ADSORPTIVE REMOVAL OF METHYLENE BLUE DYE USING ACTIVATED CARBON PREPARED FROM SEED OF TINDU (*DIOSPYROS MALABARICA*)

A DISSERTATION

SUBMITTED FOR THE PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE MASTER OF SCIENCE DEGREE IN CHEMISTRY

SUBMITTED BY

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BOARD OF EXAMINER AND CERTIFICATE OF APPROVAL

This dissertation entitled, "**Adsorptive Removal of Methylene Blue Dye Using Activated Carbon Prepared from Seed of Tindu (*Diospyros Malabarica*)**" by **Sabina Shrestha** under the supervision of **Asst. Prof. Hari Bhakta Oli**, Department of Chemistry, Amrit Campus, Tribhuvan University, Kathmandu, Nepal, and co-supervision of **Asst. Prof. Dr. Deval Prasad Bhattarai**, Department of Chemistry, Amrit Campus, Tribhuvan University, Kathmandu, Nepal, hereby submitted has been approved for partial fulfillment of the requirement for completion of her Master of Science (M.Sc.) Degree in Chemistry. This dissertation has not been submitted in any other university or institution previously for the award of a degree.

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LETTER OF RECOMMENDATION

This is to recommend that the dissertation work entitled, "**Adsorptive Removal of Methylene Blue Dye Using Activated Carbon Prepared from Seed of Tindu (*Diospyros Malabarica*)**" has been carried out by **Sabina Shrestha** as partial fulfillment for the requirements of Master of Science Degree in Chemistry. This is her original work and has been carried out under our guidance and supervision. To the best of our knowledge, this research work has not been submitted for any other degree in this institute.

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DECLARATION

I, **Sabina Shrestha,** hereby declare that the work presented here is genuine work done originally by me under the supervision of Asst. Prof. Hari Bhakta Oli and co-supervision of Asst. Prof. Dr. Deval Prasad Bhattarai, Department of Chemistry, Amrit Campus, TU, Kathmandu, Nepal. This dissertation has not been published or submitted elsewhere for the requirement of a degree program. Any literature, data, or work done by others are cited in this dissertation with due acknowledgment and listed in the reference section.

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Sabina Shrestha

January, 2024

LIST OF ABBREVIATIONS

C_e	Equilibrium concentration
C_i	Initial concentration
R^2	Correlation coefficient
DMSC	*Diospyros malabarica* seed activated carbon
FTIR	Fourier Transform Infra-red Spectroscopy
I_N	Iodine adsorption number
MB	Methylene blue
MB_N	Methylene blue number
PPM	Parts per million
PZC	Point of zero charge
FE-SEM	Field Emission Scanning Electron Microscopy
EDX	Energy Dispersive X-ray
XRD	X-ray diffraction

ABSTRACT

Methylene blue (MB) is a commonly used cationic dye used in the dyeing industries. Its contamination on the water bodies as an effluent of industries causes harmful effects on human health & environment. In this context, due attention has been paid in in its removal from waste water and industrial effluents. Several methods are used to eliminate this dye from aquatic environment but a crucial & efficient method is adsorption by using activated carbon. In this work, seeds of *Diospyros malabarica* has been used to prepare activated carbon for MB dye removal. The ground seed powder was chemically activated. The porosity and surface area was determined by methylene blue number (MB_N) and iodine number (I_N) method, respectively. Its surface was characterized by Field Emission Scanning Electron Microscopy (FESEM) equipped with Energy Dispersive X-ray (EDX). Fourier Transform Infrared Spectroscopy (FTIR) was used to characterize the functional groups associated with activated carbon. Using the prepared activated carbon materials, it has been attempted to remove the methylene blue. The optimum working pH was found to be 5. Similarly, optimum adsorbent dose of 20 mg, and equilibrium contact time of 120 minutes were achieved. Based on the result, it has been advocated that the adsorption capacity of *Diospyros malabarica* seed carbon (DMSC) is appropriate for the adsorptive removal of methylene blue and it could be used as accost-effective adsorbent for the removal of dyes from aqueous media.

Keywords: *Diospyros malabarica*, Activated carbon (AC), Methylene blue, Adsorbent

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Keywords: *Diospyros malabarica*, Activated carbon (AC), Methylene blue, Adsorbent

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CHAPTER-1

INTRODUCTION

1.1. Background

Various kinds of contaminants emanating from domestic and industrial sources in the form of sewage and sludge contains huge amount of toxic heavy metals, toxic organics, phenols, and color that pose a great threat to the public health & environment. Among the various effluents, dyes can be easily identified by the naked eye, these are mainly caused by industries like food, printing, textile, cosmetics, etc. There are thousands of dyes which are present in water as pollutants & are difficult to treat. MB dye is a cationic dye in the phenothiazine class. Effects of MB dye includes eye burns in human and animals, skin irritation, convulsions, lowering the dissolved oxygen level in water source, eutrophication, etc. (Singh et al., 2016).

Many methods of waste removal such as ozonation, adsorption, coagulation, etc. have been developed using various kinds of adsorbents like activated carbon, silica, carbon nanotubes, bio-waste (Singh et al., 2016). Bio-materials have grabbed attention of the researchers due to low cost, ease of availability also the advantages of ease of operation and high efficiency. It has been found that the bio-waste shows less adsorption capacity as compared to activated carbon. However, this can be increased by activating the surface of these bio-wastes by chemical activation (Hameed et al, 2007). Activated carbons from bio-waste materials have got much attention & various bio-waste materials have been tested. In a reported research, Argan seed shell were carbonized in N_2 environment & then were activated using KOH (Hameed et al., 2007). In a similar work, sunflower seed hull was activated in acidic condition by sulfuric acid (Thinakaran et al., 2008), orange peels were activated by $ZnCl_2$ solution and carbonization was carried out (Ahmed et al., 2021). Bio-char derived from pulp and paper sludge (Chaukura et al., 2017) have shown effective removal of pollutants. Properties of activated carbons depends upon the inherent properties of biomass precursors, methods of activation and processing. It is both art and science to choose a biomass for the preparation of activated carbon (AC) with high surface area and pore volume. In search of new adsorbent, *Diospyros malabarica* (Tindu) seed has been selected for the preparation of efficient AC for the adsorptive removal of cationic dye (MB dye).

1.2. Dye Description

Huge amount (~8,00,000 tons) of synthetic dyes are being manufactured every year globally which are soluble in water, readily adsorbed and are versatile color in nature compared to natural dye (James and Siddique, 2019). Dyes are used in foods, chemicals, paper, textiles and pharmaceutical industries, resulting in serious outcomes for human health and environment (Islam et al. 2017a, Baumer et al. 2018). Various types of dyes are used for many purposes. Among many types of dyes commercially available, methylene blue dye is one.

1.2.1 Methylene Blue Dye

Methylthioninium chloride is commonly called as methylene blue dye. Among the various dyes, methylene blue (MB) dye is cationic dye in the phenothiazine class. Methylene blue dyes have various applications in chemistry, biology and medicine (Youcef et al. 2019).

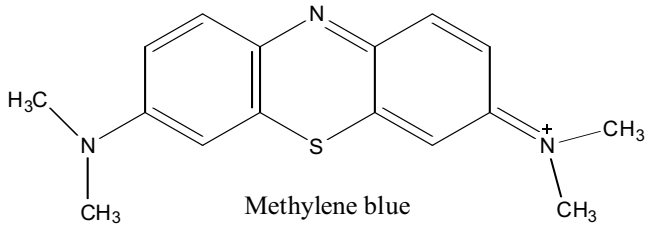


Figure 1.1: Structure of methylene blue dye

1.2.2 Sources of methylene blue contamination

One of the pollutants in industrial wastewater is dye which is extensively used in multiple industries like textiles, ink, plastics, etc. (Crini et al., 2006). Sewage sludge effluents that emanates from industries like food, printing, cosmetics, textiles, pharmaceuticals, etc. are the main sources of methylene blue contamination (Dod et al., 2012). These colored effluents contain large amount of suspended organic solids which are harmful to human being and toxic for organism. These may be mutagenic, carcinogenic and toxic in nature and harmful to health in one or, other way (Unal et al., 2013).

1.2.3 Health impact of methylene blue dye

Methylene Blue (MB) dye is one of the most widely used dyes that causes eye burns in humans and animals, methamoglobinemia, cyanosis, convulsions, skin irritation and irritation to the gastrointestinal tracts, diarrhoea and vomiting if inhaled (Cazetta et al.,

2011). Textile industries are the main contributors of MB dyes into the water source and causes serious threats to aquatic flora and fauna. Exposure to MB can cause harmful effects such as high blood pressure, gastro intestinal pain and nausea (Liu et al., 2019). The indirect impacts of MB dyes include eutrophication, acceleration of genotoxicity and microtoxicity.

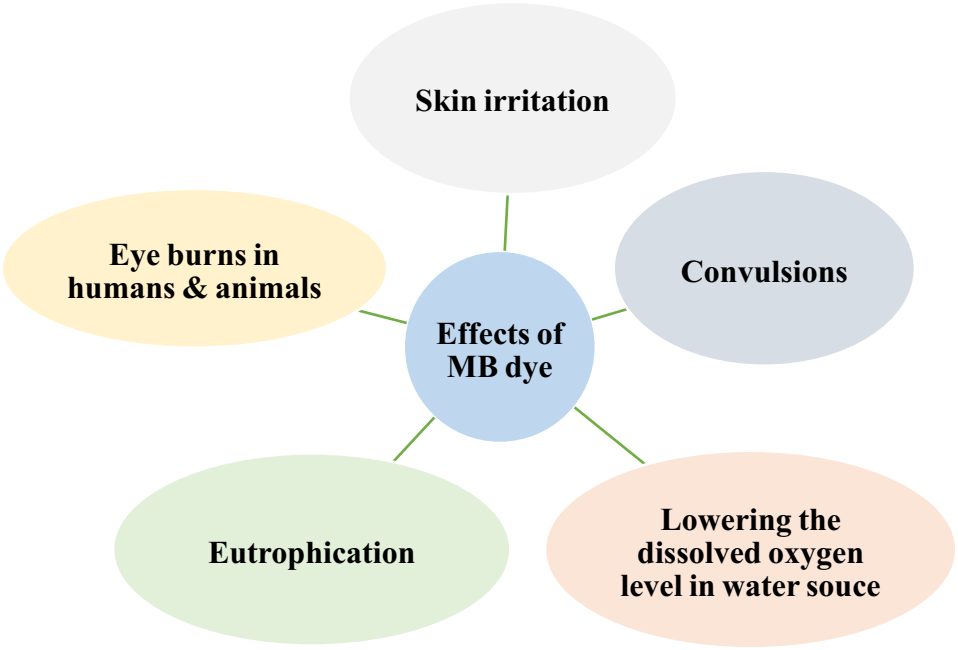


Figure 1.2: Effect of methylene blue dye

1.2.4 Removal of methylene blue dye

For the removal of pollutants from aquatic environment various methods have been employed. Some of such methods are coagulation/flocculation, precipitation, oxidation, ozonolysis, etc. (Rezakazemia et al., 2019). However, these methods are expensive and produce toxic byproducts in turn (Elmorsi et al., 2011). Thus, adsorption has been the most used treatment process since it has advantages of ease of operation and high efficiency.

- **Coagulation/Flocculation:** This method uses coagulant to form gelatinous mass to trap which then can be settled and removed by sedimentation or filtration.
- **Precipitation:** In this method, metal ions are precipitated by reacting with suitable precipitant resulting into the formation of metal hydroxide, carbonates, sulphides, phosphates and so on. Finally, such precipitates are removed by sedimentation, decantation or filtration.
- **Adsorption:** It uses various types of adsorbents at the surface of metal ions that accumulate and remove.

- **Ion exchange:** It is similar to the adsorption process, but the medium is a synthetic resign of more well-defined ion exchange capacity.

All of the above mentioned methods have been used for the effective removal of dyes from aqueous solution. However, these techniques have some limitations such as low efficiency, sensitive operation condition, and the production of secondary sludge, which increase the cost. Adsorption, as compared to the different conventional methods, appears to be more attractive due to high efficiency, cost-effective and reversible nature as adsorbent material (Rahadar et al., 2019).

Various kinds of adsorbents such as activated carbons, silica, zeolites, bio-waste, carbon nanotubes, etc. have been reported. Among these, activated carbon is the most widely used adsorbent due to its excellent color removal efficiency, high surface area and microporous structure (Ferrero et al., 2007). Materials such as rice husk, date stones, walnut shell, and sun-flower seed have been tested for dye removal.

Adsorption is the adhesion of atoms, ions or, molecules from a gas, liquid or, dissolved solid (adsorbate) onto the surface (adsorbent) (Abdelhafez et al., 2016). Adsorption is the anchoring of materials on its surface via van der Waals' force and is a surface phenomena. In this case, molecules or ions do not penetrate deep into the materials. This phenomenon is widely used in many natural, physical, biological and chemical systems involved in industrial application such as heterogenous catalysts, activated charcoal, etc. Adsorption can be either physical or, chemical or mixed type in nature. Physical adsorption or physisorption is the surface phenomena where molecules, ions or any chemical moieties get attached onto the surface by physical forces and regarded as reversible process. Adsorption is exothermic process. However, in chemical adsorption or chemisorption, adsorbates are held to a solid surface by chemical forces that are specific for each surface and each gas. Chemisorption usually occurs at higher temperature compared to those in physical adsorption. In addition, chemisorption is a bit slower process compared to physisorption (Demirbas et al., 2005, Kundu et al., 2004). The difference between physical adsorption and chemical adsorption are presented in table 1.

Table 1.1: Difference between Physisorption and chemisorption

Physisorption	Chemisorption
Physical adsorption is due to the formation of weak van der Waals' forces.	Chemical adsorption is due to the formation of chemical bonds.
It is reversible process.	It is irreversible process.
Physisorption is not specific in nature.	Chemisorption is very specific in nature.
It decreases with increase in temperature.	It increases with increase in temperature.
It may form multi-molecular layer.	It forms uni-molecular layer
Activation energy is less in physisorption.	Activation energy is high in chemisorption.
It has low adsorption enthalpy, nearly 20 -40 kJ/mol.	Chemisorption has high adsorption enthalpy, nearly 80-240 kJ/mol.

The adsorption can be batch adsorption or, column adsorption. In this study, batch adsorption method is used.

1.3. Activated carbon

Depending upon the precursor materials chosen and the activating agent used, different types of activated carbon can be generated. Granular activated carbon and powdered activated carbon are two commercially available types of carbon.

1.3.1 Granular activated carbon (GAC)

GAC are actually derived from the bio-waste materials such as coconut shells, palm kernels, and Olive stones during activation process. Granulation can be done by using low density soft bio-waste materials and also by adding binders (Nieto-Marque et al., 2017).

1.3.2 Powdered activated carbon (PAC)

PAC are proven to be cost-effective and eco-friendly materials, which can be prepared from wood, lignite, and bio-waste materials such as ground nut shells, pea nut shells, etc. (Karmacharya et al., 2016). The density of PAC depends on the type of raw material and the manufacturing process. Usually, PACs high surface area and high micro-porosity, which are the characteristic of their adsorption capacity (Sharokhi et al., 2021).

1.4. Porosity of activated carbon

Activated carbons are getting preference not only due to their high surface area but also due to their porosity. Adsorption pores are the only regions within an active carbon particle with sufficient adsorption forces to adsorb impurities and serve as a channel for the passage of solution. According to the IUPAC (International Union of Pure and Applied Chemistry), nanoporous carbon materials are classified into three groups based on their pore size: Micropores (less than 2 nm diameter), Mesopores (2-50 nm diameter) and Macropores (greater than 50 nm diameter) as shown in fig. 3

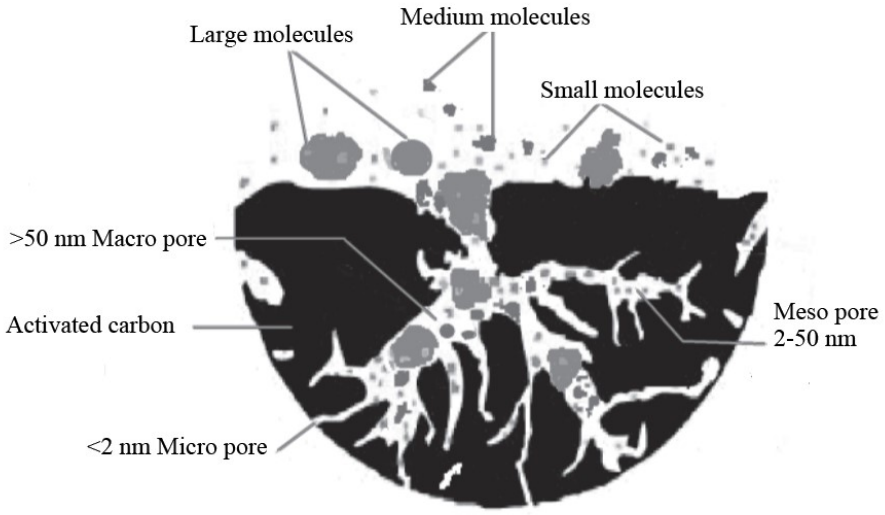


Figure 1.3 : Schematic showing the Porosity the activated carbon (Mbarki et al., 2022)

The pore size of activated carbon can be determined by using Methylene blue number and Iodine number method in a common laboratory. For more accurate work, Bruner-Emmet-Teller (BET) surface area determination can be used for the determination of surface area in addition to pore volume of materials.

1.5. *Diospyros malabarica* seeds as an adsorbent

Taxonomical Classification

Kingdom: Plantae

Phylum : Tracheophyta

Class : Magnoliopsida

Order : Ericales

Family : Ebenaceae

Genus : *Diospyros*

Species : *malabarica*

Figure 1.4: *Diospyros malabarica* tree and fruits

Diospyros malabarica is an evergreen tree with a much-branched, spreading crown, pale moon ebony, is a species of flowering tree in the family Ebanaceae that grows throughout Nepal, India and other tropical regions of the world. *D. malabarica* has been reported to have various therapeutic applications since immemorial time (Sinha et al., 2008). The tree was also reported to use in traditional medicinal practices in various diseases. Bio-active compounds like alkaloid, flavonoid, tannins vitamin C, etc. are being reported to be present, which are responsible for antioxidant, antiviral, anticancer activity (Shubhra et al., 2019).

1.6. Objectives of study

The objectives of the study are categorized into two parts:

1.6.1 General objective

The general objective of this study is preparation & characterization of adsorbent from *Diospyros malabarica* seeds & its application in removal of Methylene Blue (MB) dye.

1.6.2 Specific objectives

The specific objectives of this research work are as follows:

- Preparation of the activated carbon (AC) from *Diospyros malabarica* seeds.
- Examination of surface area of AC with the help of IAN and MBN.
- Characterization of the activated carbon using FTIR, SEM and EDX.
- Study of effectiveness of an adsorbent in removing Methylene Blue (MB) dye.
- Study of the best adsorption kinetics model among different adsorption isotherm through batch adsorption.

CHAPTER-2

1. LITERATURE REVIEW

Various methods for the removal of dyes from the polluted bodies are in operation. Each method has its own inherent limitation such as being expensive or, creating secondary pollutants. Low cost materials with high efficiency and facile techniques for the removal of dyes have yet to be developed for efficient water purification in small or large scale. In order to drop the cost of the activated carbon, waste material such as fruit seeds have been used. One of the economic adsorbents for the removal of different dyes from polluted water bodies could be activated carbon which is derived from *D. malabarica* seed.

Flavio et al., (2008), used yellow passion fruit peels as adsorbent for the removal of methylene blue from the aqueous media. The adsorption process was studied via batch process at ambient condition of temperature and pressure. The effect of agitation time and pH was studied in that experiment. In this case, the contact time of 56 h at 25 °C was achieved and argued as the suitable adsorbent for the removal of methylene blue dye from aqueous solution.

In another research, Meltem et al., (2006) investigated the mechanism for the removal of MB dyes by adsorption process through waste sludge. Effect of various parameters such as pH (3-11), dosage (1-10 g/L), contact time (5-1440 min) and initial concentration were largely studied. Results showed the increased dye removal with increased initial concentration of dyes and bio-solid adsorbent. They also studied by mathematical modeling such as Langmuir model and Freundlich model. All in all, the result revealed that such bio-solid could serve as a good adsorbent for the removal of color dyes from aqueous media.

In the work of Omar et al., (2020), Fava bean peels (*Vicia faba*) was used as as bio-sorbents for the adsorptive removal of methylene blue (MB) dye from aqueous media via novel and efficient route of sorption process. In this process, ultrasonic shaking of the material was carried out for the study. Ultrasonic rate showed four times greater than its conventional parameter of 3.6 mg/L initial dye concentration, 5 g/L adsorbent dose and pH 5.8. Under the same pH and adsorbent dosage, percent removal ranged between 70-80% at the low dye concentration range (3.6-25 mg/L) and reached to about 90% at 50 mg/L of initial dye concentration. The variable temperature equilibrium data were fitted to Langmuir adsorption model with maximum sorption capacity which was estimated to be 140 mg/g.

Uddin et al., (2009), studied the potentiality of tea waste for the adsorptive removal of methylene blue. Batch kinetics and isotherm studies were carried out under varying experimental condition of contact time, initial dye concentration, adsorbent dose and pH. The point of zero charge was estimated to be 4.3. Adsorption equilibrium of tea waste reached within 5 hr for methylene blue of 20-50 mg/L concentration. The sorption process followed the pseudo-second order. The equilibrium data were fitted to the Langmuir isotherm model. The maximum sorption capacity of methylene blue onto tea waste was found to be as high as 85.16 mg/g.

Shakoor et al., (2016), investigated the potentiality of *Citrus limetta* peel as a low cost adsorbent for the removal of methylene blue dye. Batch adsorption studies were conducted to find out how adsorption was affected by various factors like contact time, initial dye concentration, adsorbent dose, pH and temperature. The data were found to be best represented by Langmuir adsorption isotherm with maximum adsorption capacity for monolayer coverage and was found to be 227.3 mg/g. The sorption process followed pseudo-second order kinetics.

Mitrogiannis et al., (2015), studied the removal of methylene blue dye from aqueous solution by biomass of *Arthrospira platensis* as bio-sorbent. The kinetic data were better described by the pseudo-second model and equilibrium was established within 60-120 min. The increase of temperature from 298 to 318 K caused a decrease of bio-sorption capacity. The maximum monolayer adsorption capacity was 312.5 mg/g at 298 K and pH 7.5. Thermodynamic parameters indicated that MB bio-sorption onto *A. platensis* was a spontaneous, favourable and exothermic process. The bio-sorption results showed that *A. platensis* could be employed as an efficient and eco-friendly bio-sorbent for the removal of cationic dyes.

Hashem et al., (2020), utilized bio-wastes in dye adsorption from the industrial effluents, Banana peel waste (BPW) and were used as inexpensive and eco-friendly adsorbent for the MB removal. MB dye was adsorbed by mechanically pretreated BPW by 31%. The kinetics study was illustrated that the adsorption parameters indicated that the Langmuir model is better to describe the adsorption of dye with excellent maximum adsorption capacity 9.91 mg/g.

Samar et al., (2022), studied polyacrylonitrile derivatives as adsorbents to be used in waste water treatment polyacrylonitrile (PAN) derivatives were tested for the removal of methylene blue dye from aqueous solutions. Different parameters such as adsorbent dose, initial dye concentration, contact time, pH and temperature were studied to obtain

the optimum condition. The percentage of MB dye using 0.1 g adsorbent at optimum pH 8 was 99.7 % after 20 min. The rate parameters were evaluated and it was found that the adsorption process followed the pseudo-second-order kinetic model with correlation coefficient of 0.98. The adsorption data best fitted with Freudlich isotherm.

Elmorsi (2011), studied the removal of methylene blue from aqueous solution by the Miswak (Caves as low adsorbent). Equilibrium behavior of Miswak leaves was investigated by performing batch adsorption experiments. The effects of pH, contact time, adsorbent dose were evaluated. An alkaline pH (10.6) was favourable to the adsorption of MB dye. Langmuir equation was found to have the highest value of R^2 compared to other models such as Freundlich and Temkin. Furthermore, it was found that Miswak leaves have a high adsorptive capacity towards MB dye (200 mg/g) and show favourable adsorption of MB dye with separation factor ($R_L \leq 1$). Kinetic models including pseudo-second-order were used to analyze the methylene blue dye adsorption process and the results showed that the pseudo-order kinetic as proved by the high value of $R^{2.}$

Mouni et al., (2018), studied the removal of methylene blue from aqueous solutions using a raw Alergian Kaolin sample as a low-cost adsorbent. The adsorption kinetics results are adjusted to best fit the pseudo–second order model. The experimental data are analyzed by Langmuir isotherms, revealing that the maximum adsorption capacity of MB on this Kaolin sample equals 52.76 mg/g at T=25° C and pH=6.

Gupta et al., (2016), studied an agricultural waste from potato plant (Potato stem powder, Potato leaves powder) was used as an adsorbent for the removal of methylene blue dye from aqueous solution. Batch experiments were investigated the effects of parameters such as pH_{pzc}, adsorbent dose, contact time, initial concentration, and temperature. The pseudo-second order model better represented the adsorption kinetics. Equilibrium data were analyzed using Langmuir and Freundlich isotherm models.

Malik et al., (2018), investigated the potential of corn husk as a bio-sorbent for adsorption of methylene blue (MB) dye from dye synthetic effluent. The effects of operating parameters like pH, contact time, initial dye concentrations and adsorbent doses on dye uptake were examined. pH of the solution was found to have significant impact on adsorption process, and maximum dye removal was achieved at pH 6.2 within 15 minutes of contact time. The coefficient value for adsorption capacity obtained in Langmuir isotherm was 30-66 mg/g with significant value of regression R^2

=0.99. Kinetic study of the adsorption process followed the pseudo-second order kinetic model. Experimental results favor the adsorption process from corn husk based adsorbent. Some of the literature for the methylene blue (MB) removal from wastewater are listed in the following table 2.

Table 2.1: Activated carbon prepared from different biomass and their removal efficiency

S. N.	Raw material	dye	pH	Contact time	Adsorption capacity	Kinetics	Reference
1.	Yellow passion fruit	MB	alkaline	56 h	-	Langmuir isotherm, second order kinetics	(Flavio et al., 2009)
2.	Fava beans peels (*Vicia faba)*	MB	5.8	-	140 mg/g	Langmuir adsorption isotherm	(Omar et al., 2020)
3.	*Citrus limetta* peels	MB	7	-	500 mg/g	Langmuir isotherm, second order kinetics	(Singh et al., 2017)
4.	Corn Husk	MB	6.2	-	30.33 mg/g	Langmuir isotherm, second order kinetics	(Malik et al., 2016)
5.	Algerian Kaolin	MB	6	-	52.76 mg/g	Langmuir isotherm, second order kinetics	(Mouni et al., 2018)
6.	Polyacrylonitrile derivatives	MB	8	20 min.	-	Freundlich isotherm, second order kinetics	(Samar et al., 2022)

CHAPTER-3

2. MATERIALS AND METHODS

2.1. Instruments and Chemical Reagents Used

Instruments like Grinder, Sieve no. 250µm, Weighing balance (Phoenix, PH2204C), Hot air oven, Muffle Furnace, Auto Deluxe Digital pH meter (Latronics-11, India), Rotatory Flask Shaker, Filter Paper (Whatman-1, 125µm), Double Beam UV Visible Spectroscopy (Labtronics-2802), FTIR (PerkinElmer 10.6.2) and the chemicals like methylene blue (Mol. mass = 373.90, 98.5 % purity, Nacalai tesque), Hydrochloric acid (36 %, Qualigens), Sodium Hydroxide (Mol. mass= 40), Sodium thiosulphate (molecular mass=248.18, 99 %, Qualigens), Potassium dichromate (molecular mass=294.18, Fischer scientific), Iodine (253.8 molecular mass, Sara Bhai), Potassium iodide (Qualigens), were used. Chemicals used were all of laboratory grade and were used as received without any further purification.

2.2. Sample collection

Tindu (*Diospyros malabarica)* seeds were collected from Bhimsen Thapa Rural Municipality 07, Borlang, Gorkha (Latitude: 27.99, Longitude: 84.62) as in figure 3.1. Seeds were collected based on the basis of Material safety data sheet (MSDS) protocol. Collected seeds were washed with water then, dried in oven for 4 h.

Figure 3.1: Google map of the sample collection area

2.3. Preparation of Adsorbents

3.3.1 Preparation of charred Tindu seed powder

Dry seeds were grinded by Herbal Medicine Disintegrator (FW177, Ser. No. 201905051047) into fine powder. Grinded seed powder (about 300 g) was charred by 200 mL sulphuric acid in to plastic bucket of 5 L capacity. The sulphuric acid was added into bucket until the sample completely changed into black. It was stirred with the help of glass rod and left for 24 h for complete charring. The black mass was then washed repeatedly with distilled water until the pH of the sample turned to almost neutral. Then the sample mixture was filtered and residue was dried in hot air oven for 12 h with maintaining temperature 100 °C for complete removal of moisture.

3.3.2 Preparation of pre-carbonized carbon

The charred sample obtained from the previous step was taken in silica crucible with measuring weight and then put into muffle furnace for 4 h maintaining 300 °C temperature. Then the sample was allowed to cool naturally to room temperature and collected.

2.4. Preparation of Reagents

3.4.1 Preparation of 0.1 M Sodium Thiosulphate

12.4 g of sodium thiosulphate was weighed out and transferred into 500 mL volumetric flask and dissolved it completely in 100 mL distilled water. Then distilled water was added up to mark level.

3.4.2 Preparation of 0.02M Potassium Iodate

2.14 g of potassium iodate was weighed out and transferred into 500 mL of volumetric flask, dissolved it in distilled water and volume of water added up to mark level.

3.4.3 Preparation of standard potassium dichromate solution

7.35 g of potassium dichromate was weighed out and transferred into 1000 mL volumetric flask. It was dissolved in distilled water and the water was added up to mark level.

3.4.4 Preparation of starch indicator

100 mL distilled water was taken in beaker and boiled. In hot water, 1 g of starch was added and stirred continuously with glass rod up to complete dissolution. Then the

solution was allowed to cool naturally.

3.4.5 Standardization of sodium thiosulphate

As prepared sodium thiosulphate solution was filled in burette and zero level was adjusted. 10 mL of standard potassium dichromate solution was pipetted out in conical flask with the help of pipette. Half test tube distilled water, 2 mL of conc. HCl and one test tube 5% KI solution was added into the conical flask. Then, the mixture was covered with watch glass, shaken well and left in dark for five minutes. After five minutes, the solution was rinsed with distilled water and the solution was titrated with sodium thiosulphate solution with constant shaking until the faint yellow colour appeared. Then, 2 mL of freshly prepared starch solution was added when the color of titrant was like straw color. On addition of starch, the color of solution was changed to dark blue color. This is due to the absorption of iodine by starch solution. Sodium thiosulphate solution was added drop by drop until the blue color got discharged. The volume of thiosulphate consumed was recorded and concentration was calculated. This process was repeated to get concurrent readings. After calculation, the concentration of sodium thiosulphate was determined to be 0.103 M.

3.4.6 Standardization of Iodine solution

Standardized sodium thiosulphate solution was taken into burette and zero level was adjusted. 25.0 mL of iodine solution was taken in conical flask and titrated with sodium thiosulphate solution until the iodine solution was light yellow color. Then, starch indicator was added which yielded a dark blue color. Then the titration of iodine solution with sodium thiosulphate was continued by adding drop by drop until the solution turned to colorless. The volume of thiosulphate was noted and the concentration of iodine solution was calculated. The process was repeated to get concurrent readings. After calculation, the concentration of iodine was determined to be 0.172 M.

3.4.7 Preparation of the stock solution (1000 ppm) of methylene blue solution

0.1 g of methylene blue was weighed out and transferred into 100 mL volumetric flask and dissolved in distilled water. Then the volume was made up to mark by adding distilled water.

3.4.8 Preparation of 0.1 M HCl

Decimolar HCl solution was prepared by diluting 2.24 mL of concentrated acid into 250 mL of volumetric flask containing 150 mL of distilled water. The dilute solution was allowed to cool and then volume was made up to mark by adding distilled water.

3.4.9 Preparation of 0.1 M NaOH

1 g of sodium hydroxide pellets was transferred into 250 mL volumetric flask and dissolved by adding distilled water and volume made up to mark.

2.5. Point of zero charge

It is the pH at which the net charge of total particle surface is zero. This concept has been introduced in the studies dealing with colloidal flocculation to explain the effect of pH. The point of zero charge shows the acidity and basicity of activated carbons and the net surface charge of the activated carbons in solution. It was measured as follows: 0.1 g of pre-carbonized carbon was taken into conical flask and 50 mL NaCl was added to it for 9 separate system. pH of separate sample system was maintained 2-10 using HCl and NaOH as per requirement. Then each conical flask was placed in rotatory flask shaker and shaken for 48 h with constant agitation of 200 rpm. After 48 h, the solution was filtered and final pH was measured. The graph of initial pH versus change in pH was plotted. The point of intersection by the plot at x-axis is the point zero charge (PZC).

2.6. Porosity determination of adsorbent

3.6.1 Iodine number determination

The removal of Iodine may reflect the micro porosity of an activated carbon that defines the ability of activated carbons to adsorb small compounds. It is a measure of micro-pore content of the activated carbon. The higher percentage removal of iodine of the prepared activated carbon may be attributed to the presence of micro-pore nature structure and the high surface area of the activated carbon due to the enlargement of their pore structure.

Iodine number was determined using standard protocol. At first the concentration of iodine solution was determined by standardization and then this solution was used for further process. For determination of iodine number, 0.5 g carbon sample was weighed

and transferred into beaker. 25 mL standard iodine solution was added in it. Then, the mixture was swirled vigorously for 30 minutes and then solution mixture was filtered using Whatmann 41. Filtrate was titrated with standard thiosulphate solution to a persistence of a pale yellow color. 5 mL of freshly prepared starch solution was added and titrate slowly until the solution becomes colorless. The process was repeated for two more times. The blank titration was also done. Iodine number of activated carbon was calculated using following equation,

Iodine consumed = No. of milligram of Iodine consumed (before adsorption) – No. of milligram of Iodine consumed (after adsorption)

$$Iodine\ number = \frac{Amount\ of\ iodine\ consumed\ by\ carbon\ in\ mg}{Weight\ of\ carbon\ taken\ in\ gram}(mg\ /\ g) \quad \ldots (1)$$

3.6.2 Methylene blue number determination

It is the amount of methylene blue in milligram which is adsorbed by one gram of carbon. It is expressed in terms of gram of methylene blue per gram of adsorbent. Molecular mass of methylene blue is 373.9 g/mol. The amount of methylene blue adsorbed (q) per unit mass of the adsorbent (mm/g) at time 't' is given by the equation,

$$q = \frac{(Co - Ce)\ V}{W} \qquad \ldots (2)$$

Where, Co and Ce are initial and equilibrium final concentration of methylene blue solution in mg/L (ppm). W is the weight of adsorbent taken in gram and V is the volume of solution taken in liter.

The methylene blue adsorption number of carbon sample was determined by batch adsorption experiments. 0.01g of activated carbon was mixed with each 100 mL of 10, 25, 50 and 100 ppm concentrated methylene blue solution and was agitated for four hours in a shaker at 200 rpm and left for 24 h. Then, the solution was filtered using Whattman (42) filter paper and absorbance of filtrate was recorded.

2.7. Characterization of adsorbent

For the efficient removal of methylene blue dye, charred Tindu seed powder was pre-carbanized at 300 °C. Then, it was characterized in order to analyze the surface structure, morphology and functional group present in the adsorbent, which demonstrates the adsorbent's capacity for the adsorption. For which following tools

were used.

3.7.1 Fourier Transform Infrared Spectroscopy

FTIR is an analytical technique which can be used for the identification of types of functional group present at the surface of adsorbent. Among IR radiation passed through the sample in FTIR spectroscopy, some of radiation is absorbed by the sample and some of radiation is transmitted by the sample. Fourier transform refers to a fairly recent development in the manner in which the data are collected and converted from an interference pattern to a spectrum. By interpreting these spectrum different functional groups present in the surface of adsorbent can be determined. More complex molecular structures lead to more adsorption bands and more complex spectra.

The functional group present in the sample was examined using Fourier transform infra -red spectroscopy in the wave number range of 4000-450 cm^{-1}. The FTIR spectrum of charred sample and pre-carbonized sample were recorded using Perkin Elmer version 10.6.2 in the department of chemistry, Amrit Campus, Kathmandu, Nepal.

3.7.2 Field Emission Scanning electron microscopy (FE-SEM)

FESEM is one of the most powerful and useful tools for the examination and characterization of surface morphologies of the activated carbon. FE-SEM images obtained at microscopic level through SEM are primarily used to observe the structure and distribution of the pores present on the surface of activated carbon can be seen through the high resolution magnification of FE-SEM image. Activated carbon possessing more pores and irregular surfaces are considered to have high surface area and good adsorption capacity.

The morphology of as prepared activated carbon was studied using field emission scanning electron microscopy (FE-SEM) at the accelerating voltage of 5.0 kV. A field emission source releases electrons, and they accelerated and refracted in a strong electric field gradient. These so called as primary electrons are focused and refracted by electronic lenses within the high vacuum column to create a narrow scan beam that bombards the target. Each point emits secondary electrons. These secondary electrons angles and velocities are related to the objects surface structure. The secondary electrons are captured by a detector, which then generates as electrical signal. A video scan image is created by amplification and transformation of the signal.

2.8. Adsorption study

3.8.1 Batch Adsorption study

Batch adsorption is performed to evaluate the adsorption isotherms of metal ion or, dye onto the surface of the adsorbent. In batch adsorption method, a known amount of adsorbent is mixed with the required volume of solvent, concentration, pH of the solution was taken in conical flask with covering followed by continuous agitation at room temperature for 4 hours in a mechanical shaker with a speed of 200 rpm to reach adsorption equilibrium. Initial and equilibrium concentration of dye are determined and amount of dye adsorbed was determined. Adsorption of methylene blue dye on adsorbent is influenced by various parameters such as pH, adsorbent dose, initial concentration, contact time, etc. (Ghimire et al, 2002). The amount of dye adsorbed at equilibrium per unit mass is calculated as,

$$q = \frac{Ci - Ce}{w / V} \qquad \ldots (3)$$

And, percentage removal of dye is calculated by using the following relation (Acharya et al, 2008),

$$R\,(\%) = \frac{Ci - Ce}{Ci} \times 100 \qquad \ldots (4)$$

Where Ci is the initial concentration, Ce is the equilibrium concentration, V is the volume of the adsorbate solution in milliliter and w is the weight of adsorbent in milligram.

3.8.2 Calibration curve

Plotting a calibration curve is a fundamental aspect in UV-Vis absorption. It is based on the Lambert-Beer's law. A plot of absorbance versus concentration gives a straight line for a particular concertation range. This benefit is executed for the determination of absorbance of the material under the irradiation of UV-Vis radiation. The calibration curve is based on Beer-Lamberts law which states that there is a linear relationship between the absorbance and concentration of sample. In order to determine the equilibrium concentration of the methylene blue in every batch adsorption study, the

calibration curve was used. For the preparation of calibration curve, firstly, the wavelength of maximum observation was determined using 5 ppm methylene blue solution. Then, the absorbance of 10 different solutions of 1-10 ppm concentration were recorded. Finally, the absorbance versus concentration graph was plotted as calibration curve.

3.8.3 Effect of pH

pH greatly influences on the adsorption process. In this experiment, the influence of pH was determined by putting 25 mg activated carbon sample into 25 mL of 25 ppm MB solution in separate 9 conical flasks maintaining the pH 2-10 by appropriate amount of 0.1 M HCl and 0.1M NaOH. Then each container was covered with cork and placed into rotatory flask shaker for 4 hours at a speed of 200 rpm. After shaking, the solution was filtered and the absorbance of the filtrate was recorded. Final concentration was calculated from slope from calibration curve and absorbance. Then, amount of dye adsorbed and % removal of dye were calculated.

3.8.4 Effect of adsorbent dose

Amount of adsorbent dose required for maximum removal of dyes from specified volume of simulated solution was studied. For this, 25 mL of 50 ppm MB solution was taken in separate conical flasks containing 10, 20, 30, … 100 mg activated carbon and the pH 5 (optimum) was maintained for each mixture solutions. Then, each conical flask was placed in shaker for 4 hours with constant agitation of 200 rpm. After 4 hours of shaking, the solution was filtered and absorbance of the filtrate was measured by UV - spectrophotometer.

3.8.5 Effect of initial concentration

Initial concentration of adsorbate was optimized by taking different concentrations of MB dye solutions. For this, 25 mL of MB dye solution of 25, 50, 100, 150 ppm concentration was taken in separate four beakers. Then, pH 5 was maintained to each solution and transferred into conical flask. 20 mg carbon sample was added in each conical flask and placed in shaker for 4 hours. Finally, the solution was filtered and absorbance of the filtrate was recorded.

3.8.6 Effect of contact time

Adsorption kinetics study was the major point of this study. In order to determine the equilibrium time, 25 mL of 25 ppm MB solution was taken in eight beakers and pH 5 was maintained for each. Then, those solutions were transferred into eight different conical flasks and 20 mg of carbon sample each was added into all conical flasks. Then, each conical flask was placed in shaker shaken at 200 rpm for different time. Solution mixture in first conical flask was filtered after 15 minute and the absorbance of the filtrate was recorded. Similar process was applied for all remaining solutions in each 15 -minute successive time interval up to 180 minute.

CHAPTER 4

3. RESULTS AND DISCUSSIONS

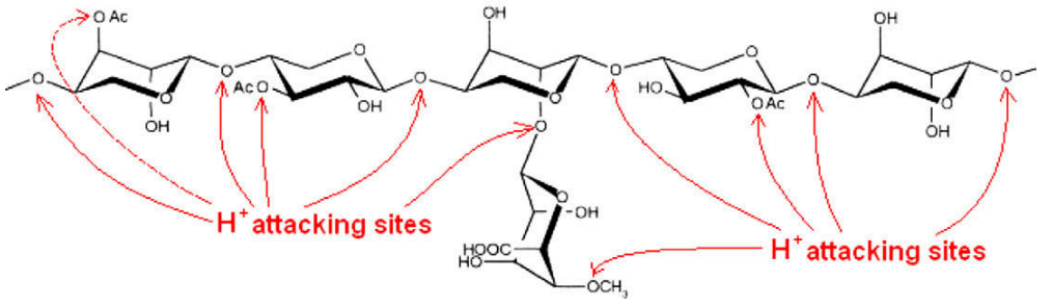
3.1. Observation and Chemical changes in charring process

Diospyros malabarica seed powder was treated with concentrated sulphuric acid, a black powder was obtained which was washed several times by deionized water to obtain neutral material. Here, concentrated sulphuric acid has dehydration capacity. The hydrates parts of carbon (i.e. Water molecules) gets adsorbed by conc. sulphuric acid by its dehydrating action. The mechanism of dehydration and ring opening by sulphuric acid is given in scheme 1. The charring process is assumed to proceed as follows.

$C_n(H_2O)_n + H_2SO_4 \rightarrow nC + H_2SO_4.nH_2O$

Carbohydrates acid carbon hydrated Hydrated sulphuric acid

There are many sites for the attack by proton onto the cellulose structure. Consequently, cellulose converts into black carbon. The released water molecules are hydrated with conc. sulphuric acid.



Scheme 4.1: Dehydration and ring opening by sulphuric acid during charring process (Hu et al., 2010)

3.2. Fourier transformed infrared spectroscopic findings

FTIR is the crucial tool for the identification of functional groups associated with sample. Here, the possible functional groups that remain in the activated carbon were determined. The FTIR spectra of the activated carbon sample is shown in figure 4.2. A broad band at around 3592 cm^{-1} indicates the presence of phenolic group or hydroxyl group associated with the cellulose moieties. An absorbance band at around 1510-1654 cm^{-1} indicates the presence of carbon to carbon double bond. Peak around 1102 cm^{-1} indicates the presence of C-O-C stretching group. IR absorbance around 665-700 cm^{-1} indicates C=C bending. The presence of functional group indicates the presence

of some unsaturated carbon in the bio-char and hydroxyl groups associated with phenolic group or moisture associated with the sample retained due to moisture.

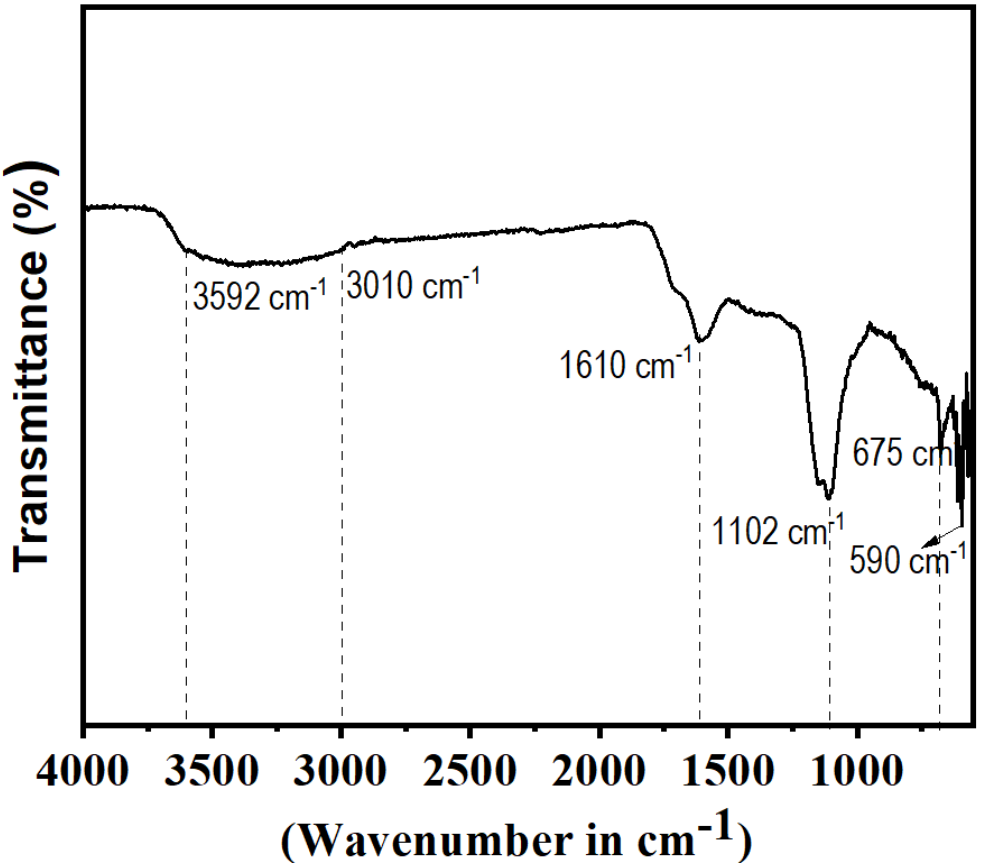


Figure 4.2: FTIR spectra of the activated carbon prepared from *Diospyros malabarica* seed powder

3.3. Field Emission Scanning Electron microscopy

The surface morphology of sulphuric acid treated carbon sample at different magnification are displayed as in figure 4.3. The carbon derived by treating the *Diospyros malabarica* with sulphuric acid shows different layered structure which reveals the presence of porosity and layers. This indicates that the adsorption has taken place properly.

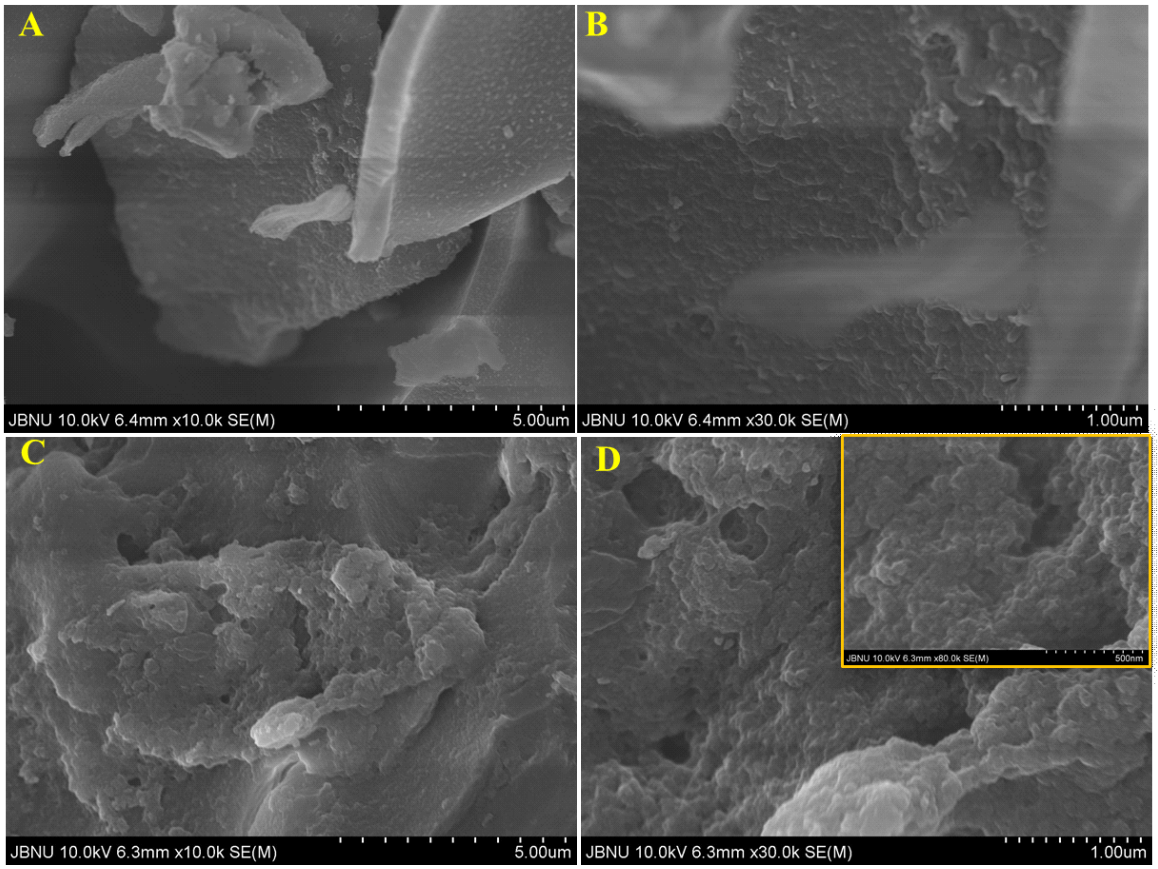
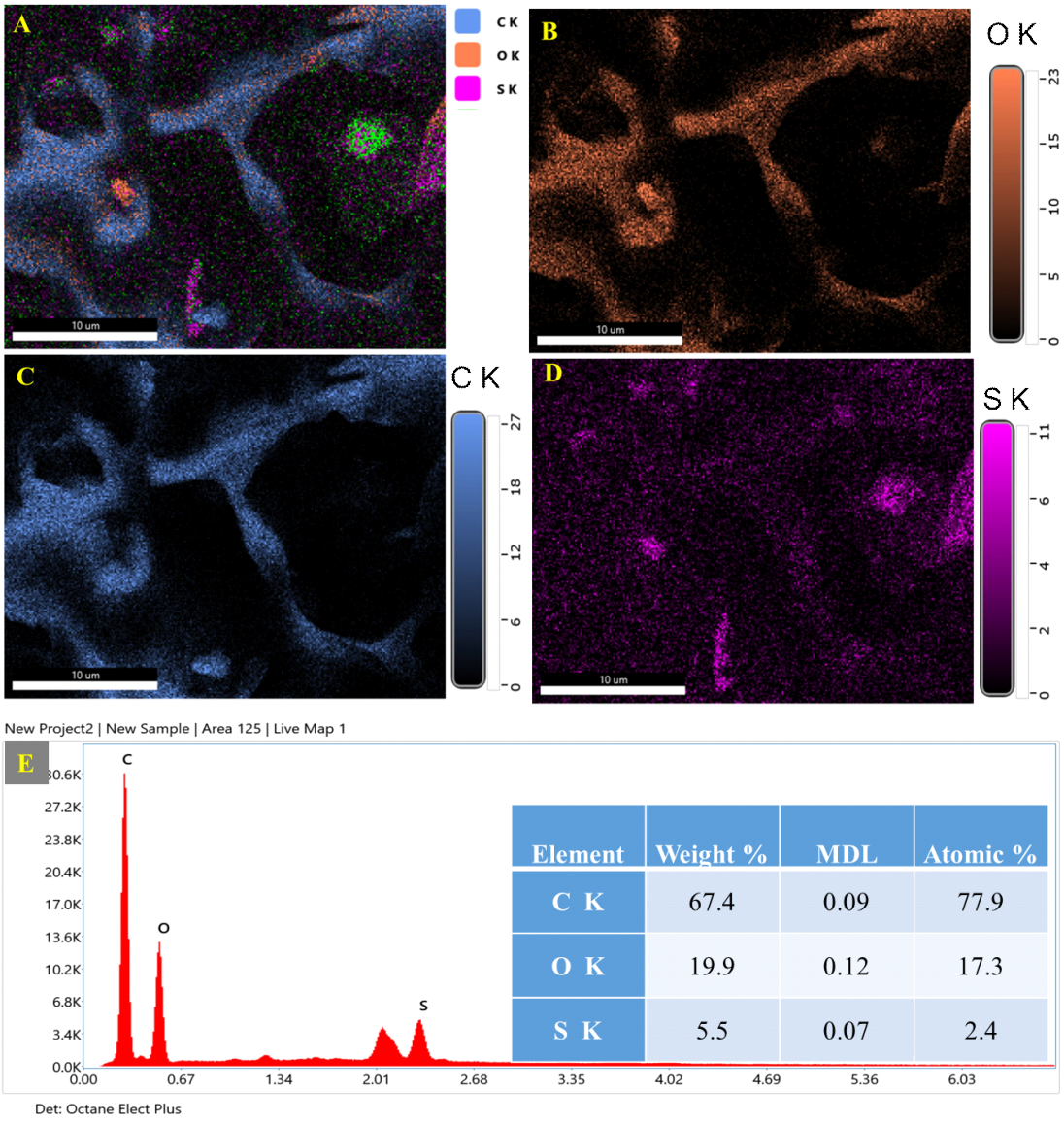


Figure 4.3: FESEM image of (A, B) precarbonized sample at 300 °C and (C, D) sulphuric acid treated activated carbon at different magnification (Image A and C have 5.00µm scale bar,B and D have 1.0µm scale bar. The inset at D has 500 nm scale bar)

3.4. EDX

The EDX image in figure 4.4 showed that carbon derived from *Diospyros malabarica* seed includes carbon (C), oxygen (O), sulphur (S). The EDX spectrum with elemental composition was expressed in percentage as shown in figure (4.3 A-E). The elemental mapping and EDX shows that sulphuric acid treated activated carbon consists of carbon, oxygen and sulphur as major elemental constituent. The percentage of carbon is the highest. The oxygen element in the carbon could be associated with the adsorbed oxygen or some functional moieties like epoxy group, carbonyl group or carboxylate group. In addition, there is possibility of doping of sulphate group indicating the presence of Sulphur and oxygen in the activated carbon. The atomic and weight percentage of all elements present in the sample are presented in figure 4.3 (E).



Element	Weight %	MDL	Atomic %
C K	67.4	0.09	77.9
O K	19.9	0.12	17.3
S K	5.5	0.07	2.4

Figure 4.4 : Elemental composition of sulphuric acid treated activated carbon and its EDX spectrum.

3.5. Point of zero charge

Point zero charge is the pH value at which the net charge of the materials (here, activated carbon) is zero. The concept of PZC is very important where adsorption depends upon pH value. Below the PZC value, hydrogen ions would be adsorbed in priority compared to other cations developing positive surface charge onto the adsorbent. In that condition, anions can be adsorbed onto the adsorbent. On the other hand, above the PZC value, hydroxyl ions gets adsorbed in priority compared to anions developing negative charge onto the adsorbent surface. Therefore, above the PZC value, the surface charge of the adsorbent is negative and cation can be adsorbed. In this

experiment, point of zero charge was determined by observing the change in pH of the solution before and after equilibrium as given in table 4.1. The difference in pH values were plotted against initial pH value of the reaction mixture as shown in figure 4.5. From graph, PZC of carbon sample is 5.2. Below the PZC value, surface charge is positive and above the PZC value, the surface charge is negative. Since methylene blue is a cationic dye, it is appropriate to adsorb above the PZC value.

Table 4.1 Initial and final pH value of solution of sulphuric acid treated activated carbon

Initial pH	Final pH	ΔpH
2	2.7	-0.7
3	4.2	-1.2
4	5.4	-1.4
5	5.2	-0.2
6	5.2	0.8
7	5.5	1.5
8	5.4	2.6
9	5.5	3.5
10	6	4

A plot of ΔpH versus initial pH of activated carbon treated solution is shown in figure 4.5. It shows that the plot cuts the x-axis at pH 5.2. This is the PZC value. Below this pH value, the surface of the AC bears positive charge and above this pH value, it bears negative charge.

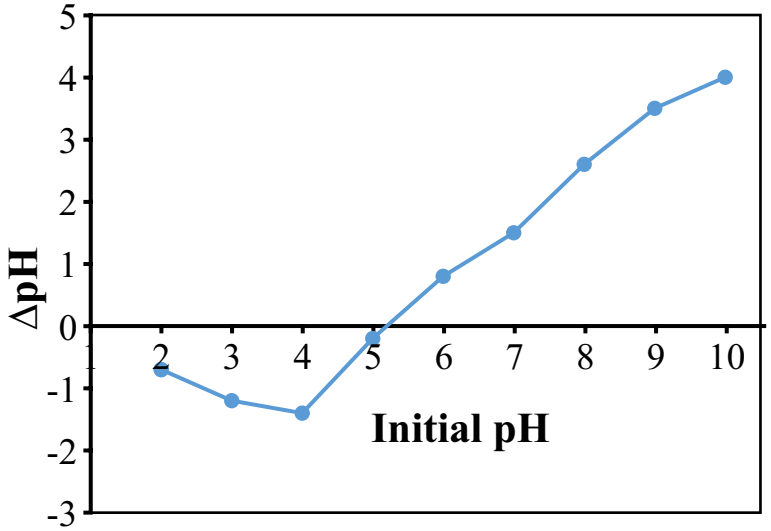


Figure 4.5: Diagram showing PZC value of activated carbon

3.6. Porosity Determination or Adsorbent

4.6.1 Iodine Number

Iodine number of activated carbon was studied. The sodium thiosulphate solution and iodine solution were standardized before carrying out the experiment. After shaking with activated carbon, the concentration of iodine solution was determined. Iodine number is the amount of iodine in milligram adsorbed by one gram of carbon. The size of iodine is similar to the micropore range. Higher value of iodine number indicates the concentration of micropore in the activated carbon. Higher value of iodine number suggests more porosity and higher levels of activity (Itodo et al, 2010). In this experiment, the iodine number of activated carbon was found to be 146.19 mg/g. This value of iodine number indicates the satisfactory mesoporosity of the activated carbon.

4.6.2 Methylene blue number

Methylene blue number of activated carbon was measured by recording the absorbance of the solution in UV-Visible spectrometer at the maximum wavelength. The maximum absorbance of the methylene blue solution of 5 ppm concentration was determined and found to be 662 nm as shown in figure 4.6.

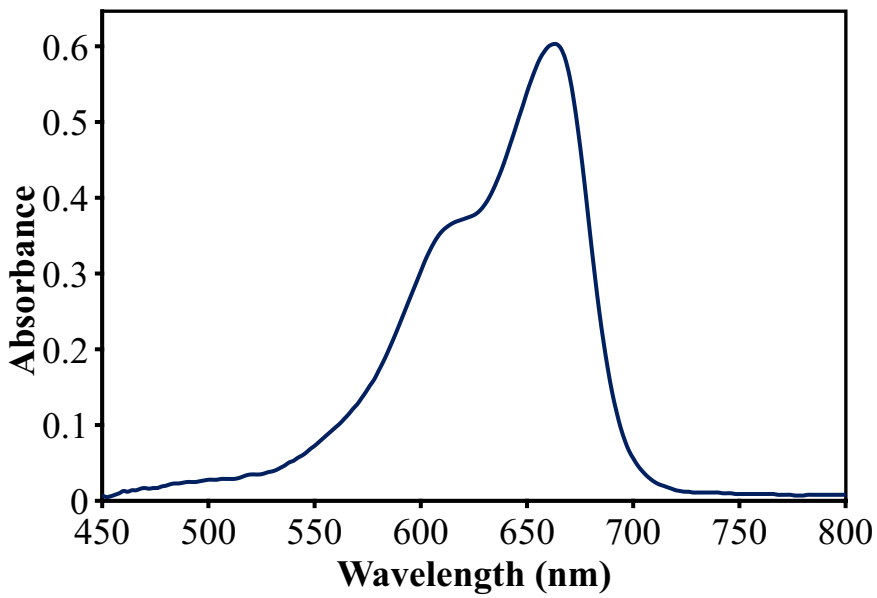


Figure 4.6: Wavelength for maximum absorbance shown by 5 ppm methylene blue solution.

From graph, maximum absorbance of MB dye was found at the wavelength of 662 nm.

Then, calibration curve of the system was created using methylene blue solutions of concentrations 1-9 ppm. The absorbance of these solutions were plotted against these concentrations and a straight line passing through origin was obtained as in figure 4.7. Based on this calibration curve and the methylene blue number as well as the batch adsorption isotherm experiments were performed.

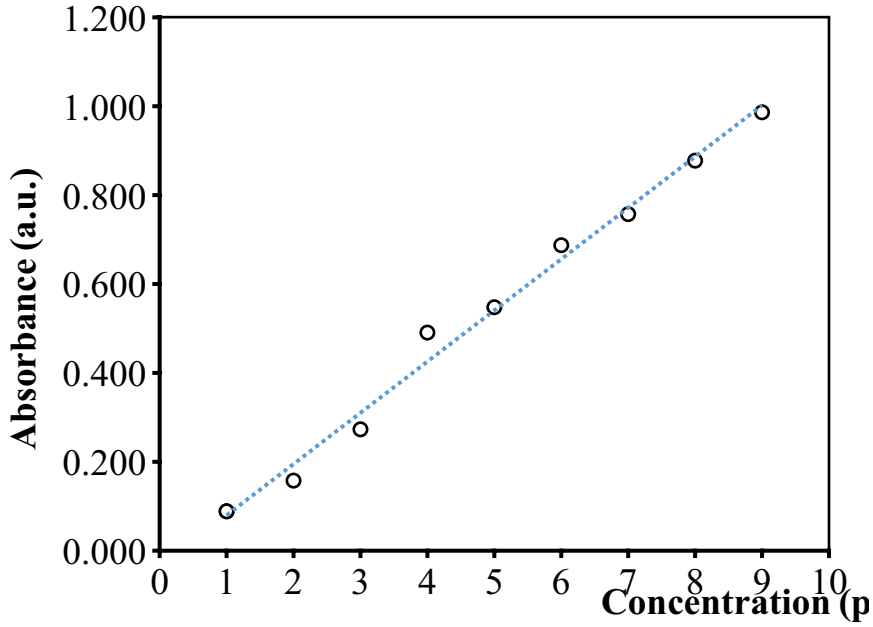


Figure 4.7: Calibration curve for the determination of MB number

Methylene blue number of the activated carbon sample determined using the calibration curve for 100 ppm solution was found to be 966.0. This value of MB number is comparable to those of other researcher's finding.

3.7. Adsorption study

Adsorption study was performed in order to determine the effect of pH of the adsorption system, effect of adsorbent dose, effect of initial concentration of adsorbate, and effect of contact time. These parameters were optimized based on the removal efficiency of methylene blue dyes from simulated solution. The detailed findings of each parameter are explained below.

4.7.1 Effect of pH

The pH of the solution is the most important parameter in the study of adsorption of methylene blue onto the surface of carbon. In this section, effect of pH on adsorption process with their adsorption efficiency was analyzed at different pH ranging from 2-

10. Here, percentage removal of methylene blue dye has comparable percentage in between pH 5 (90.763 %**)** and pH 6 (90.659 %). As per the findings of PZC value, the adsorption of cationic dye would be maximum above the pH 5.2. This is in agreement with result of optimum pH value finding for the removal of MB dye. Figure 4.7 shows that higher adsorption capacity of methylene blue in the range of pH 5-6 (90.76-90.65 %) is attributed to increase protonation by neutralization of the negative charges at the surface of adsorbent. Initially, as the pH of solution goes on increasing, the negative charge of the adsorbent goes on increasing and become maximum in the pH range of 5-6. Above this pH value, the percentage removal of MB dye go on decreasing. However, the percentage removal of MB dye is significant compared to those in acidic range. However, at pH 2, the MB adsorption is found abruptly high but not the highest.

Table 4.2: Percentage removal of MB dye from simulated solution using AC carbon

pH	Absorbance	Concentration	%Removal
2	0.285	2.4739	90.104
3	0.697	6.0503	75.798
4	0.403	6.9965	72.013
5	0.266	2.309	90.763
6	0.269	2.335	90.659
7	0.930	8.0729	67.708
8	0.3616	3.1388	87.444
9	0.8423	7.3116	70.753
10	0.5016	4.354	82.583

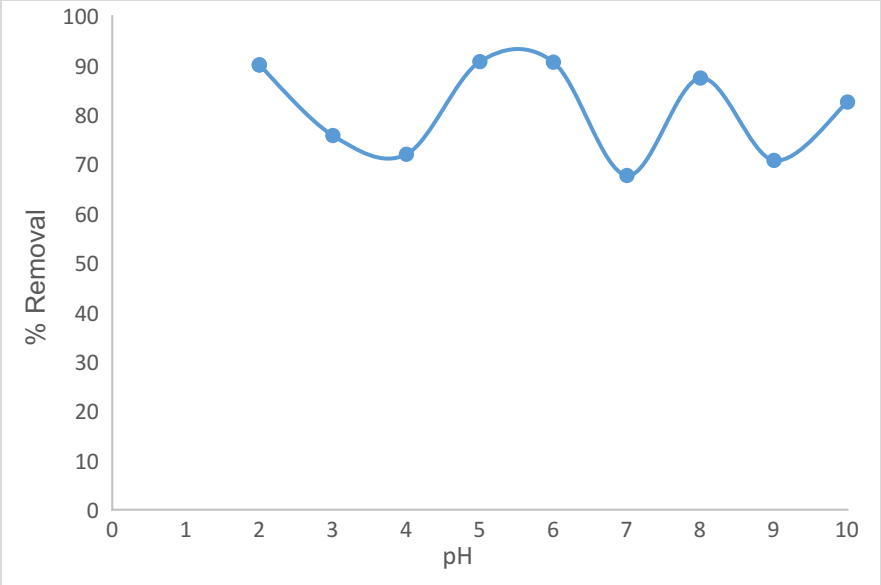


Figure 4.8 pH effect for the removal of MB

4.7.2 Effect of adsorbent dose

Adsorbent dose is another important factor in batch adsorption experiment. The effect of the dependency of adsorption efficiency on adsorbent dose is illustrated by figure 4.8. It was observed that the highest percentage removal was found at 30 mg. This suggest that increase in the adsorbent dose resulted in an increase in the available surface area and the availability of additional adsorption sites. At 30 mg of adsorbent dose of activated carbon, percentage removal of MB was maximum.

Table 4.3: Effect of adsorbent dose

Dose (mg)	Absorbance	Concentration	Dye adsorbed	% Removal
10	0.579	20.1041	74.739	59.79
20	0.4926	17.1041	41.1198	65.79
30	0.568	4.93	37.5583	90.14
40	0.51225	17.7864	20.1335	64.43
50	0.5936	15.4583	17.2708	69.08
60	0.5966	15.5364	14.3598	68.93
70	0.996	8.6458	14.7693	82.71
80	0.6753	17.5859	10.1294	64.83
90	0.691	5.9982	12.227	88.04
100	0.8376	14.5416	8.8646	70.92

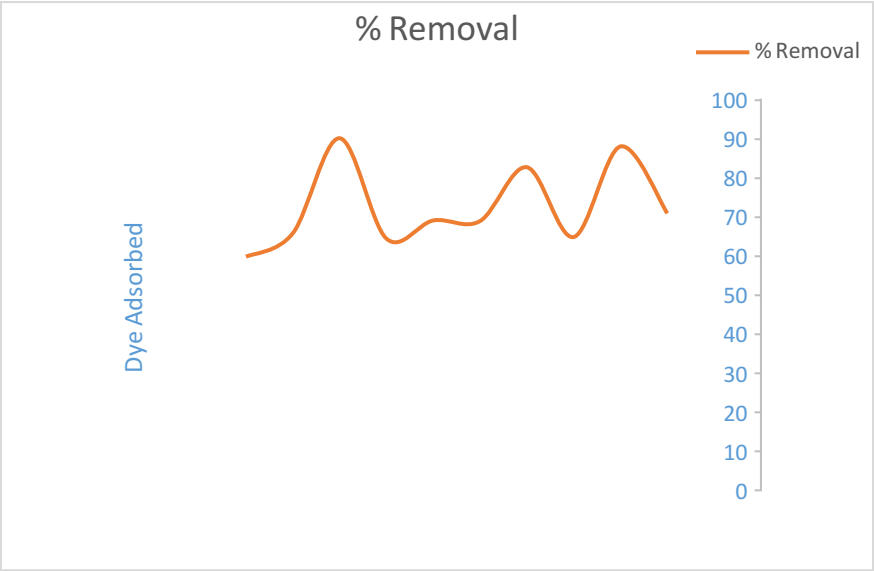


Figure 4.9: Effect of dosage of carbon for the removal of MB

4.7.3 Effect of initial concentration

The effect of initial concentration on the adsorption of methylene blue dye was studied by using different initial concentration. From figure 4.9, it can be seen that increase in initial concentration from 25-150 ppm, resulted in a decrease in the adsorption efficiency from 78.81% to 52.71%. This implies that dye adsorption efficiency get reduced as the initial concentration. The reason behind this is that at lower concentrations, there are sufficient active sites that the sorbate can easily occupy. The maximum adsorption of MB dye was found to be 25 ppm of initial concentration.

Table 4.4: Effect of initial concentration

Initial concentration(ppm)	Absorbance	Final concentration	% Removal
25	0.610	5.2951	78.819
50	0.859	14.9131	70.173
100	1.0676	27.802	72.197
150	0.817	70.92	52.719

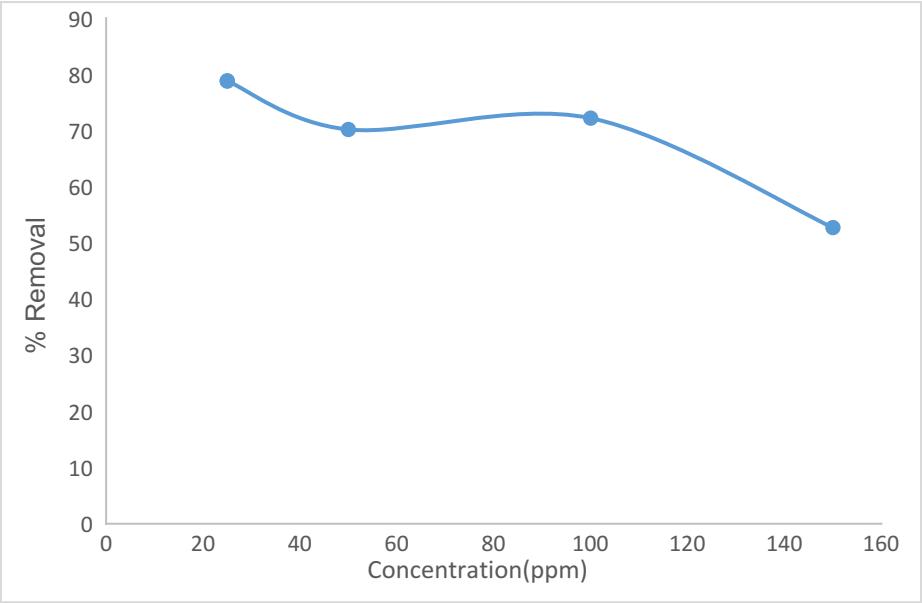


Figure 4.10: Effect of initial concentration for the removal of MB

4.7.4 Effect of contact time

The effect of contact time on adsorption of methylene blue dye was studied by varying the time interval from 15 to 180 minutes. From contact time data, it can be seen that the extent of adsorption is rapid in the initial stages (15-120 minutes) as in figure 4.10. The rate of adsorption gets decreased in later stages till saturation is attained. The adsorption at the initial stages may be due to the higher driving force making fast transfer of methylene blue to the surface of adsorbent particles. The maximum percentage removal of MB was found to be at 120 minutes.

Table 4.5: Effect of contact time

Contact Time(min)	Absorbance	Concentration	% Removal
15	0.792	6.875	72.50
30	0.856	7.4305	70.27
45	0.84	7.2916	70.83
60	0.883	7.6649	69.34
90	0.845	7.335	70.66
120	0.728	6.3194	74.72
150	0.834	7.2395	71.04
180	0.759	6.5885	73.65

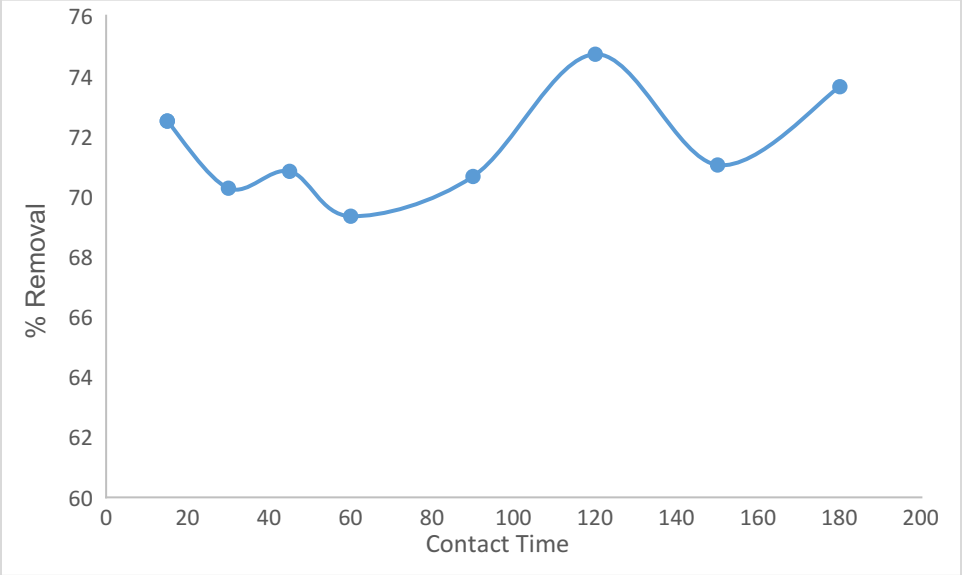


Figure 4.11: Effect of agitation time for the removal of MB

Based on the findings, it can be revealed that the activated carbon derived from *D. malabarica* can be an alternative materials for water purification. The high value of methylene blue and iodine number suggest the high surface area of the activated carbon. Such activated carbon could remove the methylene blue up to 90.67 %. This is good result. Further optimization and activation can be helpful in the development of the activated carbon materials form the same source. In the continuation of this work, chemical activation and high temperature activation under inert atmosphere would be considered. This would aid up high surface area of the activated carbon. This will increase the adsorptive capacity of the dyes such as methylene blue. However, in contrast of time and budget some work such as chemical activation of carbon under inert atmosphere could not be performed. On the other hand, the surface area determination from BET surface area measurement could not be done due to these cause. In the continuation of the work, the kinetics and modeling of adsorption (Langmuir and Freundlich adsorption) will be considered.

CHAPTER 5

4. CONCLUSIONS AND RECOMMENDATION

4.1. Conclusions

In the present work, Tindu seeds were successfully charred and pre-carbonized. The different physico-chemical properties of the as developed adsorbents were investigated. Its efficiency for the removal of methylene blue was determined by varying different parameters such as pH, adsorbent dose, initial concentration, contact time, etc. The point of zero charge of adsorbent was found to be 5.2. The surface area and porosity were determined by methylene blue number and Iodine number method. The functional group present in bio-adsorbents was characterized by FTIR analysis. The adsorption of methylene blue dye was found to be strongly dependent upon the pH of the solution and the optimum pH was found to be 5. At optimum pH, DMSC lead to 90.67% removal of methylene blue dye from aqueous solution.

The maximum adsorption capacity was found to be 30 mg/g of the adsorbent dose. The equilibrium concentration for the adsorption of methylene blue dye was found to be 25 ppm. The equilibrium time for the adsorption of of MB dye was found to be 120 min.

4.2. Limitation of the study

Every experiment in this work was performed carefully and wisely as far as possible to minimize errors and limitations. However, the following limitations of the study are subjected.

a. Chemicals weren't subjected to further purification before the experiment.
b. Characterization like XPS, XRD and TEM became impossible due to lack of time and budget.
c. The experiment in column method could not be performed.

4.3. Suggestion for further study

In this study activated carbon was prepared by chemical activation or, using sulphuric acid. Thus, DMSC has shown good ability to remove MB from aqueous solution. So, it can be used to remove a variety of different heavy metal ions including lead, mercury, cadmium, copper, etc. as well as other dyes found in industrial waste water like

Malachite green, Congo red, etc. *Diospyros malabarica* seeds can also be used to fabricate super capacitor electrodes due to their capacitance, high electrical conductivity. To investigate the impact of the additional parameter, the experiment can also be run in column mode.

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