Preparation of Adsorbent using *Punica Granatum* to Removal of Dye from Aqueous Solution

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ABSTRACT

Activated carbon prepared from Punica granatum peel has been utilized as the adsorbent for the removal of Methylene Blue and Indigo carmine dye from an aqueous solution. Punica Granatum peel was used to prepare activated carbon by pyrolysis using H_2SO_4 activation. 30g of dried and powdered punica granatum peels were taken to prepare activated carbon. Punica granatum treated at a temperature of 400 degree Celsius for 2 hours. After removing the moisture content. 30g Punica granatum was coverted into 24 g. The activated carbon was tested for dye removal of methylene blue and indigo carmine and the results were recorded The FTIR and Sem analysis were used to characterize the activated carbon. Terminalia catappa based activated carbon could be employed as a low cost alternative to commercial activated carbon in the removal of methylene blue and indigo carmine dye from wastewater. Based on the SEM analysis pore size distribution of PG activated carbon is 5-30µm, porosity is 70% and specific surface area is 1000m³/g. Result of FTIR defines the range of peak from 1000 cm^{-1} - 669.44 cm^{-1} (0-H to C-H bends).

Key Words: Chemical Activation, Adsorbent. Dye Removal, Methylene blue,Indigo carmine.

1. INTRODUCTION

Activated carbon, a versatile material renowned for its adsorption capabilities, finds wide-ranging applications in various industries including water purification, air filtration, and pharmaceuticals. The process of producing activated carbon involves the activation of carbonaceous materials through physical or chemical means to create a highly porous structure, maximizing its surface area and enhancing its adsorption properties. One promising source for producing activated carbon is punica granatum peel, commonly known as the pomengrate. Punica granatum is abundant in tropical regions and has shown potential as a sustainable feedstock for activated carbon production due to its high carbon content and availability. This report aims to explore the production of activated carbon utilizing punica granatum as a precursor material, examining the process, properties, and potential applications of the resulting activated carbon. Through a comprehensive analysis, this report seeks to provide insights into the feasibility and effectiveness of using punica granatum peels for the sustainable production of activated carbon.

1.1 BIOMASS

Biomass, an abundant and renewable resource, holds significant promise for the sustainable production of activated carbon a highly versatile material known for its exceptional adsorption properties. In recent years, there has been a growing interest in exploring various biomass sources for activated carbon production, aiming to mitigate environmental impact and reduce dependence on non-renewable resources. Punica granatum, commonly known as a pomgrenate, emerges as a compelling candidate for this purpose due to its widespread availability in tropical regions and high carbon content. This report delves into the utilization of pomegranate wastes biomass for the production of activated carbon. examining the production process, properties of the resulting activated carbon, and its potential applications across different industries. By leveraging punica granatum as a renewable precursor, this report seeks to contribute to the advancement of sustainable solutions in activated carbon production and address the growing demand for eco-friendly alternatives in various sectors.

1.2 ACTIVATED CARBON

Among several biomass sources for producing activated carbon,punica granatum stands out for its advantageous properties punica granatum derived activated carbon exhibits a pore size of 0.1-0.3 mmg and an increased surface arca, making it a promising material for various applications. This study aims to explore the production of activated carbon from punica granatum and assess its potential as a cost-effective adsorbent for removing brilliant indigo carmine and methylene blue dye from aqueous solutions.

The physical characteristics of punica granatum biomass are determined through proximate analysis, providing insights into moisture content, volatile matter, ash content, and fixed carbon. Additionally, the morphology of the resulting activated carbon is analyzed using Scanning Electron Microscope (SEM) studies.

2. MATERIALS AND METHODS

Punica granatum peela, sulphuric acid, carbonization and activation equipment, drying and washing equipment, grinding tools, and safety gear are needed supplies. After being carbonized without oxygen, the peels are powedered soaked with sulphuric acid to activate them. The activated carbon is ground arein fine powder or granules following washing with distilled water and kept them drying. When handling sulphuric acid, safety measures need to be taken, such as donning protective clothing and making sure there is enough ventilation for ventilation of air supply.

2.1 ADSORBENT PREPARATION

The preparation of the adsorbent from Punica granatum (pomegranate) peels involved several key steps including collection, drying, chemical activation with sulphuric acid, and carbonization. Using sulphuric acid (H2SO4) as the activating agent and impregnation ratios of 11 and 1:2, a chemical activation method was utilized to prepare the activated carbon generated from punica granatum biomass.

Step 1: Collection and Pre-treatment

Fresh pomegranate peels were collected from local fruit vendors and thoroughly washed with tap water followed by distilled water to remove dirt, dust, and impurities.

The cleaned peels were then air-dried under sunlight for 2–3 days to remove surface moisture.

After sun drying, the peels were further oven-dried at 80°C for 24 hours to ensure complete removal of moisture content.

Step 2: Chemical Activation

The dried peels were cut into small pieces and soaked in concentrated sulphuric acid in a 1:2 weight-to-volume ratio

The mixture was allowed to react for 24 hours at room temperature with occasional stirring to ensure uniform activation.

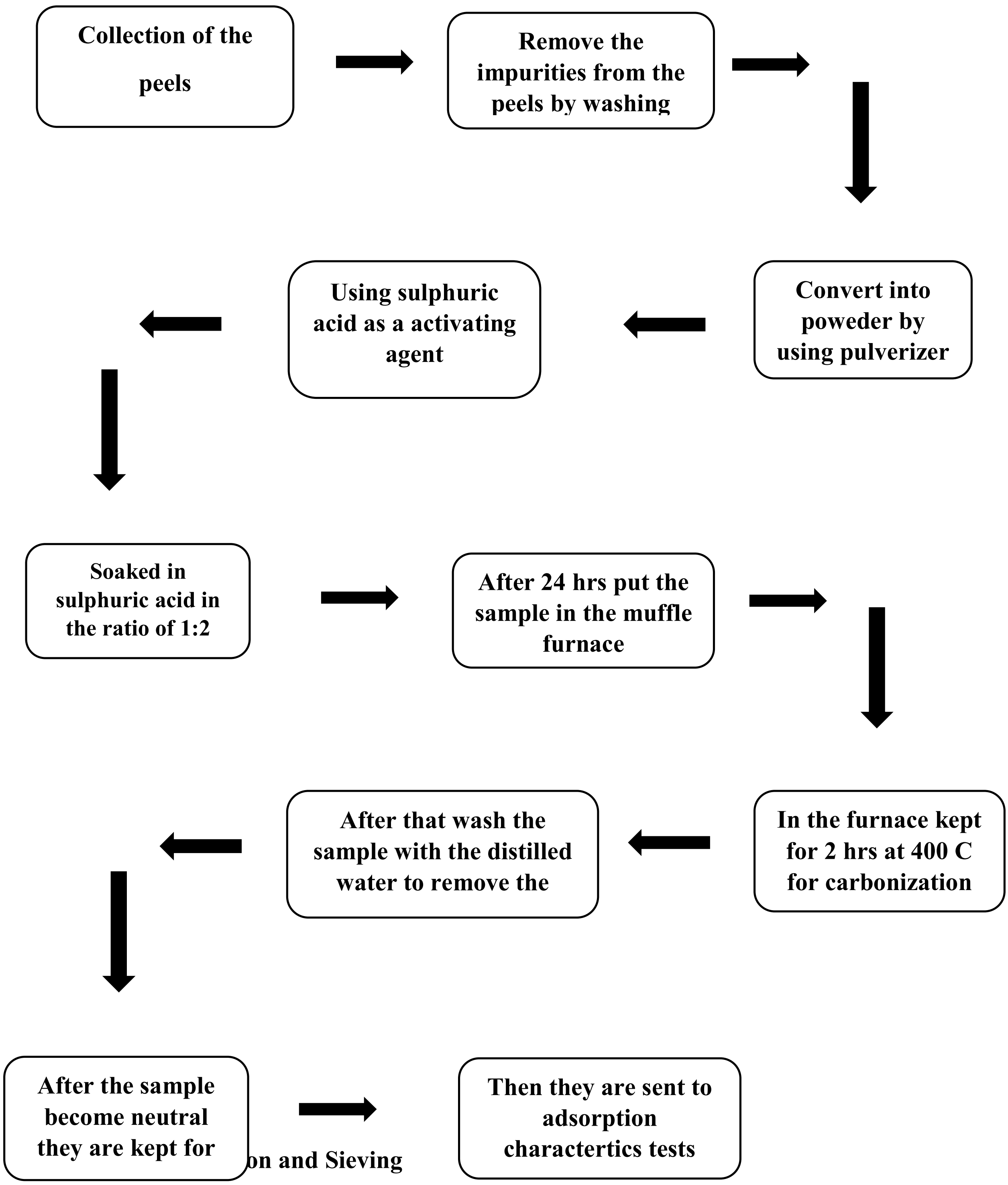
After activation, the mixture was carefully filtered and washed repeatedly with distilled water to remove residual acid until the filtrate reached a neutral pH (~7).Caution: The washing process was performed with care, as the exothermic neutralization of acid can be hazardous

Step 3: Carbonization

The neutralized, acid-treated peels were then oven-dried again at 105°C for 12 hours.

The dried material was placed in a muffle furnace and carbonized at 400–500°C for 2 hours under limited air supply to prevent combustion.

This process produced activated carbon with enhanced porosity and surface area.



The carbonized material was ground using a mortar and pestle or grinder to a fine powder.

The powdered adsorbent was then sieved to obtain uniform particle size (e.g., <250 µm).

Finally, the prepared adsorbent was stored in clean, airtight containers to prevent moisture absorption until further use.

FIG : PUNICA GRANATUM

FIG : DRIED PEEL

FIG : POWDERED PEELS


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TABLE: ACTIVATION OF PUNICA GRANATUM

Activating agent	H_2SO_4
Impregrnation ratio	1:2
Time	2 Hr
Temperature	400 C

2.2 SELECTION OF ADSORBATE

Wastewater has many colours, and activated carbon made from punica granatum peels has good adsorption capacity for dyes. The tannins found in the bark make them attracted to organic chemicals, making it easier for dye molecules to stick. Activated carbon made from punica granatum peels has a porous structure and functional groups on the surface, making it safe and environmentally friendly in removing paint. This helps businesses comply with regulations and reduce water pollution. Methylene blue is a heterocyclic aromatic chemical compound with the chemical formula C16H18N3SC.

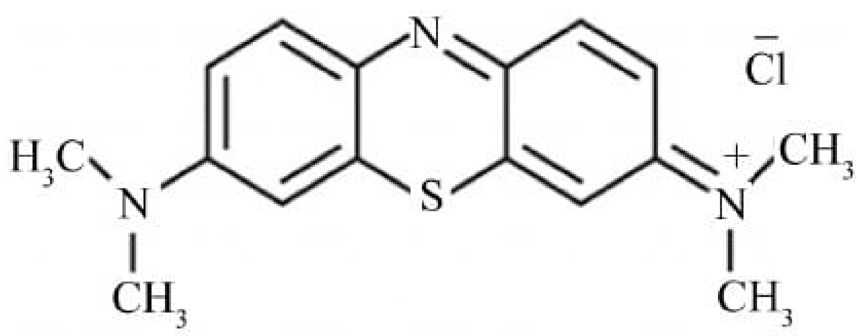

Fig: Structure of Methylene blue

Indigo Carmine is a synthetic organic compound used as a pH indicator and a colorant with the chemical formula C16H8N2Na2O8S2

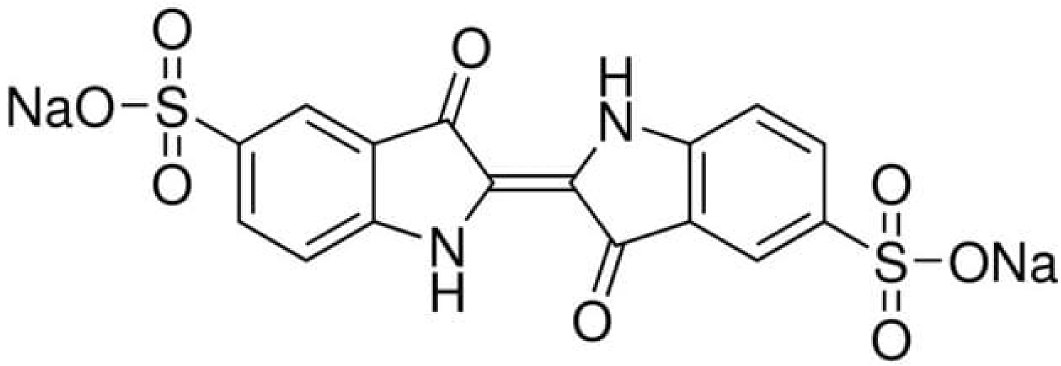

Fig: Structure of Indigo Carmine

The adsorbent showed better performance for methylene blue, likely due to its cationic nature, which allows stronger electrostatic attraction to the acid-treated (negatively charged) surface of the pomegranate peel.

Indigo carmine, being anionic, experiences less attraction, and may face competition or repulsion at active sites, resulting in lower adsorption efficiency.

3. RESULT AND DISCUSSION

SEM ANALYSIS

Surface characterization of activated carbon derived from Punica granatum is conducted using a Scanning Electron Microscope (SEM). The SEM parameters include a working distance set to 10.5 mm, a magnification range of 1000-5000X, and an acceleration voltage of 10kV. Comparative analysis is performed between raw Punica granatum and chemically activated Punica granatum. Results indicate that chemically activated Pumica granatum exhibits larger pore sizes, enhancing its capacity to adsorb organic pollutants to a significantly greater extent. The Scanning Electron Microscope is used to used to assess the morphological feature and surface characteristic of Punica granatum peels before and after Indigo Carmine and methylene blue dye removal.

The Scanning Electron Microscopy (SEM) technique was employed to study the surface morphology of Punica granatum (pomegranate) peel adsorbents before and after chemical activation with sulphuric acid. SEM analysis provides insights into surface texture, porosity, and structural modifications which are directly related to adsorption performance.

Before Sulphuric Acid Treatment:

The untreated pomegranate peels exhibited a smooth, dense, and compact surface with minimal visible pores or cracks.

The lack of significant porosity indicates fewer active sites available for adsorption, thereby limiting its efficiency as an adsorbent.

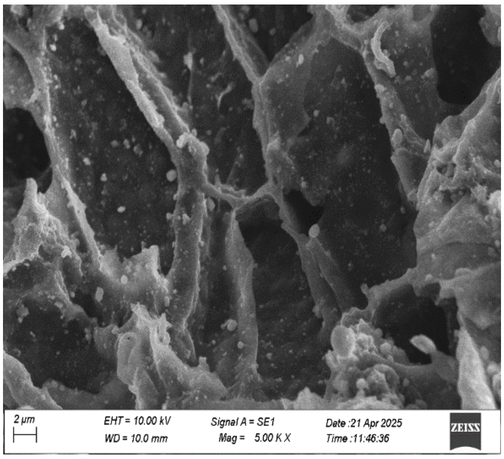

Fig 3.1(a)

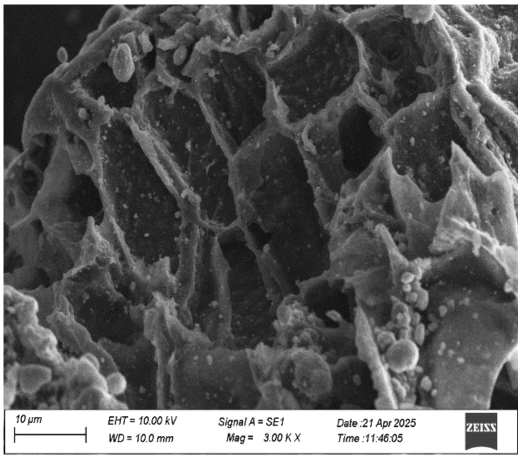

Fig 3.1(b)

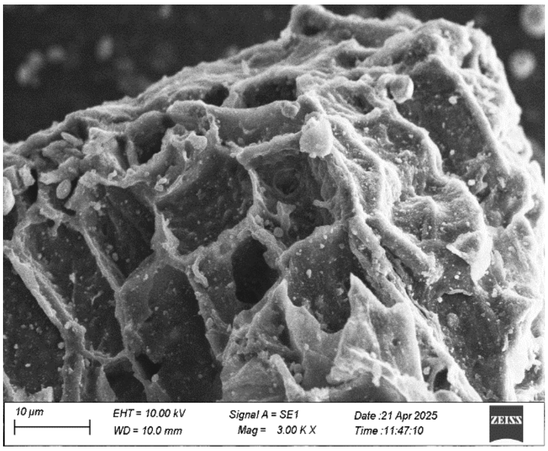

Fig 4.1 (c)

PUNICA GRANATUM SAMPLE BEFORE ACTIVATION

After Sulphuric Acid Treatment:

The surface morphology underwent drastic changes, becoming rougher and more irregular.

SEM images revealed the formation of numerous pores, cavities, and cracks, which significantly increased the surface area and pore volume.

These structural changes are attributed to the dehydration, carbonization, and chemical degradation of the lignocellulosic matrix by concentrated sulphuric acid.

The porous structure enhances dye uptake by facilitating greater dye molecule diffusion and interaction with surface functional groups.

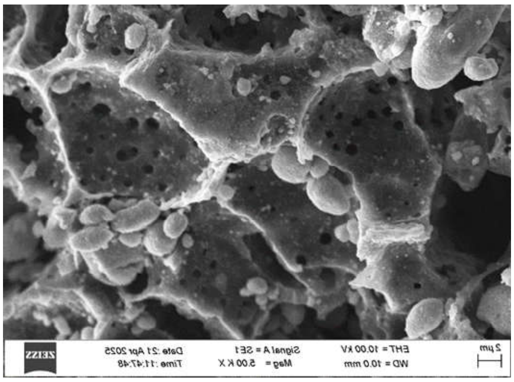

Fig 4.2 (a)

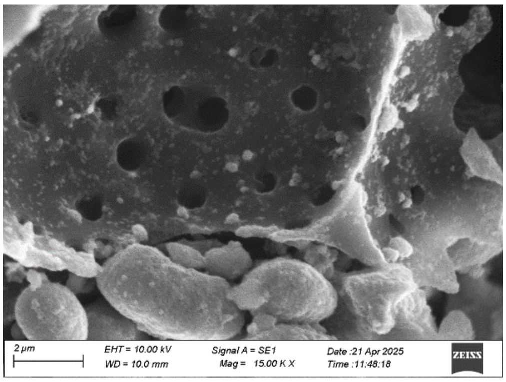

Fig 4.2 (b)

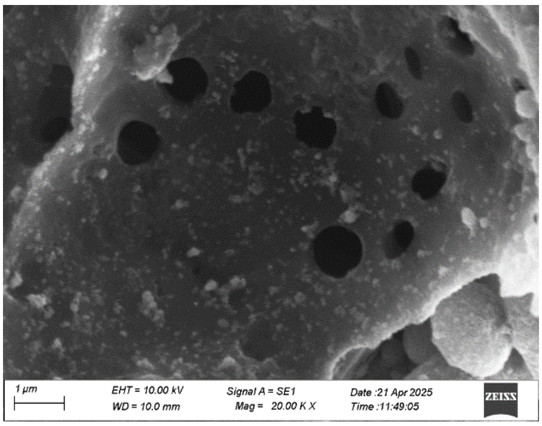

Fig 4.2 (c)

PUNICA GRANATUM SAMPLE AFTER ACTIVATION

The SEM analysis clearly demonstrates that sulphuric acid treatment of pomegranate peel powder enhances the surface roughness and porosity, making it a more effective adsorbent for dye removal from wastewater.

Fig: 4.1(a), 4.1(b) and 4,1(c) shows the SEM image in 1000 magnification for Punica granatum peels with highly porous and small in size before contacted with Indigo Carmine and Methylene Blue dye. Fig: 4.2(a), 4.2(b) and 4.2(c) shows the SEM image in <1000 magnification for PG shell after contacted with IC dye

FTIR ANALYSIS

The FTIR (Fourier Transform Infrared) analysis was conducted to characterize the chemical composition of the activated carbon derived from Punica granatum. Spectral analysis revealed distinctive peaks corresponding to functional groups present in the sample. The FTIR spectrum displayed peaks at specific wave numbers, indicating the presence of various chemical bonds and functional groups such as hydroxyl (-OH), carbonyl (C-O), and carboxyl (-COOH) groups. These findings provide valuable insights into the structural properties and surface chemistry of the activated carbon, which are crucial for understanding its adsorption capabilities and potential applications.

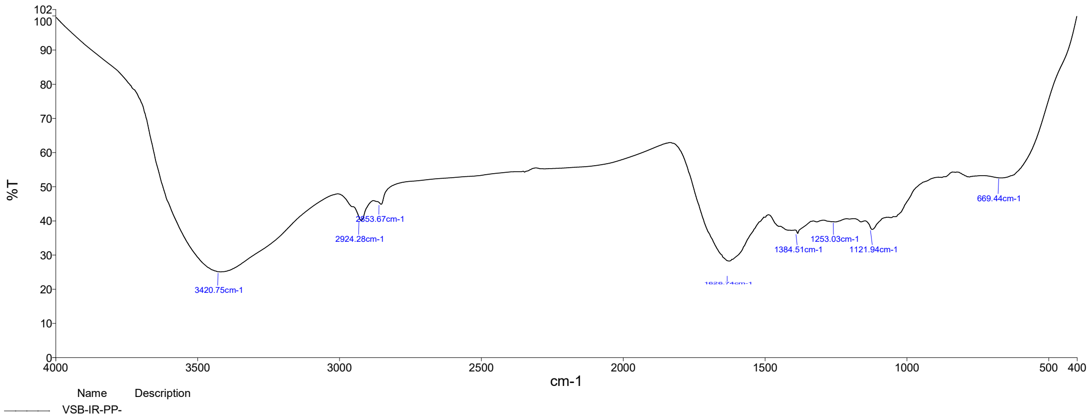

Fig 3.3 FTIR analysis

Fig: 4.3 shows the FTIR spectra of the biosorbent before and after MB removal. The wavenumber of some of the Punica granatum functional groups shifted due to chemical interaction between the biosorbent and Methylene Blue and Indigo Carmine. From the spectra, there was the strong O-H stretching at 3413-3853 cm. The peak at 2923-3000 cm is assigned to C-H stretching. The C=O was observed at 2855-2900 cm. Other functional groups observed on the biosorbent were the C-O and C-O-C stretching at 1587-1800cm, C-C asymmetric 1384-1450 cm^3, C-H bending, C-O stretching at 620-720 cm and then the peak at 1400-1600 cm.

FTIR Peak Analysis

1. **3420.75 cm^{-1}**
   - **Assignment:** O–H stretching (broad)
   - **Possible Groups:** Alcohols, phenols, or water (moisture). Often seen as a broad peak due to hydrogen bonding.
2. **2924.28 cm^{-1} & 2853.67 cm^{-1}**
   - **Assignment:** C–H stretching (sp^3 hybridized carbon)
   - **Possible Groups:** Alkanes, $–CH_2–$ and $–CH_3$ groups in long hydrocarbon chains.
3. **1626.74 cm^{-1}**
   - **Assignment:** C=O stretching (carbonyl group) or C=C stretching in alkenes/aromatic rings
   - **Possible Groups:** Ketones, aldehydes, carboxylic acids, or amides.
4. **1384.51 cm^{-1}**
   - **Assignment:** Bending vibration of C–H (methyl groups, CH_3 symmetric deformation)
   - **Possible Groups:** Alkanes, methyl-substituted compounds.
5. **1253.03 cm^{-1} & 1121.94 cm^{-1}**
   - **Assignment:** C–O stretching or C–N stretching
   - **Possible Groups:** Ethers, esters, carboxylic acids, or amines.
6. **669.44 cm^{-1}**
   - **Assignment:** Out-of-plane bending vibrations
   - **Possible Groups:** Aromatic C–H bending (indicative of substituted benzene rings)

Interpretation Summary

- The presence of **O–H** and **C=O** stretches may suggest compounds like **carboxylic acids** or **esters**.
- The **C–H stretches** and **bends** suggest **alkyl chains**, common in **lipids or polymers**.
- Aromatic or ring structures may be indicated by the peak at **669.44 cm^{-1}**.

ADSORPTION ISOTHERM

The interactions between the adsorbent and the adsorbate are described by the equilibrium isotherms. Understanding the mechanisms of adsorption and its significance in the real-world design and operation of systems can be aided by the linkage of experimental data to the adsorption model. There are two widely used isotherm models namely Langmuir and Freundlich

LANGMUIR ISOTHERM

This theory was proposed by Langmuir to explain the adsorbate monolayer coverage over a homogenous adsorbent surface. Based on the presumption that sorption occurs at particular homogeneous locations within the adsorbent, the adsorption isotherm is calculated. Following an adsorbate once a molecule occupies a site, it is no longer available for adsorption. Thus, a linear equation can be used to reach an equilibrium value.

$$1/(qe) = (1 / (KL*qm))*(1/(ce)) + (1/(qm))$$

Where Ce is the equilibrium concentration (mg / L) qe is the equilibrium adsorption capacity ie, amount of brilliant yellow adsorbed on activated carbon (mg / g) qm is the monolayer sorption capacity (mg / g) L is the energy of the adsorption (L / m * g) The slope and intercept were determined by plotting 1/qe versus 1/Ce

$$RL = 1(1 + LCo)$$

Where, Co is the highest initial solute concentration.

RL values indicate whether the adsorption is unfavorable (RL > 1) , linear (RL = 1) favorable (0 < RL < 1) or irreversible (RL = 0).

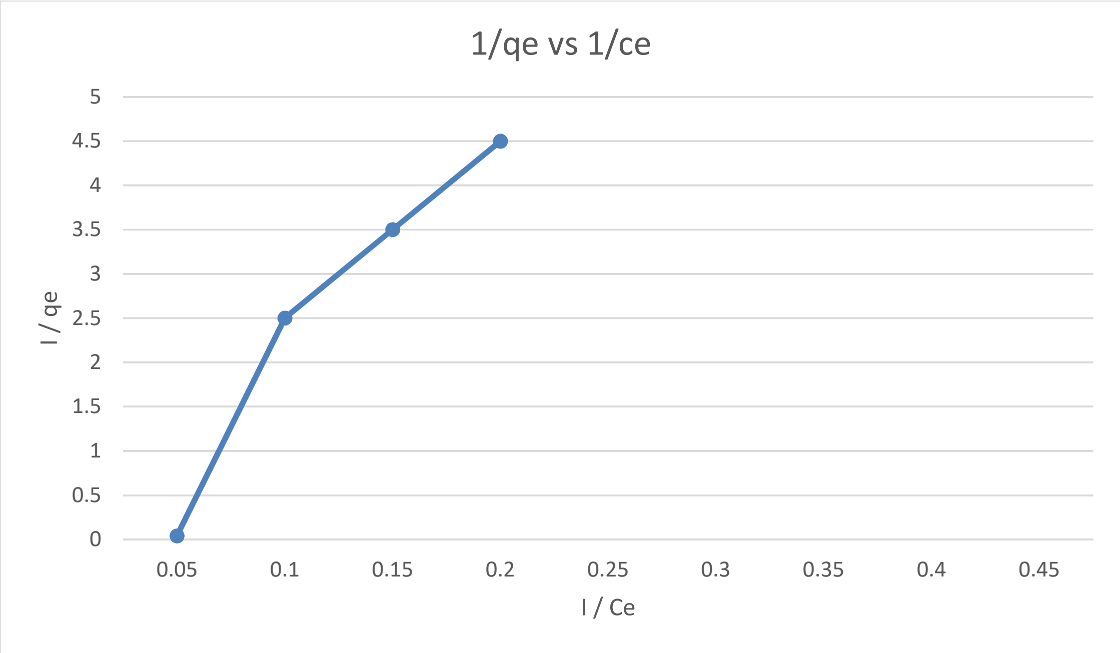

Fig 3.4 Langumir Isotherm

FREUNDLICH ISOTHERM

The model proposed by Freundlich explains the characteristics of heterogeneous systems. In heterogeneous adsorption systems, this model has been frequently used. particularly for organic chemicals and highly interacting species on activated carbon Consequently, Freundlich's research demonstrated that the relationship between the solute concentration in the solution and the amount of solute adsorbed onto a specific mass of adsorbent was not constant across a range of values. For heterogeneous surfaces, he introduced this multiple adsorption isotherm, which is expressed as

$$\log qe = \log kf + 1/n * \log Ce$$

Where Kfand n are Freundlich constants. In general, n 1 suggests that adsorbate is favorably adsorbed on the adsorbent. The higher then value stronger the adsorption intensity The Freundlich constants were y = 9.513x + 0.033 R^2 = 0.953 0 0.10.2.0.30.40.50.60.700.02

0.04 0.06 0.08 1/QE 1/CE 1/qe vs 1/Ce l/ce Linear (1/ce) 34 determined from the slope and intercept by plotting log qe versus log Ce

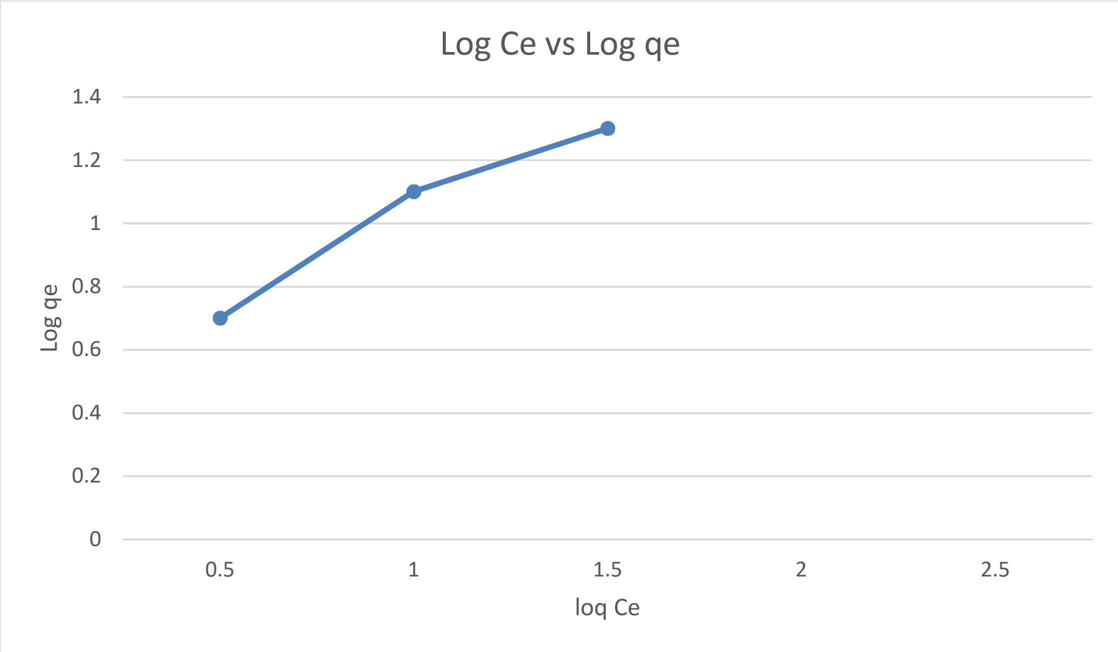

Fig 3.5 Freundlich isotherm

4. CONCLUSION

This research investigated the utilisation of nitric acid modified Punica granatum as biosorbent in the removal of indigo carmine and methylene blue dye from aqueous solution. Nitric acid modification was to open Punica granatum surface pores and to encourage more Punica granatum functional groups. Indigo Carmine and Methylene Blue removal increased with time and initial concentration. The optimum conditions for punica granatum biosorption of Indigo Carmine and Methylene Blue dye were at pH 5 and 3 respectively, contact time 30 min for both and initial concentration 500 mg/L. The experimental biosorption capacity was 26.77 mg/g Thermodynamic parameters for biosorption showed that the process was exothermic and spontaneous throughout a temperature range of 300-400 K. When compared to other substances used to extract indigo carmine and methylene blue dye from aqueous solution, the terminalia catappa biosorbent performed admirably. punica granatum has the potential to be used as a biosorbent to lower the concentration of indigo carmine and methylene blue in aqueous solutions. The Langmuir Isotherm was high and adsorption follows monolayer,

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