

Adsorption of Metformin Hydrochloride from Aqueous Medium Using *Azadirachta Indica* Bark Derived Biochar and GO-Biochar Composite

Submitted in partial fulfillment of the requirements for the award of
Bachelor of Technology degree in Chemical Engineering

by

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**DEPARTMENT OF CHEMICAL ENGINEERING
SCHOOL OF BIO AND CHEMICAL ENGINEERING**

SATHYABAMA

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

**Accredited with Grade "A++" by NAAC
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DEPARTMENT OF CHEMICAL ENGINEERING

BONAFIDE CERTIFICATE

This is to certify that this Project Report is the bonafide work of **MALIKAL MULKI.A (40190012)** and **PRITHIVIRAJAN.D (40190017)** who carried out the project entitled **"ADSORPTION OF METFORMIN HYDROCHLORIDE FROM AQUEOUS MEDIUM USING AZADIRACHTA INDICA BARK DERIVED BIOCHAR AND GO-BIOCHAR COMPOSITE"** under our guidance from December 2023 to April 2024.

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We, **MALIKAL MULKI.A (40190012)** and **PRITHIVIRAJAN.D (40190017)** hereby declare that the Project Report entitled "**ADSORPTION OF METFORMIN HYDROCHLORIDE FROM AQUEOUS MEDIUM USING AZADIRACHTA INDICA BARK DERIVED BIOCHAR AND GO-BIOCHAR COMPOSITE**" done by me under the guidance of **Prof. A. Annam Renita** (Internal) of Sathyabama Institute of Science and Technology and **Mr. Bharath Balji, M. Tech** (External) at SSN College of Engineering is submitted in partial fulfillment of the requirements for the award of Bachelor of Technology degree in Chemical Engineering.

DATE: 06-04-2024

PLACE: Chennai

SIGNATURE OF THE CANDIDATES

The block contains two handwritten signatures in blue ink. The top signature is 'Prithvi' with a horizontal line underneath it. The bottom signature is 'Malik' with a horizontal line underneath it.

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ABSTRACT

In this study the removal of antidiabetic pharmaceutical pollutant (Metformin Hydrochloride) from aqueous medium was investigated with *Azadirachta indica* bark derived biochar (AIB) and Graphene Oxide doped biochar composite (GAIB) under different process conditions. The AIB adsorbent was prepared by physical activation. Graphene oxide was synthesized using modified hummers method and a GAIB composite was prepared. Batch mode experiments were carried out to investigate the influence of adsorbent dosage, pH, contact time and temperature. The optimum experimental conditions were determined for both of the prepared adsorbents. The optimum experimental conditions for AIB were as follows pH 6, contact time 120 minutes, initial concentration 10 mg/L, adsorbent dosage 10 g/L and temperature 30°C. Optimal experimental conditions of GAIB were as follows pH 6, contact time 120 minutes, initial concentration 10 mg/L, adsorbent dosage 5 g/L, and temperature 30°C. For both the adsorbents isotherm data followed Freundlich model and pseudo-first order adsorption. The $Q_{\max}$ value increased from 5.878 mg/g to 11.84 mg/g from AIB to GAIB which has reportedly increased by 99%. The reaction was found to be endothermic from the obtained thermodynamic properties. This study highlighted the potential of AIB, GAIB composite as cost-effective and eco-friendly sustainable adsorbent providing a promising approach of adsorption of pharmaceutical pollutants from waste water.

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LIST OF ABBREVIATIONS

AIB - *Azadirachta Indica* bark derived biochar

GAIB – Graphene Oxide doped *Azadirachta India* bark biochar composite

MH – Metformin Hydrochloride

GO – Graphene Oxide

FT-IR - Fourier transform infrared spectroscopy

FESEM - Field Emission Scanning Electron Microscopy

XRD - X-ray diffraction

BET - Brunauer–Emmett–Teller

EDAX - Energy Dispersive X-ray Analysis

EDS - Energy-dispersive X-ray spectroscopy

BJH - Barrett-Joyner-Halenda

UV – Ultra Violet visible spectrophotometer

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND

Our existence on Earth hinges upon three fundamental resources: water, air, and soil. These are nature's invaluable offerings to humanity. Among them, water takes precedence as it serves as the primary medium for the genesis of life. Water pollution from emerging contaminants is on the rise due to the increasing effects of urbanization, industrialization, and agricultural practices. Emerging contaminants encompass substances that are not currently subject to regulatory monitoring or public disclosure requirements regarding their existence in our water source and wastewater. Industrial formulations, chemicals, food additives, food packaging materials, metalloids, rare earth elements, pharmaceuticals, cosmetics, personal care items, surfactants, cleaning agents, and pathogens are just a few examples of the diverse components that fall under this area.

The main sources of these emerging pollutants include leachates from landfills, agricultural runoff, hospital effluents, industrial wastewater discharges, and livestock and aquaculture operations. Especially, the effluents from municipal wastewater treatment plants are a major source of recently identified pollutants in aquatic habitats.

1.2 PHARMACEUTICAL CONTAMINANTS: A MAJOR CONCERN

Pharmaceuticals are biologically active substances with well-defined mechanisms of action in both humans and animals. Prior to the 19th century, the primary source of therapeutics was natural compounds. This included the use of crude extracts from plants and various shrubs, which served as herbal medicines. These natural remedies were employed for purposes such as pain relief, wound healing, and the treatment of various illnesses. Progress in the realm of medical science played a pivotal role in the emergence of numerous synthetic therapeutic compounds during the latter part of the 19th century and throughout the 20th century. These compounds included substances like naphthalene, acetanilide, aspirin, ephedrine, and arsphenamine.

The widespread use of pharmaceuticals has raised alarm about their detection in the environment. This concern arises because a significant portion of these medicinal substances cannot be absorbed and processed by the human body, resulting in their excretion through feces and urine, ultimately entering municipal wastewater treatment facilities.

The key origins of pharmaceutical contaminants in the environment encompass pharmaceutical industries, hospitals, the disposal of expired medications, research projects employing therapeutic compounds, and animal waste. Among the sources, hospitals emerge as the predominant contributors to the release of pharmaceuticals into the environment. Wastewater discharged from hospitals carries a mixture of components, including pathogens, pharmaceutical residues and their metabolites, drug conjugates, radioactive elements, and various other chemical substances.

Individuals can potentially come into contact with pharmaceuticals that contaminate water environments by either consuming drinking water or ingesting aquatic organisms. Ongoing risk assessment studies are being conducted for both aquatic species and humans. However, it has been observed that the risk of exposure to pharmaceuticals is generally greater for aquatic species than for humans.

These small quantities of pharmaceuticals remain present in the environment for lengthy periods of time, affecting both targeted and non-targeted species. Moreover, medicinal drugs are frequently present in complex combinations containing a variety of unrelated compounds, each of which has unique pharmacological properties that may have additive or synergistic effects. This raises questions regarding the possible risks that medications dissolved in water offer to aquatic life's survival and function, as well as the possibility that these chemicals may cause genetic abnormalities or modifications.

1.3 METFORMIN HYDROCHLORIDE: AN EMERGING CONTAMINANT

Metformin Hydrochloride, an oral medication designed for managing type 2 diabetes, has become increasingly prevalent in medical practice due to the worldwide surge in diabetes cases. Due to its increasing use and subsequent discharge into wastewater, there is a growing concern regarding the environmental impact of Metformin Hydrochloride.

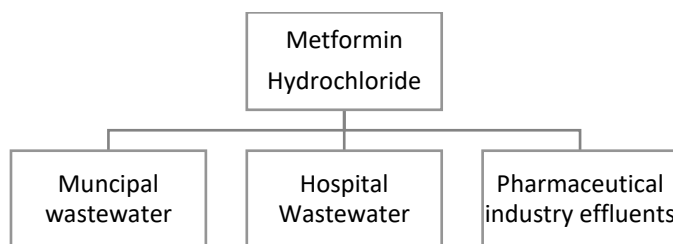


Fig 1.1 Sources of Metformin Hydrochloride

Metformin Hydrochloride, alternatively labeled as 1,1-Dimethylbiguanide hydrochloride, possesses the chemical composition $C_4H_{12}ClN_5$. This compound exists in a crystalline state and exhibits a molecular weight of 165.62 g/mol. Within its structure, there are six C—N bonds, and an examination of bond order reveals that four of these bonds exhibit bond orders nearing $4/3$, while the remaining two bonds can be characterized as single bonds. The structure of Metformin Hydrochloride can be given as follows.

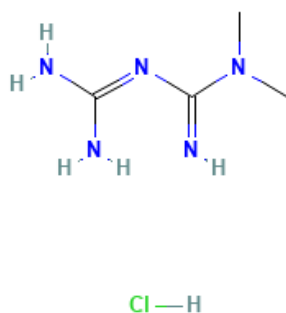


Fig 1.2 2-D Chemical structure depiction of Metformin Hydrochloride

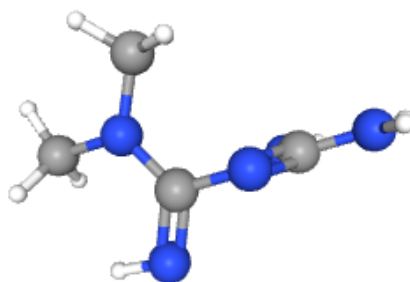


Fig 1.3 3-D Ball and stick structure of Metformin Hydrochloride

Metformin and one molar equivalent of hydrogen chloride combine to make metformin hydrochloride. It performs a number of tasks, including xenobiotic, hypoglycemia, and environmental contaminant roles.

Because of its extensive utilization, metformin and its derivatives are detected in wastewater and subsequently enter aquatic ecosystems. Consequently, metformin accumulates within organisms and the environment, potentially causing health issues when concentration levels exceed safe limits. Recent research indicates a global rise in the number of individuals diagnosed with diabetes. Among the medications frequently prescribed for type 2 diabetes, Metformin Hydrochloride stands out as a widely used option. In recent times, Metformin Hydrochloride has gained more attention for being one of the pharmaceuticals that is frequently found in aquatic ecosystems. This prevalence is attributed to its low K_{ow} , high pKa, and excellent solubility in water, resulting in concentration levels ranging from 64 to 98 $\mu\text{g/L}$ in domestic wastewater.

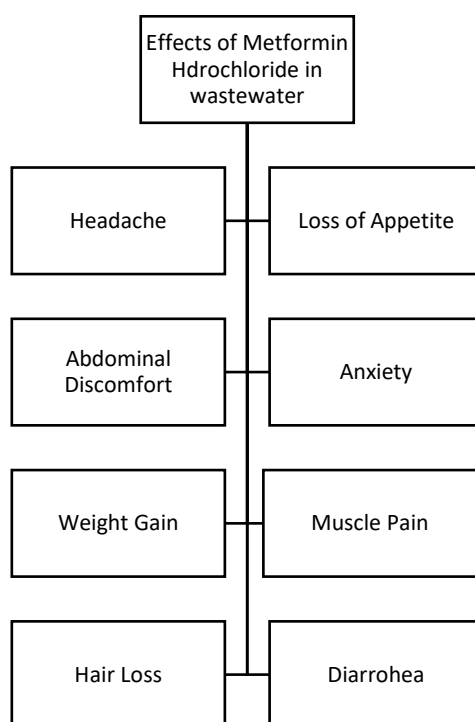


Fig 1.4 Effects of Metformin Hydrochloride

There are a lot of negative effects that have been reported from metformin being present in surface waterways. Surface waterways are becoming more and more contaminated with medicines, even with pre-discharge municipal water treatment. As conventional wastewater treatment methods are not consistently tailored to effectively eliminate various organic compounds, in addition to other inorganic and biological contaminants.

1.4 BIOCHAR AS AN ADSORBENT

Pharmaceuticals have been removed from wastewater employing a variety of physical and biochemical methods, such as oxidative catalytic processes, adsorption, membrane bioreactor treatment, and bio-system recovery. Adsorption is one of these techniques that has shown to be the most effective in eliminating dissolved organic contaminants from wastewater that is used in both industrial and domestic settings. This method has gained extensive usage due to its simplicity, high effectiveness, and cost-effectiveness. Nevertheless, a significant hurdle lies in the quest for effective and appropriate adsorbents capable of adsorbing a broad spectrum of pollutants. Utilizing cost-effective biochar adsorbents for the elimination of organic and inorganic contaminants in aqueous solutions is likely to offer a more cost-efficient approach compared to conventional methods for purifying water.

In the realm of adsorbing pollutants in aqueous environments, biochar presents unique advantages over activated carbon under certain circumstances. While activated carbon is recognized for its high surface area and specialized pore structure, biochar offers distinct benefits in specific contexts. With its porous composition, biochar demonstrates efficacy in capturing certain organic compounds and contaminants from water. Additionally, when utilized as a soil amendment, biochar facilitates water filtration as it traverses through soil integrated with biochar, thereby reducing the influx of pollutants into water bodies. In situations prioritizing sustainable solutions and considering soil-water interactions, biochar provides a comprehensive approach to pollutant adsorption in aqueous settings compared to activated carbon.

Through the pyrolysis of biomass in an oxygen-limited atmosphere, biochar is a solid matter rich in carbon. Neem (*Azadirachta indica*) is a tree species belonging to the Meliaceae family. Is found in large numbers in Indian subcontinent. The primary focus on cultivation of neem tree lies on utilization of neem leaves, seeds and oil. Often the barks are left behind after harvest of these primary components. 65.63% cellulose, 23.55% hemicellulose, and 9.04% lignin make up neem bark. All of which significantly influence the characteristics of biochar produced during pyrolysis. Notably, Neem is commonly found in Asian countries and is known for its medicinal properties.



Fig 1.5 Wood bark of Azadirachta indica tree



Fig 1.6 Biochar produced from wood bark of Neem

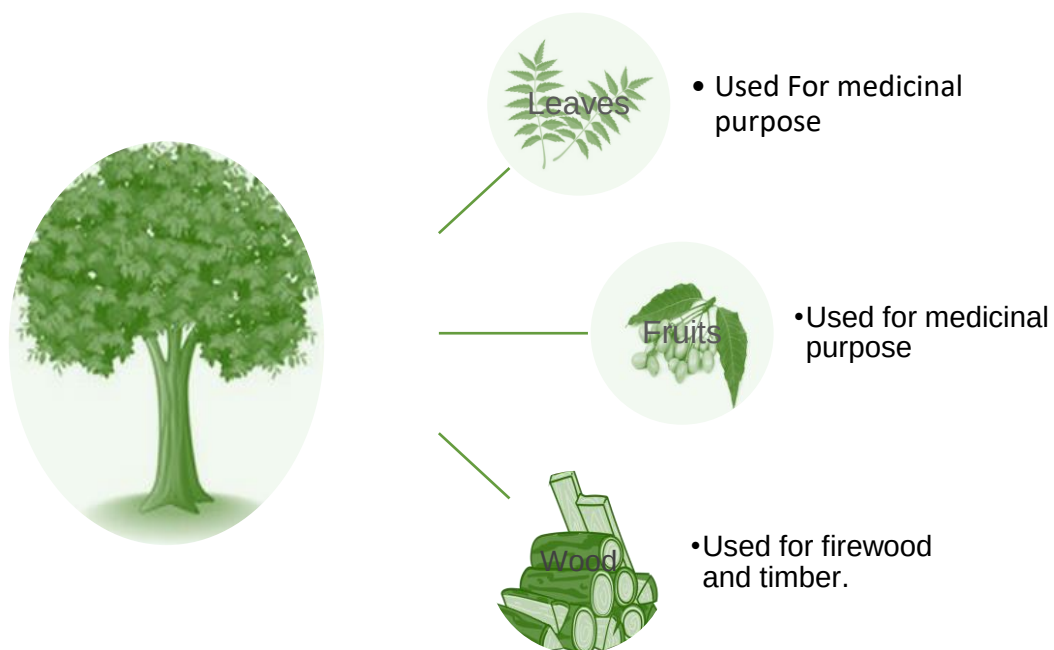


Fig 1.7 Uses of neem tree parts

1.5 GRAPHENE OXIDE

Graphene oxide is an incredibly thin layer of carbon atoms structured in a two-dimensional lattice. Its remarkable features have drawn attention from all over the world in a number of disciplines. Its remarkable qualities, which make it extremely adaptable, include great electrical conductivity, mechanical strength, optical transparency, and simplicity of modification. Many potential uses are available for graphene due to its exceptional properties and planar structure, especially in the domains of electronics and energy storage. Different methods for creating graphene with different sizes, forms, and qualities have been developed over time. Recently, research on graphene's potential use in environmental contexts—particularly in pollutant adsorption has taken center stage. Understanding graphene's effectiveness and basic mechanisms as an adsorbent for various contaminants, including organic molecules, has been the subject of research.

In the past, activated carbon has been a traditional adsorbent for waste water treatment because of its adaptability, safety, and broad range of applications. However, because of its high regeneration costs and chemical rigidity, it is not as effective as it might be. Graphene meets the demand for a superior carbon-based substitute because, in addition to being carbonaceous, its planar sheet-like form gives it a large surface area. As a result of graphene's polyaromatic π -system, which readily reacts with the aromatic rings of organic substances in water through π - π stacking interactions or a potent hydrophobic effect, graphene-based materials are highly effective adsorbents and have been used to remove dyes such as methylene blue (MB) and Rhodamine B (RhB), as well as pollutants like naphthalene and 1-naphthyl-amine and aspirin.

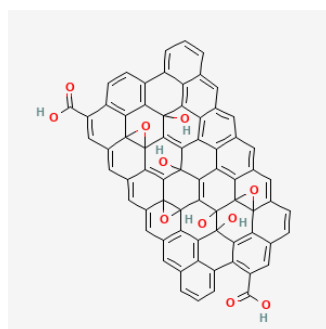


Fig 1.8 Structure of Graphene Oxide

CHAPTER 2

LITERATURE REVIEW

Menala Kalumpha et al.,(2019) Conducted research on affordable activated carbon was synthesized from Zea mays tassel by employing phosphoric acid as a crucial reagent. This activated carbon exhibited remarkable effectiveness in the removal of Metformin Hydrochloride, a prevalent pharmaceutical contaminant found in wastewater. Through a series of experiments, the optimal conditions for the adsorption process were meticulously identified. It was observed that the adsorption behavior followed both Langmuir isotherm and pseudo-second-order kinetics, underscoring the reliability and spontaneity of the process. These findings not only demonstrate the potential of Zea mays tassel as a precursor for producing efficient adsorbents but also highlight its suitability for targeted applications in pharmaceutical wastewater treatment. Overall, the study contributes to the advancement of sustainable and cost-effective solutions for mitigating pharmaceutical pollution in water bodies.

Mohamed E et al.,(2020) Conducted research on evaluated biochars derived from artichoke leaves through pyrolysis, further modified with sodium hydroxide, as potential adsorbents for the removal of Metformin Hydrochloride (MFH) from water. Among the tested variants, Artich-Bch-NaOH demonstrated superior performance compared to Artich-Bch. The study investigated various parameters, including shaking time, adsorbent dosage, initial MFH concentration, solution pH, temperature, and interfering ions, which were found to influence the removal of MFH. The adsorption process was effectively described by Langmuir and pseudo-second-order models. Furthermore, thermodynamic analyses conducted indicated the spontaneity and exothermic nature of the process.

Mohammad et al.,(2022) Researched on study involved in synthesizing of activated carbons from water hyacinth biomass through H_3PO_4 chemical activation and controlled carbonization. Different impregnation ratios (ranging from 0.5 to 3.0) and carbonization temperatures (ranging from 400°C to 800°C) were investigated to assess their impact on the resulting activated carbons. Notably, the sample

identified as 1.5 AC/600 exhibited the highest specific surface area at $1421 \text{ m}^2 \text{ g}^{-1}$, which positioned it as a promising candidate for metformin removal. The adsorption process was effectively described by Langmuir and pseudo-second-order models, indicating its spontaneity and endothermic nature. Successful desorption was achieved using a 0.1 M HCl/ethanol mixture, and the adsorbent showed potential for multiple cycles of reuse, thereby demonstrating its practical applicability in water treatment efforts.

Ferda Civan et al., (2021) Researched on synthesizing of novel magnetic-carbon composites (M-CCs) by incorporating Fe (II) and Fe (III) oxides onto various matrices (PAC, GNP, MWCNT), with the goal of assessing their effectiveness in removing Metformin Hydrochloride from water. Among the kinetic models that we evaluated, the pseudo-second-order model showed the best fit, with M-GNP demonstrating the highest adsorption rate. We found the Langmuir isotherm model to be applicable, indicating that M-GNP was the most efficient adsorbent under standard conditions, while M-MWCNT performed better at elevated temperatures. Additionally, in desorption tests, M-GNP exhibited superior effectiveness, with approximately 66% recovery of Metformin Hydrochloride after each cycle of use.

K.Balasubramani et al., (2020) Researched on the issue of micro-pollutants, such as pharmaceuticals in water, which posed a threat to living organisms. We looked at graphene oxide (GO) as a potential efficient adsorbent to remove model micropollutant metformin from water. The Hummers technique was used to synthesize GO, and its characteristics were carefully described. It was found that the material had notable pore volume, breadth, and surface area, all of which were indicative of mesoporous properties. Various adsorption parameters, including pH, temperature, time, adsorbent dose, and metformin concentration, were systematically investigated using statistical design techniques to establish optimal conditions for maximum removal efficiency. The maximal metformin adsorption capacity was discovered to be 122.61 mg/g , and a pseudo-first-order kinetic model described the adsorption process. The adsorption was shown to be exothermic and spontaneous by thermodynamic analysis. Additionally, desorption studies demonstrated that GO could be effectively regenerated using a 1 N sodium hydroxide solution for up to six cycles, underscoring its potential for practical application in water treatment processes.

Xixian Huang et al., (2016) Metformin hydrochloride (MF) adsorption was studied using hydrogen peroxide modified biochar (mBC) produced from *Alternanthera philoxeroides* (AP) biomass. The effects of pH and Cu (II) on MF adsorption were also investigated. The pseudo-second-order model described the adsorption process, according to an analysis of the adsorption kinetics, and the Freundlich model suited the adsorption isotherms the best. Thermodynamic analysis indicated that MF adsorption occurred spontaneously and was endothermic. It has been found that because MF species (cationic, zwitterionic, and anionic) vary depending on pH, pH had a substantial impact on MF adsorption capability. Furthermore, it was shown that MF adsorption was enhanced by Cu (II) in the pH range of 3.0–7.0, but that MF adsorption was decreased by higher Cu (II) concentrations. Cu (II) had no effect on MF adsorption at pH values higher than 7 or lower than 3.

S Zhu et al., (2017) investigated the possibility that newly discovered pollutants in water supplies may endanger living things. Effective removal strategies for these pollutants were judged required due to insufficient wastewater treatment. Graphene oxide (GO) was assessed for its ability to remove the emerging contaminant metformin. The research involved conducting systematic adsorption and kinetic experiments, which revealed that GO efficiently reduced metformin concentrations, offering a potential solution to this issue. The uptake of metformin on GO was influenced by factors such as temperature, pH, ionic strength, and background electrolyte. The adsorption kinetics showed rapid removal, with approximately 80% removal achieved within 20 minutes. Thermodynamic analysis indicated spontaneous and exothermic adsorption. A pH of 6.0 and a temperature of 288 K yielded the highest adsorption capacity. GO demonstrated excellent adsorption capacity over multiple desorption/adsorption cycles, with π – π interactions and hydrogen bonds playing a crucial role in metformin adsorption onto GO.

G De Bhowmick et al., (2022) For the purpose of batch sorption of metformin hydrochloride (MET), a specifically prepared biochar combination including macroalgae (MAC), microalgae (MIC), rice husk, and pine sawdust was investigated. The MAC and MIC algae combination was pyrolyzed to create the biochar mix, which was then chemically activated using hydrogen peroxide. The impact of pH was the main focus of the MET adsorption experiment. The isotherms were described using the Freundlich model, which showed values for the Freundlich

exponent and variable non-linearity. The presence of surface functional groups on the modified biochar was identified as the cause of the variability in MET adsorption that was observed. The most advantageous MET adsorption was shown by activated macroalgae biochar (MACAC) and microalgae biochar (MICAC) out of the four biochars examined; at pH 7, the maximum removal efficiency was attained, reaching up to 76%. The production of oxygen-containing surface functional groups was confirmed, and the chemisorption process was established as the main sorption mechanism, using a variety of analytical methods. Zeta potential measurements indicated a lower zeta potential at pH 7, enhancing the electrostatic attraction for both biochars, thereby making them effective at adsorbing positively charged contaminants. Economically speaking, the manufacture of pyrolyzed biochar from algal biomass seemed to offer promise, especially for high-end applications, even if capital expenditure figures were not given.

OS Jimoh et al., (2023) Researched on orange peels which were subjected to acid modification using ortho-phosphoric acid (OPAC) and were subsequently characterized. The functional groups and pore diameters of these OPAC materials were appropriate for the adsorption of metformin (MET) from water. At a contact period of 240 minutes, an initial MET concentration of 5 mg/L, a temperature of 323 K, and a pH of 7, optimal MET adsorption onto OPAC was found, yielding an astounding 97.23% clearance rate of MET. With a high affinity found at 303 K, the Freundlich isotherm model offered the greatest match for the sorption data. At 323 K, the monolayer sorption capacity was 50.99 mg/g, according to the Langmuir isotherm model. Kinetic studies favored the pseudo-second-order model, suggesting a physisorption mechanism. Thermodynamic analysis unveiled the process to be spontaneous, feasible, and endothermic. Overall, OPAC demonstrated efficiency as an adsorbent for removing MET from aqueous solutions.

L Hellmann et al., (2021) Researched on the potential of peach pits as a biosorbent for removing Metformin Hydrochloride from water was investigated. Experiments were conducted in a closed batch system, where various factors such as solution pH, temperature, stirring speed, and chemical treatments were considered. The biosorbent underwent multiple tests and characterizations, including kinetics, equilibrium, and thermodynamic parameters analysis. The ideal parameters were found to be pH 7, 25°C, and 100 rpm for both the untreated and chemically treated

biosorbents. As a consequence, following basic treatment and acid, the highest removal capacity was 49.14 mg/g. The Langmuir model suited the equilibrium data in the kinetic research, but the pseudo-second-order model gave the best explanation of the data. When compared to the raw biosorbent, the chemically treated biomasses showed much better drug removal capabilities. After basic treatment and acid, the greatest absorption capacity of 82.54 ± 1.34 mg/g was noted. According to these results, peach pits may be used as an affordable biosorbent to remove drugs from water.

CHAPTER 3

AIM AND SCOPE

3.1 AIM:

This research aims to develop and investigate the adsorption of Metformin Hydrochloride, an antidiabetic pharmaceutical pollutant, from an aqueous medium employing biochar (AIB) generated from *Azadirachta indica* bark and Graphene oxide doped biochar (GAIB). To prepare graphene oxide through modified hummers method and prepare a composite of AIB with GO which GAIB, and conduct comparative studies among these prepared adsorbents and investigate their efficiency by varying the adsorption parameters through batch studies.

3.2 OBJECTIVE:

- To prepare and characterize cost effective and efficient adsorbent i.e., *azadirachta indica* bark derived biochar, Graphene oxide by using modified hummers method and composite of biochar and graphene oxide.
- To conduct batch tests to ascertain the produced adsorbents' adsorption capacity and effectiveness for the removal of metformin hydrochloride from the aqueous solution.
- To determine the optimal conditions for carrying out adsorption of Metformin Hydrochloride from aqueous system by including factors such as concentration, adsorbent dosage, pH, temperature, and contact time.
- To conduct a comparative study on adsorption among the prepared adsorbents.

3.3 SCOPE:

- Application in pharmaceutical manufacturing industries to treat the effluents containing the toxic pollutants before discharged from the industries.
- These adsorbents can be used in water treatment plants to prevent the pharmaceutical pollutants from entering the water bodies.
- Reduction in environmental impact of the toxic pharmaceutical pollutants from affecting the aquatic ecosystems and public health.

CHAPTER 4

MATERIALS AND EXPERIMENTAL METHODS

4.1 MATERIALS REQUIRED:

Neem tree barks were procured from the surroundings of Kalpakkam in Tamil Nadu. Synthetic graphite powder (98% pure, SRL Chemicals), sulphuric acid (Thermo Fisher), Potassium Permanganate (extrapure 99%, SRL Chemicals), Metformin Hydrochloride (98% purity, Dhamtec), HCl (Thermo Fisher), hydrogen peroxide (SRL Chemicals), Double distilled water, Acetone (Thermo Fisher).

4.2 STOCK SOLUTION PREPERATION:

1000 mg/l stock solution was prepared initially by dissolving 0.1 g of Metformin Hydrochloride in 100 ml of distilled water. From the prepared stock solution series of dilutions were done according to the experimental demands and requirements. Analytical quantification of MH solution was confirmed with the help of double beam UV visible spectrophotometer. By analyzing the UV response curve, the maximum adsorption (λ_{max}) level occurred at 233 nm with quartz cuvettes. A standard curve for MH was plotted which was used to calculate the concentrations of MH in the studies.

4.3 ADSORBENT PREPARATION:

Dried barks from *azadirachta indica* trees commonly known as neem trees were collected from the surroundings of Kalpakkam, Tamil Nadu. The collected barks were washed thoroughly for several times using distilled water to remove the dirt particles from it. Then the washed barks were dried in an oven at 120°C for 8 hours. The dried bark was compacted using a domestic mixer-grinder and stored in an air tight container away from moisture.

In order to prepare the *azadirachta indica* bark biochar (AIB). The *azadirachta indica* bark powder was weighed and the *azadirachta indica* bark powder was pyrolyzed in a muffle furnace at 500°C for 2 hours. Then obtained AIB was washed several times and stored in an air tight container.



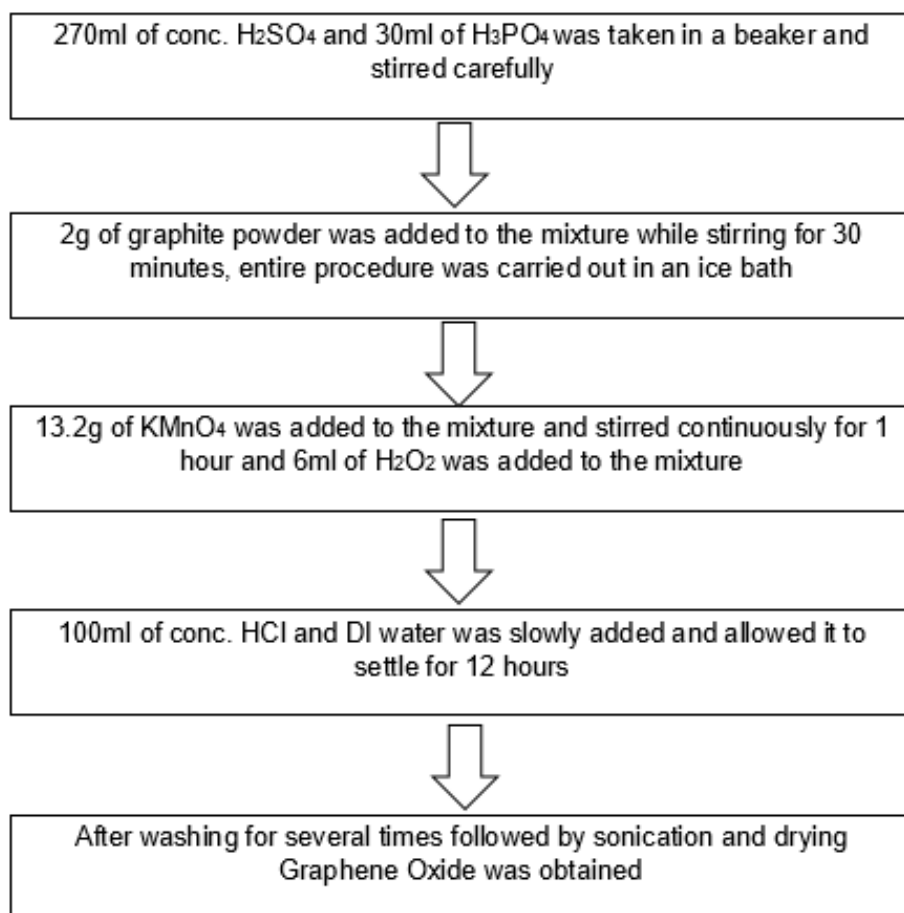
(a)

(b)

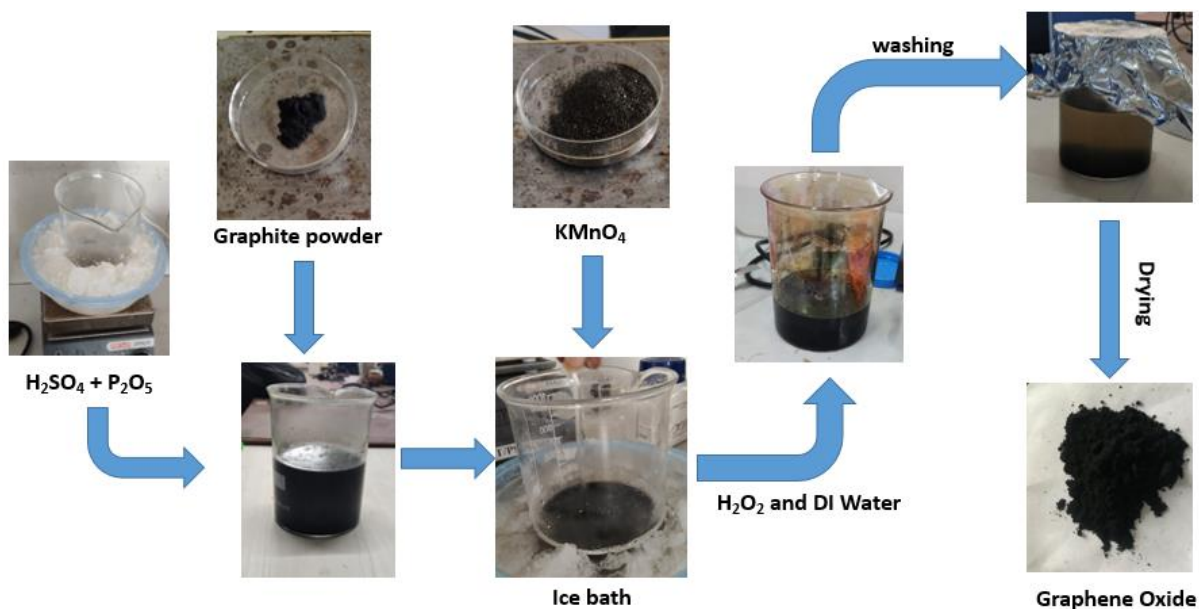
Fig 4.1 (a) Powdered Bark (b) AIB Biochar

4.4 SYNTHESIS OF GO:

The preparation of graphene oxide [GO] is carried out using Modified Hummer's method. Initially, 270 ml of concentrated H_2SO_4 and 30 ml of phosphoric acid was taken in a beaker and stirred carefully using a glass rod. Then, 2 g of synthetic graphite powder was measured and added to the mixture while stirring for 30 mins. This entire procedure was carried out below in an ice bath which was measured at $10\text{ }^\circ\text{C}$. This is done to control the high exothermic reaction. After ensuring the proper mixing, 13.2 g of potassium permanganate [KMnO_4] was added slowly to the mixture and stirred for 1 hour during which the color change from black to dark green colored solution was observed. This was followed by the addition of 6 ml of hydrogen peroxide [H_2O_2] to the slurry mixture. Later, 100 ml of concentrated hydrochloric acid and 300 ml of deionized water was added slowly and carefully. This final mixture is allowed to settle for 12 hours and left undisturbed. When the pH of the mixture was measured it was found to be highly acidic, which is why the mixture is neutralized by washing it using distilled water several times. It is then subjected to sonication process for exfoliation of graphene oxide layers. Finally, the settled graphene oxide slurry was filtered and dried in a hot air oven at $95\text{ }^\circ\text{C}$ for 10 hours.



(a)



(b)

Fig 4.2 (a)(b) Synthesis of Graphene Oxide

4.5 PREPERATION OF COMPOSITE ADSORBENT

The biochar which was previously prepared through pyrolysis and graphene oxide synthesized through modified hummer's method were used to prepare the composite adsorbent (GAIB). 200 milliliters of acetone have been added to five grams of AIB in a conical flask, and the mixture was sonicated for two hours. Simultaneously in the other hand 0.5g of GO was taken with 50ml of acetone and sonicated for 2 hours. The AIB mixture from the stirrer and GO mixture from the sonicator are mixed together in a beaker then allowed to sonicate in a sonicator for 2 hours. The obtained slurry was dried overnight at 50°C using tray drier. Finally the obtained composite adsorbent was stored in an air tight container.

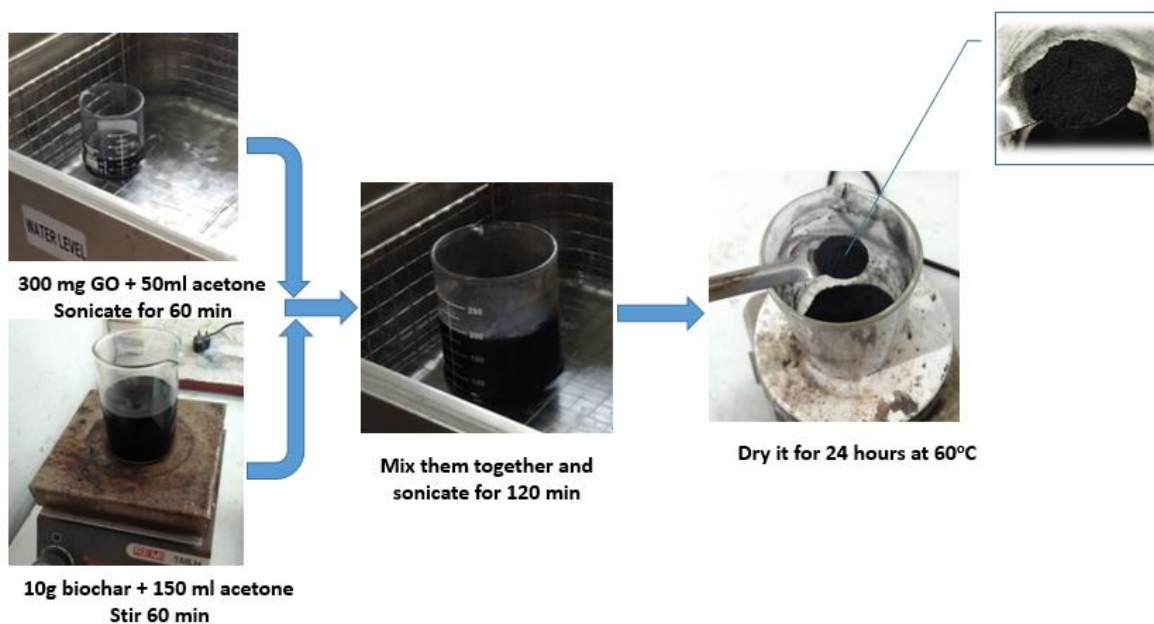


Fig 4.3 Synthesis of GAIB

4.6 CHARACTERIZATION OF ADSORBENTS:

Fourier Transform Infrared (FTIR) Spectroscopy was employed to analyze surface functional groups of AIB, GO and GAIB. The spectrum was obtained by recording wavelengths ranging from 4500 to 500 cm^{-1} in transmission mode. X-Ray Diffraction (XRD) was utilized to examine structural variations in the prepared adsorbents. Field-emission scanning electron microscopy (FESEM) with energy dispersive X-ray spectroscopy (EDX) was done to study the morphological structure of the adsorbents and the specific surface area of adsorbents was measured using the BET (Brunauer-Emmett-Teller) test.

4.7 ADSORPTION EXPERIMENTS:

The pace at which adsorption may possibly approach equilibrium was evaluated by batch adsorption tests. Batch adsorption experiments were conducted using AIB and GAIB in 100 mL of Metformin Hydrochloride (MH) solution. The determination of Metformin Hydrochloride (MH) was carried out using a UV spectrophotometer at a wavelength of 233 nm. Batch experiments were then conducted to assess the behavior of Metformin Hydrochloride (MH) on AIB and GAIB.

The batch study parameters, including pH (2,4,6,8,10) and dose rate (2,4,6,8,10,12,14 g/L) for AIB and (1,2,3,4,5,6,7 g/L) for GAIB, the effect of initial concentration (10,20,30,40,50 mg/L), contact time (30,60,90,120,150,180 minutes), and temperature (303,308,313,323 K) were evaluated. The pH of the mixture was adjusted using 0.1 N solutions of both HCl and Noah. Following the completion of adsorption, the filtrate underwent filtration through whatman filter papers. Subsequently, the Metformin Hydrochloride (MH) was conducted using a UV-Visible spectrophotometer at a wavelength of 233 nm.

The following formulas were used to determine the removal efficiency and amount of adsorbate absorbed by the adsorbent (q_e ; mg/g).

$$\text{removal efficiency} = \frac{C_i - C_e}{C_i} \times 100$$

$$q_e = \frac{C_i - C_e}{W} \times V$$

Where W is the mass of the adsorbent taken (g), V is the volume of the solution (L), C_i is the initial concentration (mg/L), and C_e is the equilibrium concentration (mg/L).

CHAPTER 5

RESULTS AND CHARACTERIZATION

This section attempts to clarify the effectiveness and processes behind the adsorption process of Metformin Hydrochloride by *Azadirachta Indica* bark-derived biochar and its composite with graphene oxide by rigorous experiments and careful analysis. The results reported here offer insightful information on the adsorbents adsorption capacity, kinetics, thermodynamics, and structural properties, opening the door to a fuller comprehension of their possible uses in pharmaceutical waste management and water treatment.

5.1 UV SPECTROSCOPY:

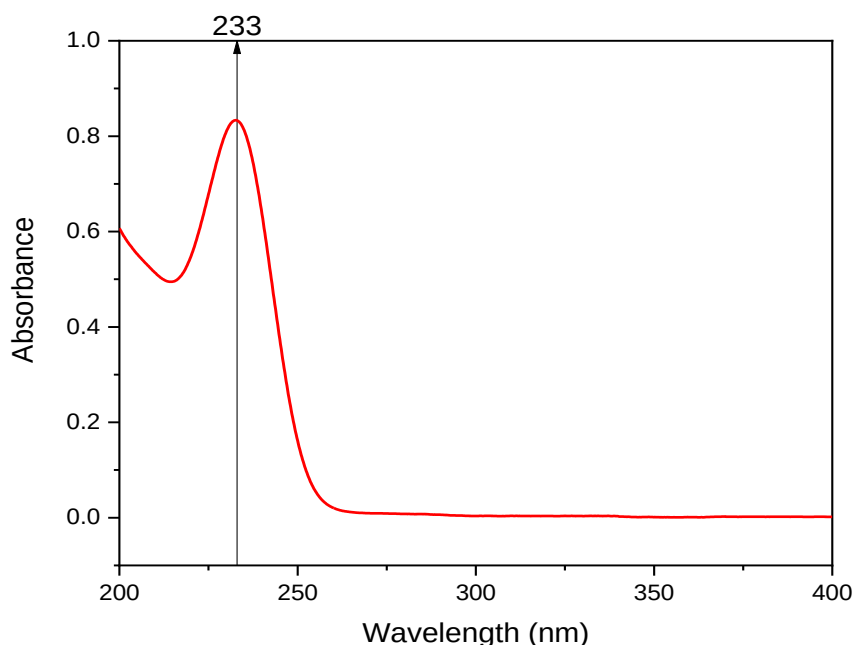


Fig 5.1 UV Spectra of Metformin Hydrochloride

A solution with a concentration of 10 ppm was created in order to calculate the ($\lambda_{\max}$) of MH. By using UV-Vis spectroscopy, the absorbance spectra was captured between 200 and 800 nm in wavelength. It was discovered that the $\lambda_{\max}$ was 233 nm, as Fig. 5.1 illustrates.

5.2 FT-IR ANALYSIS:

5.2.1 FT-IR of AIB:

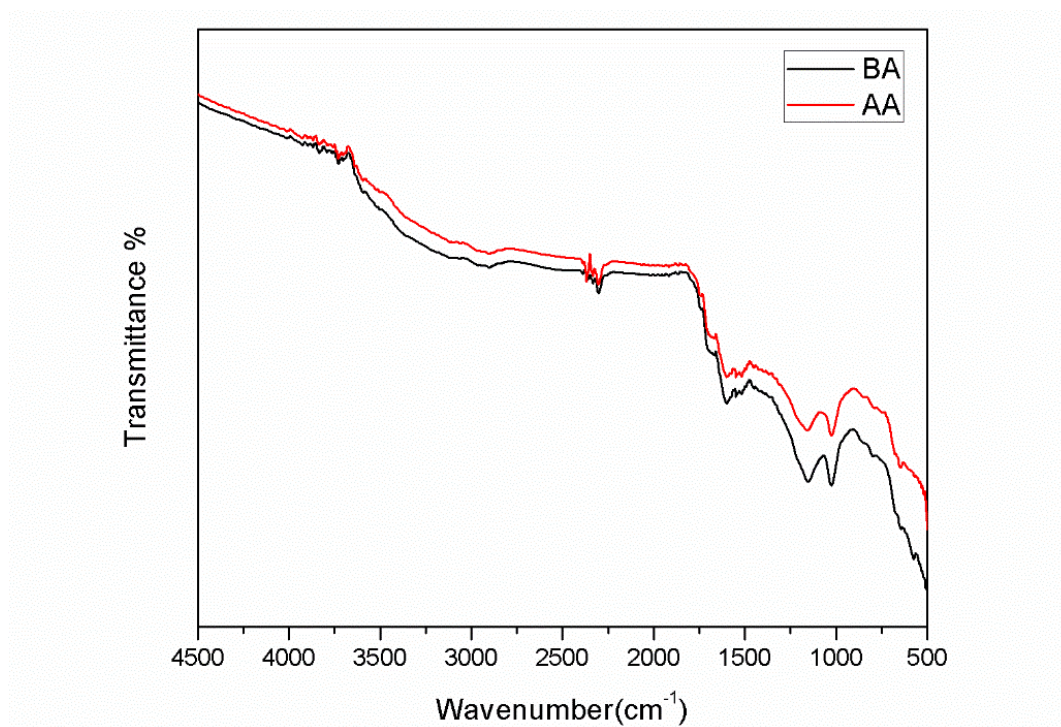


Fig 5.2 FT-IR Spectra of AIB before and after adsorption

In the FTIR spectrum of AIB before adsorption (BA) and after adsorption (AA), the presence of aromatic C=C (carbon-carbon double bonds) stretching vibrations often corresponds to a peak that is approximately 1597 cm⁻¹. The observed peak in the context of biochar could suggest that the material comprises aromatic carbon structures. Following the pyrolysis process used to form biochar, lignin, a component of plant biomass, can break down to yield aromatic carbon structures. This peak, which is indicative of aromatic chemicals, often appears in biochar spectra as a result of the burnt plant matter present. A peak at about 1154 cm⁻¹ often corresponds to C-O stretching vibrations, which are commonly symptomatic of C-O single bonds. This peak could point to that there is a presence of ethers, other oxygen-containing functional groups, or aliphatic hydroxyl groups (alcohols) in the structure of biochar. A peak roughly 1025 cm⁻¹ is frequently connected to C-O-C (carbon-oxygen-carbon) stretching vibrations, which are a sign that ether functional groups have been discovered in a sample. This peak could point to that there is a presence of ethers or other organic molecules containing oxygen in the chemical structure of biochar.

5.2.2 FT-IR of GO:

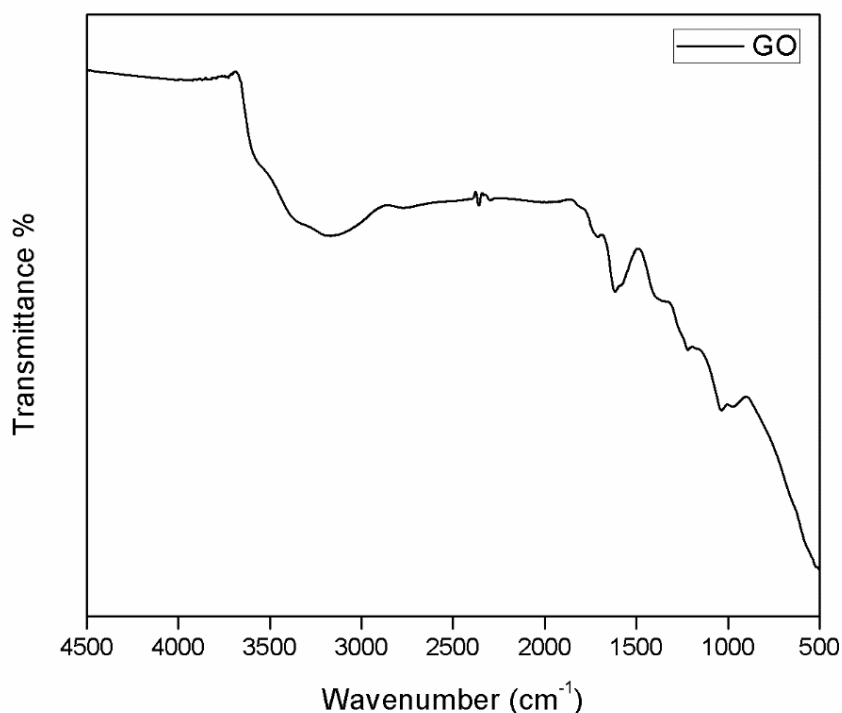


Fig 5.3 FT-IR Spectra of GO

The FTIR (Fourier-Transform Infrared) spectrum of graphene oxide (GO) has a peak at 3167 cm^{-1} that is most likely related to O-H stretching vibrations, which show the presence of hydroxyl (alcohol) groups. Oxygen-containing functional groups are the hallmark of GO, and its FTIR spectra is characterized by O-H stretching vibrations. In an FTIR (Fourier-Transform Infrared) spectrum, a peak at around 1035 cm^{-1} is frequently linked to C-O (carbon-oxygen) stretching vibrations, which are generally suggestive of the existence of oxygen-containing functional groups in a substance. A peak at 1035 cm^{-1} is significant in the context of graphene oxide (GO), which is well-known for having functional groups that include oxygen. Graphite is converted into GO through an oxidation process that adds groups containing oxygen.

5.2.3 FTIR OF GAIB:

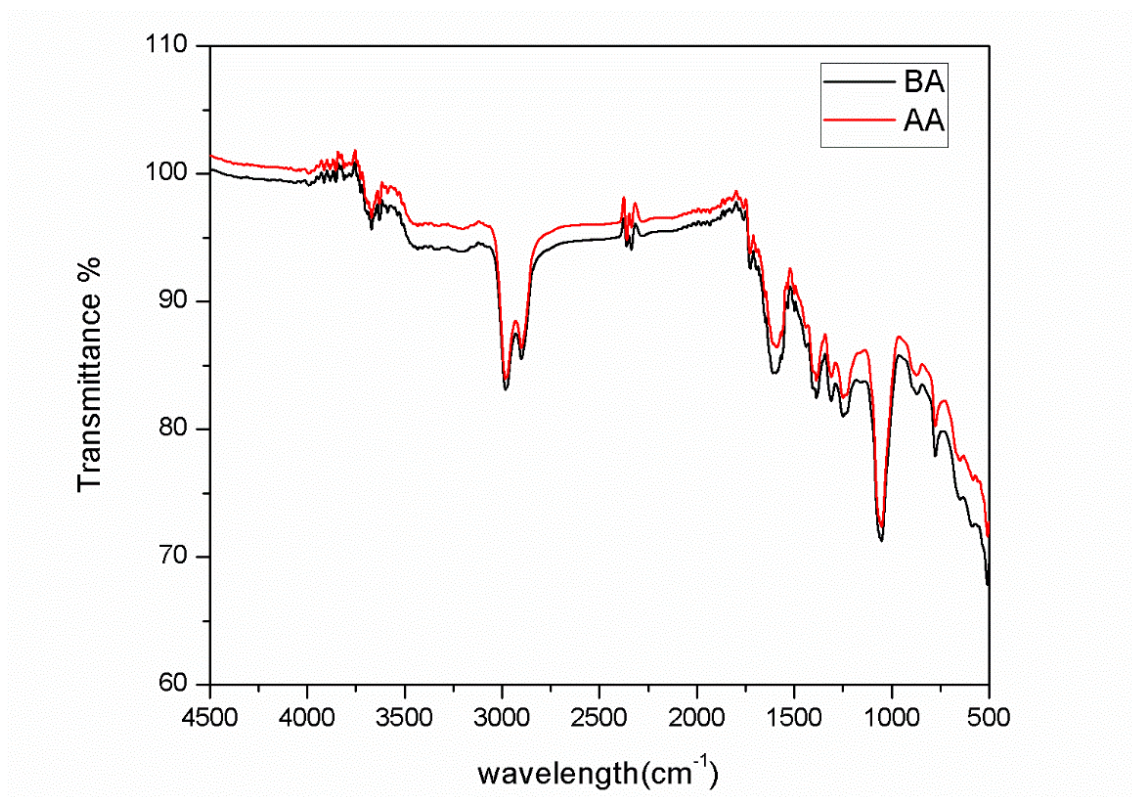


Fig 5.4 FTIR spectra of GAIB

The FTIR (Fourier-Transform Infrared) spectrum of GAIB before adsorption (BA) and after adsorption (AA), has a peak at 3992, 3669, cm⁻¹ that is most likely related to O-H stretching vibrations, which show the presence of hydroxyl (alcohol) groups. The FTIR peak detected at 2982 cm⁻¹ is commonly in connection with the stretching vibration of C-H (carbon-hydrogen) bonds, which are frequently present in alkane functional groups, peak detected at 1610 cm⁻¹ is commonly in connection with the stretching vibration of C=C (carbon-carbon double bonds), which are frequently present in aromatic compounds or conjugated systems. The FTIR peak detected at 2279 cm⁻¹ is often in connection with the stretching vibration of a carbon-carbon triple bond (C≡C), which is commonly found in alkynes.

5.3.1 XRD ANALYSIS OF AIB:



A promising technique for evaluating the structural makeup of biochar, a material rich in carbon that is produced by pyrolyzing material that is organic, is X-ray diffraction (XRD). Rather than featuring distinct, sharp peaks, patterns usually have wide, diffuse ones. This quality is a reflection of the amorphous, disordered carbon structure of biochar.

5.3.2 XRD SPECTRA OF GAIB:



The GAIB sample before adsorption were subjected to x-ray diffraction (XRD) analysis. The X-ray diffraction (XRD) analysis of GAIB unveiled a prominent peak at 24.73 degrees, alongside peaks at 15.63, 30.44, and 38.62 degrees at 2 θ . These peaks signify diffraction from distinct crystallographic planes within the composite material, offering crucial insights into its structural properties. From which can we infer that GAIB has crystalline structure due to more number of sharp and higher peaks compared to XRD results of AIB.

5.4 FESEM ANALYSIS:

5.4.1 AIB FESEM ANALYSIS:

To comprehend the structural and morphological changes that take place throughout the adsorption process, FESEM analysis is a vital method for evaluating biochar both prior to and during adsorption tests.

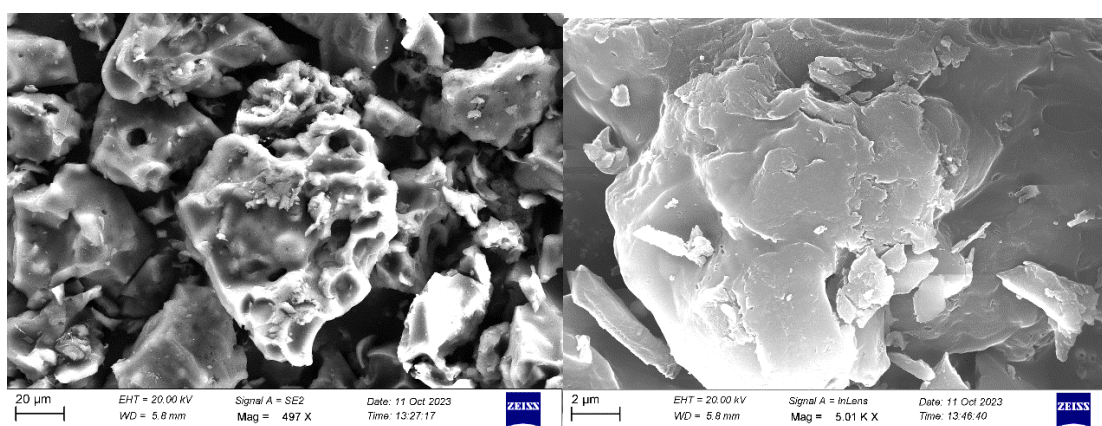


Fig 5.7 FESEM images of AIB before adsorption

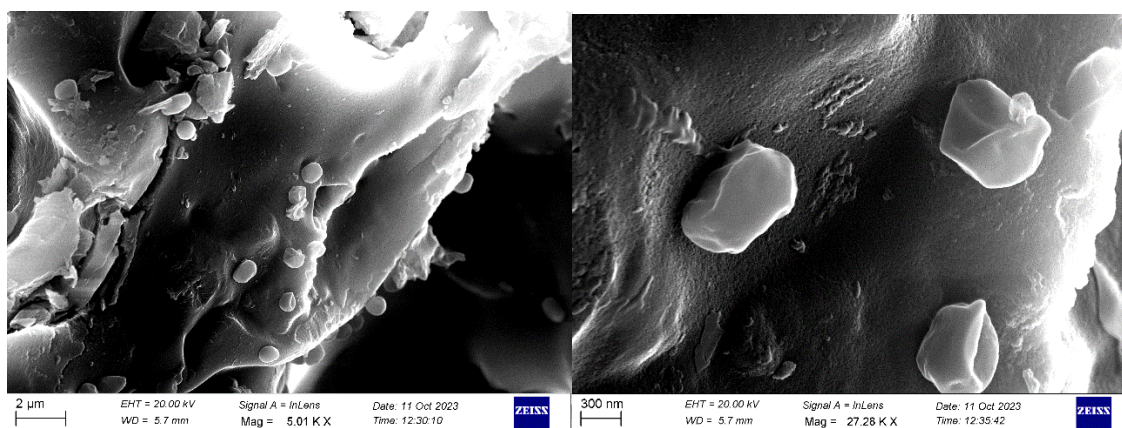


Fig 5.8 FESEM Images of AIB after adsorption

AIB samples were examined to Field Emission Scanning Electron Microscopy (FESEM) before and after adsorption. By comparing the images of before and after adsorption we can very clearly visualize from the structure that adsorption has taken place by seeing the pollutants being attached to the surface after adsorbent and prominent changes in the surface of the biochar after adsorption.

5.4.2 GAIB FESEM ANALYSIS:

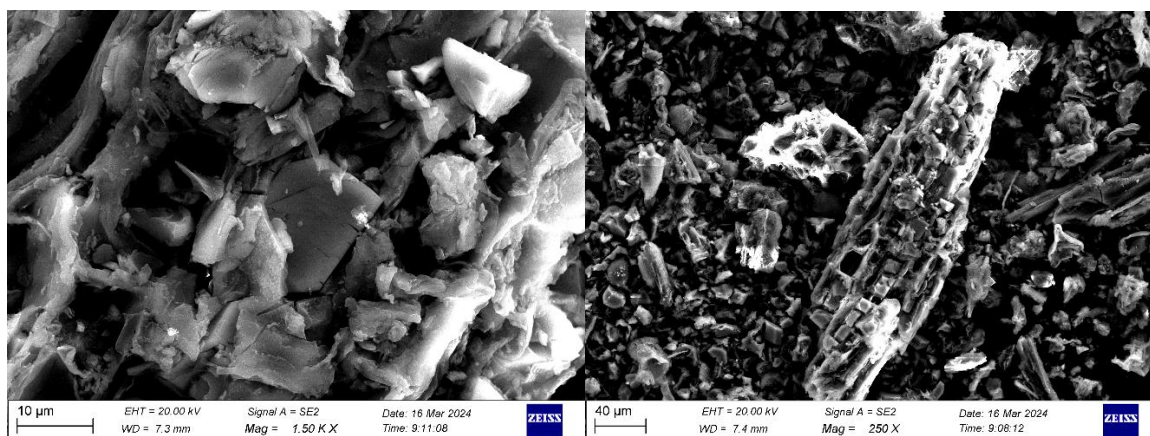


Fig 5.9 FESEM images of GAIB before adsorption

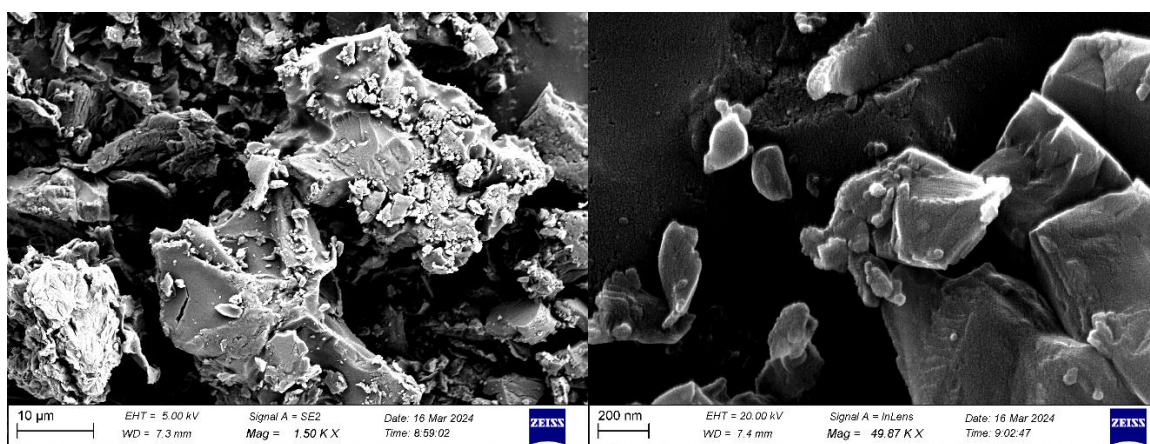


Fig 5.10 FESEM images of GAIB after adsorption

GAIB samples were examined to Field Emission Scanning Electron Microscopy (FESEM) before and after adsorption. In the before adsorption FESEM image of GAIB we can clearly see the rough and porous surface of the material which is very much essential for the adsorption to take place. In the after adsorption samples of GAIB we can see clearly that the pores of the adsorbent material surface is occupied by the adsorbate which is Metformin Hydrochloride (MH).

5.5 EDAX ANALYSIS:

EDAX, or energy dispersive X-ray analysis, is a useful analytical method for figuring out a material's constituent makeup. It can offer crucial information on the alterations in the elemental composition brought about by the adsorption process when applied to biochar both before and after adsorption of Metformin Hydrochloride.

5.6.1 EDAX ANALYSIS OF AIB:

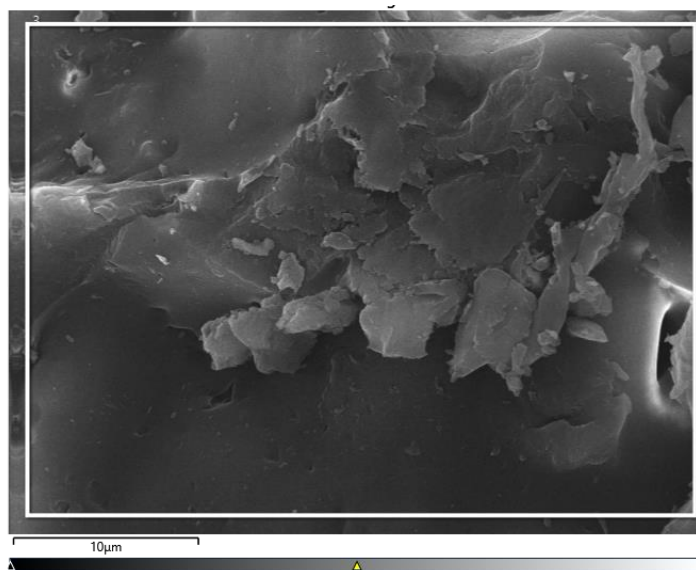


Fig 5.11 Electron image of AIB before adsorption

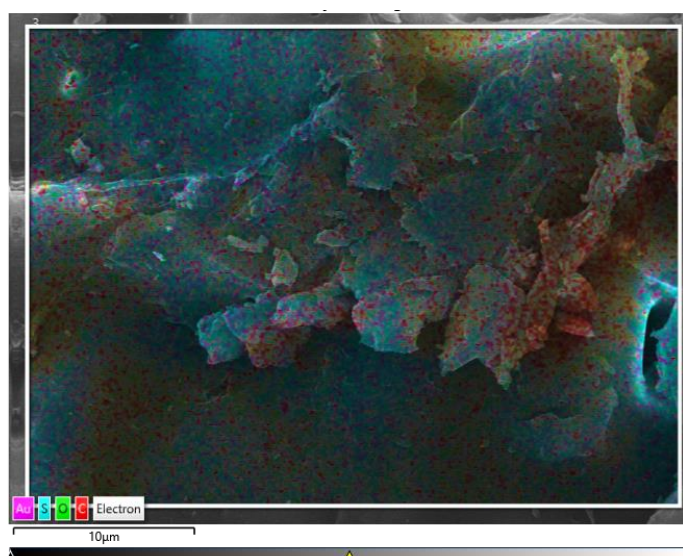


Fig 5.12 EDS Layered image of AIB before adsorption

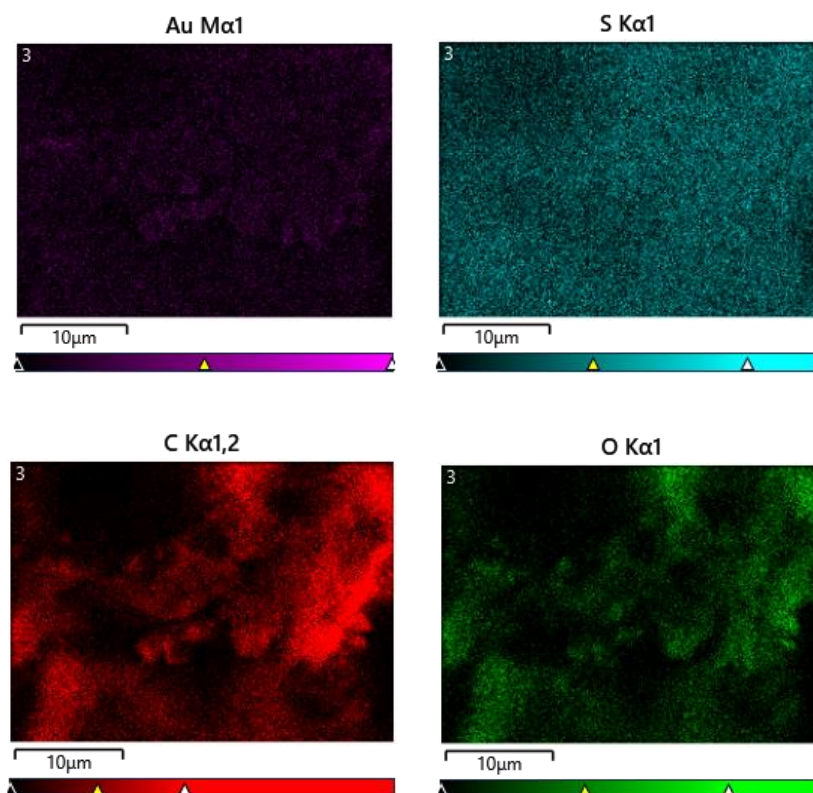


Fig 5.13 EDS Layered images of Au, S, C, O before adsorption

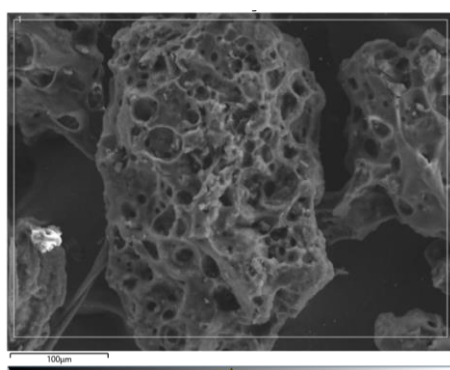


Fig 5.14 Electron image of AIB after adsorption

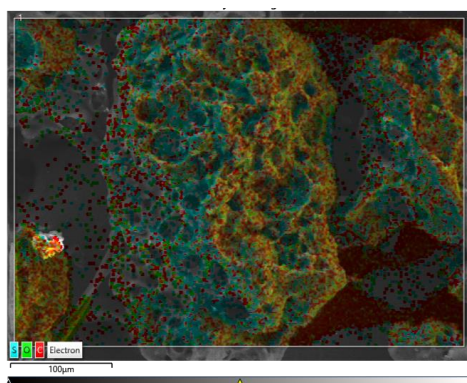


Fig 5.15 EDS Layered image of AIB after adsorption

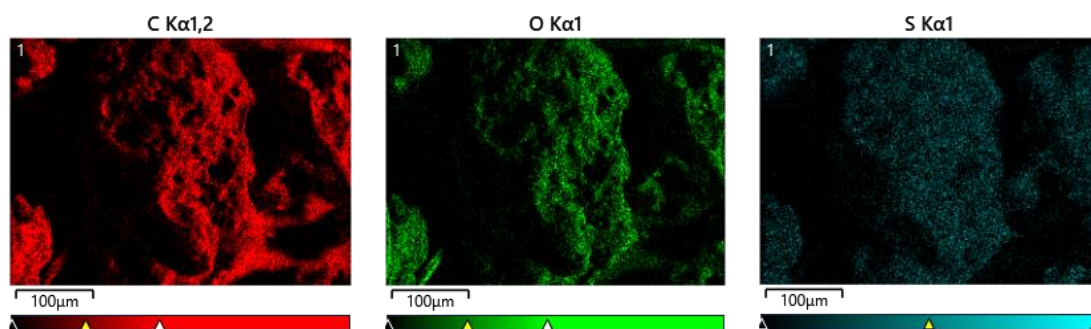


Fig 5.16 EDS Layered images of C, O, S after adsorption

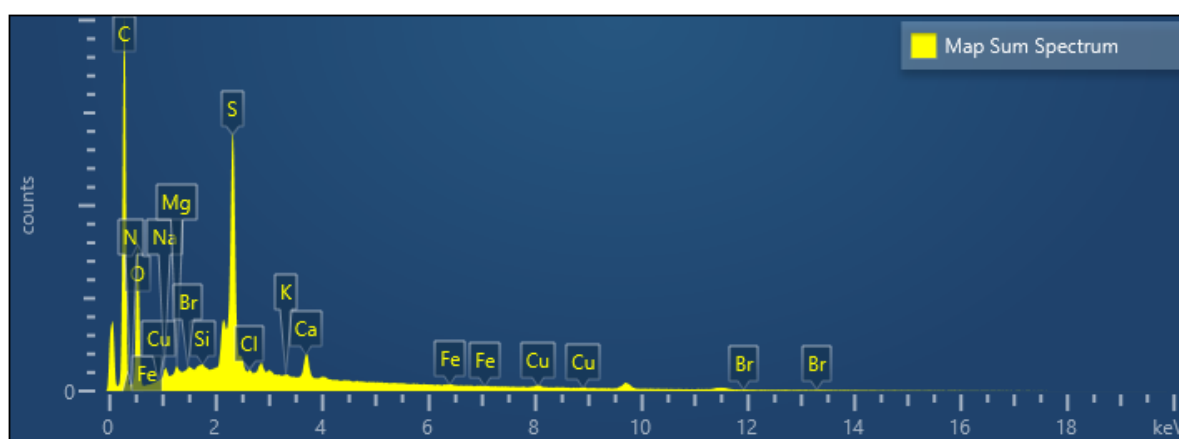


Fig 5.17 EDAX spectra of AIB before adsorption

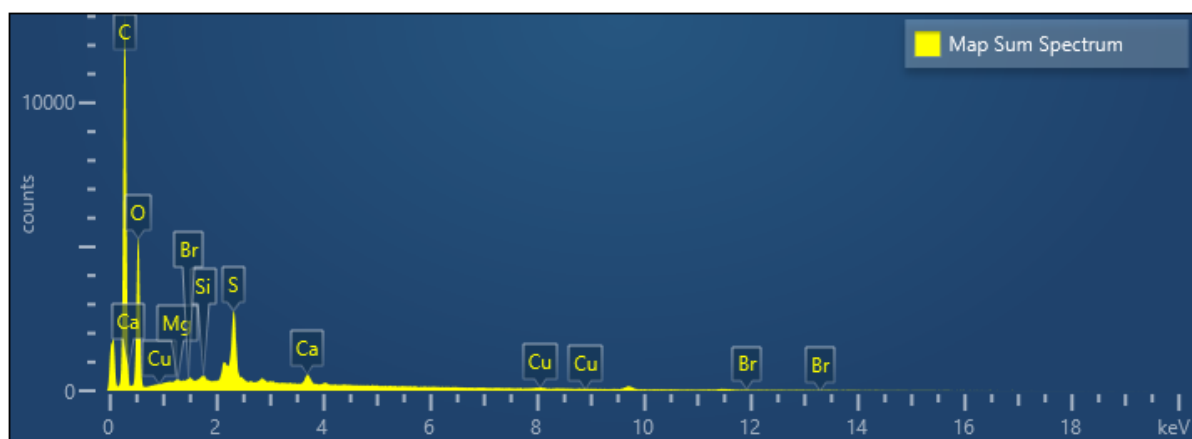


Fig 5.18 EDAX Spectra of AIB after adsorption

Table 5.1 EDAX spectra of AIB before and after adsorption

Element	Weight % before adsorption	Weight % after adsorption
C	76.29	72.73
N	0.47	-
O	20.37	26.11
Na	0.21	-
Mg	0.10	0.04
Si	0.03	0.05
S	2.03	0.81
Cl	0.05	-
K	0.02	-
Ca	0.30	0.16
Fe	0.03	-
Cu	0.09	0.06
Br	0.03	0.03

5.5.2 EDAX ANALYSIS OF GAIB:

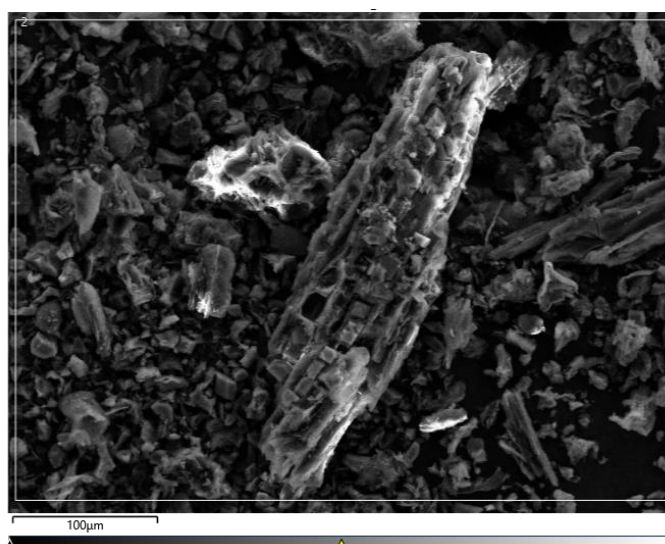


Fig 5.19 Electron image of GAIB before adsorption

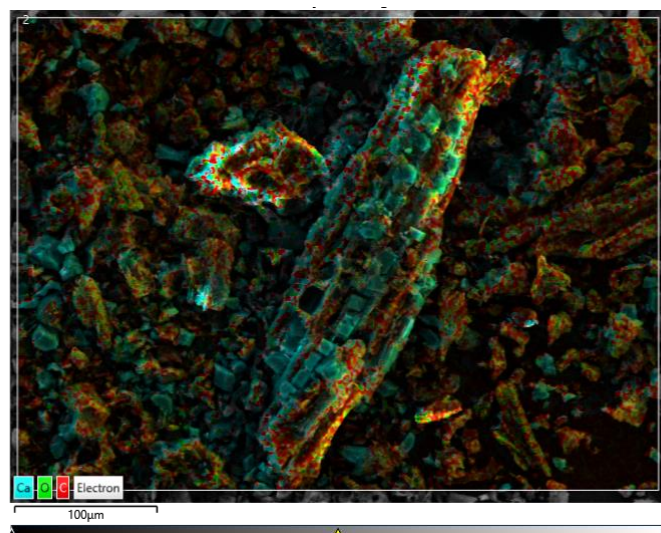


Fig 5.20 EDS layered images of GAIB before adsorption

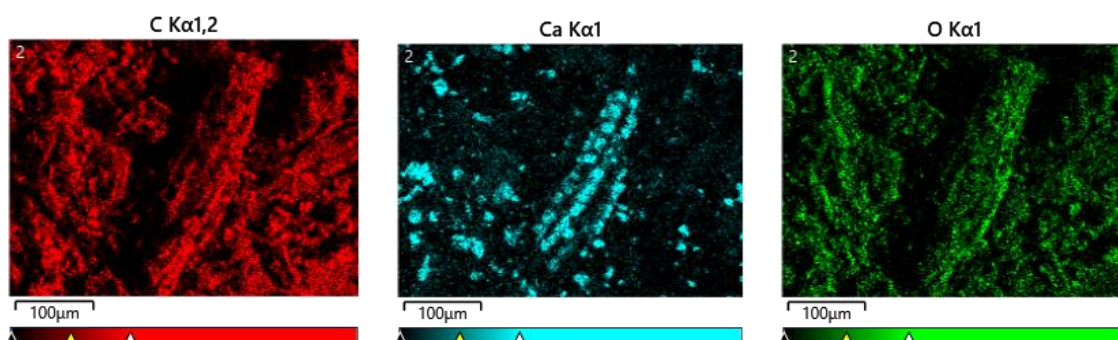


Fig 5.21 EDS Layered images of C, Ca, O before adsorption

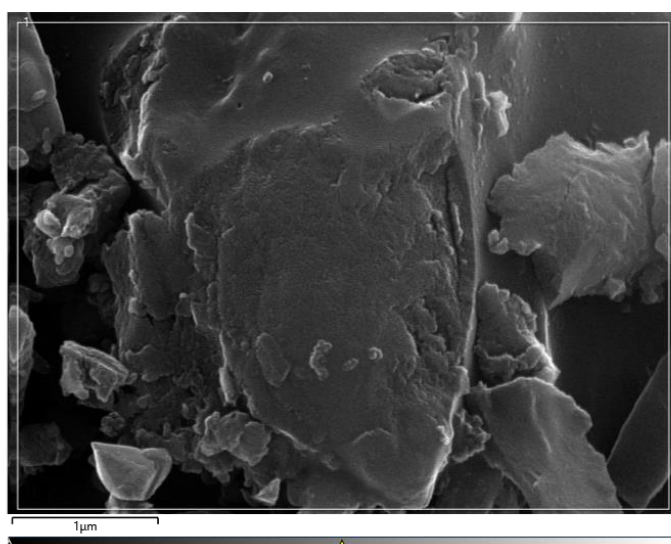


Fig 5.22 Electron image of GAIB after adsorption

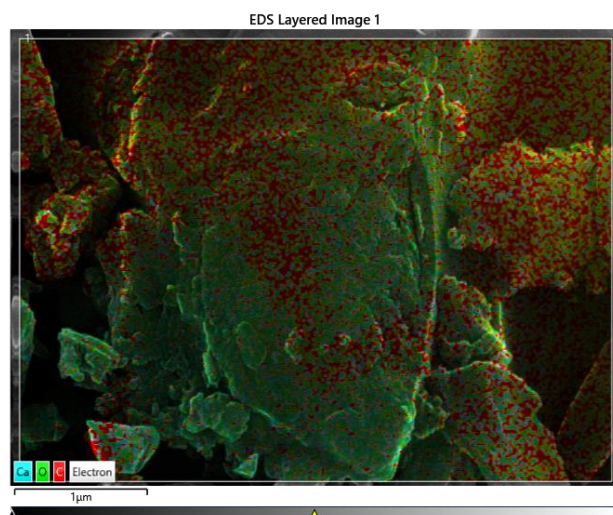


Fig 5.23 EDS layered image of GAIB after adsorption

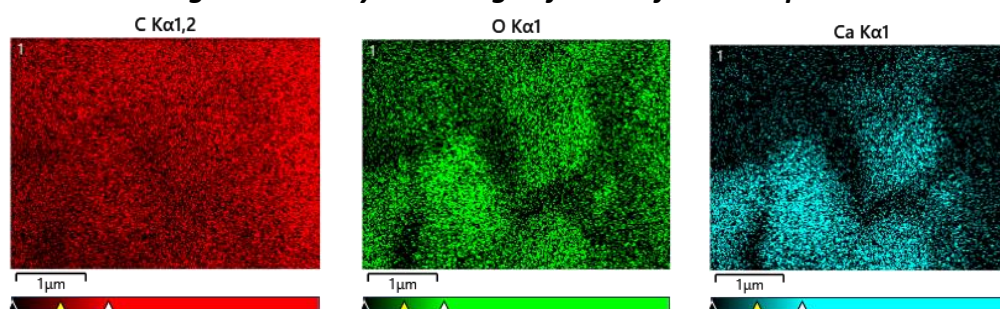


Fig 5.24 EDS layered images of C, O, and Ca after adsorption

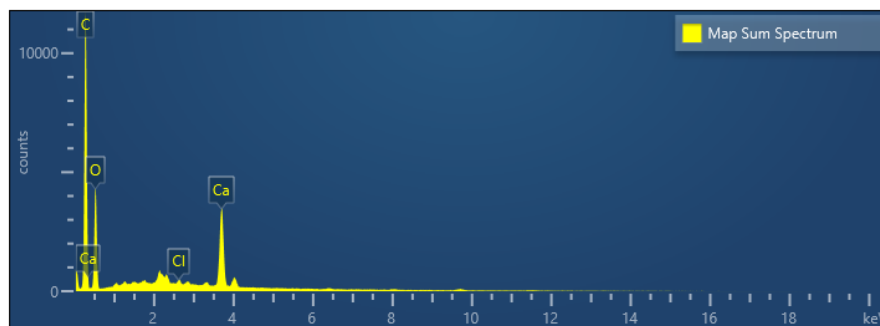


Fig 5.25 EDAX spectra of GAIB before adsorption

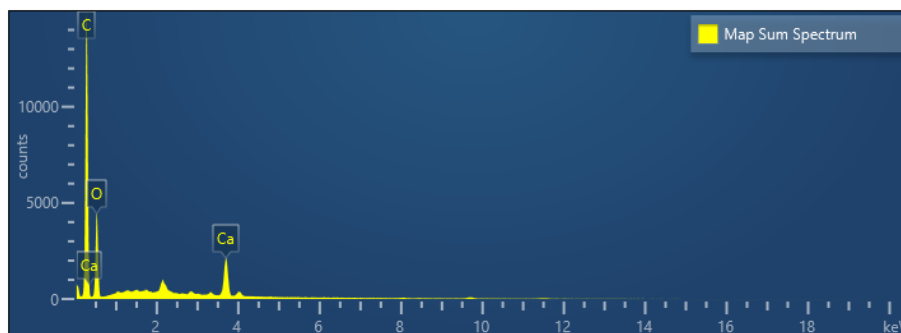


Fig 5.26 EDAX spectra of GAIB after adsorption

Table 5.2 EDAX spectra of GAIB before and after adsorption

Element	Weight % before adsorption	Weight % after adsorption
C	60.58	65.07
O	33.19	31.62
Ca	5.97	3.30
Cl	0.26	-
Total	100	100

Using energy dispersive X-ray analysis, the AIB and GAIB samples were examined. We may infer from the AIB's EDAX results that its primary constituents are carbon and oxygen. Other than C and O, other elements are too found such as N, Si, Mg, Cl, S, Br, K, Ca, Fe, Cu and Na but which are present only in trace amount and is negligible. The carbon content have decreased after adsorption experiment this is due to coverage of Metformin Hydrochloride particles on the surface of the sample Adsorption mechanisms led to the displacement or obscuration of carbon atoms by adsorbed molecules, impacting their detectability via EDX. The increase in oxygen content following adsorption stemmed from interactions between oxygen-containing molecules in the adsorbate and surface functional groups of the adsorbent, resulting in the formation of new oxygen species. Chemisorption processes resulted in the chemical bonding of oxygen atoms to the adsorbent surface, contributing to the elevated oxygen content.

GAIB was examined using energy dispersive X-ray analysis (EDAX) before and after the adsorption have taken place. From the results we can infer that, the prepared adsorbent GAIB was mainly composed of C, O and Ca. The increase in carbon content was observed after adsorption which was due to the preferential adsorption of carbon-containing species onto the composite surface. During the adsorption process, organic molecules or contaminants from the solution interacted with the surface functional groups of the composite, leading to the immobilization of carbon-rich molecules onto its surface. As a result, the composite material's apparent carbon content increased.

5.6 BET ANALYSIS

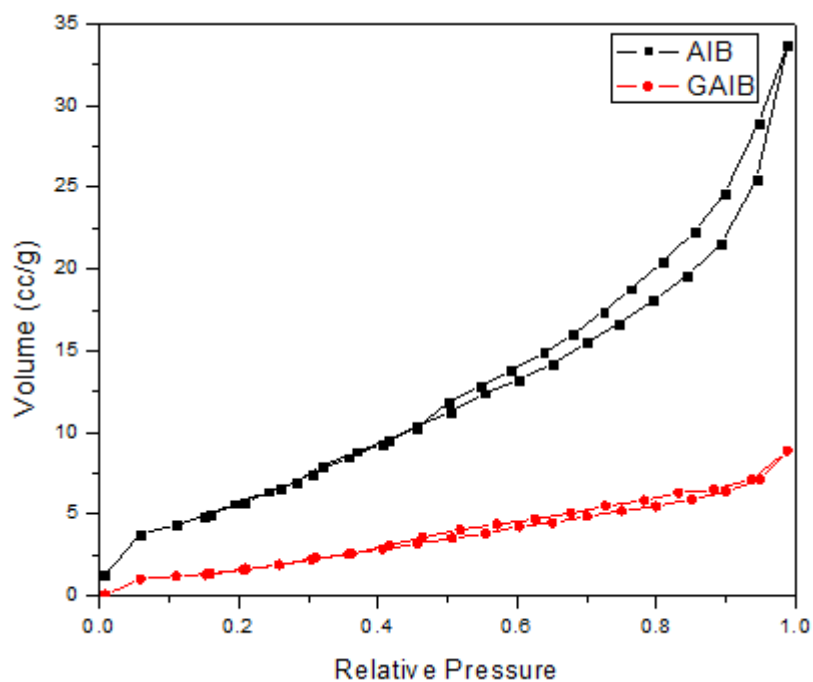


Fig 5.27 Adsorption/Desorption isotherm curve for AIB and GAIB

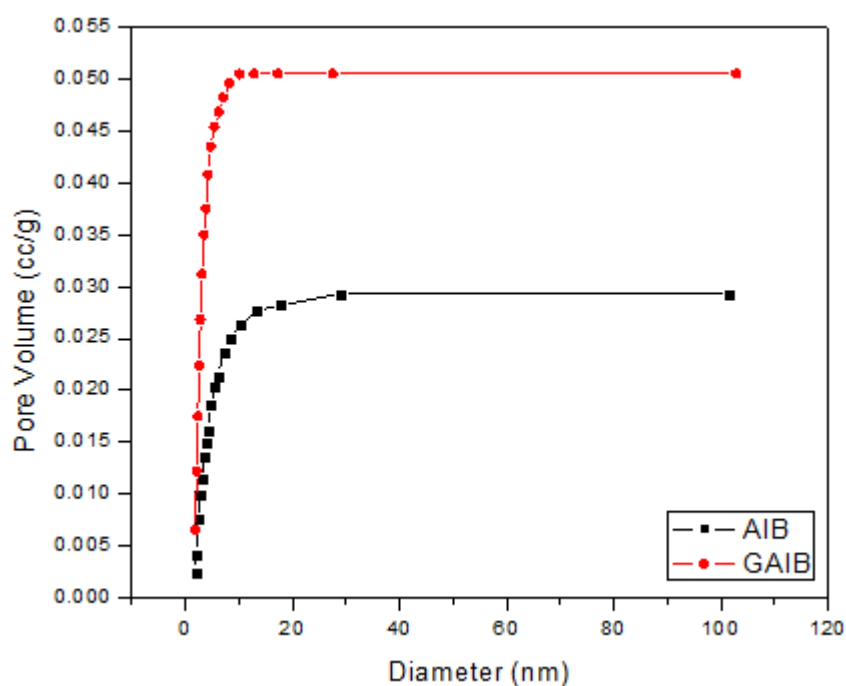


Fig 5.28 BJH pore size distribution for AIB and GAIB

Figure 5.27 shows the Brunauer, Emmett, and Teller (BET) adsorption isotherms and Fig 5.28 shows the Barrett-Joyner-Halenda (BJH) pore size distribution curves for AIB and GAIB. The N₂ isotherm of AIB and GAIB reveals a meso-porous structure with a type IV isotherm and an H₃-type hysteresis loop. The type IV isotherm hysteresis closed-loop verified the mesoporous structure occluded with voids in the shape of the narrow slit, while the N₂ adsorption isotherm demonstrated the microporous nature of the material.

The AIB has a surface area (S_{BET}), pore diameter (d), and total pore volume (V_{tot}) of 6.425 m²/g, 1.925 nm, and 0.029 cc/g, in that order. Whereas in the case of GAIB the surface area (S_{BET}), pore diameter (d), and total pore volume (V_{tot}) were in the order of 25.812 m²/g, 1.923 nm and 0.050 cc/g. From this it is evident that the surface area has increased, from AIB to GAIB which is favorable for adsorption. Thus, GAIB can be considered as a more potential adsorbent.

Table 5.3 BET Surface area and Pore volume

Adsorbent	Surface Area (S_{BET}) (m ² /g)	Pore Diameter (d) (nm)	total pore volume (V_{tot}) (cc/g)
AIB	6.425	1.925	0.029
GAIB	25.812	1.923	0.050

5.7 FACTORS IMPACTING ADSORPTION OF METFORMIN HYDROCHLORIDE:

5.7.1 EFFECT OF pH:

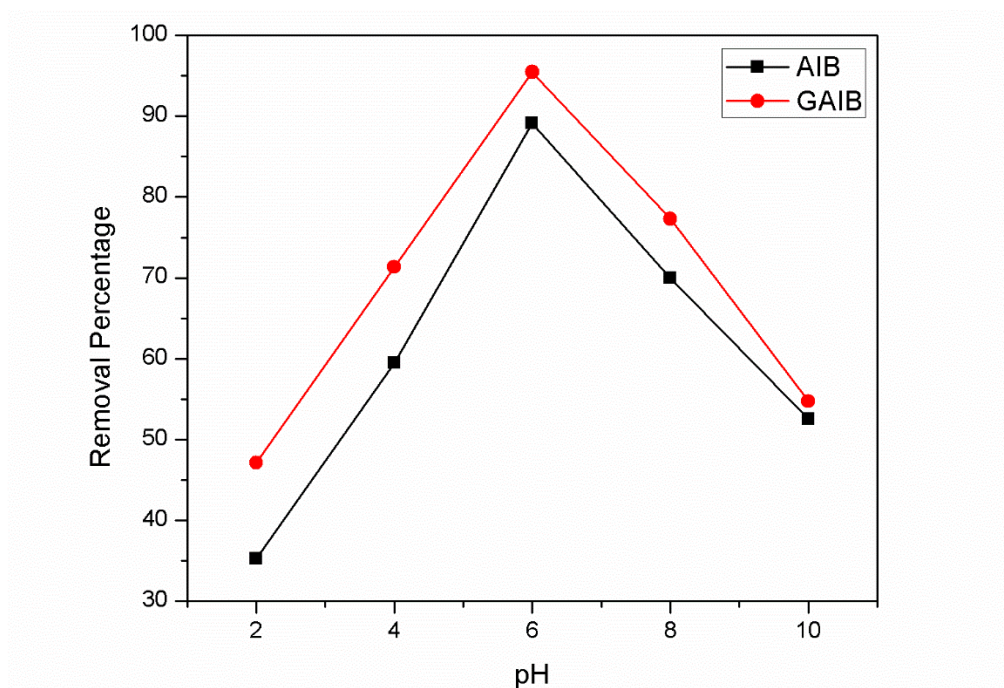


Fig 5.29 effect of pH vs Removal Percentage

The pH level of the solution was changed between 2 and 10 in order to evaluate the impact of pH. All other parameters were held constant during the adsorption studies, which were conducted in the pH range of 2 to 10. (MH concentration = 10 mg/L; adsorbent dosage = 10g/L for AIB and 5g/L for GAIB; contact period = 120 min). According to Figure 5.29, it is evident that the adsorption of the Metformin Hydrochloride for AIB and GAIB increased when the pH of the mixture rose from 35.23 to 89.17% for AIB and 47.14 to 95.47% for GAIB. From 2 to 6 and started to decrease after reaching maximum at pH 6. The maximum adsorption of Metformin Hydrochloride by AIB and GAIB at pH 6 attributed to optimal surface charge and chemical speciation, favoring effective binding of neutral metformin molecules to adsorbent surface. Additionally, the surface functional groups were likely in an optimal state for interaction with MH molecules at this pH. At pH 6, minimized competition from other ionic species and enhanced chemical stability further facilitated efficient adsorption of MH onto AIB and GAIB, resulting in maximum adsorption capacity at this pH level.

5.7.2 EFFECT OF ADSORBENT DOSAGE:

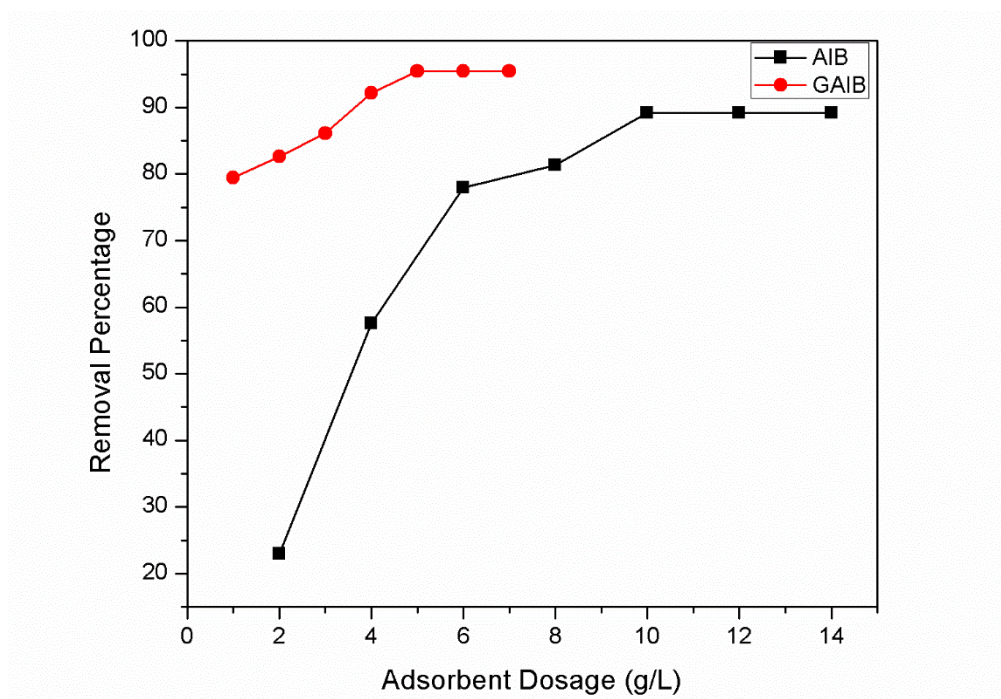


Fig 5.30 Effect of adsorbent dosage vs Removal percentage

The influence of AIB and GAIB dose rate was studied by adjusting the AIB dosage from 1 to 14 g/L and GAIB dosage from 1 to 7 g/L. while maintaining pH at 6, shaking time at 120 minutes, MH concentration at 10 mg/L, and temperature at 30°C. Graphical representation in Figure 5.30 indicates that as AIB and GAIB dosage increased, the removal efficiency of MH also rose. Notably, a substantial improvement in MH removal, from 22.93% to 89.17% in AIB and 79.47% to 95.47% in GAIB was observed with the increase in dosage. Nevertheless, when the surface attained MH molecule saturation, additional adsorbent dose increases had little effect on removal effectiveness. This saturation shows that MH molecules occupy every accessible active site on the adsorbent surface. The inclusion of more active sites and the increased surface area of GAIB and AIB most likely contributed to the increased removal efficiency. Notably, since the pores are already full of dye molecules, adsorption stops as soon as equilibrium is reached.

5.7.3 EFFECT OF INITIAL CONCENTRATION:

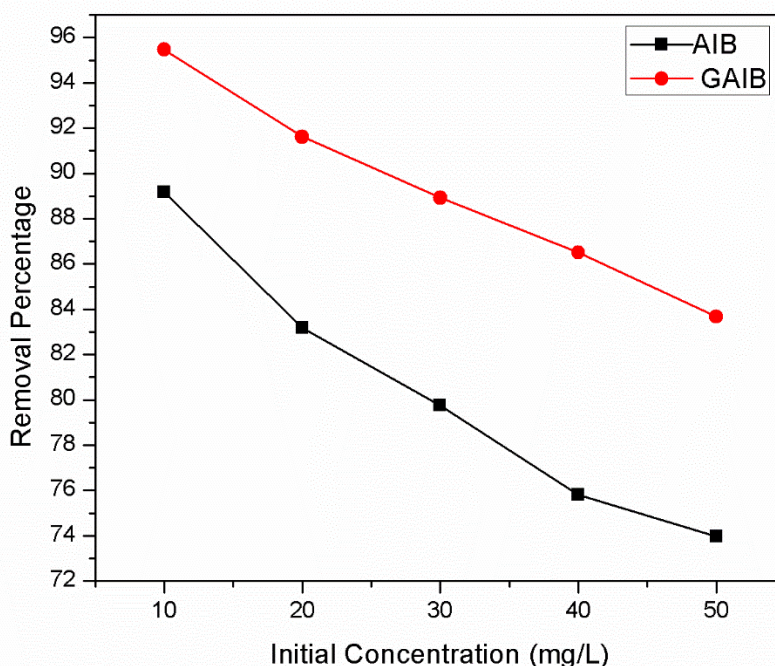


Fig 5.31 Effect of initial concentration vs removal percentage

The experimental results of the effect of initial MH concentration on the removal of MH by AIB and GAIB was shown in Figure 5.31. The removal of MH by AIB and GAIB was studied by varying the initial concentration (10, 20, 30, 40, 50 mg/L) in aqueous system with temperature (30°C) and pH (6) and 120 min as shaking time. It was evident from Figure 5.20 that the removal of MH decreased with increasing initial MH concentration. The results indicated that the optimum pollutant concentration was 10 mg/L for AIB and GAIB. The removal percentage of AIB decreased from 89.17% to 73.97% at 50 mg/L, for GAIB it decreased from 95.47% to 83.67% at 10 mg/L. At lower MH concentrations, there was a higher availability of adsorption sites, making it easier for MH to be adsorbed. On the other hand, a decrease in MH removal was noted at greater starting MH concentrations because there were fewer adsorption sites available overall. Absorbance levels increased noticeably when the concentration of metformin hydrochloride was more than 50 mg/L during UV detection. This elevated absorbance could introduce significant interference, thereby compromising the precision of the analytical results obtained. Consequently, it was crucial to ensure that the concentration remained below 50 ppm to uphold the accuracy and reliability of UV detection analyses.

5.7.4 EFFECT OF CONTACT TIME:

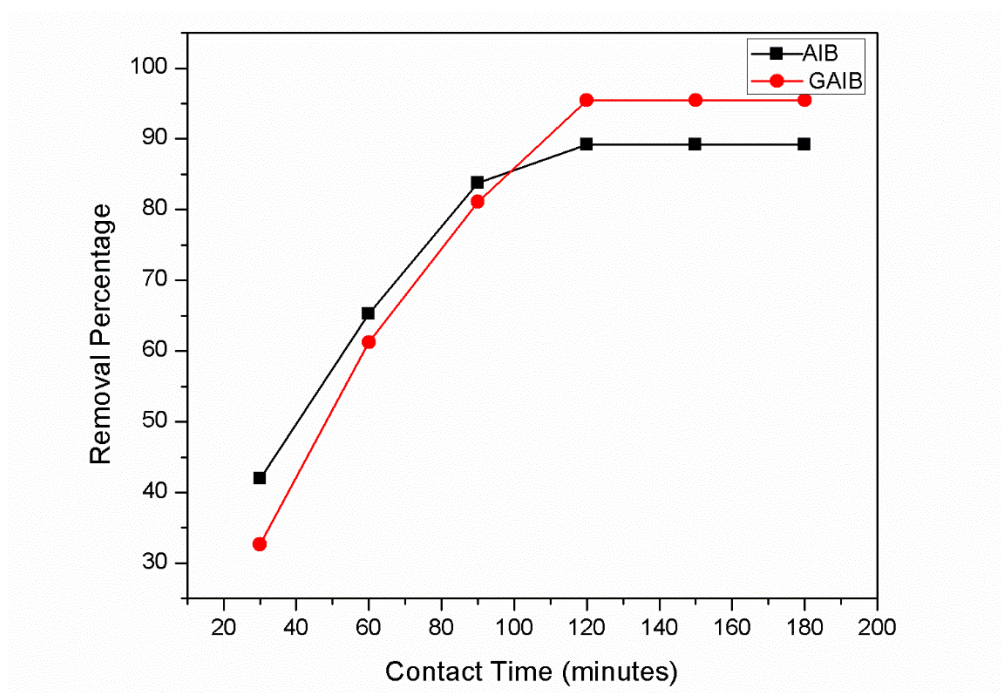


Fig 5.32 Effect of contact time vs removal percentage

One of the crucial factors utilized to evaluate the efficiency of the adsorbent in removing the adsorbate is the impact of contact time of AIB and GAIB on MH. The rate of MH removal was examined by varying the agitation time from 30 minutes to 180 minutes, while keeping other parameters constant at pH 6, MH concentration at 10 mg/L, dose rate at 10 g/L for AIB and 5 g/L for GAIB, and temperature at 30°C. The results are illustrated graphically in Figure 5.32. For AIB the removal percentage of MH molecules increased from 41.93% at 30 minutes to 89.17% at 120 minutes, whereas for GAIB the removal percentage increased from 32.64% at 30 minutes to 95.47% at 120 minutes. The figure clearly shows a significant increase up to 120 minutes, at which point the rate at which MH molecules are adsorption by the active sites equals the rate at which MH molecules are desorption from previously bound sites, resulting in an equilibrium condition. Further adsorption stops when equilibrium is established because MH molecules have saturated the active sites and pores. After this time, the three diffusion processes of film, pore, and surface responses cause any residual active sites to become saturated.

5.7.5 EFFECT OF TEMPERATURE

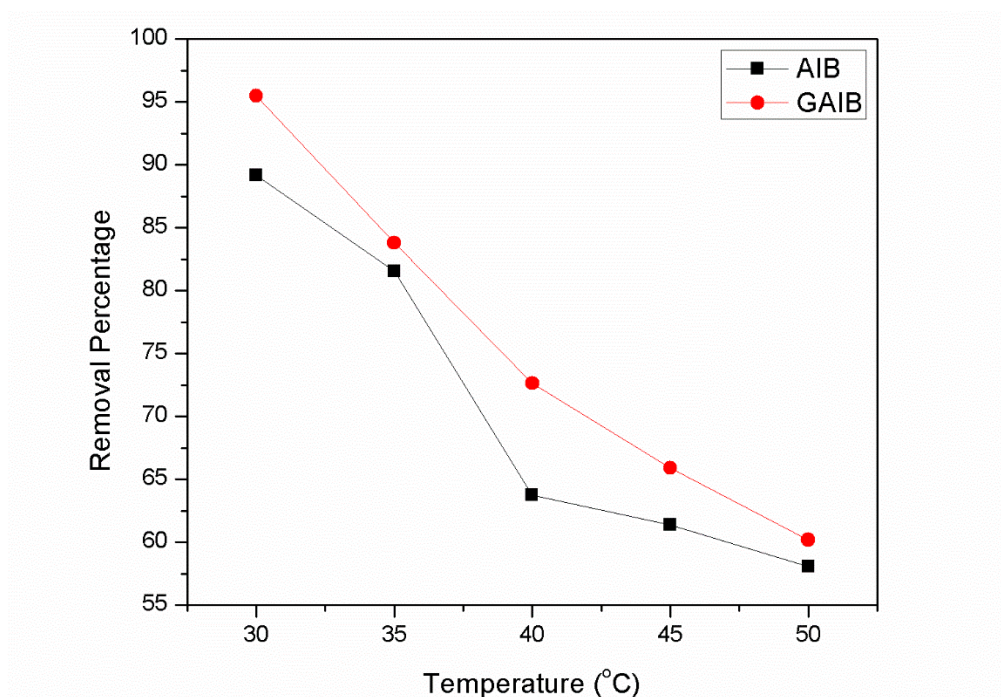


Fig 5.33 Effect of temperature vs removal percentage

To investigate the suitable temperature, experiments were conducted by varying the temperature from 303 K to 318 K while maintaining other parameters constant, such as pH 6, MH concentration 10 mg/L, shaking time 120 min, and dose rate was 10 g/L for AIB and 5 g/L for GAIB. As depicted in Figure 5.33, it is observed that increasing the temperature leads to a decrease in adsorption efficiency from 89.17% to 58.09% for AIB and for GAIB in decreased from 95.47% to 60.18% with increase in temperature. The weakening of the electrostatic field of attraction, which causes the AIB and GAIB to absorb less MH at higher temperatures, may be the cause of this decline in efficiency. MH molecules have a tendency to desorb from the adsorbed active sites at higher temperatures. As a result, it is clear that utilizing AIB and GAIB as the adsorbent, MH will adsorb more effectively at lower temperatures.

5.8 ADSORPTION ISOTHERM MODELS

An adsorption isotherm is essentially a critical curve that clarifies the mechanisms controlling the retention, release, or mobility of a material under constant pH and temperature from aqueous porous media or aquatic habitats to a solid phase. The adsorption of MH by AIB and GAIB adsorbents was examined in this work using three adsorption isotherm models: the Langmuir, Freundlich, and Temkin isotherms.

For monolayer adsorptions, where the adsorbent surface is thought to be homogenous and the adsorbate is thought to adsorb in a monolayer, the Langmuir isotherm model works well. Here is the mathematical expression that has been provided.

$$q_e = \frac{q_{max}K_L C_e}{1 + K_L C_e},$$

Where q_e is the quantity of MH adsorbed per gram of the adsorbent at equilibrium (mg^{-1}), K_L is known as the Langmuir constant (L/mg), C_e is the equilibrium concentration of the MH (mg/L), and q_{max} is the monolayer adsorption capacity (mg/g).

The Freundlich isotherm, an early empirical model of adsorption phenomena which extend beyond the formation of monolayers, characterizes non-ideal and reversible adsorption processes. It accommodates multilayer adsorption with varying distribution of adsorption heat and affinities across heterogeneous surfaces. The equation that represents this isotherm shall be the following

$$q_e = K_F C_e^{1/n},$$

Where, q_e is the amount of adsorbate adsorbed per unit mass of adsorbent at equilibrium (mg^{-1}), C_e is the equilibrium concentration, K_F is the Freundlich constant and $1/n$ is the empirical parameter related to adsorption intensity.

The Temkin isotherm is a tool used to explain solid surface adsorption processes. Adsorbent-adsorbate interactions are assumed to cause the adsorption heat of molecules to decrease linearly with surface coverage. A parameter is included to account for the potential energy of adsorption sites. Here is an expression for the Temkin equation:

$$qe = \frac{RT}{b_T} \ln (K_T C_e),$$

Where, q_e is the amount of adsorbate adsorbed per unit mass of adsorbent at equilibrium (mg^{-1}), C_e is the equilibrium concentration, K_T is the Temkin constant, R represents the universal gas constant, and T represents the absolute temperature in Kelvin.

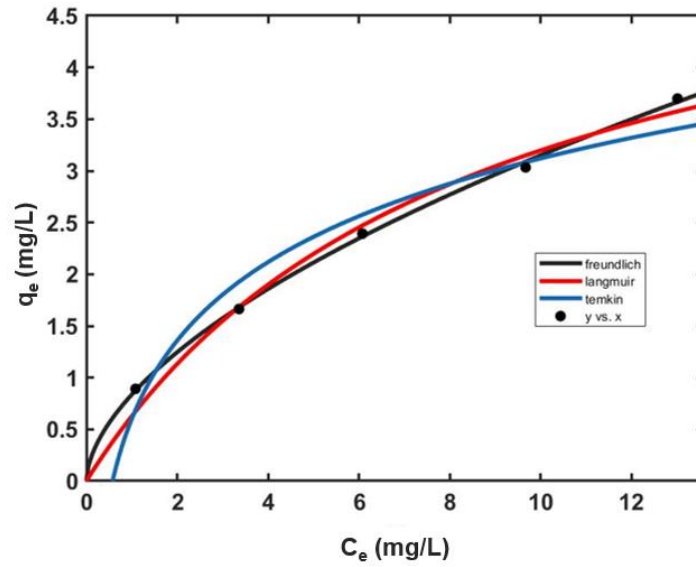


Fig 5.34 Isotherm evaluation for removal of MH by AIB

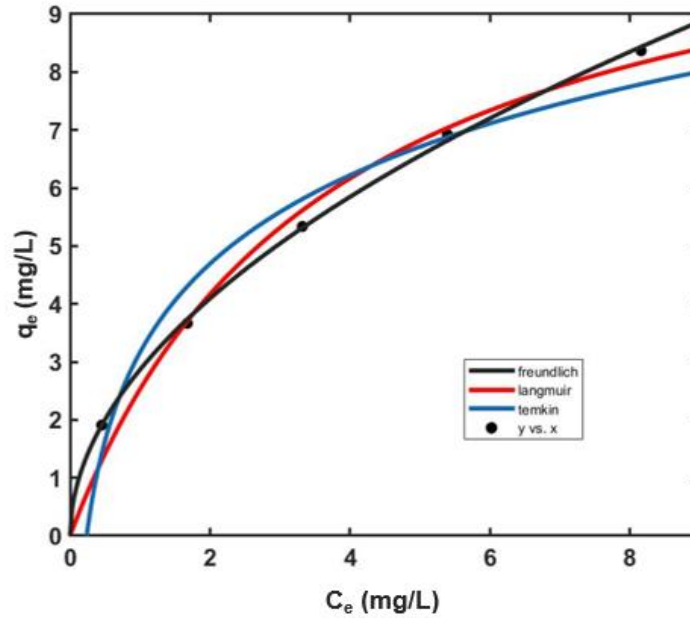


Fig 5.35 Isotherm evaluation for removal Of MH by GAIB

Table 5.4 Adsorption Isotherm Parameters

Models	AIB		GAIB	
	Parameters	Values	Parameters	Values
Langmuir	$q_{\max}$ (mg/g)	5.878	$q_{\max}$ (mg/g)	11.84
	K_L (L/mg)	0.1193	K_L (L/mg)	0.2712
	R^2	0.983	R^2	0.9805
	SSE	0.0832	SSE	0.5107
	RMSE	0.1665	RMSE	0.4126
Freundlich	K_f ((mg/g) (L/mg) ^{1/n})	0.8352	K_f ((mg/g) (L/mg) ^{1/n})	2.865
	N	1.735	n	1.945
	R^2	0.9988	R^2	0.9992
	SSE	0.00564	SSE	0.02118
	RMSE	0.04336	RMSE	0.08403
Temkin	R^2	0.9526	R^2	0.9387
	K_T (L/mg)	1.729	K_T (L/mg)	4.205
	SSE	0.2313	SSE	1.204
	RMSE	0.2776	RMSE	0.6334

Table 5.4 displays the isotherm analysis parameters as well as the equilibrium evaluation. The R^2 value and error readings were used to pick the model that was most appropriate for this adsorption process. Given Table 5.4's higher R^2 value and lower SSE and RMSE error values, it is evident that the system adheres to the Freundlich isotherm. The SSE and RMSE mathematical equations are shown below.

$$SSE = \sum_{i=1}^n (A_i - P_i)^2,$$

$$RMSE = \sqrt{\sum_{i=1}^n \frac{(A_i - P_i)^2}{n}},$$

5.9 ADSORPTION KINETIC MODELS

The kinetic models offer insights into the time needed to reach adsorption equilibrium, serving as a crucial aspect in designing adsorption systems. They provide valuable information about the process rate and the efficacy of the adsorbent material. Pseudo-first-order (PFO), pseudo-second-order (PSO) and elovich kinetic models were used to evaluate the prepared adsorbents. The equilibrium time needed to complete the adsorption process is disclosed by these kinetic models. It is a crucial instrument in the development of an adsorption system. It delivers information on the process's pace and the material's efficiency.

Pseudo-first order kinetic model is given as:

$$q_t = q_e(1 - \exp(-k_1 t))$$

Pseudo-second order kinetic model is given as:

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t}$$

Elovich Kinetic model is given as:

$$q_t = \frac{1}{\beta} \ln(1 + \alpha \beta t)$$

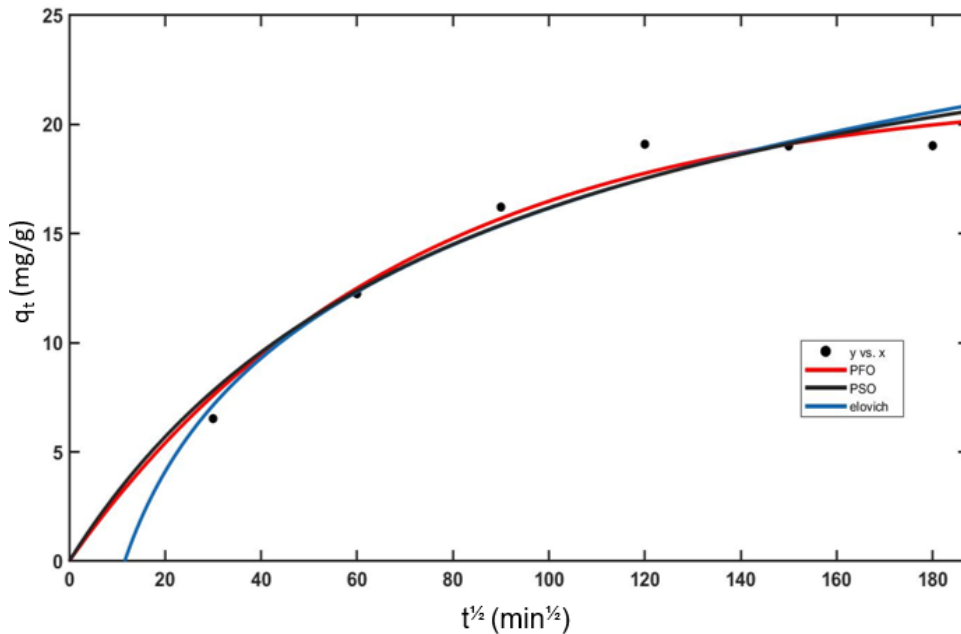


Fig 5.36 Kinetics of AIB

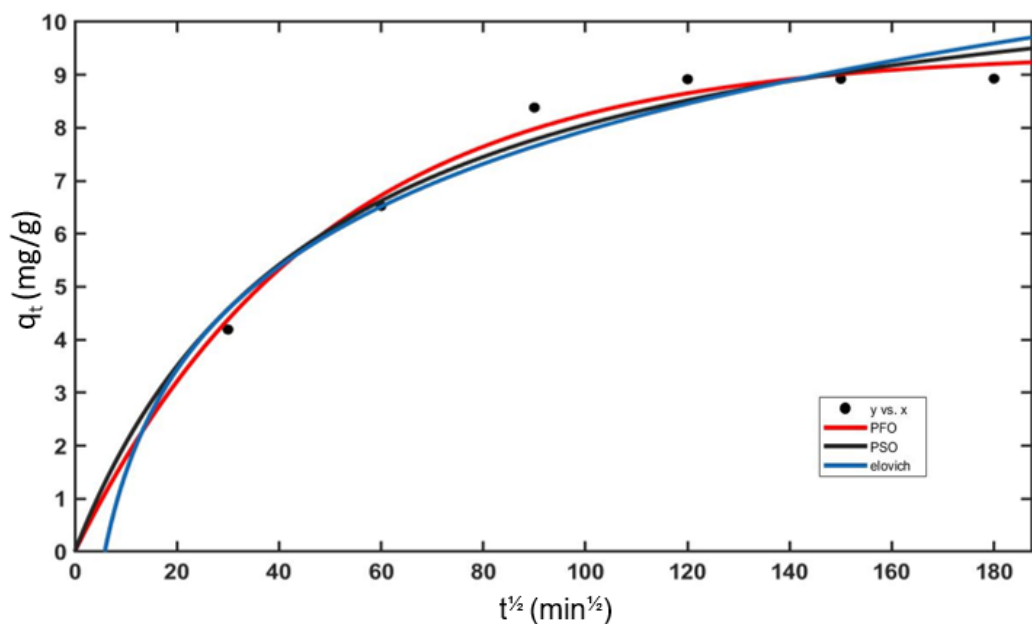


Fig 5.37 Kinetics of GAIB

Table 5.5 Kinetic parameters of AIB and GAIB

Kinetic Models	AIB		GAIB	
	Parameters	Values	Parameters	Values
Pseudo-First Order	K_1 (min^{-1})	0.02082	K_1 (min^{-1})	0.01442
	q_e (mg/g)	9.427	q_e (mg/g)	21.59
	R^2	0.979	R^2	0.968
	SSE	0.3905	SSE	4.314
	RMSE	0.3125	RMSE	1.017
Pseudo-Second Order	K_2 (g/mg·min)	0.000173	K_2 (g/mg·min)	0.000391
	q_e (mg/g)	11.94	q_e (mg/g)	29.98
	R^2	0.9496	R^2	0.9495
	SSE	0.9387	SSE	6.518
	RMSE	0.4844	RMSE	1.277
Elovich	α ($\text{mg g}^{-1}\text{min}^{-1}$)	0.2072	α ($\text{mg g}^{-1}\text{min}^{-1}$)	0.2812
	β (g mg $^{-1}$)	0.8216	β (g mg $^{-1}$)	0.3074
	R^2	0.927	R^2	0.9539
	SSE	1.358	SSE	5.95
	RMSE	0.5827	RMSE	1.22

5.10 ADSORPTION THERMODYNAMICS:

Determining the nature and spontaneity of the adsorption process is the main goal of thermodynamic assessment. The following equations demonstrate how thermodynamic parameters for adsorption experiments are determined using Van't Hoff's equations:

$$KL = \frac{C_{Ae}}{C_e}$$

$$\Delta G^\circ = -RT \ln KL$$

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ$$

$$\ln KL + \frac{\Delta S^\circ}{2.303R}$$

$$\log KL = -\frac{\Delta H^\circ}{2.303 RT} + \frac{\Delta S^\circ}{2.303 R}$$

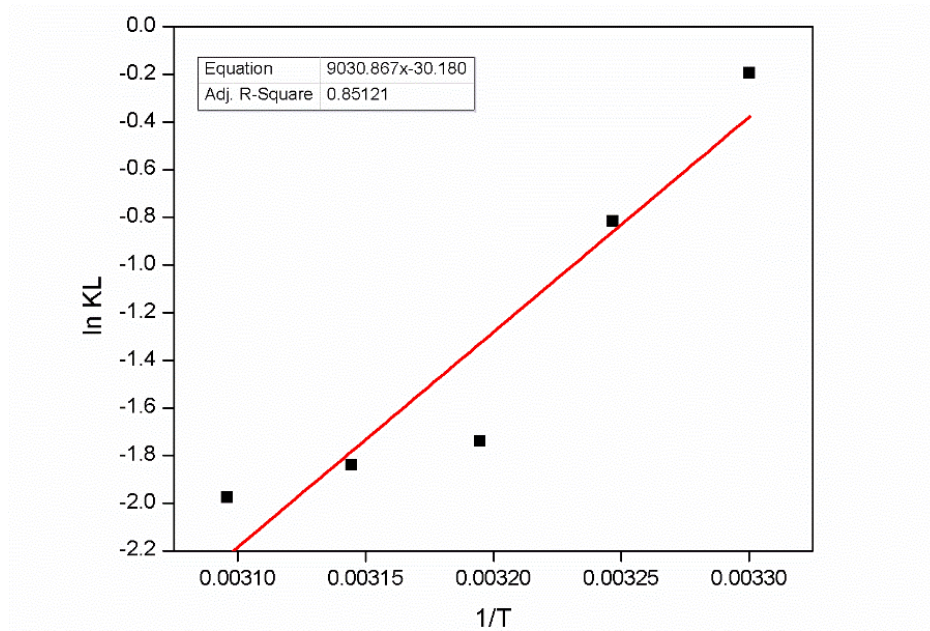


Fig 5.38 Thermodynamics of AIB

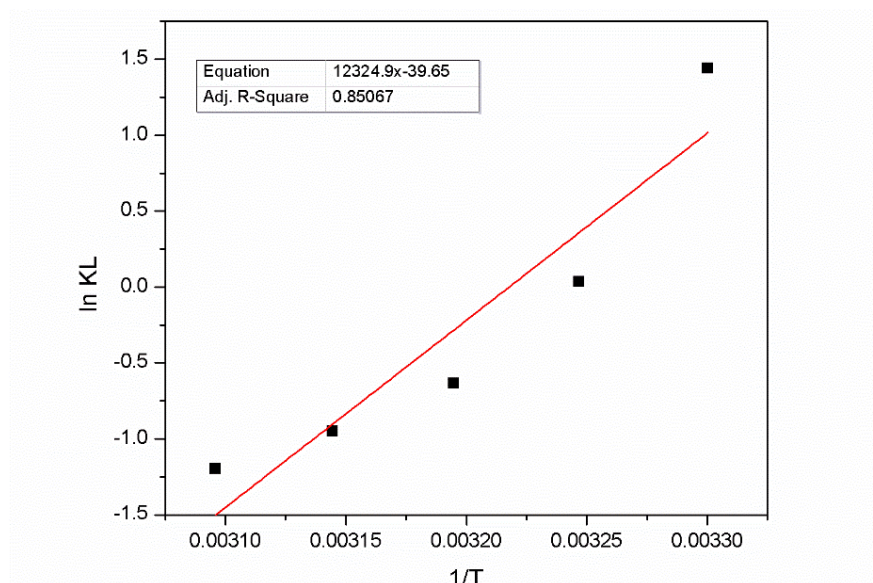


Fig 5.39 Thermodynamics of GAIB

Table 5.6 Thermodynamic parameters

Adsorbents	Parameters			
	$\Delta H^\circ (\text{KJmol}^{-1})$	$\Delta S^\circ (\text{JK}^{-1} \text{mol}^{-1})$	$\Delta G^\circ (\text{KJ mol}^{-1})$	
			Temp (K)	Values
AIB	-7.687164384	-250.9215084	303	-14.322
			308	-10.437
			313	-8.654
			318	-8.112
			323	-6.967
GAIB	-10.48365708	-329.916148	303	-12.328
			308	-10.243
			313	-10.013
			318	-7.239
			323	-6.752

Using temperatures ranging from 303 to 323 K, the MH's adsorption was investigated. Figure 5.42 and 5.43 was used to get the thermodynamic parameters, such as ΔH° and ΔS° , and the formula was used to get ΔG . The parameters used in the thermodynamic analysis are listed in Table 5.3. The negative value of ΔG for

AIB and GAIB indicates the reaction is spontaneous. The negative values of ΔH° indicated that the MH adsorption was exothermic for both the prepared adsorbents and the negative ΔS° values conclude to decrease in randomness of the adsorption for both AIB and GAIB.

CHAPTER 6

CONCLUSION

In this study, the focus was on investigating the removal of an antidiabetic pharmaceutical pollutant (Metformin Hydrochloride), from aqueous solutions using *Azadirachta indica* bark derived biochar (AIB) and a composite of graphene oxide doped biochar (GAIB) under various process conditions. The AIB adsorbent was prepared through physical activation, while graphene oxide was synthesized using a modified Hummers method, and subsequently, a GAIB composite was synthesized. Batch mode experiments were conducted to explore the influence of factors such as adsorbent dosage, pH, contact time, and temperature on the adsorption process.

Analysis techniques such as FT-IR spectroscopy, BET, XRD and FESEM were employed to characterize the prepared adsorbents. Optimal experimental conditions were determined for both AIB and GAIB. For AIB, the optimal conditions were pH 6, contact time 120 minutes, initial concentration 10 mg/L, adsorbent dosage 10 g/L, and temperature 30°C. Similarly, for GAIB, the optimal conditions were pH 6, contact time 120 minutes, initial concentration 10 mg/L, adsorbent dosage 5 g/L, and temperature 30°C.

The adsorption isotherm data for both adsorbents followed the Freundlich model, indicating non-ideal multilayer and reversible adsorption behavior. Additionally, the adsorption process followed pseudo-first-order kinetics. A significant increase in the maximum adsorption capacity ($Q_{\max}$) was observed from 5.878 mg/g to 11.84 mg/g when transitioning from AIB to GAIB, representing a 99% enhancement. Thermodynamic study of the measured thermodynamic characteristics indicated that the adsorption process was endothermic and spontaneous. Overall, this study underscores the potential of AIB and GAIB composite as cost-effective and environmentally friendly adsorbents for the removal of pharmaceutical pollutants from wastewater, offering a promising avenue for sustainable water treatment approaches.

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CHAPTER 1

INTRODUCTION

1.1 BACKGROUND

Our existence on Earth hinges upon three fundamental resources: water, air, and soil. These are nature's invaluable offerings to humanity. Among them, water takes precedence as it serves as the primary medium for the genesis of life. Water pollution from emerging contaminants is on the rise due to the increasing effects of urbanization, industrialization, and agricultural practices. Emerging contaminants encompass substances that are not currently subject to regulatory monitoring or public disclosure requirements regarding their existence in our water source and wastewater. Industrial formulations, chemicals, food additives, food packaging materials, metalloids, rare earth elements, pharmaceuticals, cosmetics, personal care items, surfactants, cleaning agents, and pathogens are just a few examples of the diverse components that fall under this area.

The main sources of these emerging pollutants include leachates from landfills, agricultural runoff, hospital effluents, industrial wastewater discharges, and livestock and aquaculture operations. Especially, the effluents from municipal wastewater treatment plants are a major source of recently identified pollutants in aquatic habitats.

1.2 PHARMACEUTICAL CONTAMINANTS: A MAJOR CONCERN

Pharmaceuticals are biologically active substances with well-defined mechanisms of action in both humans and animals. Prior to the 19th century, the primary source of therapeutics was natural compounds. This included the use of crude extracts from plants and various shrubs, which served as herbal medicines. These natural remedies were employed for purposes such as pain relief, wound healing, and the treatment of various illnesses. Progress in the realm of medical science played a pivotal role in the emergence of numerous synthetic therapeutic compounds during the latter part of the 19th century and throughout the 20th century. These compounds included substances like naphthalene, acetanilide, aspirin, ephedrine, and arsphenamine.

The widespread use of pharmaceuticals has raised alarm about their detection in the environment. This concern arises because a significant portion of these medicinal substances cannot be absorbed and processed by the human body, resulting in their excretion through feces and urine, ultimately entering municipal wastewater treatment facilities.

The key origins of pharmaceutical contaminants in the environment encompass pharmaceutical industries, hospitals, the disposal of expired medications, research projects employing therapeutic compounds, and animal waste. Among the sources, hospitals emerge as the predominant contributors to the release of pharmaceuticals into the environment. Wastewater discharged from hospitals carries a mixture of components, including pathogens, pharmaceutical residues and their metabolites, drug conjugates, radioactive elements, and various other chemical substances.

Individuals can potentially come into contact with pharmaceuticals that contaminate water environments by either consuming drinking water or ingesting aquatic organisms. Ongoing risk assessment studies are being conducted for both aquatic species and humans. However, it has been observed that the risk of exposure to pharmaceuticals is generally greater for aquatic species than for humans.

These small quantities of pharmaceuticals remain present in the environment for lengthy periods of time, affecting both targeted and non-targeted species. Moreover, medicinal drugs are frequently present in complex combinations containing a variety of unrelated compounds, each of which has unique pharmacological properties that may have additive or synergistic effects. This raises questions regarding the possible risks that medications dissolved in water offer to aquatic life's survival and function, as well as the possibility that these chemicals may cause genetic abnormalities or modifications.

1.3 METFORMIN HYDROCHLORIDE: AN EMERGING CONTAMINANT

Metformin Hydrochloride, an oral medication designed for managing type 2 diabetes, has become increasingly prevalent in medical practice due to the worldwide surge in diabetes cases. Due to its increasing use and subsequent discharge into wastewater, there is a growing concern regarding the environmental impact of Metformin Hydrochloride.

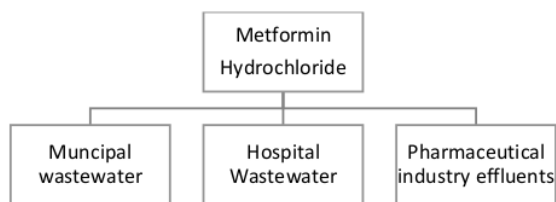


Fig 1.1 Sources of Metformin Hydrochloride

Metformin Hydrochloride, alternatively labeled as 1,1-Dimethylbiguanide hydrochloride, possesses the chemical composition $C_4H_{12}ClN_5$. This compound exists in a crystalline state and exhibits a molecular weight of 165.62 g/mol. Within its structure, there are six C—N bonds, and an examination of bond order reveals that four of these bonds exhibit bond orders nearing 4/3, while the remaining two bonds can be characterized as single bonds. The structure of Metformin Hydrochloride can be given as follows.

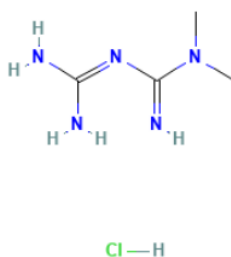


Fig 1.2 2-D Chemical structure depiction of Metformin Hydrochloride

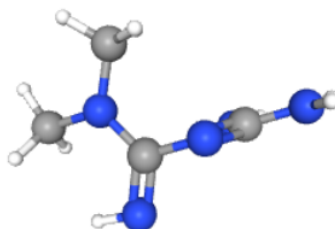


Fig 1.3 3-D Ball and stick structure of Metformin Hydrochloride

Metformin and one molar equivalent of hydrogen chloride combine to make metformin hydrochloride. It performs a number of tasks, including xenobiotic, hypoglycemia, and environmental contaminant roles.

Because of its extensive utilization, metformin and its derivatives are detected in wastewater and subsequently enter aquatic ecosystems. Consequently, metformin accumulates within organisms and the environment, potentially causing health issues when concentration levels exceed safe limits. Recent research indicates a global rise in the number of individuals diagnosed with diabetes. Among the medications frequently prescribed for type 2 diabetes, Metformin Hydrochloride stands out as a widely used option. In recent times, Metformin Hydrochloride has gained more attention for being one of the pharmaceuticals that is frequently found in aquatic ecosystems. This prevalence is attributed to its low K_{ow} , high pKa, and excellent solubility in water, resulting in concentration levels ranging from 64 to 98 $\mu\text{g/L}$ in domestic wastewater.

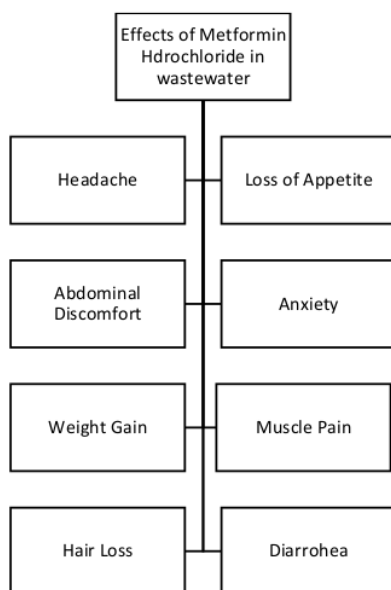


Fig 1.4 Effects of Metformin Hydrochloride

There are a lot of negative effects that have been reported from metformin being present in surface waterways. Surface waterways are becoming more and more contaminated with medicines, even with pre-discharge municipal water treatment. As conventional wastewater treatment methods are not consistently tailored to effectively eliminate various organic compounds, in addition to other inorganic and biological contaminants.

1.4 BIOCHAR AS AN ADSORBENT

Pharmaceuticals ⁷² have been removed from wastewater employing a variety of physical and biochemical methods, such as oxidative catalytic processes, adsorption, membrane bioreactor treatment, and bio-system recovery. Adsorption is one of these techniques that has shown to be the most effective in eliminating dissolved organic contaminants from wastewater that is used in both industrial and domestic settings. This method has gained extensive usage due to its simplicity, high effectiveness, and cost-effectiveness. Nevertheless, a significant hurdle lies in the quest for effective and appropriate adsorbents capable of adsorbing a broad spectrum of pollutants. Utilizing cost-effective biochar adsorbents for the elimination of organic and inorganic contaminants in aqueous solutions is likely to offer a more cost-efficient approach compared to conventional methods for purifying water.

In the realm of adsorbing pollutants in aqueous environments, biochar presents unique advantages over activated carbon under certain circumstances. While activated carbon is recognized for its high surface area and specialized pore structure, biochar offers distinct benefits in specific contexts. With its porous composition, biochar demonstrates efficacy in capturing certain organic compounds and contaminants from water. Additionally, when utilized as a soil amendment, biochar facilitates water filtration as it traverses through soil integrated with biochar, thereby reducing the influx of pollutants into water bodies. In situations prioritizing sustainable solutions and considering soil-water interactions, biochar provides a comprehensive approach to pollutant adsorption in aqueous settings compared to activated carbon.

¹ Through the pyrolysis of biomass in an oxygen-limited atmosphere, ¹¹ biochar is a solid matter rich in carbon. ¹¹ Neem (*Azadirachta indica*) is a tree species belonging to the Meliaceae family. Is found in large numbers in Indian subcontinent. The primary focus on cultivation of neem tree lies on utilization of neem leaves, seeds and oil. Often the barks are left behind after harvest of these primary components. ¹¹ 65.63% cellulose, 23.55% hemicellulose, and 9.04% lignin make up neem bark. All of which significantly influence the characteristics of biochar produced during pyrolysis. Notably, Neem is commonly found in Asian countries and is known for its medicinal properties.



Fig 1.5 Wood bark of Azadirachta indica tree



Fig 1.6 Biochar produced from wood bark of Neem

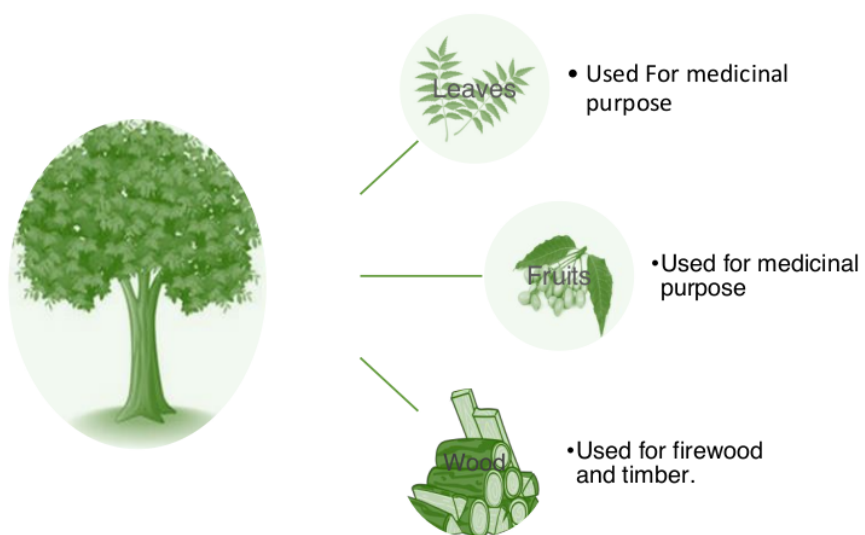


Fig 1.7 Uses of neem tree parts

1.5 Graphene Oxide

Graphene oxide is an incredibly thin layer of carbon atoms structured in a two-dimensional lattice. Its remarkable features have drawn attention from all over the world in a number of disciplines. Its remarkable qualities, which make it extremely adaptable, include great electrical conductivity, mechanical strength, optical transparency, and simplicity of modification. Many potential uses are available for graphene due to its exceptional properties and planar structure, especially in the domains of electronics and energy storage. Different methods for creating graphene with different sizes, forms, and qualities have been developed over time. Recently, research on graphene's potential use in environmental contexts—particularly in pollutant adsorption has taken center stage. Understanding graphene's effectiveness and basic mechanisms as an adsorbent for various contaminants, including organic molecules, has been the subject of research.

In the past, ²¹ activated carbon has been a traditional adsorbent for waste water treatment because of its adaptability, safety, and broad range of applications. However, because of its high regeneration costs and chemical rigidity, it is not as effective as it might be. Graphene meets the demand for a superior carbon-based substitute because, in addition to being carbonaceous, its planar sheet-like form gives it a large surface area. As a result of graphene's polyaromatic π -system, which readily reacts with the aromatic rings of organic substances in water through π - π stacking interactions or a potent hydrophobic effect, graphene-based materials are highly effective adsorbents and have been used to remove dyes such as methylene blue (MB) and Rhodamine B (RhB), as well as pollutants like naphthalene and 1-naphthyl-amine and aspirin.

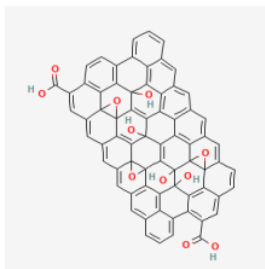


Fig 1.8 Structure of Graphene Oxide

CHAPTER 2

LITERATURE REVIEW

Menala Kalumpha et al.,(2019) Conducted research on affordable activated carbon was synthesized from Zea mays tassel by employing phosphoric acid as a crucial reagent. This activated carbon exhibited remarkable effectiveness in the removal of Metformin Hydrochloride, a prevalent pharmaceutical contaminant found in wastewater. Through a series of experiments, the optimal conditions for the adsorption process were meticulously identified. It was observed that the adsorption behavior followed both Langmuir isotherm and pseudo-second-order kinetics, underscoring the reliability and spontaneity of the process. These findings not only demonstrate the potential of Zea mays tassel as a precursor for producing efficient adsorbents but also highlight its suitability for targeted applications in pharmaceutical wastewater treatment. Overall, the study contributes to the advancement of sustainable and cost-effective solutions for mitigating pharmaceutical pollution in water bodies.

Mohamed E et al.,(2020) Conducted research on evaluated biochars derived from artichoke leaves through pyrolysis, further modified with sodium hydroxide, as potential adsorbents for the removal of Metformin Hydrochloride (MFH) from water. Among the tested variants, Artich-Bch-NaOH demonstrated superior performance compared to Artich-Bch. The study investigated various parameters, including shaking time, adsorbent dosage, initial MFH concentration, solution pH, temperature, and interfering ions, which were found to influence the removal of MFH. The adsorption process was effectively described by Langmuir and pseudo-second-order models. Furthermore, thermodynamic analyses conducted indicated the spontaneity and exothermic nature of the process.

Mohammad et al.,(2022) Researched on study involved in synthesizing of activated carbons from water hyacinth biomass through H_3PO_4 chemical activation and controlled carbonization. Different impregnation ratios (ranging from 0.5 to 3.0) and carbonization temperatures (ranging from 400°C to 800°C) were investigated to assess their impact on the resulting activated carbons. Notably, the sample

identified as 1.5 AC/600 exhibited the highest specific surface area at $1421 \text{ m}^2 \text{ g}^{-1}$, which positioned it as a promising candidate for metformin removal. The adsorption process was effectively described by Langmuir and pseudo-second-order models, indicating its spontaneity and endothermic nature. Successful desorption was achieved using a 0.1 M HCl/ethanol mixture, and the adsorbent showed potential for multiple cycles of reuse, thereby demonstrating its practical applicability in water treatment efforts.

Ferda Civan et al., (2021) Researched on synthesizing of novel magnetic-carbon composites (M-CCs) by incorporating Fe (II) and Fe (III) oxides onto various matrices (PAC, GNP, MWCNT), with the goal of assessing their effectiveness in removing Metformin Hydrochloride from water. Among the kinetic models that we evaluated, the pseudo-second-order model showed the best fit, with M-GNP demonstrating the highest adsorption rate. We found the Langmuir isotherm model to be applicable, indicating that M-GNP was the most efficient adsorbent under standard conditions, while M-MWCNT performed better at elevated temperatures. Additionally, in desorption tests, M-GNP exhibited superior effectiveness, with approximately 66% recovery of Metformin Hydrochloride after each cycle of use.

K.Balasubramani et al., (2020) Researched on the issue of micro-pollutants, such as pharmaceuticals in water, which posed a threat to living organisms. We looked at graphene oxide (GO) as a potential efficient adsorbent to remove model micropollutant metformin from water. The Hummers technique was used to synthesize GO, and its characteristics were carefully described. It was found that the material had notable pore volume, breadth, and surface area, all of which were indicative of mesoporous properties. Various adsorption parameters, including pH, temperature, time, adsorbent dose, and metformin concentration, were systematically investigated using statistical design techniques to establish optimal conditions for maximum removal efficiency. The maximal metformin adsorption capacity was discovered to be 122.61 mg/g , and a pseudo-first-order kinetic model described the adsorption process. The adsorption was shown to be exothermic and spontaneous by thermodynamic analysis. Additionally, desorption studies demonstrated that GO could be effectively regenerated using a 1 N sodium hydroxide solution for up to six cycles, underscoring its potential for practical application in water treatment processes.

Xixian Huang et al., (2016) Metformin hydrochloride (MF) adsorption was studied using hydrogen peroxide modified biochar (mBC) produced from *Alternanthera philoxeroides* (AP) biomass. The effects of pH and Cu (II) on MF adsorption were also investigated. The pseudo-second-order model described the adsorption process, according to an analysis of the adsorption kinetics, and the Freundlich model suited the adsorption isotherms the best. Thermodynamic analysis indicated that MF adsorption occurred spontaneously and was endothermic. It has been found that because MF species (cationic, zwitterionic, and anionic) vary depending on pH, pH had a substantial impact on MF adsorption capability. Furthermore, it was shown that MF adsorption was enhanced by Cu (II) in the pH range of 3.0–7.0, but that MF adsorption was decreased by higher Cu (II) concentrations. Cu (II) had no effect on MF adsorption at pH values higher than 7 or lower than 3.

S Zhu et al., (2017) investigated the possibility that newly discovered pollutants in water supplies may endanger living things. Effective removal strategies for these pollutants were judged required due to insufficient wastewater treatment. Graphene oxide (GO) was assessed for its ability to remove the emerging contaminant metformin. The research involved conducting systematic adsorption and kinetic experiments, which revealed that GO efficiently reduced metformin concentrations, offering a potential solution to this issue. The uptake of metformin on GO was influenced by factors such as temperature, pH, ionic strength, and background electrolyte. The adsorption kinetics showed rapid removal, with approximately 80% removal achieved within 20 minutes. Thermodynamic analysis indicated spontaneous and exothermic adsorption. A pH of 6.0 and a temperature of 288 K yielded the highest adsorption capacity. GO demonstrated excellent adsorption capacity over multiple desorption/adsorption cycles, with π – π interactions and hydrogen bonds playing a crucial role in metformin adsorption onto GO.

G De Bhowmick et al., (2022) For the purpose of batch sorption of metformin hydrochloride (MET), a specifically prepared biochar combination including macroalgae (MAC), microalgae (MIC), rice husk, and pine sawdust was investigated. The MAC and MIC algae combination was pyrolyzed to create the biochar mix, which was then chemically activated using hydrogen peroxide. The impact of pH was the main focus of the MET adsorption experiment. The isotherms were described using the Freundlich model, which showed values for the Freundlich

exponent and variable non-linearity. The presence of surface functional groups on the modified biochar was identified as the cause of the variability in MET adsorption that was observed. The most advantageous MET adsorption was shown by activated macroalgae biochar (MACAC) and microalgae biochar (MICAC) out of the four biochars examined; at pH 7, the maximum removal efficiency was attained, reaching up to 76%. The production of oxygen-containing surface functional groups was confirmed, and the chemisorption process was established as the main sorption mechanism, using a variety of analytical methods. Zeta potential measurements indicated a lower zeta potential at pH 7, enhancing the electrostatic attraction for both biochars, thereby making them effective at adsorbing positively charged contaminants. Economically speaking, the manufacture of pyrolyzed biochar from algal biomass seemed to offer promise, especially for high-end applications, even if capital expenditure figures were not given.

OS Jimoh et al., (2023) Researched on orange peels which were subjected to acid modification using ortho-phosphoric acid (OPAC) and were subsequently characterized. The functional groups and pore diameters of these OPAC materials were appropriate for the adsorption of metformin (MET) from water. At a contact period of 240 minutes, an initial MET concentration of 5 mg/L, a temperature of 323 K, and a pH of 7, optimal MET adsorption onto OPAC was found, yielding an astounding 97.23% clearance rate of MET. With a high affinity found at 303 K, the Freundlich isotherm model offered the greatest match for the sorption data. At 323 K, the monolayer sorption capacity was 50.99 mg/g, according to the Langmuir isotherm model. Kinetic studies favored the pseudo-second-order model, suggesting a physisorption mechanism. Thermodynamic analysis unveiled the process to be spontaneous, feasible, and endothermic. Overall, OPAC demonstrated efficiency as an adsorbent for removing MET from aqueous solutions.

L Hellmann et al., (2021) Researched on the potential of peach pits as a biosorbent for removing Metformin Hydrochloride from water was investigated. Experiments were conducted in a closed batch system, where various factors such as solution pH, temperature, stirring speed, and chemical treatments were considered. The biosorbent underwent multiple tests and characterizations, including kinetics, equilibrium, and thermodynamic parameters analysis. The ideal parameters were found to be pH 7, 25°C, and 100 rpm for both the untreated and chemically treated

biosorbents. As a consequence, following basic treatment and acid, the highest removal capacity was 49.14 mg/g. The Langmuir model suited the equilibrium data in the kinetic research, but the pseudo-second-order model gave the best explanation of the data. When compared to the raw biosorbent, the chemically treated biomasses showed much better drug removal capabilities. After basic treatment and acid, the greatest absorption capacity of 82.54 ± 1.34 mg/g was noted. According to these results, peach pits may be used as an affordable biosorbent to remove drugs from water.

CHAPTER 3

AIM AND SCOPE

3.1 AIM:

This research aims to develop and investigate the adsorption of Metformin Hydrochloride, an antidiabetic pharmaceutical pollutant, from an aqueous medium employing biochar (AIB) generated from *Azadirachta indica* bark and Graphene oxide doped biochar (GAIB). To prepare graphene oxide through modified hummers method and prepare a composite of AIB with GO which GAIB, and conduct comparative studies among these prepared adsorbents and investigate their efficiency by varying the adsorption parameters through batch studies.

3.2 OBJECTIVE:

- To prepare and characterize cost effective and efficient adsorbent i.e., *azadirachta indica* bark derived biochar, Graphene oxide by using modified hummers method and composite of biochar and graphene oxide.
- To conduct batch tests to ascertain the produced adsorbents' adsorption capacity and effectiveness for the removal of metformin hydrochloride from the aqueous solution.
- To determine the optimal conditions for carrying out adsorption of Metformin Hydrochloride from aqueous system by including factors such as concentration, adsorbent dosage, pH, temperature, and contact time.
- To conduct a comparative study on adsorption among the prepared adsorbents.

3.3 SCOPE:

- Application in pharmaceutical manufacturing industries to treat the effluents containing the toxic pollutants before discharged from the industries.
- These adsorbents can be used in water treatment plants to prevent the pharmaceutical pollutants from entering the water bodies.
- Reduction in environmental impact of the toxic pharmaceutical pollutants from affecting the aquatic ecosystems and public health.

MATERIALS AND EXPERIMENTAL METHODS

4.1 MATERIALS REQUIRED:

Neem tree barks were procured from the surroundings of Kalpakkam in Tamil Nadu. Synthetic graphite powder (98% pure, SRL Chemicals), sulphuric acid (Thermo Fisher), Potassium Permanganate (extrapure 99%, SRL Chemicals), Metformin Hydrochloride (98% purity, Dhamtec), HCl (Thermo Fisher), hydrogen peroxide (SRL Chemicals), Double distilled water, Acetone (Thermo Fisher).

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4.2 STOCK SOLUTION PREPERATION:

1000 mg/l stock solution was prepared initially by dissolving 0.1 g of Metformin Hydrochloride in 100 ml of distilled water. From the prepared stock solution series of dilutions were done according to the experimental demands and requirements. Analytical quantification of MH solution was confirmed with the help of double beam UV visible spectrophotometer. By analyzing the UV response curve, the maximum adsorption ($\lambda_{\max}$) level occurred at 233 nm with quartz cuvettes. A standard curve for MH was plotted which was used to calculate the concentrations of MH in the studies.

4.3 ADSORBENT PREPARATION:

Dried barks from *azadirachta indica* trees commonly known as neem trees were collected from the surroundings of Kalpakkam, Tamil Nadu. The collected barks were washed thoroughly for several times using distilled water to remove the dirt particles from it. Then the washed barks were dried in an oven at 120°C for 8 hours. The dried bark was compacted using a domestic mixer-grinder and stored in an air tight container away from moisture.

In order to prepare the *azadirachta indica* biochar (AIB). The *azadirachta indica* powder was weighed and the *azadirachta indica* bark powder was pyrolyzed in a muffle furnace at 500°C for 2 hours. Then obtained AIB was washed several times and stored in an air tight container.



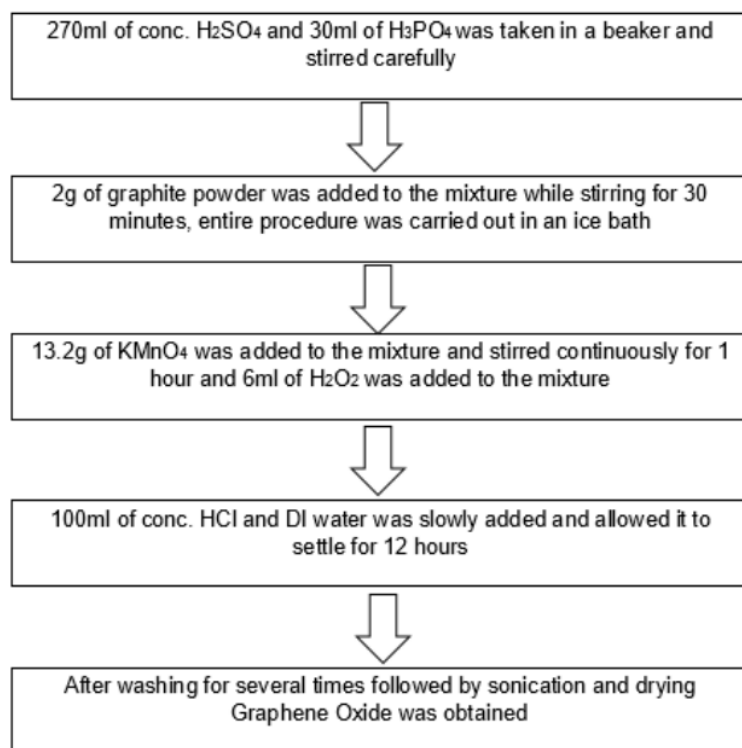
(a)

(b)

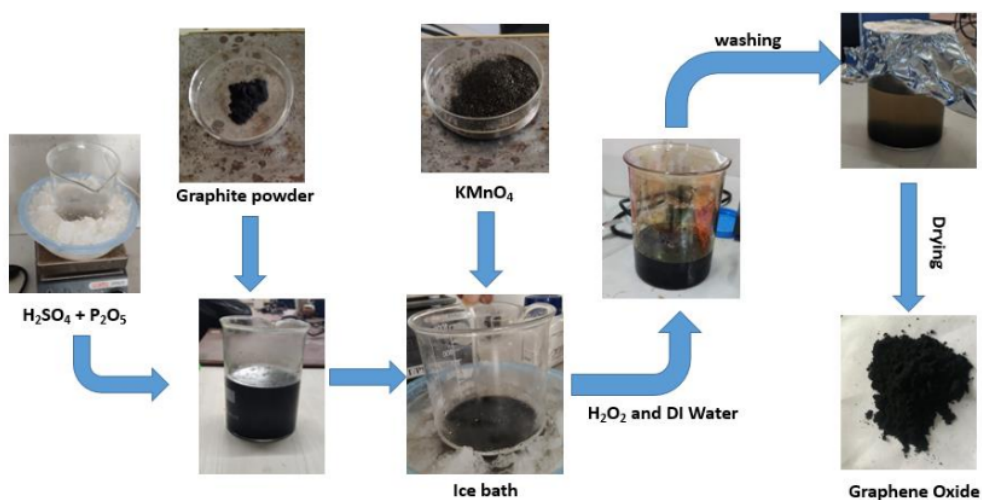
Fig 4.1 (a) Powdered Bark (b) AIB Biochar

4.4 SYNTHESIS OF GO:

The preparation of graphene oxide [GO] is carried out using Modified Hummer's method. Initially, 270 ml of concentrated H_2SO_4 and 30 ml of phosphoric acid was taken in a beaker and stirred carefully using a glass rod. Then, 2 g of synthetic graphite powder was measured and added to the mixture while stirring for 30 mins. This entire procedure was carried out below in an ice bath which was measured at 10 °C. This is done to control the high exothermic reaction. After ensuring the proper mixing, 13.2 g of potassium permanganate [KMnO_4] was added slowly to the mixture and stirred for 1 hour during which the color change from black to dark green colored solution was observed. This was followed by the addition of 6 ml of hydrogen peroxide [H_2O_2] to the slurry mixture. Later, 100 ml of concentrated hydrochloric acid and 300 ml of deionized water was added slowly and carefully. This final mixture is allowed to settle for 12 hours and left undisturbed. When the pH of the mixture was measured it was found to be highly acidic, which is why the mixture is neutralized by washing it using distilled water several times. It is then subjected to sonication process for exfoliation of graphene oxide layers. Finally, the settled graphene oxide slurry was filtered and dried in a hot air oven at 95 °C for 10 hours.



(a)



(b)

Fig 4.2 (a)(b) Synthesis of Graphene Oxide

4.5 PREPERATION OF COMPOSITE ADSORBENT

The biochar which was previously prepared through pyrolysis and graphene oxide synthesized through modified hummer's method were used to prepare the composite adsorbent (GAIB). 200 milliliters of acetone have been added to five grams of AIB in a conical flask, and the mixture was sonicated for two hours. Simultaneously in the other hand 0.5g of GO was taken with 50ml of acetone and sonicated for 2 hours. The AIB mixture from the stirrer and GO mixture from the sonicator are mixed together in a beaker then allowed to sonicate in a sonicator for 2 hours. The obtained slurry was dried overnight at 50°C using tray drier. Finally the obtained composite adsorbent was stored in an air tight container.

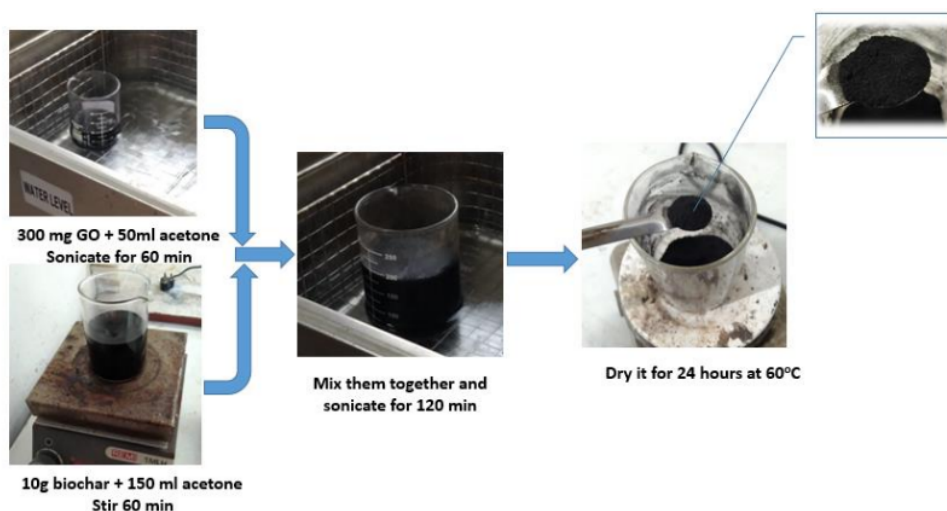


Fig 4.3 Synthesis of GAIB

4.6 CHARACTERIZATION OF ADSORBENTS:

Fourier Transform Infrared (FTIR) Spectroscopy was employed to analyze surface functional groups of AIB, GO and GAIB. The spectrum was obtained by recording wavelengths ranging from 4500 to 500 cm^{-1} in transmission mode. X-Ray Diffraction (XRD) was utilized to examine structural variations in the prepared adsorbents. Field-emission scanning electron microscopy (FESEM) with energy dispersive X-ray spectroscopy (EDX) was done to study the morphological structure of the adsorbents and the specific surface area of adsorbents was measured using the BET (Brunauer-Emmett-Teller) test.

4.7 ADSORPTION EXPERIMENTS:

The pace at which adsorption may possibly approach equilibrium was evaluated by batch adsorption tests. Batch adsorption experiments were conducted using AIB and GAIB in 100 mL of Metformin Hydrochloride (MH) solution. The determination of Metformin Hydrochloride (MH) was carried out using a UV spectrophotometer at a wavelength of 233 nm. Batch experiments were then conducted to assess the behavior of Metformin Hydrochloride (MH) on AIB and GAIB.

The batch study parameters, including pH (2,4,6,8,10) and dose rate (2,4,6,8,10,12,14 g/L) for AIB and (1,2,3,4,5,6,7 g/L) for GAIB, the effect of initial concentration (10,20,30,40,50 mg/L), contact time (30,60,90,120,150,180 minutes), and temperature (303,308,313,323 K) were evaluated. The pH of the mixture was adjusted using 0.1 N solutions of both HCl and Noah. Following the completion of adsorption, the filtrate underwent filtration through whatman filter papers. Subsequently, the Metformin Hydrochloride (MH) was conducted using a UV-Visible spectrophotometer at a wavelength of 233 nm.

The following formulas were used to determine the removal efficiency and amount of adsorbate absorbed by the adsorbent (q_e ; mg/g).

$$\text{removal efficiency} = \frac{C_i - C_e}{C_i} \times 100$$

$$q_e = \frac{C_i - C_e}{W} \times V$$

Where W is the mass of the adsorbent taken (g), V is the volume of the solution (L), C_i is the initial concentration (mg/L), and C_e is the equilibrium concentration (mg/L).

CHAPTER 5

RESULTS AND CHARACTERIZATION

This section attempts to clarify the effectiveness and processes behind the adsorption process of Metformin Hydrochloride by *Azadirachta Indica* bark-derived biochar and its composite with graphene oxide by rigorous experiments and careful analysis. The results reported here offer insightful information on the adsorbents adsorption capacity, kinetics, thermodynamics, and structural properties, opening the door to a fuller comprehension of their possible uses in pharmaceutical waste management and water treatment.

5.1 UV SPECTROSCOPY:

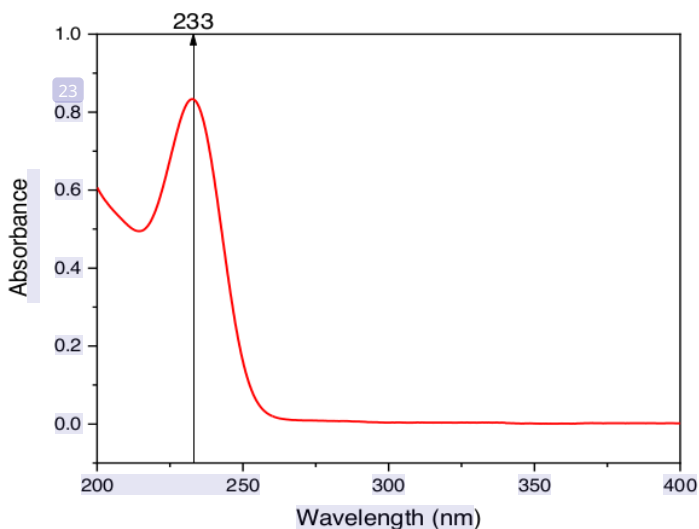


Fig 5.1 UV Spectra of Metformin Hydrochloride

A solution with a concentration of 10 ppm was created in order to calculate the ($\lambda_{\max}$) of MH. By using UV-Vis spectroscopy, the absorbance spectra was captured between 200 and 800 nm in wavelength. It was discovered that the $\lambda_{\max}$ was 233 nm, as Fig. 5.1 illustrates.

5.2 FT-IR Analysis:

5.2.1 FT-IR of AIB:

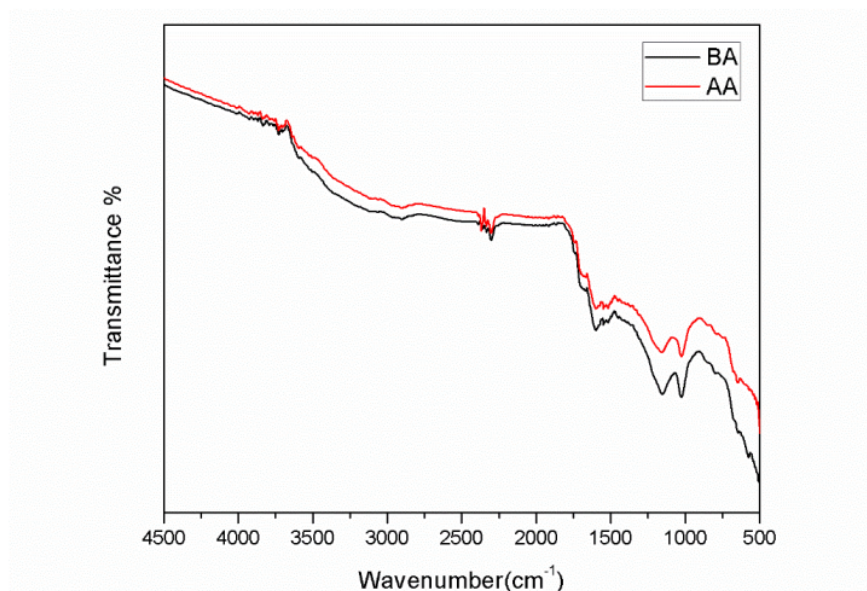


Fig 5.2 FT-IR Spectra of AIB before and after adsorption

In the FTIR spectrum of AIB before adsorption (BA) and after adsorption (AA), the presence of aromatic C=C (carbon-carbon double bonds) stretching vibrations often corresponds to a peak that is approximately 1597 cm⁻¹. The observed peak in the context of biochar could suggest that the material comprises aromatic carbon structures. Following the pyrolysis process used to form biochar, lignin, a component of plant biomass, can break down to yield aromatic carbon structures. This peak, which is indicative of aromatic chemicals, often appears in biochar spectra as a result of the burnt plant matter present. A peak at about 1154 cm⁻¹ often corresponds to C-O stretching vibrations, which are commonly symptomatic of C-O single bonds. This peak could point to that there is a presence of ethers, other oxygen-containing functional groups, or aliphatic hydroxyl groups (alcohols) in the structure of biochar. A peak roughly 1025 cm⁻¹ is frequently connected to C-O-C (carbon-oxygen-carbon) stretching vibrations, which are a sign that ether functional groups have been discovered in a sample. This peak could point to that there is a presence of ethers or other organic molecules containing oxygen in the chemical structure of biochar.

5.2.2 FT-IR of GO:

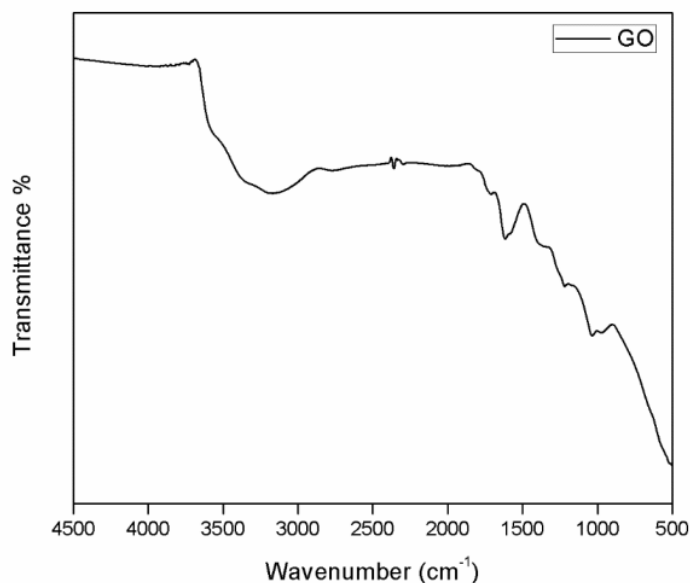


Fig 5.3 FT-IR Spectra of GO

The FTIR (Fourier-Transform Infrared) spectrum of graphene oxide (GO) has a peak at 3167 cm^{-1} that is most likely related to O-H stretching vibrations, which show the presence of hydroxyl (alcohol) groups. Oxygen-containing functional groups are the hallmark of GO, and its FTIR spectra is characterized by O-H stretching vibrations. In an FTIR (Fourier-Transform Infrared) spectrum, a peak at around 1035 cm^{-1} is frequently linked to C-O (carbon-oxygen) stretching vibrations, which are generally suggestive of the existence of oxygen-containing functional groups in a substance. A peak at 1035 cm^{-1} is significant in the context of graphene oxide (GO), which is well-known for having functional groups that include oxygen. Graphite is converted into GO through an oxidation process that adds groups containing oxygen.

5.2.3 FTIR OF GAIB:

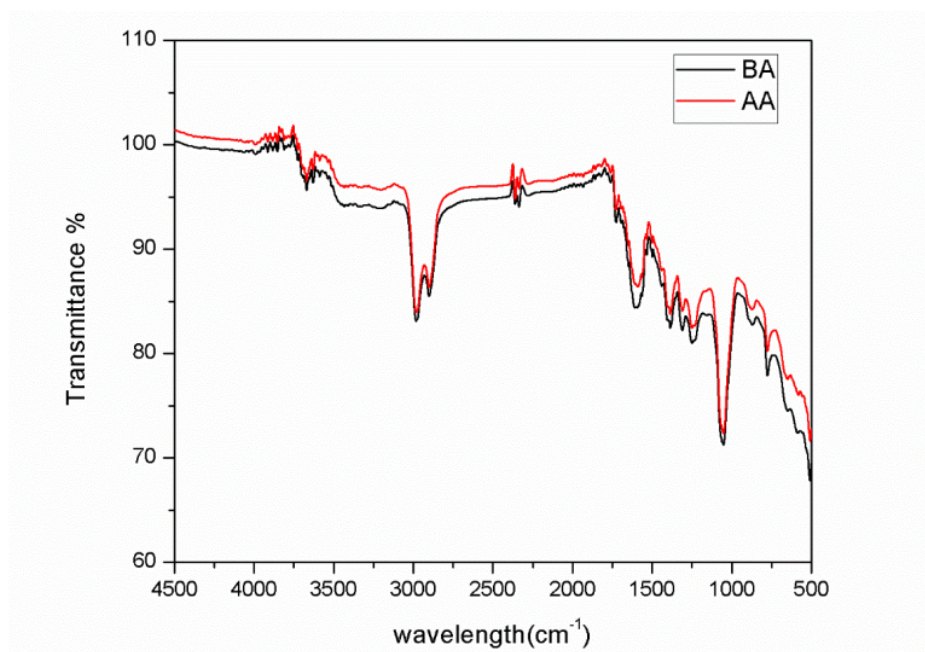


Fig 5.4 FTIR spectra of GAIB

The FTIR (Fourier-Transform Infrared) spectrum of GAIB before adsorption (BA) and after adsorption (AA), has a peak at 3992, 3669, cm⁻¹ that is most likely related to O-H stretching vibrations, which show the presence of hydroxyl (alcohol) groups. The FTIR peak detected at 2982 cm⁻¹ is commonly in connection with the stretching vibration of C-H (carbon-hydrogen) bonds, which are frequently present in alkane functional groups, peak detected at 1610 cm⁻¹ is commonly in connection with the stretching vibration of C=C (carbon-carbon double bonds), which are frequently present in aromatic compounds or conjugated systems. The FTIR peak detected at 2279 cm⁻¹ is often in connection with the stretching vibration of a carbon-carbon triple bond (C≡C), which is commonly found in alkynes.

5.3 XRD Analysis:

5.3.1 XRD ANALYSIS OF AIB:

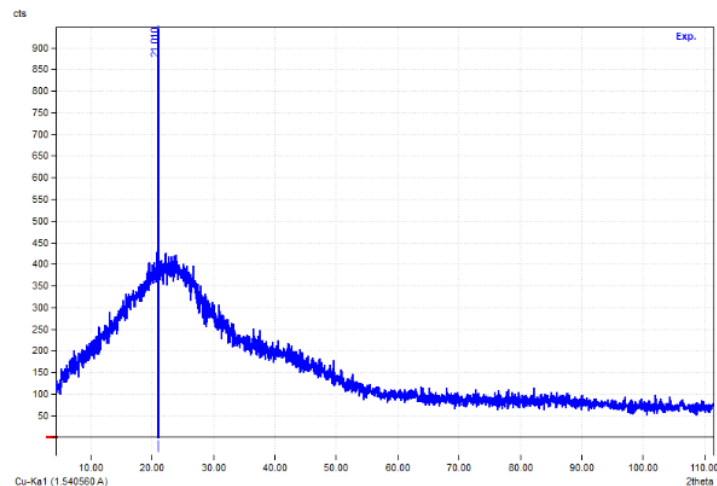


Fig 5.5 XRD Spectra of AIB

A promising technique for evaluating the structural makeup of biochar, a material rich in carbon that is produced by pyrolyzing material that is organic, is X-ray diffraction (XRD). Rather than featuring distinct, sharp peaks, patterns usually have wide, diffuse ones. This quality is a reflection of the amorphous, disordered carbon structure of biochar.

5.3.2 XRD SPECTRA OF GAIB:

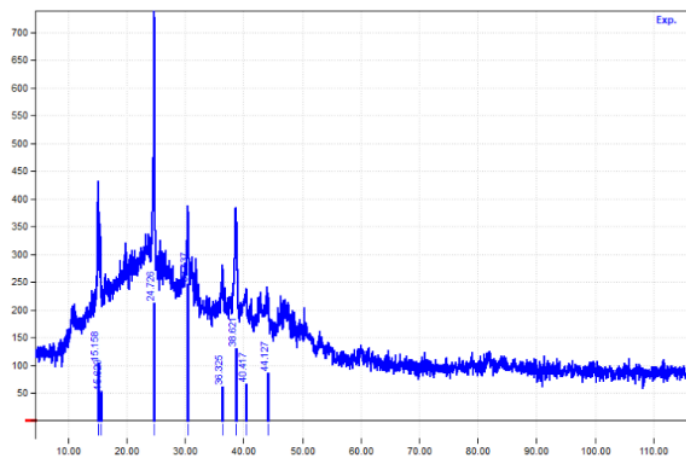


Fig 5.6 XRD spectra of GAIB

The GAIB sample before adsorption were subjected to x-ray diffraction (XRD) analysis. The X-ray diffraction (XRD) analysis of GAIB unveiled a prominent peak at 24.73 degrees, alongside peaks at 15.63, 30.44, and 38.62 degrees at 2 θ . These peaks signify diffraction from distinct crystallographic planes within the composite material, offering crucial insights into its structural properties. From which can we infer that GAIB has crystalline structure due to more number of sharp and higher peaks compared to XRD results of AIB.

5.4 FESEM Analysis:

5.4.1 AIB FESEM ANALYSIS:

To comprehend the structural and morphological changes that take place throughout the adsorption process, FESEM analysis is a vital method for evaluating biochar both prior to and during adsorption tests.

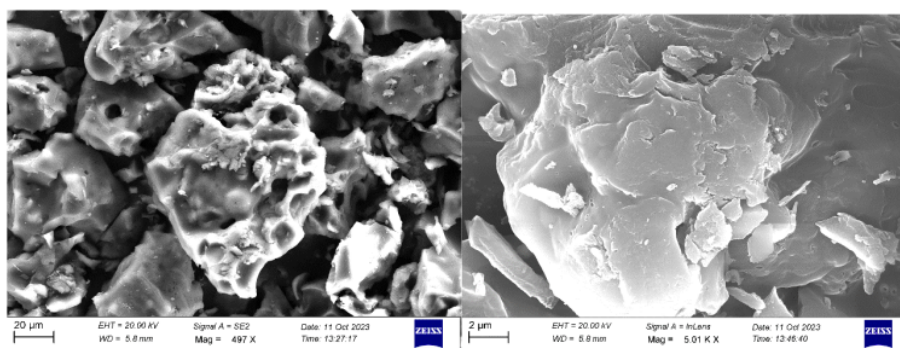


Fig 5.7 FESEM images of AIB before adsorption

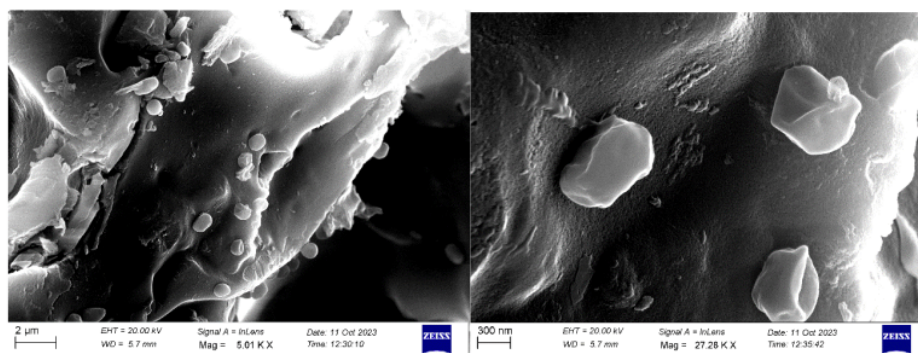


Fig 5.8 FESEM Images of AIB after adsorption

¹⁹ AIB samples were examined to Field Emission Scanning Electron Microscopy (FESEM) before and after adsorption. By comparing the images of before and after adsorption we can very clearly visualize from the structure that adsorption has taken place by seeing the pollutants being attached to the surface after adsorbent and prominent changes in the surface of the biochar after adsorption.

5.4.2 GAIB FESEM ANALYSIS:

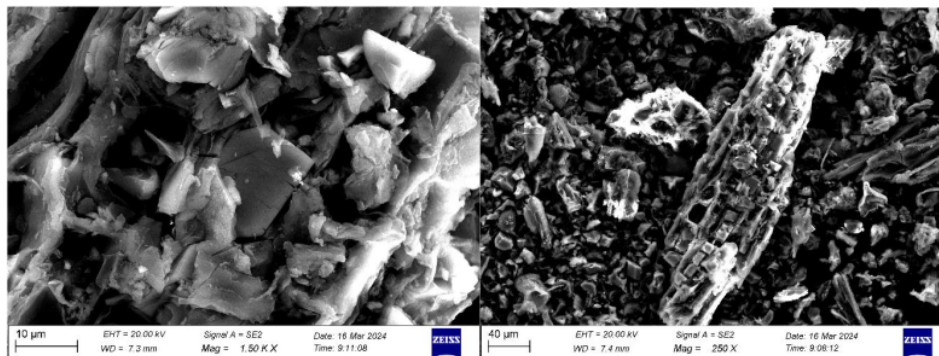


Fig 5.9 FESEM images of GAIB before adsorption

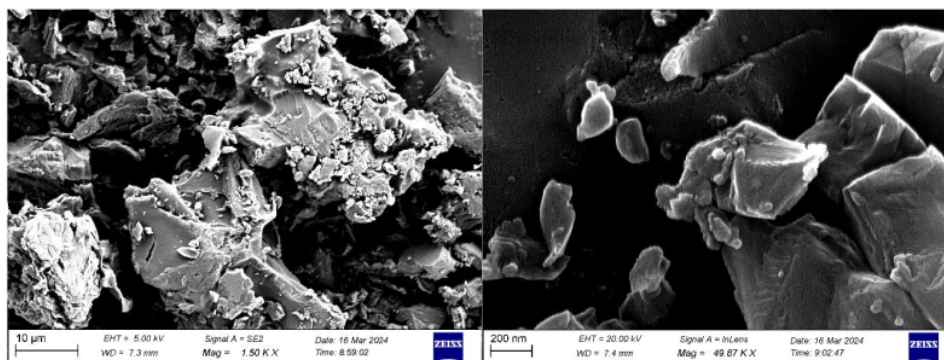


Fig 5.10 FESEM images of GAIB after adsorption

¹⁹ GAIB samples were examined to Field Emission Scanning Electron Microscopy (FESEM) before and after adsorption. In the before adsorption FESEM image of GAIB we can clearly see the rough and porous surface of the material which is very much essential for the adsorption to take place. In the after adsorption samples of GAIB we can see clearly that the pores of the adsorbent material surface is occupied by the adsorbate which is Metformin Hydrochloride (MH).

5.5 EDAX Analysis:

EDAX, or energy dispersive X-ray analysis, is a useful analytical method for figuring out a material's constituent makeup. It can offer crucial information on the alterations in the elemental composition brought about by the adsorption process when applied to biochar both before and after adsorption of Metformin Hydrochloride.

5.6.1 EDAX ANALYSIS OF AIB:

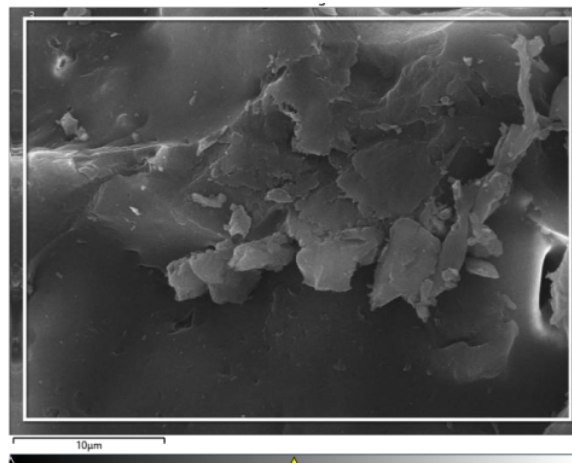


Fig 5.11 Electron image of AIB before adsorption

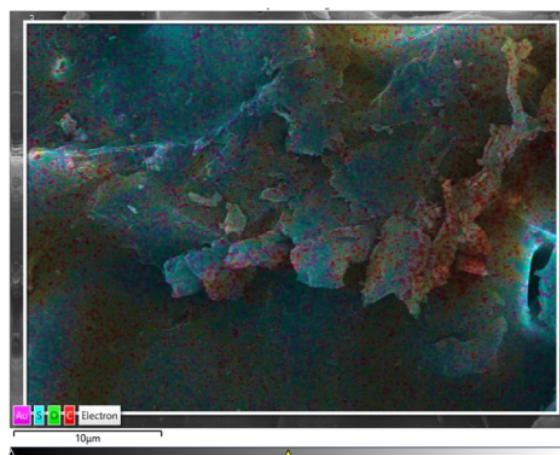


Fig 5.12 EDS Layered image of AIB before adsorption

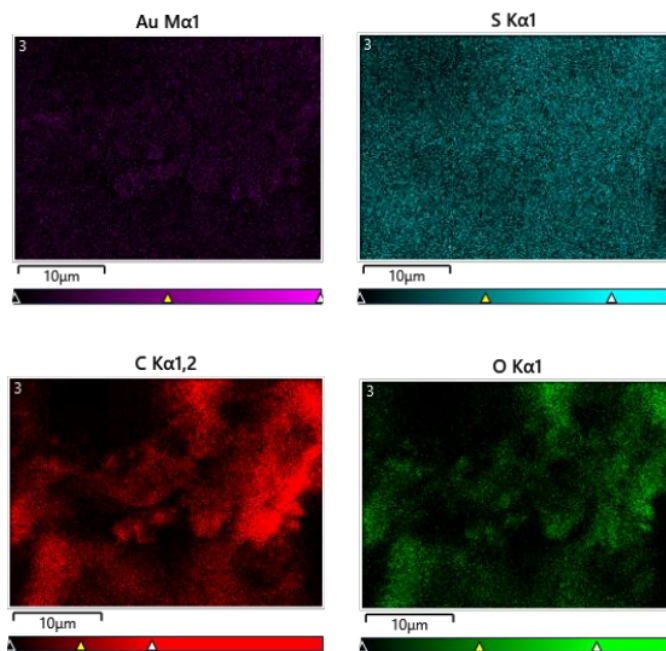


Fig 5.13 EDS Layered images of Au, S, C, O before adsorption

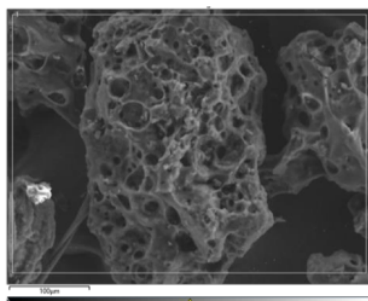


Fig 5.14 Electron image of AIB after adsorption

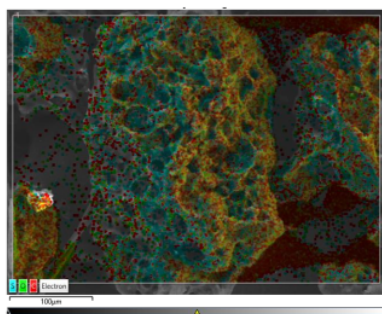


Fig 5.15 EDS Layered image of AIB after adsorption

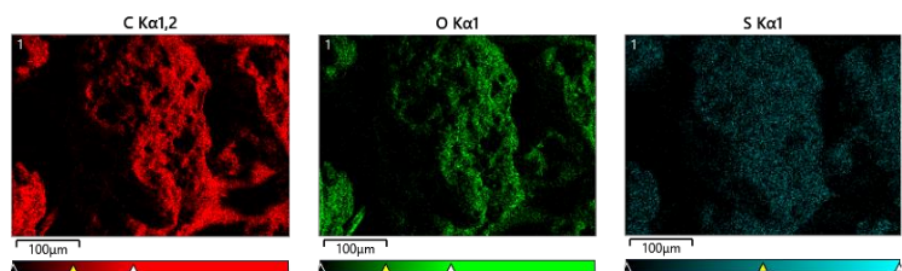


Fig 5.16 EDS Layered images of C, O, S after adsorption

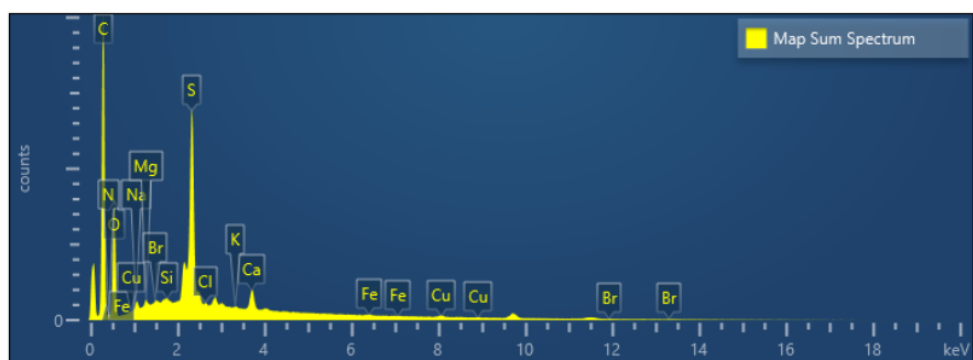


Fig 5.17 EDAX spectra of AIB before adsorption

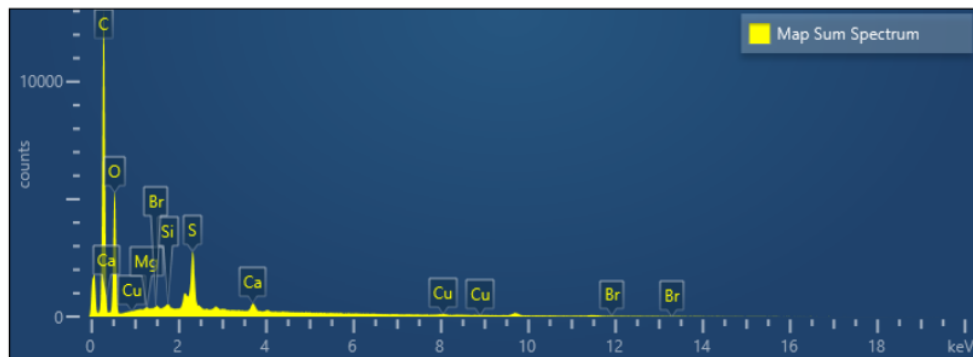


Fig 5.18 EDAX Spectra of AIB after adsorption

5
Table 5.1 EDAX spectra of AIB before and after adsorption

Element	Weight % before adsorption	Weight % after adsorption
C	76.29	72.73
N	0.47	-
O	20.37	26.11
Na	0.21	-
Mg	0.10	0.04
Si	0.03	0.05
S	2.03	0.81
Cl	0.05	-
K	0.02	-
Ca	0.30	0.16
Fe	0.03	-
Cu	0.09	0.06
Br	0.03	0.03

5.5.2 EDAX ANALYSIS OF GAIB:

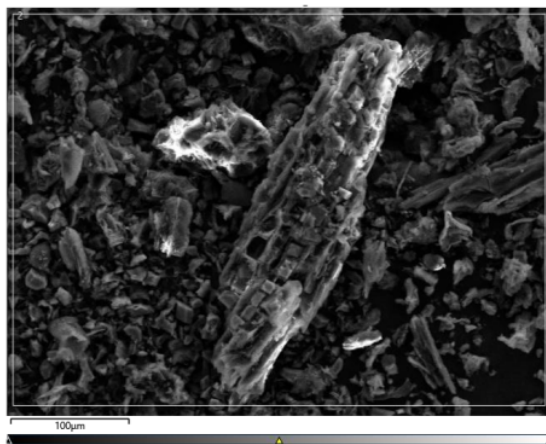


Fig 5.19 Electron image of GAIB before adsorption

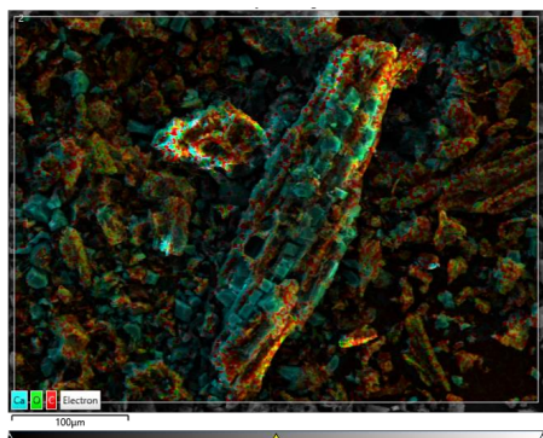


Fig 5.20 EDS layered images of GAIB before adsorption

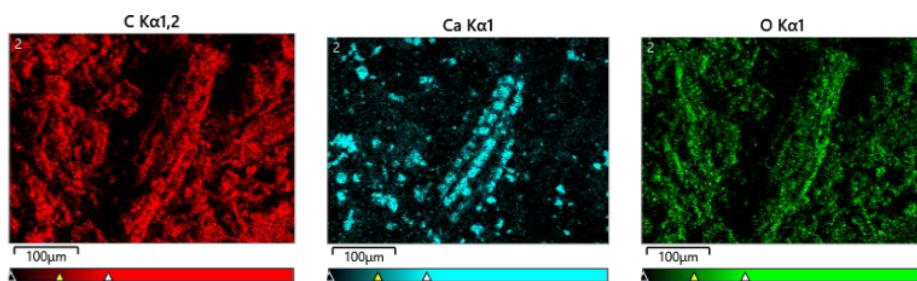


Fig 5.21 EDS Layered images of C, Ca, O before adsorption

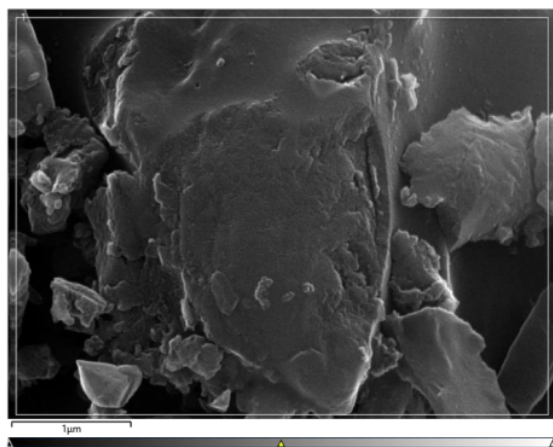


Fig 5.22 Electron image of GAIB after adsorption

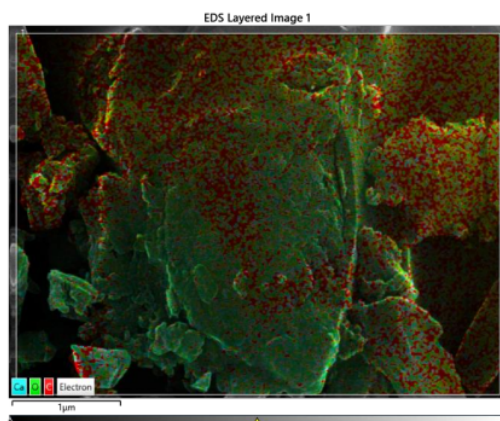


Fig 5.23 EDS layered image of GAIB after adsorption

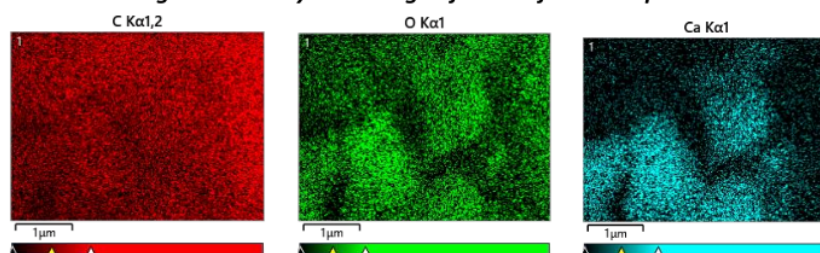


Fig 5.24 EDS layered images of C, O, and Ca after adsorption

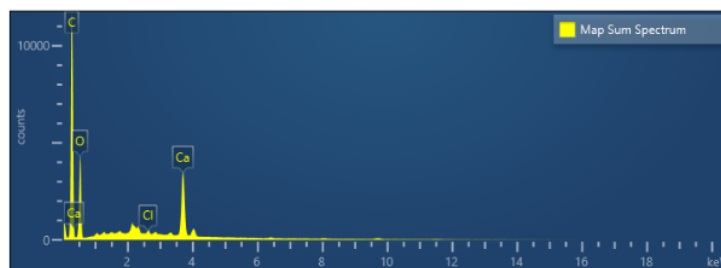


Fig 5.25 EDAX spectra of GAIB before adsorption

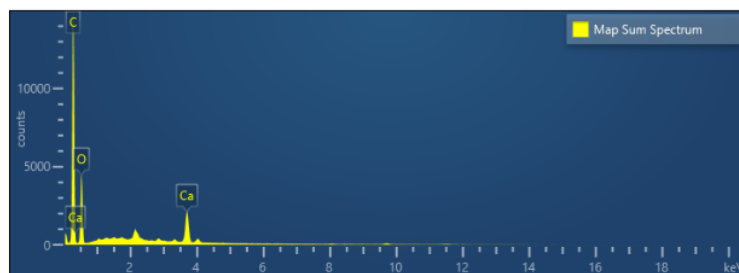


Fig 5.26 EDAX spectra of GAIB after adsorption

Table 5.2 EDAX spectra of GAIB before and after adsorption

Element	Weight % before adsorption	Weight % after adsorption
C	60.58	65.07
O	33.19	31.62
Ca	5.97	3.30
Cl	0.26	-
Total	100	100

Using energy dispersive X-ray analysis, the AIB and GAIB samples were examined. We may infer from the AIB's EDAX results that its primary constituents are carbon and oxygen. Other than C and O, other elements are too found such as N, Si, Mg, Cl, S, Br, K, Ca, Fe, Cu and Na but which are present only in trace amount and is negligible. The carbon content have decreased after adsorption experiment this is due to coverage of Metformin Hydrochloride particles on the surface of the sample Adsorption mechanisms led to the displacement or obscuration of carbon atoms by adsorbed molecules, impacting their detectability via EDX. The increase in oxygen content following adsorption stemmed from interactions between oxygen-containing molecules in the adsorbate and surface functional groups of the adsorbent, resulting in the formation of new oxygen species. Chemisorption processes resulted in the chemical bonding of oxygen atoms to the adsorbent surface, contributing to the elevated oxygen content.

GAIB was examined using energy dispersive X-ray analysis (EDAX) before and after the adsorption have taken place. From the results we can infer that, the prepared adsorbent GAIB was mainly composed of C, O and Ca. The increase in carbon content was observed after adsorption which was due to the preferential adsorption of carbon-containing species onto the composite surface. During the adsorption process, organic molecules or contaminants from the solution interacted with the surface functional groups of the composite, leading to the immobilization of carbon-rich molecules onto its surface. As a result, the composite material's apparent carbon content increased.

5.6 BET ANALYSIS

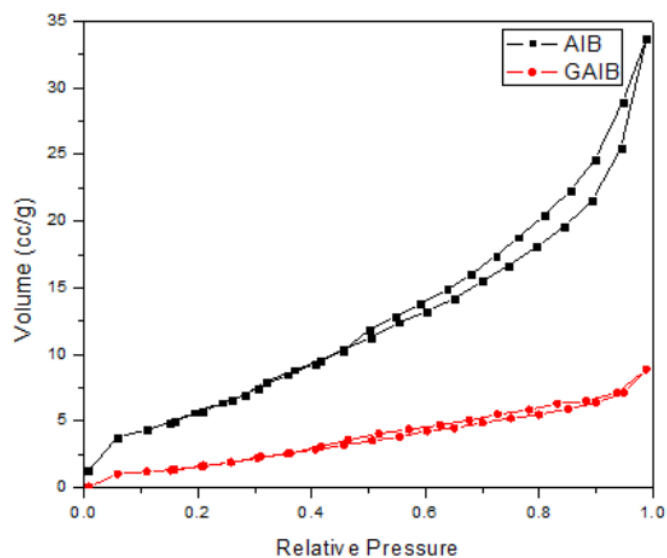


Fig 5.27 Adsorption/Desorption isotherm curve for AIB and GAIB

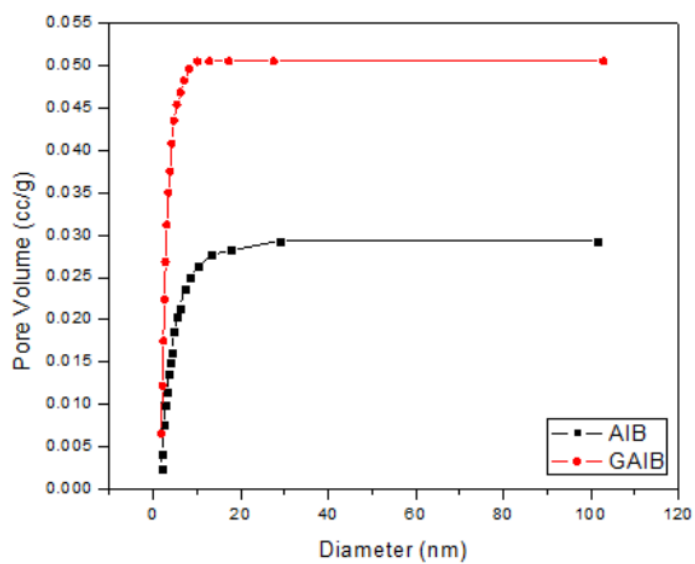


Fig 5.28 BJH pore size distribution for AIB and GAIB

Figure 5.27 shows the Brunauer, Emmett, and Teller (BET) adsorption isotherms and Fig 5.28 shows the Barrett-Joyner-Halenda (BJH) pore size distribution curves for AIB and GAIB. The N₂ isotherm of AIB and GAIB reveals a meso-porous structure with a type IV isotherm and an H₃-type hysteresis loop. The type IV isotherm hysteresis closed-loop verified the mesoporous structure occluded with voids in the shape of the narrow slit, while the N₂ adsorption isotherm demonstrated the microporous nature of the material.

The AIB has a surface area (S_{BET}), pore diameter (d), and total pore volume (V_{tot}) of 31.612 m²/g, 1.925 nm, and 0.029 cc/g, in that order. Whereas in the case of GAIB the surface area (S_{BET}), pore diameter (d), and total pore volume (V_{tot}) were in the order of 68.713 m²/g, 1.923 nm and 0.050 cc/g. From this it is evident that the surface area has increased 117% from AIB to GAIB which is favorable for adsorption. Thus, GAIB can be considered as a more potential adsorbent.

Table 5.3 BET Surface area and Pore volume

Adsorbent	Surface Area (S_{BET}) (m ² /g)	Pore Diameter (d) (nm)	total pore volume (V_{tot}) (cc/g)
AIB	31.612	1.925	0.029
GAIB	68.713	1.923	0.050

5.7 FACTORS IMPACTING ADSORPTION OF METFORMIN HYDROCHLORIDE:

5.7.1 EFFECT OF pH:

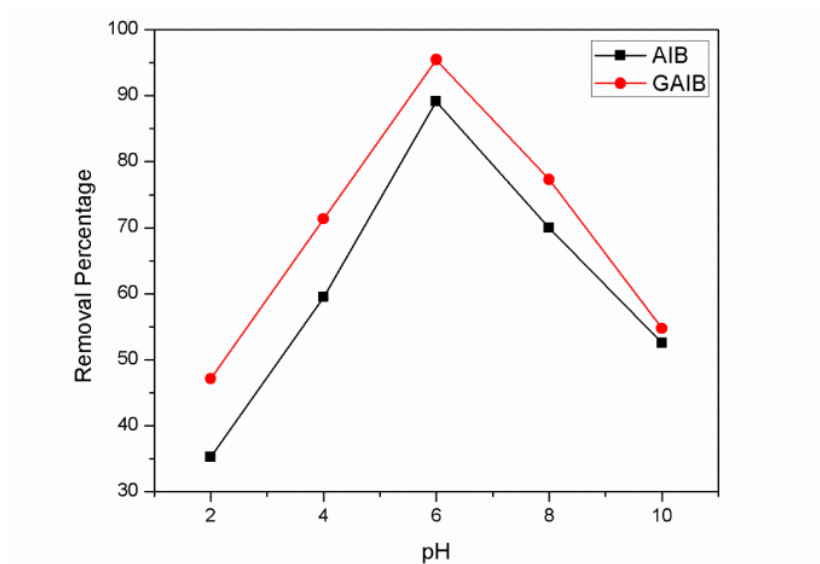


Fig 5.29 effect of pH vs Removal Percentage

The pH level of the solution was changed between 2 and 10 in order to evaluate the impact of pH. All other parameters were held constant during the adsorption studies, which were conducted in the pH range of 2 to 10. (MH concentration = 10 mg/L; adsorbent dosage = 10g/L for AIB and 5g/L for GAIB; contact period = 120 min). According to Figure 5.29, it is evident that the adsorption of the Metformin Hydrochloride for AIB and GAIB increased when the pH of the mixture rose from 35.23 to 89.17% for AIB and 47.14 to 95.47% for GAIB. From 2 to 6 and started to decrease after reaching maximum at pH 6. The maximum adsorption of Metformin Hydrochloride by AIB and GAIB at pH 6 attributed to optimal surface charge and chemical speciation, favoring effective binding of neutral metformin molecules to adsorbent surface. Additionally, the surface functional groups were likely in an optimal state for interaction with MH molecules at this pH. At pH 6, minimized competition from other ionic species and enhanced chemical stability further facilitated efficient adsorption of MH onto AIB and GAIB, resulting in maximum adsorption capacity at this pH level.

5.7.2 EFFECT OF ADSORBENT DOSAGE:

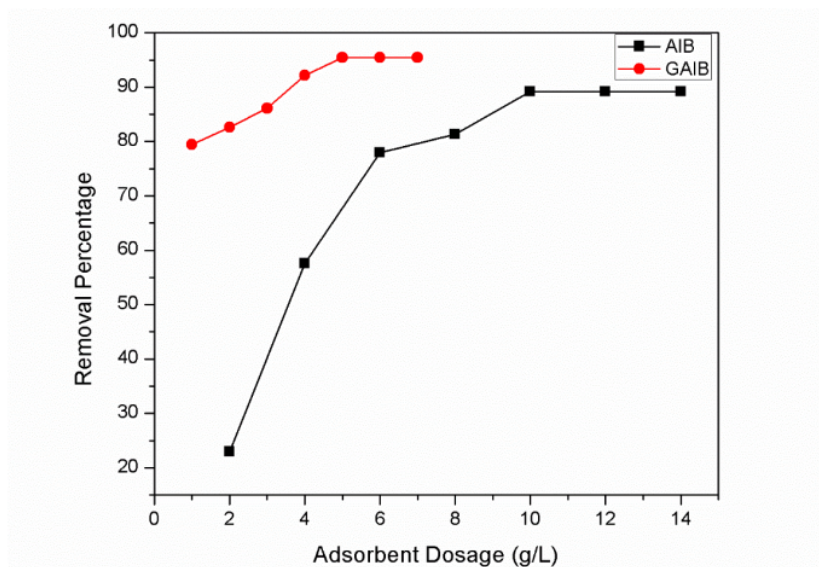


Fig 5.30 Effect of adsorbent dosage vs Removal percentage

The influence of AIB and GAIB dose rate was studied by adjusting the AIB dosage from 1 to 14 g/L and GAIB dosage from 1 to 7 g/L, while maintaining pH at 6, shaking time at 120 minutes, MH concentration at 10 mg/L, and temperature at 30°C. Graphical representation in Figure 5.30 indicates that as AIB and GAIB dosage increased, the removal efficiency of MH also rose. Notably, a substantial improvement in MH removal, from 22.93% to 89.17% in AIB and 79.47% to 95.47% in GAIB was observed with the increase in dosage. Nevertheless, when the surface attained MH molecule saturation, additional adsorbent dose increases had little effect on removal effectiveness. This saturation shows that MH molecules occupy every accessible active site on the adsorbent surface. The inclusion of more active sites and the increased surface area of GAIB and AIB most likely contributed to the increased removal efficiency. Notably, since the pores are already full of dye molecules, adsorption stops as soon as equilibrium is reached.

5.7.3 EFFECT OF INITIAL CONCENTRATION:

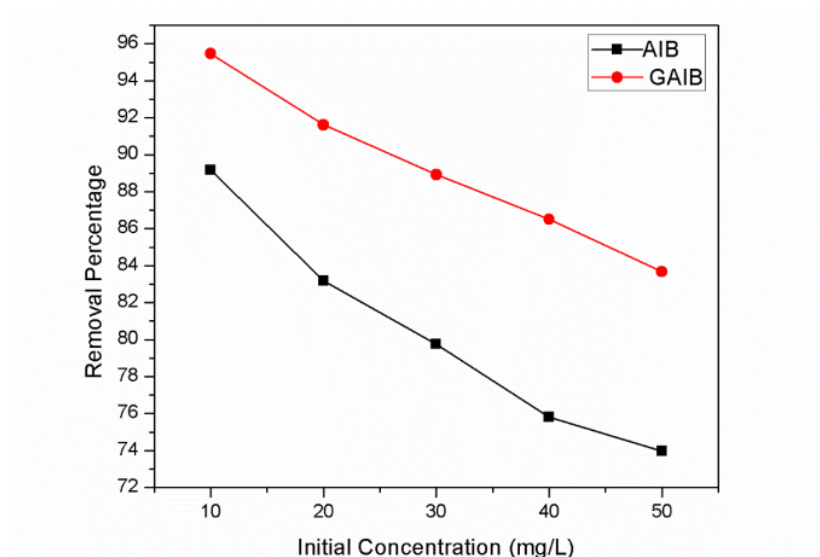


Fig 5.31 Effect of initial concentration vs removal percentage

The experimental results of the effect of initial MH concentration on the removal of MH by AIB and GAIB was shown in Figure 5.31. The removal of MH by AIB and GAIB was studied by varying the initial concentration (10, 20, 30, 40, 50 mg/L) in aqueous system with temperature (30°C) and pH (6) and 120 min as shaking time. It was evident from Figure 5.20 that the removal of MH decreased with increasing initial MH concentration. The results indicated that the optimum pollutant concentration was 10 mg/L for AIB and GAIB. The removal percentage of AIB decreased from 89.17% to 73.97% at 50 mg/L, for GAIB it decreased from 95.47% to 83.67% at 10 mg/L. At lower MH concentrations, there was a higher availability of adsorption sites, making it easier for MH to be adsorbed. On the other hand, a decrease in MH removal was noted at greater starting MH concentrations because there were fewer adsorption sites available overall. Absorbance levels increased noticeably when the concentration of metformin hydrochloride was more than 50 mg/L during UV detection. This elevated absorbance could introduce significant interference, thereby compromising the precision of the analytical results obtained. Consequently, it was crucial to ensure that the concentration remained below 50 ppm to uphold the accuracy and reliability of UV detection analyses.

5.7.4 EFFECT OF CONTACT TIME:

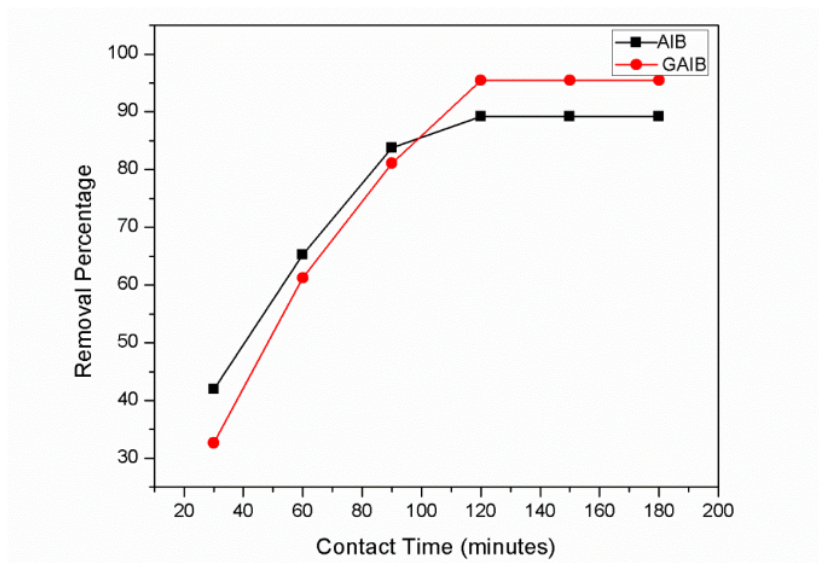


Fig 5.32 Effect of contact time vs removal percentage

One of the crucial factors utilized to evaluate the efficiency of the adsorbent in removing the adsorbate is the impact of contact time of AIB and GAIB on MH. The rate of MH removal was examined by varying the agitation time from 30 minutes to 180 minutes, while keeping other parameters constant at pH 6, MH concentration at 10 mg/L, dose rate at 10 g/L for AIB and 5 g/L for GAIB, and temperature at 30°C. The results are illustrated graphically in Figure 5.32. For AIB the removal percentage of MH molecules increased from 41.93% at 30 minutes to 89.17% at 120 minutes, whereas for GAIB the removal percentage increased from 32.64% at 30 minutes to 95.47% at 120 minutes. The figure clearly shows a significant increase up to 120 minutes, at which point the rate at which MH molecules are adsorption by the active sites equals the rate at which MH molecules are desorption from previously bound sites, resulting in an equilibrium condition. Further adsorption stops when equilibrium is established because MH molecules have saturated the active sites and pores. After this time, the three diffusion processes of film, pore, and surface responses cause any residual active sites to become saturated.

5.7.5 EFFECT OF TEMPERATURE

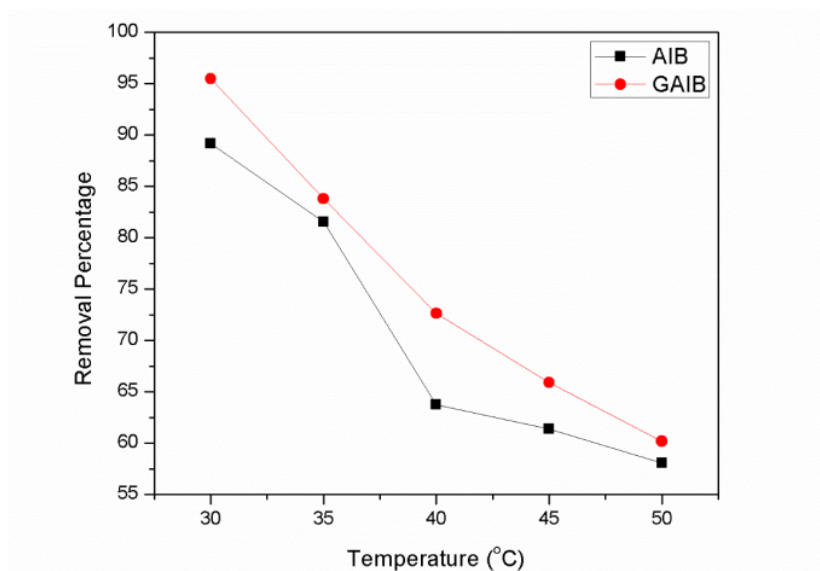


Fig 5.33 Effect of temperature vs removal percentage

To investigate the suitable temperature, experiments were conducted by varying the temperature from 303 K to 318 K while maintaining other parameters constant, such as pH 6, MH concentration 10 mg/L, shaking time 120 min, and dose rate was 10 g/L for AIB and 5 g/L for GAIB. As depicted in Figure 5.33, it is observed that increasing the temperature leads to a decrease in adsorption efficiency from 89.17% to 58.09% for AIB and for GAIB in decreased from 95.47% to 60.18% with increase in temperature. The weakening of the electrostatic field of attraction, which causes the AIB and GAIB to absorb less MH at higher temperatures, may be the cause of this decline in efficiency. MH molecules have a tendency to desorb from the adsorbed active sites at higher temperatures. As a result, it is clear that utilizing AIB and GAIB as the adsorbent, MH will adsorb more effectively at lower temperatures.

5.8 ADSORPTION ISOTHERM MODELS

An adsorption isotherm is essentially a critical curve that clarifies the mechanisms controlling the retention, release, or mobility of a material under constant pH and temperature from aqueous porous media or aquatic habitats to a solid phase. The adsorption of MH by AIB and GAIB adsorbents was examined in this work using three adsorption isotherm models: the Langmuir, Freundlich, and Temkin isotherms.

For monolayer adsorptions, where the adsorbent surface is thought to be homogenous and the adsorbate is thought to adsorb in a monolayer, the Langmuir isotherm model works well. Here is the mathematical expression that has been provided.

$$q_e = \frac{q_{max}K_L C_e}{1 + K_L C_e},$$

Where q_e is the quantity of MH adsorbed per gram of the adsorbent at equilibrium (mg^{-1}), K_L is known as the Langmuir constant (L/mg), C_e is the equilibrium concentration of the MH (mg/L), and q_{max} is the monolayer adsorption capacity (mg/g).

The Freundlich isotherm, an early empirical model of adsorption phenomena which extend beyond the formation of monolayers, characterizes non-ideal and reversible adsorption processes. It accommodates multilayer adsorption with varying distribution of adsorption heat and affinities across heterogeneous surfaces. The equation that represents this isotherm shall be the following

$$q_e = K_F C_e^{1/n},$$

Where, q_e is the amount of adsorbate adsorbed per unit mass of adsorbent at equilibrium (mg^{-1}), C_e is the equilibrium concentration, K_F is the Freundlich constant and $1/n$ is the empirical parameter related to adsorption intensity.

The Temkin isotherm is a tool used to explain solid surface adsorption processes. Adsorbent-adsorbate interactions are assumed to cause the adsorption heat of molecules to decrease linearly with surface coverage. A parameter is included to account for the potential energy of adsorption sites. Here is an expression for the Temkin equation:

$$qe = \frac{RT}{b_T} \ln(K_T C_e),$$

Where, q_e is the amount of adsorbate adsorbed per unit mass of adsorbent at equilibrium (mg^{-1}), C_e is the equilibrium concentration, K_T is the Temkin constant, R represents the universal gas constant, and T represents the absolute temperature in Kelvin.

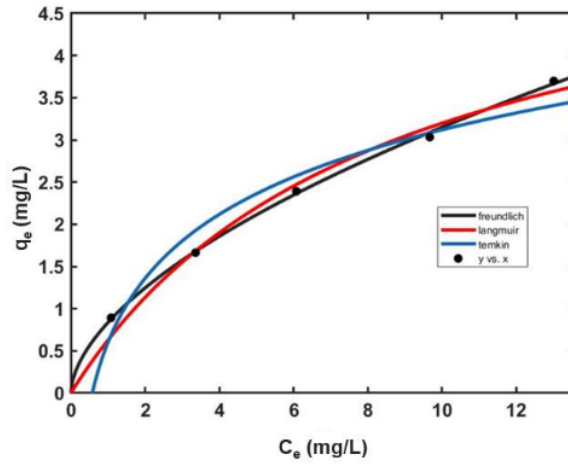


Fig 5.34 Isotherm evaluation for removal of MH by AIB

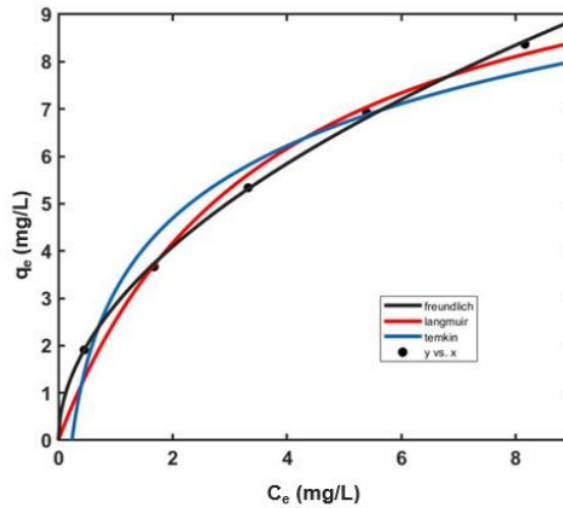


Fig 5.35 Isotherm evaluation for removal Of MH by GAIB

Table 5.4 Adsorption Isotherm Parameters

Models	AIB		GAIB	
	Parameters	Values	Parameters	Values
Langmuir	$q_{\max}$ (mg/g)	5.878	$q_{\max}$ (mg/g)	11.84
	K_L (L/mg)	0.1193	K_L (L/mg)	0.2712
	R^2	0.983	R^2	0.9805
	SSE	0.0832	SSE	0.5107
	RMSE	0.1665	RMSE	0.4126
Freundlich	K_f ((mg/g) (L/mg) ^{1/n})	0.8352	K_f ((mg/g) (L/mg) ^{1/n})	2.865
	n	1.735	n	1.945
	R^2	0.9988	R^2	0.9992
	SSE	0.00564	SSE	0.02118
	RMSE	0.04336	RMSE	0.08403
Temkin	R^2	0.9526	R^2	0.9387
	K_T (L/mg)	1.729	K_T (L/mg)	4.205
	SSE	0.2313	SSE	1.204
	RMSE	0.2776	RMSE	0.6334

Table 5.1 displays the isotherm analysis parameters as well as the equilibrium evaluation. The R^2 value and error readings were used to pick the model that was most appropriate for this adsorption process. Given Table 5.1's higher R^2 value and lower SSE and RMSE error values, it is evident that the system adheres to the Freundlich isotherm. The SSE and RMSE mathematical equations are shown below.

$$SSE = \sum_{i=1}^n (A_i - P_i)^2,$$

$$RMSE = \sqrt{\sum_{i=1}^n \frac{(A_i - P_i)^2}{n}},$$

5.9 ADSORPTION KINETIC MODELS

The kinetic models offer insights into the time needed to reach adsorption equilibrium, serving as a crucial aspect in designing adsorption systems. They provide valuable information about the process rate and the efficacy of the adsorbent material. Pseudo-first-order (PFO), pseudo-second-order (PSO) and elovich kinetic models were used to evaluate the prepared adsorbents. The equilibrium time needed to complete the adsorption process is disclosed by these kinetic models. It is a crucial instrument in the development of an adsorption system. It delivers information on the process's pace and the material's efficiency.

Pseudo-first order kinetic model is given as:

$$q_t = q_e(1 - \exp(-k_1 t))$$

Pseudo-second order kinetic model is given as:

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t}$$

Elovich Kinetic model is given as:

$$q_t = \frac{1}{\beta} \ln(1 + \alpha \beta t)$$

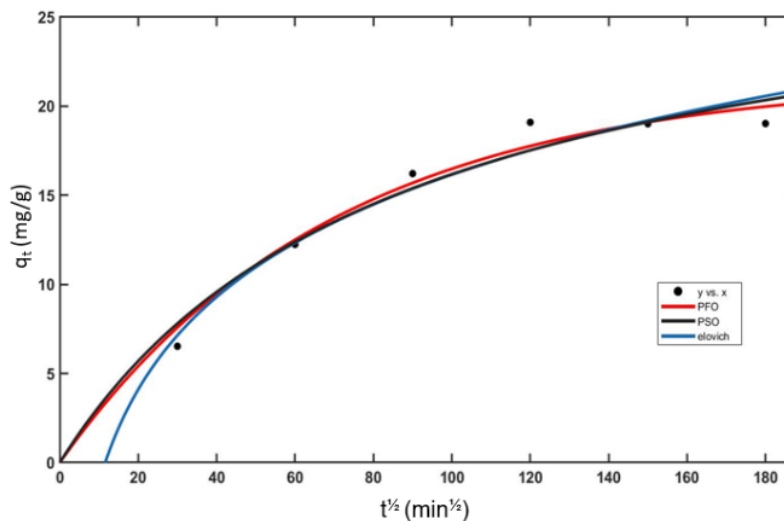


Fig 5.36 Kinetics of AIB

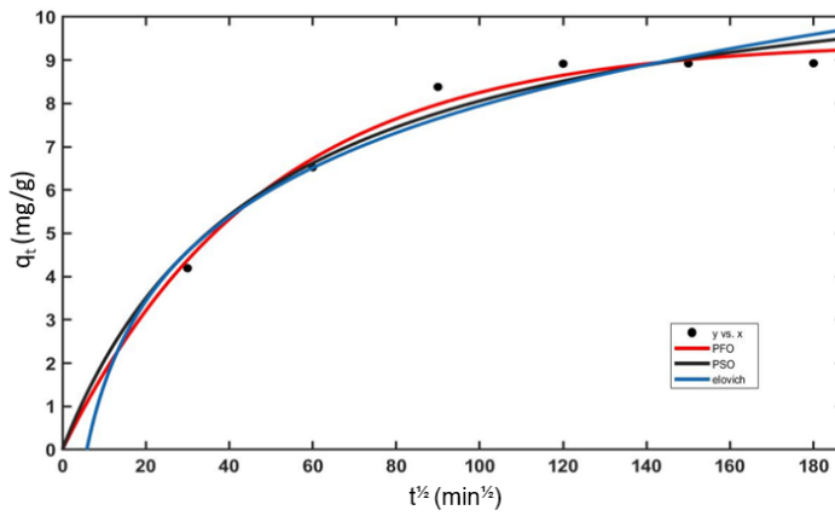


Fig 5.37 Kinetics of GAIB

Table 5.5 Kinetic parameters of AIB and GAIB

Kinetic Models	AIB		GAIB	
	Parameters	Values	Parameters	Values
31 Pseudo-First Order	K_1 (min ⁻¹)	0.02082	31 K_1 (min ⁻¹)	0.01442
	q_e (mg/g)	9.427	q_e (mg/g)	21.59
	R^2	0.979	R^2	0.968
	SSE	0.3905	SSE	4.314
	RMSE	0.3125	RMSE	1.017
62 Pseudo-Second Order	K_2 (g/mg·min)	0.000173	62 K_2 (g/mg·min)	0.000391
	q_e (mg/g)	11.94	q_e (mg/g)	29.98
	R^2	0.9496	R^2	0.9495
	SSE	0.9387	SSE	6.518
	RMSE	0.4844	RMSE	1.277
79 Elovich	α (mg g ⁻¹ min ⁻¹)	0.2072	55 α (mg g ⁻¹ min ⁻¹)	0.2812
	β (g mg ⁻¹)	0.8216	β (g mg ⁻¹)	0.3074
	R^2	0.927	R^2	0.9539
	SSE	1.358	SSE	5.95
	RMSE	0.5827	RMSE	1.22

5.10 ADSORPTION THERMODYNAMICS:

Determining the nature and spontaneity of the adsorption process is the main goal of thermodynamic assessment. The following equations demonstrate how thermodynamic parameters for adsorption experiments are determined using Van't Hoff's equations:

$$KL = \frac{C_{Ae}}{C_e}$$

$$\Delta G^\circ = -RT \ln KL$$

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ$$

$$\ln KL + \frac{\Delta S^\circ}{2.303R}$$

$$\log KL = -\frac{\Delta H^\circ}{2.303 RT} + \frac{\Delta S^\circ}{2.303 R}$$

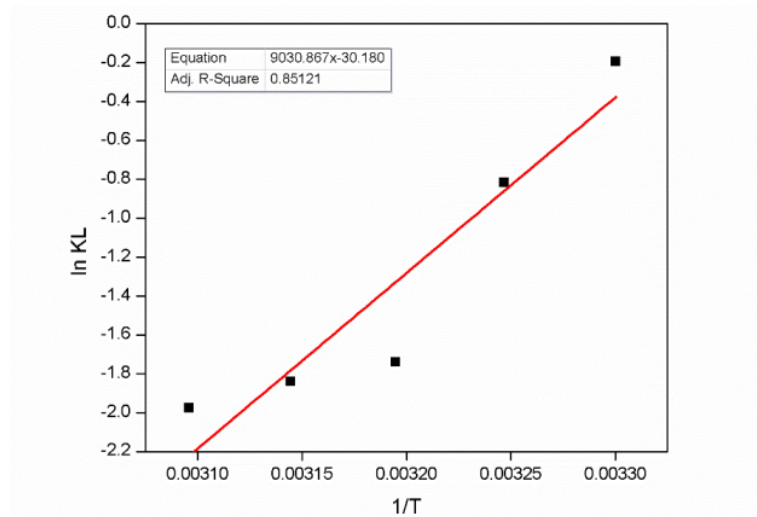


Fig 5.38 Thermodynamics of AIB

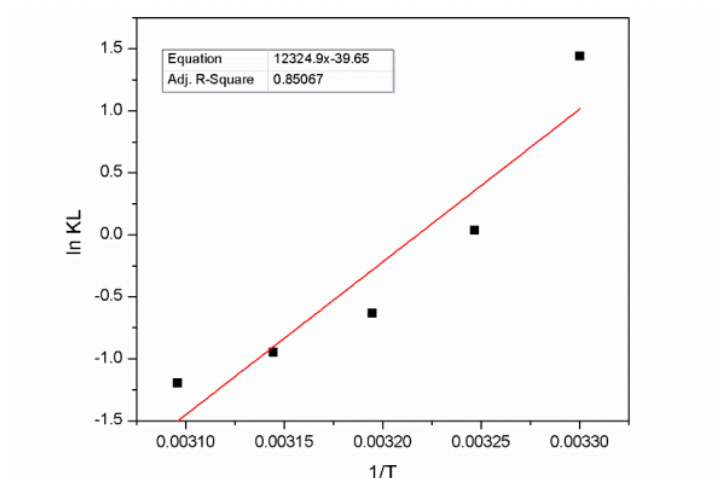


Fig 5.39 Thermodynamics of GAIB

Table 5.6 Thermodynamic parameters

Adsorbents	Parameters			
	$\Delta H^\circ (\text{KJmol}^{-1})$	$\Delta S^\circ (\text{JK}^{-1} \text{mol}^{-1})$	$\Delta G^\circ (\text{KJ mol}^{-1})$	
			Temp (K)	Values
AIB	-7.687164384	-250.9215084	303	0.489621683
			308	2.092351693
			313	4.52628761
			318	4.863876423
			323	5.306705443
GAIB	-10.48365708	-329.916148	303	-
			308	3.624169206
			313	-0.08890959
			318	1.648564841
			323	2.512060799
			323	3.21301918

Using temperatures ranging from 303 to 323 K, the MH's adsorption was investigated. Figure 5.42 and 5.43 was used to get the thermodynamic parameters, such as ΔH° and ΔS° , and the formula was used to get ΔG . The parameters used in the thermodynamic analysis are listed in Table 5.3. The positive value of ΔG for

AIB indicates the reaction is non-spontaneous whereas in the case of GAIB the ΔG value is negative, indicating that this is a spontaneous reaction. the negative values of ΔH° indicated that the MH adsorption was exothermic for both the prepared adsorbents and the negative ΔS° values conclude to decrease in randomness of the adsorption for both AIB and GAIB.

CHAPTER 6

CONCLUSION

In this study, the focus was on investigating the removal of an antidiabetic pharmaceutical pollutant (Metformin Hydrochloride), from aqueous solutions using *Azadirachta indica* bark derived biochar (AIB) and a composite of graphene oxide doped biochar (GAIB) under various process conditions. The AIB adsorbent was prepared through physical activation, while graphene oxide was synthesized using a modified Hummers method, and subsequently, a GAIB composite was synthesized. Batch mode experiments were conducted to explore the influence of factors such as adsorbent dosage, pH, contact time, and temperature on the adsorption process.

Analysis techniques such as FT-IR spectroscopy, BET, XRD and FESEM were employed to characterize the prepared adsorbents. Optimal experimental conditions were determined for both AIB and GAIB. For AIB, the optimal conditions were pH 6, contact time 120 minutes, initial concentration 10 mg/L, adsorbent dosage 10 g/L, and temperature 30°C. Similarly, for GAIB, the optimal conditions were pH 6, contact time 120 minutes, initial concentration 10 mg/L, adsorbent dosage 5 g/L, and temperature 30°C.

The adsorption isotherm data for both adsorbents followed the Freundlich model, indicating non-ideal multilayer and reversible adsorption behavior. Additionally, the adsorption process followed pseudo-first-order kinetics. A significant increase in the maximum adsorption capacity ($Q_{\max}$) was observed from 4.09 to 8.14 when transitioning from AIB to GAIB, representing a 99% enhancement. Thermodynamic study of the measured thermodynamic characteristics indicated that the adsorption process was endothermic. Overall, this study underscores the potential of AIB and GAIB composite as cost-effective and environmentally friendly adsorbents for the removal of pharmaceutical pollutants from wastewater, offering a promising avenue for sustainable water treatment approaches.

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