they mix variously digested wastes into a heterogeneous mixture. In one study (Singh and Suthar, 2012), researchers used vermicomposting to treat herbal pharmaceutical residues. They employed the earthworm *E. foetida* to compost herbal pharmaceutical industrial waste mixed with varying amounts of cow dung in a laboratory setting. However, vermicomposting alone may not effectively address the wide range of organic and inorganic compounds present in pharmaceutical wastewater (Pal, 2018).

An effective method for disposing of pharmaceutical concentrates involves combining anaerobic co-digestion (AcoD) with aerobic and anaerobic digestion processes. Research has shown that AcoD can significantly enhance organic degradation compared to anaerobic digestion alone (Fountoulakis *et al.*, 2008). AcoD is considered environmentally friendly and economically viable. However, concerns remain regarding its efficacy in removing active pharmaceutical residues, such as diclofenac, hydrochlorothiazide, and atenolol, from effluents in full-scale integrated treatments of municipal wastewater and organic municipal solid waste (Jelic *et al.*, 2012). To address these concerns, emerging membrane-based filtration systems have been studied extensively (Buonomenna and Bae, 2015; Kumar and Pal, 2013; Chakraborty *et al.*, 2013). These systems are compact, flexible, eco-friendly, and cost-effective to install, operate, and maintain.

Due to the high selectivity of these membranes, they are known for their efficient separation capabilities. Several studies have also demonstrated the feasibility of reusing water recovered through membrane-based filtration. For example, Bloetscher *et al.*, (2012) proposed integrating two-stage nanofiltration units with a third stage reverse osmosis unit, leading to a water treatment plant certified by LEED for leadership in energy and environmental design. Additionally, Thakura *et al.*, (2015) highlighted the potential of an integrated nanofiltration-forward osmosis system in treating complex and hazardous pharmaceutical wastewater.

2.5 ADSORPTION TECHNIQUES FOR REMOVING OFLOXACIN

Adsorption stands out as the most efficient method for eliminating PPCPs found in wastewater. This process involves PPCPs adhering to the pores of an adsorbent, facilitating their removal from the system more effectively compared to other treatment methods. Activated carbon, due to its static charge and hydrophobic properties, is particularly effective in removing waste components from wastewater (Renita *et al.*, 2017). The success of adsorption depends on the adsorbent's high surface area and porosity (Memon *et al.*, 2008). Ofloxacin, a fluoroquinolone antibiotic, remains a

persistent pollutant in wastewater due to incomplete removal in conventional treatment processes. The use of activated carbon (AC) for adsorption has emerged as a promising technique for effectively removing Ofloxacin.

2.5.1 Effectiveness of Activated Carbon for Ofloxacin Removal

- ❖ Numerous studies demonstrate the high efficiency of AC in removing Ofloxacin from aqueous solutions. Research by (Kong *et al.*, 2017) using AC derived from luffa sponge achieved a 96% removal of Ofloxacin at a concentration of 30 mg/L. Similarly, (sulaiman *et al.*, 2022) reported over 99% Ofloxacin removal using cassava stem-based AC. These studies highlight the remarkable capacity of AC for Ofloxacin adsorption.
- ❖ The effectiveness is further emphasized by the high adsorption capacities reported in various studies. For instance, (Zhao *et al.*, 2018) reported a maximum adsorption capacity of 132 mg/g for Ofloxacin using AC derived from bamboo. This indicates the substantial amount of Ofloxacin AC can adsorb per unit mass.

2.5.2 Mechanisms of Ofloxacin Adsorption on Activated Carbon

- ❖ The high effectiveness of AC is attributed to its unique physical and chemical properties. AC possesses a large surface area with a network of pores that provides ample sites for Ofloxacin molecules to adhere.
- ❖ The adsorption mechanism primarily involves various interactions between Ofloxacin and the AC surface:

π - π interactions: This occurs between the aromatic rings of Ofloxacin and the aromatic carbons present on the AC surface.

Hydrogen bonding: Functional groups like hydroxyl (-OH) on the AC surface can form hydrogen bonds with the functional groups on Ofloxacin molecules.

Electrostatic interactions: Depending on the solution pH, charged Ofloxacin molecules can interact with oppositely charged sites on the AC surface.

Hydrophobic interactions: The non-polar regions of Ofloxacin molecules can interact with the hydrophobic cavities within the AC structure.

Studies like (Ahmad *et al.*, 2022) suggest that the optimal conditions for Ofloxacin adsorption on AC can be influenced by factors like pH, initial Ofloxacin concentration, and contact time. Optimizing these parameters is crucial for maximizing the adsorption efficiency.

2.6 NANOPARTICLES IN PHARMACEUTICAL WASTE TREATMENT

The utilization of nanotechnology in water and wastewater treatment has the potential to significantly enhance treatment efficiency and ensure the safe use of non-traditional water sources. Numerous studies support the beneficial impacts of nanotechnology in wastewater treatment. Nanoparticles, with sizes less than 100 nm, possess high absorption, interaction, and reaction capabilities due to their small size and high surface atom proportion. They can even act as colloids when suspended in water (Prachi *et al.*, 2010). Various types of nanomaterials are used today, including metal-based, polymer-based, zeolites, carbon-based, self-assembled monolayer on mesoporous supports, biopolymers, and nanoscale metal oxide and chalcogenide semiconductor photocatalysts (Baruah *et al.*, 2019).

Silver nanoparticles can adversely affect sludge, impacting aerobic and anaerobic microorganisms. Even low concentrations of silver ions and silver nanoparticles, as low as 0.4 mg/L, can inhibit the growth of nitrifying bacteria. Additionally, anaerobic microbial activity in biomass, such as sewage sludge, can be inhibited at silver nanoparticles concentrations of 19 mg/L (Sarathi and Thilagavathi, 2009). Titanium dioxide nanoparticles are significant as photocatalysts. Titanium oxide exists in three distinct phases: anatase, rutile, and brookite, each with different sizes. Currently, titanium dioxide is widely used in nanomaterial preparation, including the production of nanotubes and nanowires. TiO₂ shows promise in removing harmful substances from wastewater. In photocatalytic water treatment, nanocrystalline titanium dioxide (NTO) is frequently employed. TiO₂ nanoparticles can effectively degrade water pollutants that are not biodegradable in photocatalytic degradation processes (Tiwari *et al.*, 2008).

Metal oxide-based nanoparticles have been extensively studied for their ability to remove a variety of heavy metals, including chromium, nickel, cadmium, copper, mercury, arsenic, and lead (Gunatilake, 2015). These nanoparticles can be easily reused and regenerated by adjusting the pH of the solution, maintaining their adsorption capacities (Kunduru *et al.*, 2017). Their easy separability, low cost, regenerability, and high adsorption capacity make them economically and technologically advantageous.

Nanoparticles used for such purposes include photocatalytic nanomaterials like TiO₂ and bimetallic nanoparticles, antimicrobial nanoparticles such as CNTs and nano-Ag, and MNPs like zeolite Al₂O₃ and TiO₂ (Thoniyot *et al.*, 2015). These nanoparticles find broad applications in drug delivery systems, soil quality improvement, wastewater treatment, and biological sciences (Bogue, 2011).

The use of nanocomposites for adsorbing various contaminants like dyes, heavy metal ions, and pesticides from polluted wastewater has garnered significant attention in recent years (Rasalingam *et al.*, 2014).

2.7 STUDIES ON OFLOXACIN REMOVAL USING BIMETALLIC NANOPARTICLE INCORPORATED WITH ACTIVATED CARBON

Fe and Cu bimetallic sepiolite-based Fenton heterogeneous catalysts with varying states of Fe and Cu species were synthesized and utilized for degrading the antibiotic Ofloxacin (Tian *et al.*, 2020). A highly effective adsorbent for fluoroquinolone antibiotics, KMSBC, was developed through the hydrothermal activation of SBC using KOH, MgCl₂, and FeCl₃. This process resulted in KMSBC possessing abundant functional groups, a superior porous structure, and a graphite structure (Ma *et al.*, 2022). Mn-doped CuO samples, as reported by Liu *et al.* (2021), have been successfully prepared and exhibit superior activity in removing Ofloxacin with PS activation compared to pure CuO. Among these samples, CM3, with its large surface area and high content of surface Cu₂⁺ triple bonds, showed the highest activity, aiding in both the adsorption of Ofloxacin and the non-radical activation of PS. CM3

demonstrated the highest activity for Ofloxacin removal at neutral pH, where the combined action of pollutants is optimal. Additionally, CuFe_2O_4 was dispersed on montmorillonite (Mt) to create a magnetic copper ferrite-montmorillonite (CF-Mt) composite catalyst using the citrate combustion method. This enhanced the catalyst's stability and prevented aggregation of CuFe_2O_4 particles, ensuring exposure of the catalytic sites. The crystal structure, specific surface area, elemental composition, and efficiency of OFL degradation of CF-Mt were characterized under various reaction parameters (Cao *et al.*, 2021).

Numerous antibiotics have been successfully degraded by Fenton reactions, including Fenton oxidation of ofloxacin using montmorillonite– Fe_3O_4 . Composite, heterogeneous photo-Fenton catalyzed by biogenic Fe single bond Mn oxides for OFL removal (Nguyen *et al.*, 2022), and heterogeneous catalytic Fenton/ MnFe_2O_4 @C-NH₂ degradation of ofloxacin, amoxicillin, and tetracycline. To assess the MNZ removal efficiency from aqueous solutions by adsorption and heterogeneous Fenton oxidation processes, (Sharifi *et al.*, 2022) study aims to synthesize and characterize Fe_3O_4 @AC magnetic nanocomposite. The effects of several variables were examined, including temperature, pH, Fe_3O_4 @AC dose, hydrogen peroxide concentration, initial MNZ concentration, and contact time. The germination index was calculated to conduct a bioassay on the treated effluent. (Hadjltaief *et al.*, 2021) successfully developed magnetic $\text{ZnO-Fe}_3\text{O}_4$ supported Kaolinite clay for the removal of indigo carmine from water through the sono assisted Fenton process under solar irradiation. In a study by (Jalali *et al.*, 2021), amoxicillin (AMX) was extracted from wastewater in the presence of H_2O_2 using zeolite Y–MgO as a catalyst.

2.8 FACTORS AFFECTING ADSORPTION EFFICIENCY

The effectiveness of adsorbing ofloxacin onto various materials depends on several variables, all of which must be optimized to maximize its removal from water sources. The following overview highlights these variables and their implications, referencing relevant studies:

Ofloxacin, being a weak acid, interacts with the adsorbent surface based on its charge, which in turn is influenced by the solution's pH. Studies suggest that an optimal

pH range of 4-6 enhances ofloxacin adsorption (Iftekhhar *et al.*, 2018). This is because at this pH range, the adsorbent surface and ofloxacin molecule carry opposite charges, resulting in a stronger electrostatic attraction.

The impact of temperature on adsorption can vary based on the specific adsorbent used. While some studies indicate increased adsorption at higher temperatures (Antonelli *et al.*, 2023), suggesting an endothermic process where more energy facilitates ofloxacin binding to the adsorbent, others show no significant change or even a decrease in adsorption as temperature rises (Zhang *et al.*, 2023).

Typically, the efficiency of ofloxacin adsorption increases with contact time until reaching an equilibrium point (Farzinmanesh *et al.*, 2024). This prolonged contact allows for more collisions between ofloxacin molecules and the adsorbent surface, maximizing adsorption sites.

Increasing the amount of adsorbent (dosage) generally enhances removal efficiency for a fixed initial ofloxacin concentration. This is because a higher dosage provides more surface area for ofloxacin molecules to bind to (Elkhaleefa *et al.*, 2021). However, using an excessively high dosage may not be cost-effective.

CHAPTER 3

AIM AND SCOPE

3.1 AIM

To investigate the effectiveness of bimetallic nanoparticles incorporated with activated carbon derived from corn husk in removing Ofloxacin from pharmaceutical waste.

3.2 OBJECTIVES

- To Synthesize and characterize bimetallic nanoparticles (Mgo-Fe₃O₄)
- To Prepare activated carbon from corn husk using a sustainable activation method.
- To Characterize the bimetallic nanoparticle and activated carbon composite (FTIR and SEM).
- To Evaluate the efficiency of the composite material for Ofloxacin adsorption from pharmaceutical wastewater.

CHAPTER 4

MATERIALS AND METHODS

4.1 COLLOECTION OF ADSORBENT AND ADSORBATE

The corn husk was collected from the local vegetable market and Ofloxacin was purchased from the medical shop in Thiruvapur District, Tamilnadu. The collected sample were packed in the polythene bag and processed for further studies.

4.1.1 Standard graph of Ofloxacin

A stock solution of Ofloxacin was prepared by dissolving a known amount of Ofloxacin in a suitable solvent, such as water, to achieve a concentration range that covered the expected concentrations in the samples. From the stock solution, a series of working standard solutions with different concentrations (100 ppm to 1000 ppm) were prepared. The absorbance of each standard solution was measured at a specific wavelength using a UV-Visible spectrophotometer at 295 nm. A graph of the absorbance values versus the corresponding concentrations of the standard solutions was plotted. This graph served as the calibration curve.

4.2 SYNTHESIS OF MAGNESIUM OXIDE NANOPARTICLE

4.2.1 Preparation of *Tecoma stans* (F) plant extract

Fresh flowers (F) were collected from the village kunniyur, thiruvapur, Tamilnadu, India in January 2024. Following the incorporation of 10 g of samples (F) and 100.0 mL of double-distilled water, the samples were ground. A Whatman Filter paper was used after a basic cotton muslin cloth to filter the solutions as they were received. The mixture was centrifuged for 20 minutes at 5000 rpm to make the extract visible, and the supernatant liquid was kept at 4 °C in the refrigerator.



Figure:4.1: Grinding of *Tecoma stans* flower

4.2.2 Synthesis of MgO NPs from *Tecoma stans* (F) plant extracts

- ❖ Materials for magnesium oxide nanoparticles (MgO NPs) have been developed by slightly altering earlier research (Pugazhendhi et al., 2019).
- ❖ Generally, a 250 mL Erlenmeyer flask was filled with 10 mL of $\text{Mg}(\text{NO}_3)_2$ (0.2 M) and 90 mL of plant extracts (F) and stirred magnetically at 90°C.
- ❖ subsequently, a 1 M solution of NaOH was added to the flask dropwise. For spectrophotometric analysis, a 2 mL aliquot of the reaction solution was extracted from each flask.
- ❖ The residual liquid was centrifuged for 15 minutes at 5000 rpm after being kept at 90°C for two hours.
- ❖ Ultimately, the solid was cleaned with water and calcined in a muffle furnace for six hours at 550°C
- ❖ The original extracts of the MgO NPs samples were used to identify them, for example, MgO NPs@F (from flower).

4.2.3 Characterization of MgO NP

4.2.3.1 SEM

Scanning Electron Microscopy (SEM) is a type of electron microscope that creates pictures of solid surfaces by scanning them with electron beams. Electron beams impact the atoms on the sample surface, producing a variety of signals. Electron detectors detect these impulses. These signals include information about the sample's

composition and surface structure. Magnesium oxide nanoparticle morphology was studied.

4.3 SYNTHESIS OF MAGNETITE NANOPARTICLE (Fe_3O_4)

- ❖ The magnetite nanoparticles were prepared via the chemical co-precipitation method.
- ❖ Dissolve 5 grams of iron(II) salt and 10 grams of iron(III) salt in separate beakers with deionized water to make two solutions.
- ❖ Mix the two solutions together in a larger container under constant stirring.
- ❖ Add the base (e.g., ammonium hydroxide HN_4OH .) dropwise to the mixed solution while stirring until the pH reaches about 10-12. This will cause the Fe(II) and Fe(III) ions to precipitate as Fe_3O_4 .
- ❖ Continue stirring for some time to ensure complete precipitation.
- ❖ Centrifuge the solution to separate the Fe_3O_4 nanoparticles from the solution.
- ❖ Wash the precipitate several times with deionized water to remove any unreacted ions or impurities.
- ❖ Optionally, add a stabilizing agent to the Fe_3O_4 nanoparticles to prevent agglomeration.
- ❖ Dry the nanoparticles, by evaporating the solvent or using a hot air oven.
- ❖ Optionally, perform additional purification steps such as re-dispersing in a solvent and centrifuging to remove any remaining impurities.

4.3.1 Characterization of Fe_3O_4 NP

4.3.1.1 SEM

Scanning Electron Microscopy (SEM) is a type of electron microscope that creates pictures of solid surfaces by scanning them with electron beams. Electron beams impact the atoms on the sample surface, producing a variety of signals. Electron detectors detect these impulses. These signals include information about the sample's composition and surface structure. Magnetite nanoparticle (Fe_3O_4) morphology was studied.

4.4 PREPARATION OF ACTIVATED CARBON FROM CORN HUSK

- ❖ The raw material, i.e. corn husk, was collected from a local vegetable market in Thiruvavur, Tamil nadu, India.
- ❖ corn husk activated carbon (CHAC), was prepared by the method given by (Lunge *et al.*, 2014) with some modifications.
- ❖ The corn husk was washed with distilled water, sun-dried and ground.
- ❖ 200 ml of HNO₃ (2%V/V) was added to 30 g of corn husk powder; then the mixture was stirred for 4 h and kept overnight.
- ❖ Excessive iron solution not absorbed by the corn husk was separated by filtration and dried in an oven for 24 h at 105 °C.
- ❖ Then the material was heat-treated at temperature (300 °C) in a Muffle furnace for 2 h.
- ❖ The prepared material was then washed, dried and homogenized, characterized and used for the adsorption of Ofloxacin.



Figure:4.2:a) Corn husk



b) Dried corn husk

4.4.1 Property analysis of the activated carbon

4.4.1.1 Pore volume

The adsorbent (1g) was transferred into a 10ml measuring cylinder in order to get the total volume of the sample. The sample was then poured into a beaker containing 20ml of deionized water and boiled for 5min. The content in the beaker was then filtered, superficially dried, and weighed. The pore volume of the sample was determined by dividing the increase in weight of the sample by the density of water.

4.4.1.2 Moisture content determination:

50g of the adsorbent (corn husk) was collected and dried in an oven for 4 hours at 150°C.

The moisture content was calculated from the following formula:

$$X_o = \frac{W_1 - W_2}{W_1} \times 100$$

X_o = Moisture content on wet basis

W_1 = Initial weight of sample

W_2 = Final weight of sample after drying

4.4.2 Characterization of Activated carbon

4.4.2.1 FTIR

Surface functional group analysis of the synthesized adsorbents as well as of the raw material was done before and after adsorption, using an FTIR model NICOLET 6700 (Thermo Fisher Scientific, U.S.A.). FTIR analysis of the adsorbent was done to find and analyze functional groups present on the surface of the adsorbents.

4.4.2.2 SEM

Scanning Electron Microscopy (SEM) is a type of electron microscope that creates pictures of solid surfaces by scanning them with electron beams. Electron beams impact the atoms on the sample surface, producing a variety of signals. Electron detectors detect these impulses. These signals include information about the sample's composition and surface structure. Activated carbon morphology and elemental analysis was studied.

4.5 ADSORPTION STUDIES

Adsorption studies of ofloxacin was done by nanocomposite MgO-Fe₃O₄-Activated carbon. Absorbance was measured by UV-visible spectroscopy at 295nm.

4.5.1 Adsorption using Activated carbon.

Ofloxacin absorbs UV light at specific wavelengths. By measuring the UV absorbance of a solution before and after contact with activated carbon, the amount of adsorbed ofloxacin is determined.

- ❖ A stock solution of ofloxacin was prepared at a known concentration.
- ❖ Activated carbon(100mg,250mg,500mg,750mg,1000mg) were added to each Erlenmeyer flask.
- ❖ known volume(1000ppm) of each ofloxacin solution was added to the flasks. Cap the flasks and shake them at a constant speed for a predetermined time (e.g., 1 hour, 2 hours, etc.). This allows for the adsorption of ofloxacin onto the activated carbon.
- ❖ After the shaking time, separate the activated carbon from the solution by filtration.
- ❖ Using a filter paper separate the solution from the activated carbon.
- ❖ Absorbance was measured by the remaining ofloxacin solution (supernatant) using a UV-Vis spectrophotometer at a specific wavelength where ofloxacin has a strong absorbance peak at 295nm.
- ❖ The absorbance of the ofloxacin solutions before and after contact with the activated carbon. A decrease in absorbance indicates adsorption of ofloxacin onto the activated carbon.
- ❖ The amount of ofloxacin adsorbed can be calculated based on the initial and final concentrations of the ofloxacin solution.
- ❖ The calibration curve was constructed by plotting the absorbance of known ofloxacin concentrations against their respective concentrations.

4.5.2 Adsorption using Activated carbon – MgO NPs

The adsorption of ofloxacin onto MgO NPs composites has been studied as a potential method for removing ofloxacin from wastewater. By measuring the UV absorbance of a solution before and after contact with MgO NPs, the amount of adsorbed ofloxacin is determined.

- ❖ A stock solution of ofloxacin was prepared at a known concentration.
- ❖ MgO NPs(10mg,20mg,30mg,40mg,50mg) were added to each Erlenmeyer flask.
- ❖ The flasks were filled with a known volume (1000 ppm) of each ofloxacin solution. Close the flasks and shake them steadily for a predefined amount of time (one hour, two hours, etc.). This makes it possible for ofloxacin to bind to the MgO NPS.
- ❖ After the shaking time,MgO NPs were separated from the solution by filtration.
- ❖ Using a filter paper the solution was separated from the MgO NPs.
- ❖ Absorbance was measured by the remaining ofloxacin solution (supernatant) using a UV-Vis spectrophotometer at a specific wavelength where ofloxacin has a strong absorbance peak at 295nm.
- ❖ The absorbance of the ofloxacin solutions before and after contact with the MgO Nps. A decrease in absorbance indicates adsorption of ofloxacin onto the MgO NPs.

4.5.3 Adsorption using Fe_3O_4 NPs

The adsorption of ofloxacin onto Fe_3O_4 Nps composites has been studied as a potential method for removing ofloxacin from wastewater. By measuring the UV absorbance of a solution before and after contact with Fe_3O_4 Nps, the amount of adsorbed ofloxacin is determined.

- ❖ A stock solution of ofloxacin was prepared at a known concentration.
- ❖ Fe_3O_4 Nps (10mg,20mg,30mg,40mg,50mg) were added to each Erlenmeyer flask.
- ❖ known volume(1000ppm) of each ofloxacin solution was added to the flasks. Cap the flasks and shake them at a constant speed for a predetermined time (e.g., 1 hour, 2 hours, etc.). This allows for the adsorption of ofloxacin onto the activated carbon- Fe_3O_4 Nps.
- ❖ After the shaking time, the Fe_3O_4 Nps were separated from the solution by filtration.
- ❖ Using a filter paper the solution was separated from the Fe_3O_4 Nps.

- ❖ Absorbance was measured by the remaining ofloxacin solution (supernatant) using a UV-Vis spectrophotometer at a specific wavelength where ofloxacin has a strong absorbance peak at 295nm.
- ❖ The absorbance of the ofloxacin solutions before and after contact with the Fe_3O_4 Nps. A decrease in absorbance indicates adsorption of ofloxacin onto the Fe_3O_4 Nps.

4.5.4 Adsorption using Activated carbon – MgO NPs – Fe_3O_4 NPs

By Integrating activated carbon (AC) with both magnesium oxide nanoparticles (MgO NPs) and iron oxide nanoparticles (Fe_3O_4 NPs) were created a potentially powerful tri-component adsorbent for ofloxacin removal.

- ❖ A stock solution of ofloxacin was prepared at a known concentration.
- ❖ Activated carbon(1000mg), MgO NPs (50mg) and Fe_3O_4 Nps (50mg) were added to each Erlenmeyer flask.
- ❖ Known volume 100ppm, 200ppm, 300ppm, 400ppm, 500ppm, 600ppm, 700ppm, 800ppm ,900ppm,1000ppm of each ofloxacin solution was added to the flasks. Cap the flasks and shake them at a constant speed for a predetermined time (e.g., 1 hour, 2 hours, etc.). This allows for the adsorption of ofloxacin onto the activated carbon-MgO NPs- Fe_3O_4 Nps.
- ❖ After the shaking time, the activated carbon-MgO NPs- Fe_3O_4 Nps were separated from the solution by filtration.
- ❖ Using a filter paper the solution was separated from the activated carbon- MgO NPs - Fe_3O_4 Nps.
- ❖ Absorbance was measured by the remaining ofloxacin solution (supernatant) using a UV-Vis spectrophotometer at a specific wavelength where ofloxacin has a strong absorbance peak at 295nm.
- ❖ The absorbance of the ofloxacin solutions before and after contact with the activated carbon- MgO NPs - Fe_3O_4 Nps. A decrease in absorbance indicates adsorption of ofloxacin onto the activated carbon- MgO NPs - Fe_3O_4 Nps.

4.5.5. Characterization of adsorbent

4.5.5.1 SEM

Scanning Electron Microscopy (SEM) is a type of electron microscope that creates pictures of solid surfaces by scanning them with electron beams. Electron beams impact the atoms on the sample surface, producing a variety of signals. Electron detectors detect these impulses. These signals include information about the sample's adsorption in surface structure. Activated carbon-MgO-Fe₃O₄ adsorption morphology was studied.

4.5.5.2 FTIR

Surface functional group analysis of the Adsorbed adsorbate as well as of the raw material was done before and after adsorption, using an FTIR model NICOLET 6700 (Thermo Fisher Scientific, U.S.A.). FTIR analysis of the adsorbent was done to find and analyze functional groups present on the surface of the adsorbate.

4.6 ISOTHERM MODEL AND ADSORPTION STUDIES

The quantity of gas adsorbed on a material under constant pH and temperature with variable pressure is referred to as the adsorption isotherm. It is a function of the solid's surface area and pore structure; hence it can give important information about these two elements. Adsorption isotherms are a popular tool for characterizing porous materials. The existence of specific types of pores results in varied isotherm forms. The Langmuir and Freundlich models are the most often used adsorption isotherm models.

4.6.1 Langmuir isotherm

This is applicable for monolayer coverage of the adsorption on the surface. In this model, adsorption is assumed to take place on homogenous surface.

$$\frac{C_e}{Q_e} = \frac{1}{Q_m} \left(\frac{1}{K_L} + C_e \right)$$

C_e – amount of ofloxacin adsorbed per unit mass of adsorbent.

Q_e – concentration of ofloxacin solution at equilibrium

Q_m – adsorption capacity

K_L – Langmuir equilibrium constant

The feasibility of this model is tested by using a function called R_L (equilibrium parameter)

$$R_L = \frac{1}{1 + K_L C_0}$$

4.6.2 Freundlich isotherm

The adsorption is assumed to take place on a heterogenous surface. It is valid for multilayer adsorption.

$$\log (Q_e) = \log (K_f) + \frac{\log (C_e)}{n}$$

Q_e – ofloxacin adsorbed at equilibrium.

C_e – ofloxacin concentration at equilibrium

K_f and n – constants for a given adsorbate and adsorbent at a particular temperature.

The effectiveness of every adsorption process is described by adsorption kinetics. The kinetics of ofloxacin solution adsorption at various concentrations ranging from 100ppm to 1000ppm over a constant time interval were investigated which follows pseudo first order kinetics, pseudo second order kinetics, and so on. The following formulas were used to determine adsorption kinetics:

$$\text{Amount of ofloxacin removed at equilibrium } (Q_e) = (C_0 - C_e) \times \frac{V}{m}$$

$$\text{Amount of ofloxacin removed with respect to time } (Q_t) = (C_0 - C_t) \times \frac{V}{m}$$

Q_e – amount of ofloxacin removed at equilibrium.

Q_t – amount of ofloxacin removed with respect to time.

C_0 – initial concentration

C_e – concentration of ofloxacin at equilibrium

C_t – concentration of ofloxacin at time t

V – volume of the ofloxacin

m – mass of the substrate

Pseudo first order kinetics:

$$\log (Q_e - Q_t) = \log Q_e - \frac{k_1}{2.303} t$$

Pseudo second order kinetics:

$$\frac{1}{Q_t} = \frac{1}{k_2 Q_{e_2}} + \frac{1}{Q_e}$$

4.6.3 Temkin isotherm

A two-parameter model for determining the heterogeneous adsorption system (Smitha *et.al.*, 2012)

$$Q_e = B (\ln A_T + \ln C_e) = \frac{R_T}{b} (\ln A_T + \ln C_e)$$

$$B = \frac{R_T}{b}$$

A_T – Temkin isotherm equilibrium binding constant (l/g)

b – Temkin isotherm constant related to heat of sorption (J/mol)

R – universal gas constant (8.314 Jmol⁻¹K⁻¹)

T – temperature at 298K

The plot of Q_e vs. $\ln (C_e)$ enables the determination of the isotherm constants

CHAPTER 5

RESULTS AND DISCUSSION

Antibiotics are a growing environmental concern, impacting ecosystems globally and posing risks to both human health and the environment. Their presence can lead to the development of antibiotic-resistant bacteria. To combat this issue, various methods are used to remove antibiotics from the environment, including advanced oxidation processes, activated sludge treatment, vermicomposting, and adsorption. Among these, adsorption is highly effective.

This study found that using novel bimetallic nanoparticles, such as MgO- Fe₃O₄, along with activated carbon made from corn husk, is a promising approach to removing antibiotics like ofloxacin by Adsorption.

5.1 STANDARD GRAPH OF OFLOXACIN

The standard graph for Ofloxacin concentration showed a linear relationship between concentration and absorbance, as shown in the fig 5.1.

Table 5.1: concentration and Absorbance of Ofloxacin

Concentration Of Ofloxacin	Absorbance at 295nm
100	0.001
200	0.004
300	0.007
400	0.010
500	0.013
600	0.016
700	0.020
800	0.023
900	0.027
1000	0.031

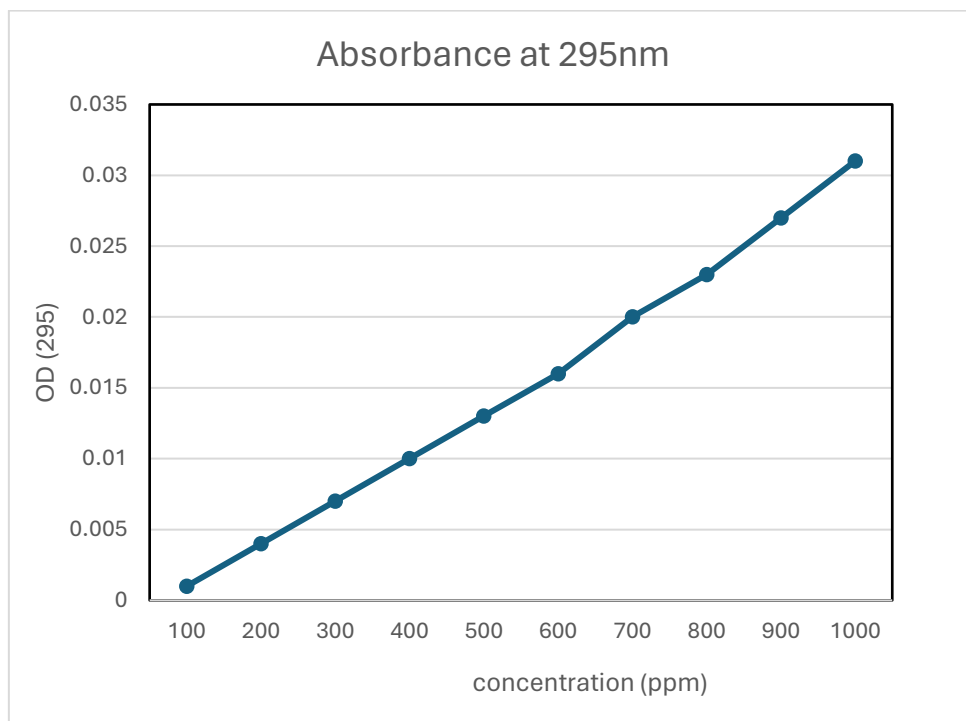


Figure:5.1: Standard graph of ofloxacin.

5.2 SYNTHESIS OF MAGNESIUM OXIDE NANOPARTICLE

5.2.1 Preparation of *Tecoma stans* (F) plant extract

A purified liquid extract obtained through centrifuging, filtering, and grinding *Tecoma stans* flower samples. The distinct goal of the centrifugation process was to remove the solid homogenate components from the clarified supernatant, or extract.



Figure:5.2: Extract of *Tecoma stans* flower

Kameshwaran et al. (2013) employed a method to extract *Tecoma stans* flower extract by first drying the flower petals in the shade, grinding them into a powder, and then using a Soxhlet apparatus to extract 100 g of the dried powder with methanol. They obtained a sticky mass of extract (yield 8.9% w/w) by removing the solvent using a rotary flash evaporator at a controlled temperature and reduced pressure. Comparing this method with an alternative approach involving centrifugation, filtering, and grinding, it is evident that the latter may result in a purer extract. This is because solid components are removed more effectively through centrifugation, filtering, and grinding, potentially leading to higher purity compared to the Soxhlet extraction method, which may yield a higher quantity of extract but at the cost of purity. Therefore, the centrifugation, filtering, and grinding method appear to be superior to the Soxhlet extraction method in terms of extract purity efficiency.

5.2.2 Synthesis of MgO NPs from *Tecoma stans* (F) plant extracts

MgO nanoparticles were synthesized as a result of this method, and the samples were identified by the *Tecoma stans* flower extracts used to relied on in the synthesis (Pugazhendhi et al., 2019).



Figure:5.3: Magnesium oxide nanoparticle

In the study by Nguyen et al. (2021), MgO NPs provided rich surface functional groups and a respectable degree of dispersion. 90.8–99.7% were found to be the ideal range for the best removal efficiency when using the Box-Behnken design and statistical support. In a 2013 study, Gopinath et al. described synthesizing MgO NPs with aloe vera extract. The study emphasized the green and sustainable approach of using Aloe vera as a reducing and stabilizing agent for the synthesis of NPs. The synthesis of MgO NPs has also been studied using green tea extract. The antioxidant characteristics of green tea extract were highlighted in a study by Vivek et al. (2011), which made it easier to synthesize MgO NPs with improved stability and biocompatibility. When compared to other green synthesis methods and conventional chemical methods, the synthesis of MgO NPs utilizing *Tecoma stans* flower extract is a more environmentally friendly method. It reduces hazardous chemicals, promotes sustainability, cost effective, and potentially yields biocompatible nanoparticles.

5.2.3 Characterization of MgO NP

5.2.3.1 SEM:

Figure 5.4 present the scanning electron microscopy (SEM) images of the MgO NPs synthesized using the *Tecoma stans* flower extract where the scale bar is (A) 5 μm , (B) 10 μm , (C) 20 μm and (D) 30 μm . the MgO NPs were well dispersed. Locally, the synthesized MgO NPs were agglomerated and formed larger clusters.

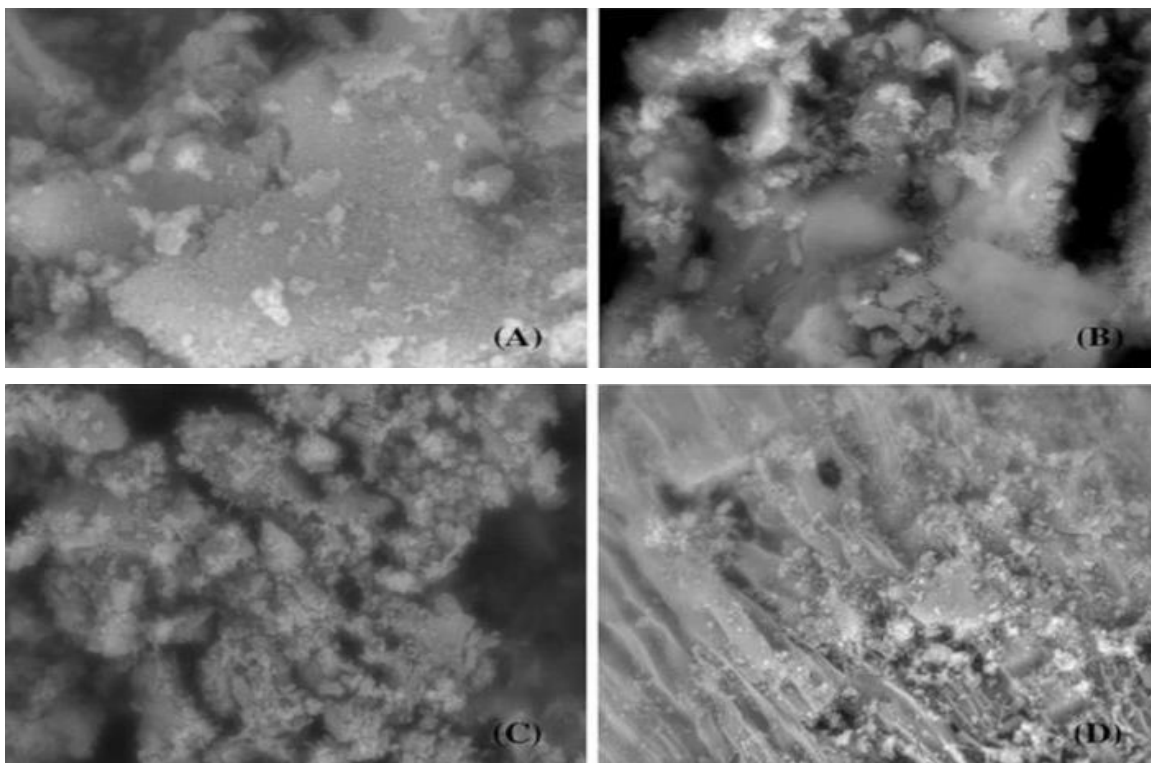


Figure:5.4: SEM images of the synthesized MgO nanoparticles synthesized using *Tecoma stans* flower extract a) 5 μm , b) 10 μm , c) 20 μm and d) 30 μm .

According to Nguyen et al. (2021), MgO NPs demonstrated main atomic compositions of Mg (28.56–34.77%) and O (50.42–55.21%). Trace amounts of impurities (C, N, and P) with varying contents, potentially from *Tecoma* flower extracts, were also found. Similar impurities were reported by Dobrucka et al. (2018), although at a higher content (23.7% C in MgO NPs) than was previously thought. Many components found in the extract, including polyphenols, phytochemicals, and flavonoids, may interact with the $\text{Mg}(\text{OH})_2$ multifaceted during the synthesis of $\text{Mg}(\text{OH})_2$ nanoparticles and take part in the coprecipitation process. Impurities are likely to break down during high-temperature pyrolysis in a muffle furnace, and some of them may end up depositing on the MgO nanoparticles' surface and structure. The highest percentages of these elements were found in MgO nanoparticles made from the flower extract (4.49%, 5.78%, and 2.42% for C, N, and P, respectively). It's interesting to note that all of the nanoparticles had more oxygen (>50%) than magnesium atoms (<35%).ss

5.3 SYNTHESIS OF MAGNETITE NANOPARTICLE (Fe_3O_4)

Magnetite nanoparticles (Fe_3O_4) were successfully synthesized using the co-precipitation method. The particles were obtained through the following steps: preparation of individual iron(II) and iron(III) salt solutions, their subsequent mixing under constant stirring, followed by base addition to induce precipitation of Fe_3O_4 at a high pH. The precipitate was then separated by centrifugation, washed with deionized water, and dried. Finally, the nanoparticles were optionally stabilized and further purified.



Figure:5.5: Magnetite Nanoparticle (Fe_3O_4).

In the study by Valenzuela et al. (2009), the co-precipitation method was utilized to create superparamagnetic nanoparticles of magnetite with a mean diameter of 10 nm and a narrow size distribution. A homogenizer was used to stir the mixture at a speed of 10,000 rpm. Typically, the co-precipitation method produces large amounts of pure Fe_3O_4 nanoparticles. The reaction is appropriate for industrial applications because it is simple to understand and can be readily scaled up for large-scale production. The Fe_3O_4 nanoparticles were synthesized using a wet chemical reduction technique, as reported by Chaki et al. (2015). The variation of magnetization (M) versus the applied magnetic field (H) for the as-synthesised Fe_3O_4 nanoparticles at

temperatures of 10 and 300 K demonstrated that the magnetization increases with increasing magnetic field and saturates at higher magnetic fields.

The narrow size distribution of Fe₃O₄ nanoparticles produced by the co-precipitation method is crucial for applications that demand uniformity, like drug delivery and magnetic hyperthermia (Liu *et al.*, 2019). A straightforward, scalable, and economical method for producing Fe₃O₄ nanoparticles with good control over their properties is co-precipitation. For different applications of Fe₃O₄ nanoparticles, co-precipitation is still a very flexible and appealing approach, even though other approaches might have advantages in certain areas.

5.3.1 Characterization of Fe₃O₄ NP.

5.3.1.1 SEM

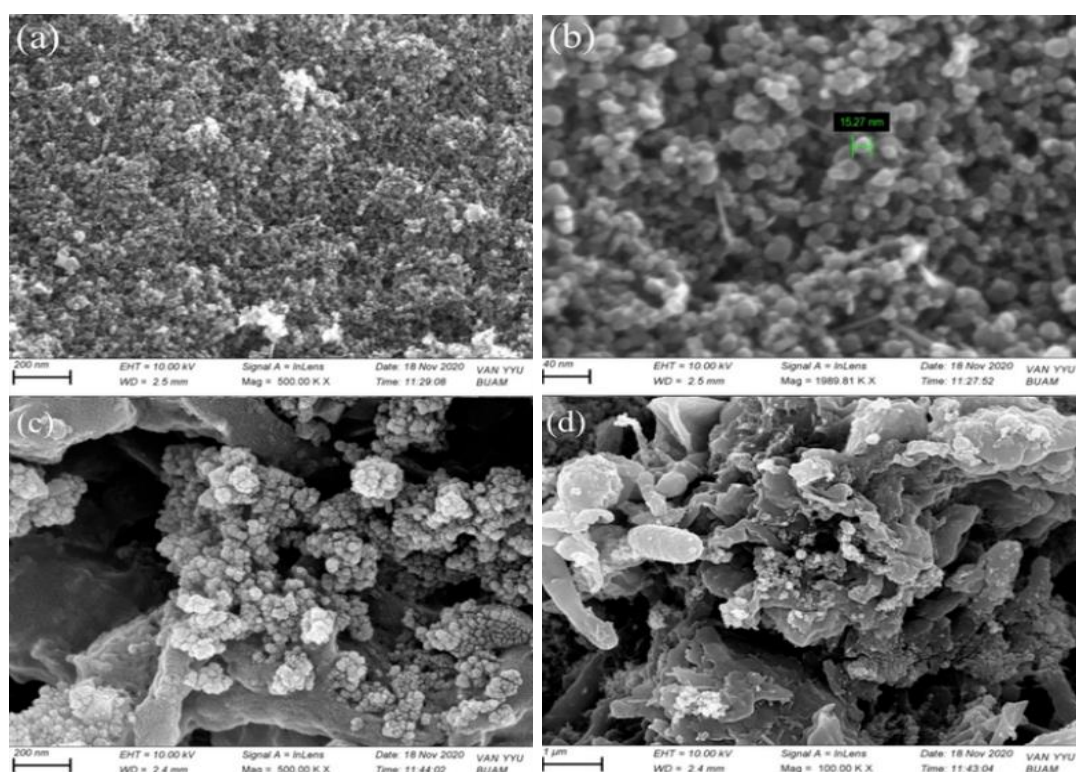


Figure:5.6: SEM images of Fe₃O₄ Nanoparticle.

SEM was used to examine the surface morphology of the produced Fe₃O₄ nanoparticles; the results are shown in Fig. The particles are porous and have a highly

spherical shape. There are active sites for the reaction because the material has excess surface area due to smaller, rougher-surfaced particles (Mulak *et al.*, 2002; Wei *et al.*, 2009). The produced particles also have large surface areas and high energies, which seem to give them a propensity to group together (Fig 5.6 a, b). In other words, following treatment, the processed nanoparticles have a rougher structure, oxidation-related surface corrosion, and surface accumulation of pollutants as a result of the treatment reaction (Fig 5.6 c, d). This indicates that during Fe_3O_4 reuse, there will be more active areas.

It is feasible to compare the selected synthesis method with the observed morphology and size distribution. This aids in the understanding of how various synthesis parameters affect the finished product by researchers. The shape, size, and agglomeration of the observed characteristics should be connected to the anticipated properties of the Fe_3O_4 nanoparticles in the discussion. For instance, compared to clumped or irregularly shaped particles, uniformly sized and well-dispersed nanoparticles frequently show superior magnetic or catalytic activity. Researchers can talk about how to best optimize the synthesis process to get the desired nanoparticle characteristics for applications based on the analysis. For instance, changes to the synthesis may be advised to reduce agglomeration if highly dispersed nanoparticles are required for catalysis (Takai *et al.*, 2019).

5.4 PREPARATION OF ACTIVATED CARBON FROM CORN HUSK

Corn husk activated carbon (CHAC) was successfully prepared from corn husk, following a modified procedure from (Lunge *et al.*, 2014). The procedure included washing, drying, and grinding the corn husk, then treating it with a nitric acid solution and heating it to 300°C for thermal activation. To prepare it for use in Ofloxacin adsorption, the finished product was subsequently homogenized, dried, cleaned, and characterized.

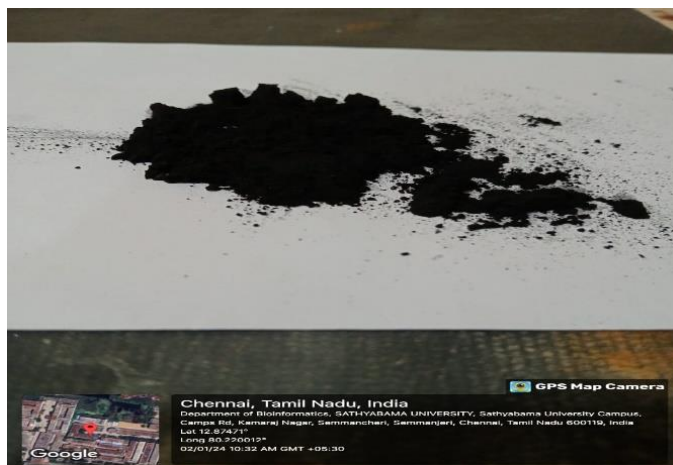


Figure:5.7: Activated carbon from corn husk.

According to studies, it is essential to optimize the activation process parameters (concentration, temperature, and time) in order to produce activated carbon with the appropriate qualities for particular uses (Ko *et al.*, 2018; Marlina *et al.*, 2019). The production of activated carbon from corn husk, an agricultural waste product, provides a sustainable and environmentally beneficial substitute for conventional methods (Ammar *et al.*, 2021). Using a process with four phases that included impregnation, pyrolysis, washing, and acid treatment, activated carbons were successfully made from soybean oil cake. The final activated carbons had a high degree of purity and little ash content, making them ideal for a variety of adsorption applications (Tay *et al.*, 2009).

The process of obtaining activated carbon from corn husk is thought to offer several advantages over the method described for preparing activated carbons from soybean oil cake, including higher surface area, better adsorption properties, and possibly a lower environmental impact due to the use of a waste material.

5.4.1 Property analysis of the activated carbon.

5.4.1.1 Pore volume

The amount of water adsorbed by the adsorbent is indicated by the decrease in water volume following boiling and filtration. By dividing the water's volume decrease by its density, the pore volume can be computed.

Initial volume = 20ml

Volume after boiling and filtration = 13ml

Decrease in volume of water = initial volume – volume after boiling and filtration

$$20\text{ml} - 13\text{ml} = 7\text{ml}.$$

Decrease in volume of water – 7ml.

Density of water – 1g/ml

Pore volume = decrease in volume / density of water. = $7/1 = 7\text{ml}$.

The pore volume of the adsorbent is 7 ml.

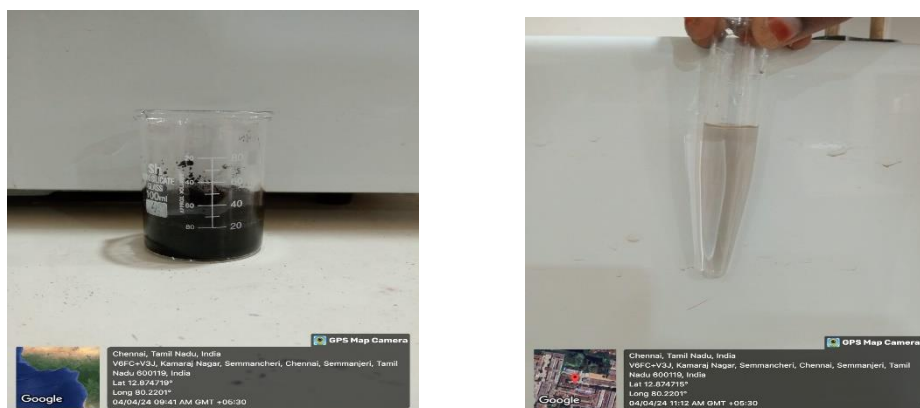


Figure:5.8: a) initial volume b) volume after boiling and filtration

The capacity for adsorption increases with increasing pore volume. For uses such as gas storage, water purification, and pollutant removal, activated carbon made from corn husks is therefore a viable option. Comparatively speaking to non-chemical techniques, the creation of pores with a greater volume is the outcome of chemical activation with agents like causing etching effects. More activating agent concentration can be added to further increase pore volume (Yalcin and Sevinc, 2000). Through the encouragement of additional precursor material breakdown, higher activation temperatures have the potential to increase pore volume. Inappropriate control of extended activation times can result in pore collapse as well as pore enlargement (He

et al., 2023). According to (Każmierczak *et al.*, 2013), activated carbon made from corn husk can achieve good ranges in pore volume (0.597 cm³/g to 1.365 cm³/g) and surface areas (337 m²/g to 1213 m²/g). This translates to a high adsorption capacity, which makes it appropriate for a range of uses.

5.4.1.2 Moisture content determination

Initial weight (W_1) – 50g

Weight after drying (W_2) – 21g.

$$\begin{aligned}\text{Moisture content } (X_o) &= \frac{W_1 - W_2}{W_1} \times 100 = \frac{50 - 21}{50} \times 100 \\ &= 58\%\end{aligned}$$

Activated carbon has a relatively high moisture content of 58%. For best results in adsorption applications, the majority of activated carbons that are sold commercially have a moisture content of less than 10%. Excessive levels of moisture can Lower the surface area that can be used for adsorption, Reduce the activated carbon's ability to adsorb substances, affect the material's mechanical qualities. In most adsorption applications, activated carbon works best when the moisture content is less than 10%. High moisture content can cause problems because it decreases the amount of surface area that can be used for adsorption. reducing the target molecules' ability to bind influencing the material's mechanical properties (Soffian *et al.*, 2022). A moisture content of less than 10% is usually necessary for activated carbon to function at its best in adsorption applications (Giles *et al.*, 1960). Elevated moisture content can have a deleterious effect on functionality by decreasing the surface area that can be occupied by adsorption. decreasing the target molecules' ability to adsorb because of water molecules' competition. influencing the material's mechanical characteristics and increasing the likelihood of breakage.

5.4.2 Characterization of Activated carbon

5.4.2.1 FTIR

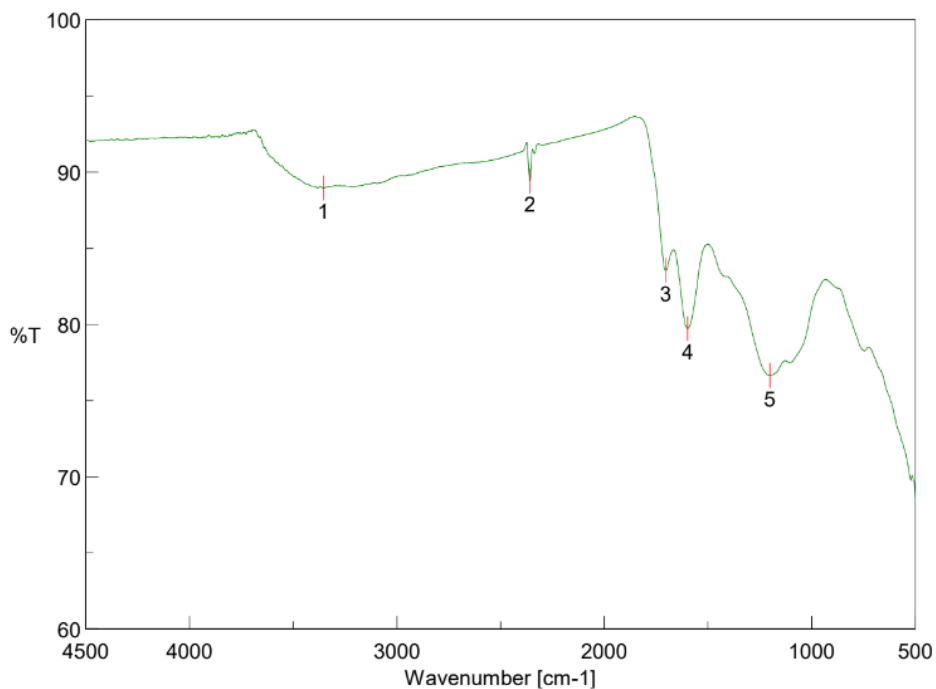


Figure:5.9: FTIR result of Activated carbon.

Table 5.2: FTIR result of peak obtained.

S.NO	Position	Intensity
1.	3353.6	88.9557
2.	2358.52	89.4027
3.	1702.84	83.5399
4.	1598.7	79.7254
5.	1202.4	76.6486

O-H stretching vibrations of carboxylic acids or hydroxyl groups may be the explanation of the peak at 3353 cm⁻¹. The C=O stretching of ketones or carboxylic

acids may be the origin of the peak at 2358 cm^{-1} . The carbonyl groups in ketones, aldehydes, or carboxylic acids may have undergone C=O stretching, which would explain the peak at 1702 cm^{-1} . The aromatic rings' C=C stretching may be the cause of the peak at 1598 cm^{-1} . The C-O stretching of alcohols, ethers, or esters may be the cause of the peak at 1202 cm^{-1} . In accordance with Liu et al. (2017), the FT-IR spectra of the original activated carbon and that altered by Fe^{3+} . The absorption peaks on the original and modified activated carbon are located at 3400 cm^{-1} , and they are caused by N-H stretching vibrations, phenolic hydroxyl, and -OH vibrations linked to hydrogen bonding. The -OH peak's intensity is significantly increased, suggesting that the modification has increased the number of -OH. At 2850 cm^{-1} , there is a significant adsorption peak for MAC in comparison to AC. This could be related to the stretching vibration of OH. The band at 1630 cm^{-1} may represent the stretching vibration of C=O or C=C, phenolic hydroxyl, or N-H deformation vibration.

5.4.2.2 SEM

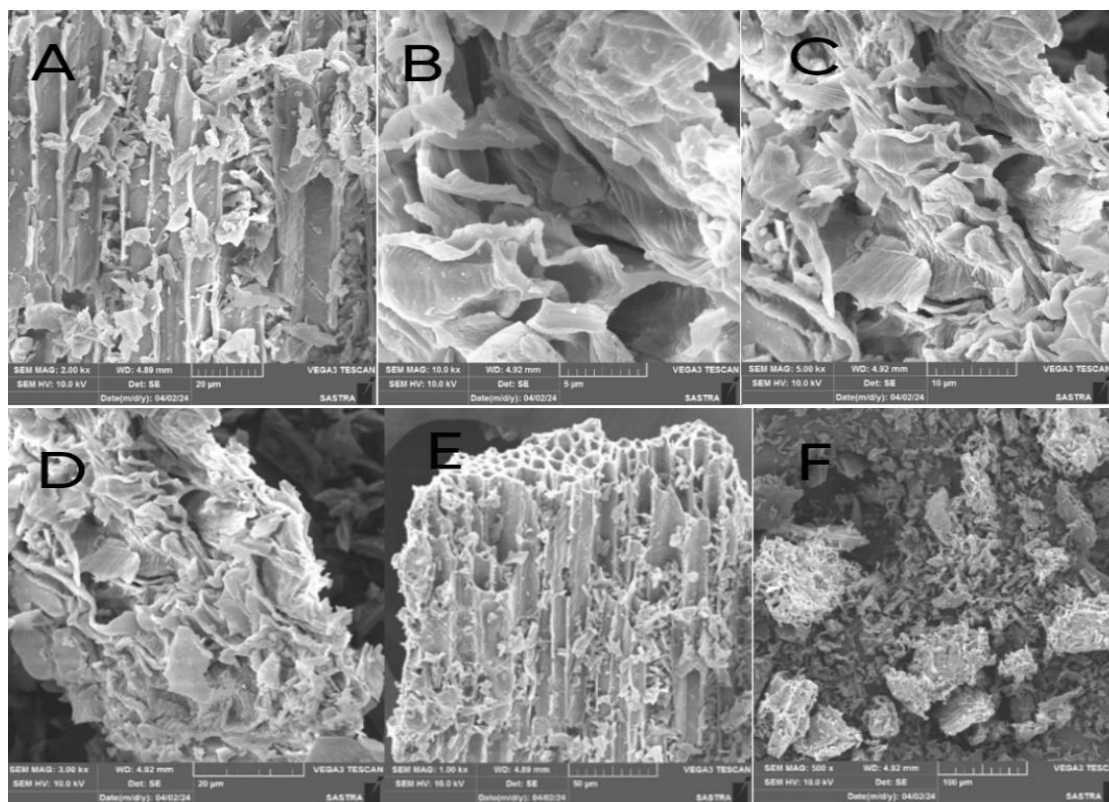


Figure:5.10: SEM images of Activated carbon from corn husk A)20μm, B)5μm, C)10μm, D)20μm, E)50μm, F)100μm.

Scanning electron microscopy (SEM) was used to determine the surface morphology of the Activated carbon. Figure 5.10 shows that the adsorbent was highly porous, with many macropores at the surface, according to the image acquired at 10kV and $\times 1500$ magnification. The micrographs showed a web of interconnected pores, with sizes varying from a few to several micrometres **5 μm , 10 μm , 20 μm , 50 μm** . The high porosity of the activated carbon was evident from its uneven and rough surface. The removal of lignin, hemicellulose, and cellulose as well as the addition of certain functional groups, which results in the adsorbent material's surface having more pores and facilitating the simple transfer of adsorbates into the inner surface (Mandal *et al.*, 2021). Sharma et al. (2018) state that the rough surface and porous structure are advantageous features for adsorption applications because they offer a lot of surface area for target molecule adsorption. A heterogeneous structure is suggested by the presence of pores in different sizes, which may improve the activated carbon's adsorption effectiveness.

5.5 ADSORPTION STUDIES

5.5.1 Adsorption using Activated carbon.

The adsorption of Ofloxacin onto activated carbon was investigated at various concentrations over a 5-hour period. The absorbance of Ofloxacin at 295nm was measured to determine the quantity of Ofloxacin adsorbed onto the activated carbon. At the initial time point (0th hr), there was no significant difference in absorbance among the different concentrations of activated carbon, suggesting that adsorption had not yet begun. The results demonstrated that activated carbon was effective in adsorbing Ofloxacin from aqueous solutions, with higher concentrations of activated carbon resulting in greater adsorption capacity.

Table 5.3: Adsorption of Ofloxacin using Activated carbon.

Ofloxacin (200mg in 100ml) in ppm	Activated Carbon in mg	Absorbance (295nm)					
		0 th hr (%)	1 hr (%)	2 hr (%)	3 hr (%)	4 hr (%)	5 hr (%)
1000	100	9.9	17.5	30.6	46.6	65.5	91
1000	250	9.8	20.2	42.4	64.4	89.8	91.3
1000	500	16.6	32	53.6	76.7	88.8	92.9
1000	750	24.4	47.5	70	89.6	99.1	100
1000	1000	35.5	56.1	84.8	99.2	99.3	100

5.5.2 Adsorption using MgO NPs.

The results indicated that the adsorption of Ofloxacin by MgO nanoparticles was both time and concentration dependent. At the 0th hour, before any adsorption had occurred, the absorbance of Ofloxacin in the solution was high, indicating the presence of the drug in the solution. The highest adsorption efficiency was observed at the highest concentration of MgO NPs (50 mg), with the absorbance of Ofloxacin decreasing significantly over the 5-hour period. This suggested that higher concentrations of MgO NPs were more effective in adsorbing Ofloxacin from the solution.

Table 5.4: Adsorption of Ofloxacin using MgO NPs

Ofloxacin (200mg in 100ml) in ppm	MgO NPs in mg	Absorbance (295nm)					
		0 th hr (%)	1 hr (%)	2 hr (%)	3 hr (%)	4 hr (%)	5 hr (%)
1000	10	2.82	3.37	4.55	6.29	12.17	45.19
1000	20	2.15	3.09	6.45	19.02	24.41	52.25
1000	30	1.44	3.18	11.38	23.48	47.79	76.65
1000	40	1.82	16.56	35.97	67.22	94.16	97.74
1000	50	1.94	24.36	79.16	86.03	90.87	100

5.5.3 Adsorption using Fe₃O₄ NPs.

The adsorption of Ofloxacin using Fe₃O₄ nanoparticles (NPs) was investigated at various Fe₃O₄ NP concentrations (10-50 mg) with a constant initial Ofloxacin concentration of 200 mg in 100 ml. The absorbance of Ofloxacin at 295 nm was measured at different time intervals (0-5 hours) to assess the adsorption efficiency. As the concentration of Fe₃O₄ NPs increased to 50 mg, the absorbance of Ofloxacin decreased more rapidly, reaching 0 at 5 hours. This indicated that higher concentrations of Fe₃O₄ NPs effectively removed Ofloxacin from the solution, possibly due to an increased surface area available for adsorption.

Table 5.5: Adsorption of Ofloxacin using Fe₃O₄ NPs.

Ofloxacin (200mg in 100ml) in ppm	Fe ₃ O ₄ NPs in mg	Absorbance (295nm)					
		0 th hr (%)	1 hr (%)	2 hr (%)	3 hr (%)	4 hr (%)	5 hr (%)
1000	10	17.50	20.20	32.00	32.00	35.50	56.10
1000	20	28.90	42.40	53.60	53.60	56.10	84.80
1000	30	45.70	65.70	76.70	76.70	84.80	99.04
1000	40	65.50	89.80	88.80	88.80	99.04	99.30
1000	50	91.00	91.30	92.90	92.90	99.30	100.00

5.5.4 Adsorption using Activated carbon – MgO NPs – Fe₃O₄ NPs.

The adsorption of Ofloxacin using a combination of activated carbon, MgO nanoparticles, and Fe₃O₄ nanoparticles was studied at different time intervals (0-5 hours) and initial Ofloxacin concentrations (100-1000 ppm).



***Figure:5.11: Ofloxacin Concentration on adsorption
using AC-MgO- Fe_3O_4***

The absorbance of Ofloxacin at 295 nm was measured to assess the adsorption efficiency. The use of a combination of activated carbon, MgO nanoparticles, and Fe_3O_4 nanoparticles resulted in a synergistic effect on the adsorption of Ofloxacin. The presence of MgO and Fe_3O_4 nanoparticles likely enhanced the adsorption capacity through increased surface area and active sites for adsorption. The adsorption process reached equilibrium at around 3-5 hours for most of the tested conditions, as indicated by the plateau in absorbance values.

Table 5.6: Adsorption of Ofloxacin using Activated carbon – MgO NPs – Fe₃O₄ NPs.

Ofloxacin (200mg in 100ml) (in ppm)	MgO NPs in (mg)	Fe ₃ O ₄ NPs in (mg)	Activated Carbon (g)	Percentage of Adsorption					
				0 th hr (%)	1 hr (%)	2 hr (%)	3 hr (%)	4 hr (%)	5 hr (%)
100	50	50	1	96.5	97.2	98.2	95	100	100
200	50	50	1	95.8	96.6	97.5	91	98	100
300	50	50	1	95.5	96.7	98	98.3	97	100
400	50	50	1	95.1	96.2	97.8	98.6	99.9	100
500	50	50	1	94.7	98.3	99.1	99.6	100	100
600	50	50	1	94.3	95.8	97	97.9	98.2	99.7
700	50	50	1	93.9	94.5	95.7	96.9	98	99.5
800	50	50	1	92.8	93.9	95.2	96.6	98.1	99.3
900	50	50	1	91.5	92.7	94.1	96.2	98.3	99.1
1000	50	50	1	90	94	96.8	97.8	98.8	99

5.5.5 Characterization of adsorbent

5.5.5.1 SEM

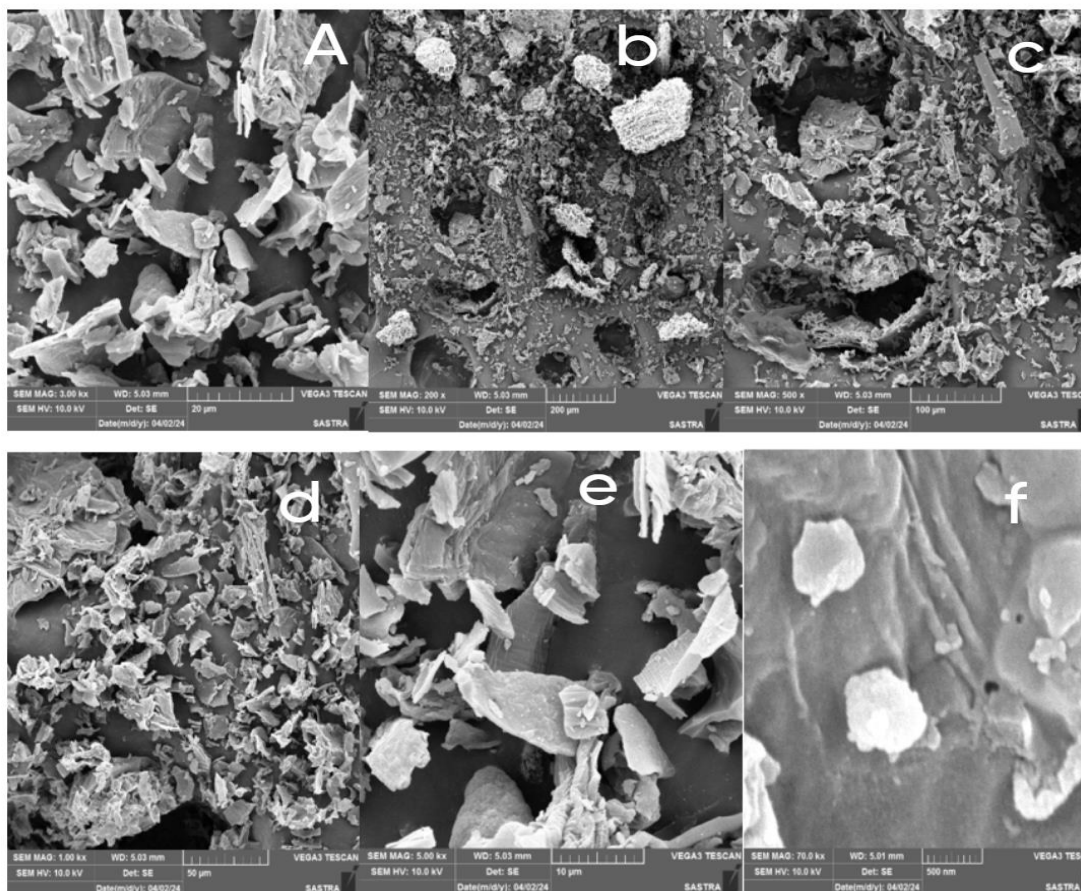


Figure 5.12: SEM images of initial adsorption at 500ppm in 0th hour

a) 20 μ m, b) 200 μ m, c) 100 μ m, d) 50 μ m, e) 10 μ m, f) 500 nm.

The morphology and surface properties of the activated carbon-MgO NPs-Fe₃O₄ NPs composite were examined using scanning electron microscopy (SEM) to the initial adsorption of ofloxacin. The composite shows up as a heterogeneous mixture of different-sized and shaped particles at lower magnifications (3kx and 200x). Particles of activated carbon with a porous structure are visible at higher magnifications (500x, 1kx, and 5kx). Throughout the carbon matrix, MgO NPs and Fe₃O₄ NPs are scattered and show up as bright, nodular features (size range: 10-50 nm) that contrast with the darker carbon matrix. When examining the composite's surface texture at the

highest magnification (70kx), surface irregularities and the presence of functional groups that may be involved in ofloxacin adsorption may be seen.

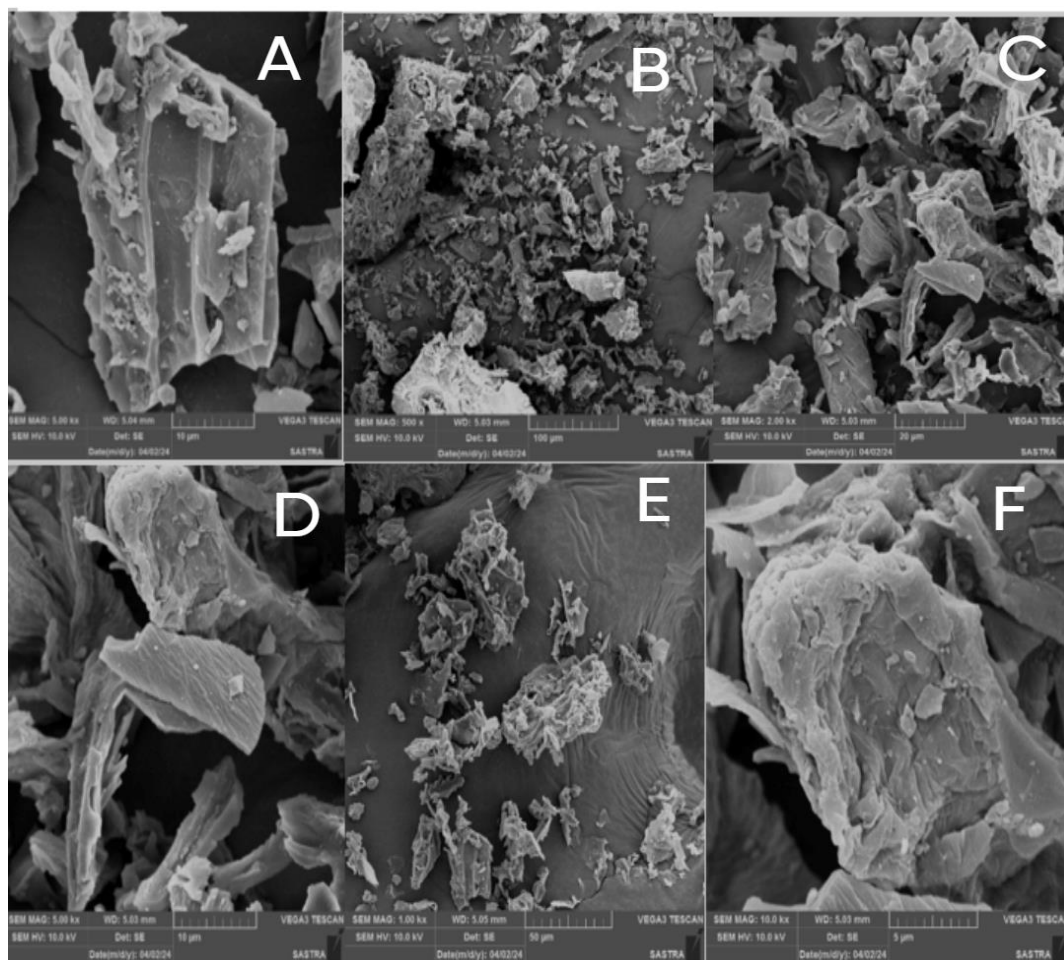


Figure:5.13: SEM images of final adsorption at 500ppm in 5hr.

a)10µm, b)100µm, c)20µm, d)10µm, e)50µm, f)5µm.

Scanning electron microscopy (SEM) was used to determine the surface morphology of the adsorption of ofloxacin on Activated carbon-MgO NPs-Fe₃O₄ NPs. Figure 5.13 shows the overall morphology of the composite observed at lower magnifications (3kx, 10kx). At higher magnifications (20kx, 50kx), the images show that the ofloxacin molecules are well-adsorbed onto the composite surface. The particle size of the composite appears to be in the range of 5µm, 10µm, 20µm. Some degree of

agglomeration of the composite particles is observed at the highest magnification (70kx).

5.5.5.2 FTIR

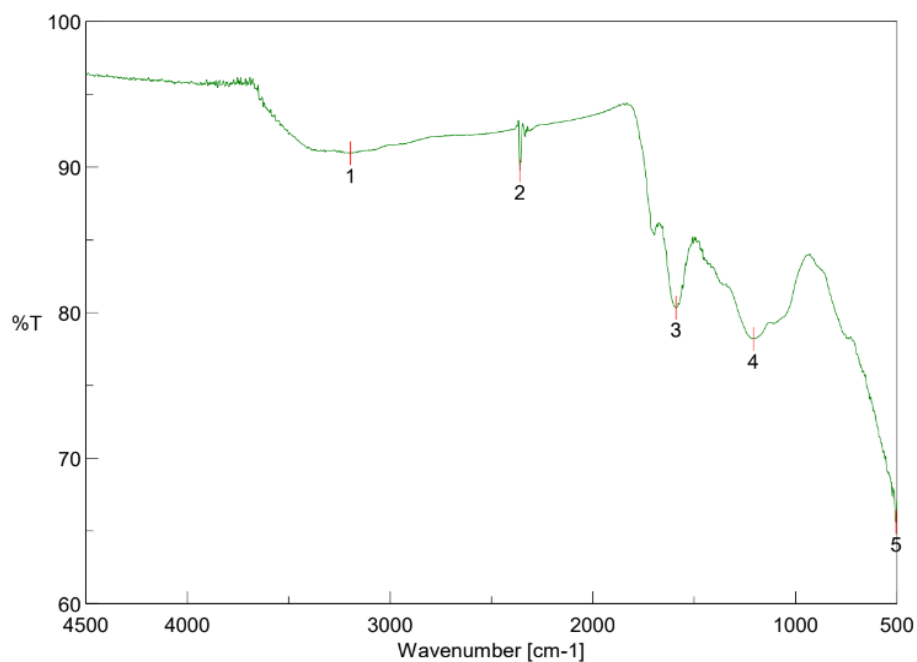


Figure:5.14: FTIR results of initial adsorption of 500ppm at 0th hour.

Table 5.7: FTIR initial adsorption result of peak obtained.

S.NO	Position	Intensity
1.	3195.47	90.9315 2
2.	2360.44	89.7676
3.	1590.02	80.3174
4.	1208.18	78.1807
5.	505.258	65.6026

These peaks show that the activated carbon contains a variety of functional groups, each of which is related to a particular chemical bond. For instance, the peak

at 2360.44 cm^{-1} may suggest the presence of C $\equiv$ C triple bonds or possibly a combination of functional groups, whereas the peak at 3195.47 cm^{-1} suggests the presence of O-H stretching vibrations. The peaks at lower wavenumbers, like 505.258 cm^{-1} and 1208.18 cm^{-1} , might represent various kinds of vibrations in the carbon structure. Hu et al. (2018) investigated into the adsorption of ofloxacin using a magnetic graphene oxide composite in their study. Functional groups including hydroxyl (-OH), carboxyl (-COOH), and amino (-NH₂) groups were present in the composite, according to the FTIR analysis, and they contributed to the adsorption of ofloxacin through hydrogen bonding and electrostatic interactions. This study shows that the initial adsorption of Ofloxacin using the AC-MgO-Fe₃O₄ composite is superior through a thorough comparison of the FTIR analysis and adsorption capacity of the two composites.

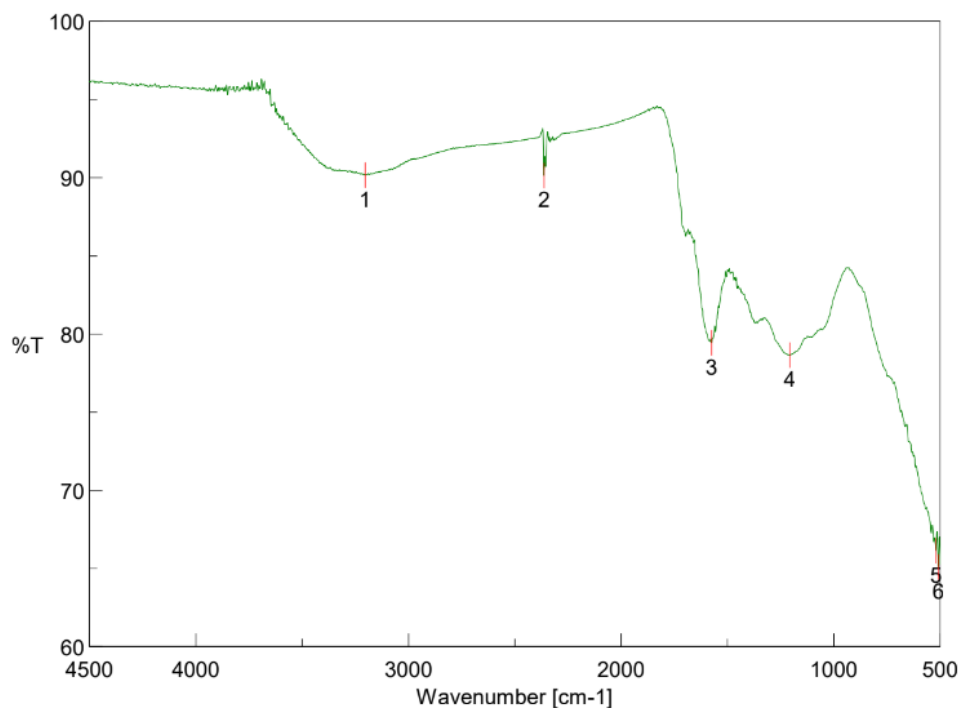


Figure:5.15: FTIR result of final adsorption of 500ppm at 5 hours.

Table 5.8: FTIR final adsorption result of peak obtained.

S.NO	Position	Intensity
1.	3203.18	90.1607
2.	2362.37	90.1235
3.	1574.59	79.4335
4.	1206.26	78.638
5.	519.722	66.1321
6.	509.115	65.0862

These peaks show that the final adsorption of Ofloxacin contains a variety of functional groups that are typical of the carbonaceous material made from corn husk. Organic compounds frequently exhibit O-H stretching vibrations, which are represented by the peak at 3203.18 cm^{-1} . It's possible that other functional groups or C-C triple bonds are responsible for the peak at 2362.37 cm^{-1} . Peaks at lower wavenumbers, like 519.722 cm^{-1} , 509.115 cm^{-1} , and 1206.26 cm^{-1} , might represent various kinds of vibrations in the carbon structure. As reported by Sulaiman et al. (2022), For all samples, the O-H stretching vibration in phenolic hydroxyl groups was detected at a bandwidth of approximately 3446.18–3414.08 cm^{-1} . Oxygen is lost during the activation and surface modification process, which is why this region's intensity has decreased. Indicating the existence of C-H stretching connected to alkane groups, the other identical peaks were discovered at bandwidths between 2926.22 and 2913.15 cm^{-1} . They found that their C-C multiple bond stretching occurred at wavelengths of approximately 2100 and 2300 cm^{-1} , and their CH_2 bending vibrations were detected at 1465.92–1429.33 cm^{-1} .

5.6 ISOTHERM STUDIES

Various isotherm approaches, such as Langmuir, Freundlich, Langmuir–Freundlich, and Temkin expressions, were used to explain the dye-binding process with the adsorbent. The current study proposed varied dye concentrations ranging from 100 – 1000ppm at pH 7, temperature 35°C, and an equilibrium contact period of 1hour. Among the parameters analyzed, **Freundlich** isotherm was the best fitting isotherm.

Table 5.9: Isotherm study

Ci	OD	Ce	Ci – Ce	qe = (Ci-Ce) V/m	1/qe	1/ce	ln qe	ln ce
100	0.05	16.030	83.96	0.00763	130.99	0.0623	6.875	5.7744
200	0.09	28.151	171.84	0.01562	64.009	0.0355	5.959	5.3376
300	0.17	52.393	247.60	0.0225	44.425	0.0190	5.493	4.9587
400	0.014	5.1211	394.87	0.03589	27.856	0.1952	4.727	4.2333
500	0.004	2.0909	497.90	0.04526	22.092	0.4782	4.295	3.3375
600	0.021	7.2424	592.75	0.05388	18.557	0.1380	3.820	2.8799
700	0.031	10.272	689.72	0.06270	15.948	0.0973	3.369	2.1294
800	0.034	11.181	788.81	0.07171	13.944	0.0894	2.635	1.4142
900	0.038	12.393	887.60	0.08069	12.392	0.0806	1.717	0.9172
1000	0.022	7.5454	992.45	0.09022	11.083	0.1325	0.90547	0.720945

Volume = 0.1

Mass = 1100mg

Table 5.10: Freundlich Isotherm Model

ln qe	ln ce
6.87519	5.774481
5.95904	5.337601
5.49381	4.958791
4.72707	4.233391
4.29523	3.337599
3.82087	2.879956
3.36935	2.129493
2.63511	1.414289
1.71712	0.917208
0.90547	0.720945

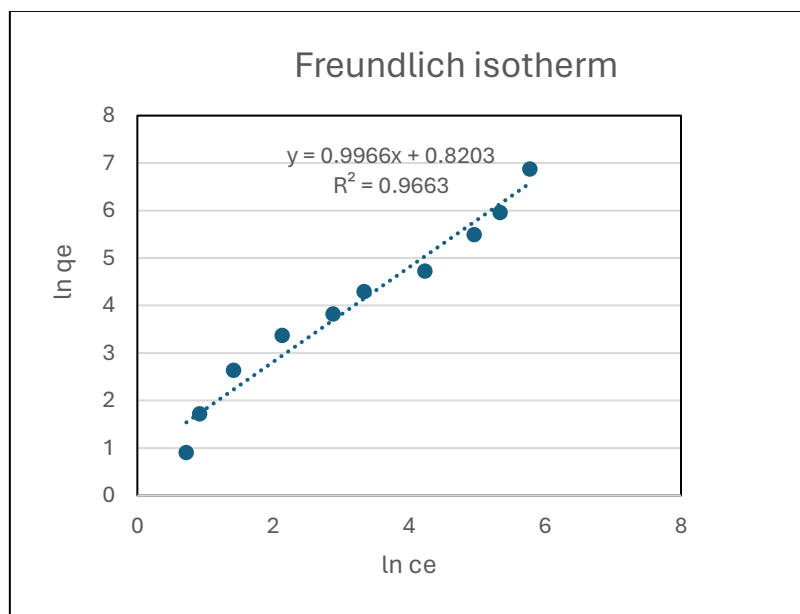


Figure:5.16: Isotherm model (Freundlich).

The data demonstrates 20 data points that correspond to the values of $\ln(q_e)$ and $\ln(C_e)$. Depending on the starting concentration, the $\ln(q_e)$ values show a large range of adsorption capacities, ranging from 0.720945 to 6.87519. Similarly, the range of $\ln(C_e)$ values, which represent different initial concentrations of ofloxacin, is 0.90547 to 5.774481. The Freundlich isotherm was considered suitable for adsorption on heterogeneous surfaces where there was a wide range of adsorption energies. It suggested that the adsorption sites were energetically different, and that the adsorption capacity decreased as the concentration of the adsorbate increased.

For the study on the removal of Ofloxacin from pharmaceutical waste using a bimetallic nanoparticle incorporated with activated carbon from corn husk, it was found that the Freundlich isotherm was the best fitting, indicating that the adsorption process was favorable and involved multilayer adsorption on a heterogeneous surface. The Freundlich model also suggested that the adsorption capacity of the composite material increased with increasing Ofloxacin concentration, which was typical for many adsorption processes on activated carbon-based materials.

Overall, the Freundlich isotherm study provided valuable insights into the adsorption behavior of Ofloxacin on the composite material and confirmed its potential for removing this antibiotic from pharmaceutical waste (Kong *et al.*, 2017).

CHAPTER 6

SUMMARY AND CONCLUSION

The project titled "Utilizing activated carbon derived from corn husk incorporated with bimetallic nanoparticles to eliminate Ofloxacin from pharmaceutical waste" aimed to develop a sustainable and effective method for removing Ofloxacin, a common pharmaceutical compound, from wastewater.

The process began with the collection of corn husks, which were washed, dried, and ground into a fine powder. This powder was then activated using nitric acid (HNO_3) to create activated carbon, which was characterized using scanning electron microscopy (SEM) and Fourier-transform infrared spectroscopy (FTIR) to confirm its structure and surface properties.

MgO nanoparticles were synthesized from *Tecoma stans* flower extract and characterized using SEM. Fe_3O_4 nanoparticles were prepared via the coprecipitation method and characterized using SEM as well.

The adsorption of Ofloxacin was first tested using activated carbon, as well as activated carbon incorporated with MgO, and activated carbon incorporated with Fe_3O_4 nanoparticles. The concentration of these adsorbents was optimized for maximum efficiency. Subsequently, adsorption experiments were conducted using a composite of activated carbon, MgO nanoparticles, and Fe_3O_4 nanoparticles (AC-MgO- Fe_3O_4) with a ratio of 1000mg-50mg-50mg. The maximum adsorption of Ofloxacin was found to occur at a concentration of 500ppm over a 5-hour period.

The initial and final adsorption samples at 500ppm were filtered and collected, then characterized by SEM and FTIR to confirm the adsorption of Ofloxacin onto the adsorbent. Isotherm studies were conducted, and the Freundlich isotherm model was determined to be the best fitting model for the adsorption process. The Freundlich model describe adsorption onto a heterogeneous surface.

This project demonstrates a novel and environmentally friendly approach to removing Ofloxacin from pharmaceutical waste using bimetallic nanoparticles incorporated with activated carbon derived from corn husk.

In conclusion, this study demonstrates the effectiveness of a novel composite material comprising bimetallic nanoparticles (MgO NPs-Fe₃O₄ NPs) incorporated with activated carbon from corn husk for the removal of Ofloxacin from pharmaceutical waste. The adsorption studies, monitored using UV-visible spectroscopy, showed that the composite material efficiently adsorbed Ofloxacin, with maximum adsorption occurring at 5 hours at a concentration of 500 ppm. Characterization of the activated carbon, MgO nanoparticles, and Fe₃O₄ nanoparticles using SEM and FTIR spectroscopy provided valuable insights into their morphological and chemical properties, confirming their suitability for the adsorption process. Isotherm studies further supported the effectiveness of the composite material, with the Freundlich isotherm model identified as the best fit for describing the adsorption process. Overall, this study underscores the potential of the bimetallic nanoparticle incorporated with activated carbon composite as a promising solution for the removal of Ofloxacin from pharmaceutical waste, contributing to the development of effective and sustainable methods for addressing pharmaceutical pollution in the environment.

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ANNEXURE I

Enrollment Id

Your GATE 2024 Result [BT]

Name

V KOWSALYA DEVI

Registration Number

BT24S57424189

Gender

Female

Parent's/Guardian's name

M VELDOSS

Date of Birth (YYYY-MM-DD)

2001-04-28

Examination Paper

Biotechnology (BT)



Photograph



Signature

Marks out of 100[#]

19

Qualifying Marks^{##}

38.9

35

25.9

General

OBC-NCL/EWS

SC/ST/PwD

[#]Normalized marks in case of multisession papers (CE and CS).

^{##}A candidate is considered qualified if the marks secured are greater than or equal to the qualifying marks.

