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# Synthesis of mesoporous carbon from non-biodegradable plastic bags for water purification: methylene blue removal

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**SYNTHESIS OF MESOPOROUS CARBON FROM  
NON-BIODEGRADABLE PLASTIC BAGS FOR WATER  
PURIFICATION: METHYLENE BLUE REMOVAL**

**Kazula Henry**

**A Dissertation Submitted in Partial Fulfillment of the Requirement for the Degree of  
Master's in Environmental Science and Engineering of the Nelson Mandela African  
Institution of Science and Technology**

**Arusha, Tanzania**

**December, 2017**

## ABSTRACT

In the present work, the mesoporous carbon materials with pore diameter of 14.2 nm and specific surface areas of 15.18 ( $\text{m}^2\text{g}^{-1}$ ) identified by Brunauer, Emmett, and Teller (BET) were synthesized from non-biodegradable plastic bags (LDPE) wastes using hard template technique with alpha-manganese (IV) oxide by optimizing plastic scraps to  $\alpha\text{-MnO}_2$  mass ratio i.e. 1:1, 1:2, and 1:3 and temperature between 400°C and 600°C for each sample. Powder X-ray diffraction (XRD) identified the morphological structural order and textural properties of mesoporous carbon to be amorphous.  $\alpha\text{-MnO}_2$  as template was prepared following literature procedure by redox titration under reflux heating for 24 h.

The mesoporous carbon materials were tested for efficiency on Methylene Blue dye removal whereby samples obtained from plastic scraps to  $\alpha\text{-MnO}_2$  mass ratios of 1:1, 1:2 and 1:3 at a temperature of 400°C and 600°C were used. Mesoporous carbon from plastic scraps to  $\alpha\text{-MnO}_2$  mass ratio 1:1 at 600 °C suited for further adsorption experiments in batch technique due to its lower absorbance of 0.143 as compared to the rest samples of plastic scraps to  $\alpha\text{-MnO}_2$  mass ratio.

The Langmuir and Freundlich models were used to analyze the equilibrium data that described how mesoporous carbon interacts with Methylene Blue in aqueous solution in adsorption process. Results revealed that the isotherm data fitted Langmuir model with maximum dye adsorption of 1.644 mg/g at 80°C than Freundlich model whereby, the mesoporous carbon material adsorbed over 80% of the Methylene Blue dye in less than 35 min. The results provided evidence that mesoporous carbon is effective for the removal of dyes from aqueous dye solutions and industrial effluents. Also, the work provides another technique to plastic bags recycling into useful material-mesoporous carbon for industrial dye removal by adsorption.

**DECLARATION**

I, Kazula Henry do hereby declare to the Senate of Nelson Mandela African Institution of Science and Technology that this dissertation is my own original work and that it has neither been submitted nor being concurrently submitted for degree award in any other institution.

**Name of a candidate:** KAZULA HENRY

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The above declaration is confirmed by

**Name of Supervisor 1:** Dr. CECIL K. KING'ONDU

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**Signature**.....**Date**.....

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## CERTIFICATION

The undersigned certify that have read and hereby recommend for acceptance by the Nelson Mandela African Institution of Science and Technology a research report entitled: **Synthesis of Mesoporous carbon from non-biodegradable plastic bags for water purification: Methylene Blue removal**, in partial fulfillment of the requirements for the degree of Master's in Environmental Science and Engineering of the Nelson Mandela African Institution of Science and Technology.

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(Supervisor 2)

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## **DEDICATION**

*In remembrance of my late father Mr. Matthew Kazula, May his soul rest in eternal peace.*

*Amen.*



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## LIST OF ABBREVIATIONS AND SYMBOLS

<b>UNEP</b>	United Nation Environmental Programme
<b>HDPE</b>	High Density Polyethylene
<b>LDPE</b>	Low Density Polyethylene
<b>q<sub>e</sub></b>	The amount of dye adsorbed at equilibrium (mg/g)
<b>M</b>	The amount of mesoporous carbon used (g)
<b>C<sub>0</sub></b>	Initial dye concentrations (mg/ L)
<b>C<sub>e</sub></b>	The equilibrium dye concentrations (mg/ L)
<b>Q<sub>eq</sub></b>	The amount adsorbed dye per unit weight of adsorbents at equilibrium (mg/g)
<b>Q<sub>max</sub></b>	The maximum amount of dye adsorbed per unit weight of adsorbents (mg/g)
<b>C<sub>eq</sub></b>	The equilibrium concentration of the adsorbate (mg/L)

## CHAPTER ONE

### GENERAL INTRODUCTION

#### 1.0 Introduction

This Dissertation consists of four chapters. Chapter one includes the general introduction of the problem and some few literature reviews that are closely related to this study. This chapter focuses on the background information of the study, the problem statement and justification, objectives, and research questions.

Chapter two is based on the first paper titled “*Synthesis and Characterization of Mesoporous Carbons from Plastic Bags using  $\alpha$ -MnO<sub>2</sub> Template.*” This chapter concentrates on synthetic approach with optimizing necessary conditions and determining physical-chemical properties of mesoporous carbon for water purification-Methylene Blue removal in aqueous solution by adsorption.

Chapter three presents the second paper title “*Removal of Methylene Blue using Mesoporous Carbon Prepared from Disposable Plastic Bags.*” This chapter focused on the application side of mesoporous carbon synthesized in chapter two. In chapter four covers general discussion, conclusion and recommendation.

#### 1.1 Background Information

In Tanzania, most people use plastic bags to carry different stuff including food such as chips. These bags are normally dumped after serving their purpose. Plastic shopping bags rapidly became popular among retailers and consumers worldwide in the last decade or so due to their function and strength in carrying various stuffs at low cost (UNEP, 2004), even freely provided to please customers. This makes them the best choice for packing and carrying materials for both large and small business entities. Plastic Disclosure Project (PDP) showed that about 33% of plastics are single use and approximately 85% of total global plastic used is not recycled (PDP, 2014).

Due to the above-mentioned challenges, recycling of disposable plastic bags has recently attracted considerable interest. Plastic bags have been used in small scale to make valuable materials with novel applications, for instance, in synthesis of carbon nanotubes (CNTs), (Altalhi *et al.*, 2013), making power poles and traditionally in making carpets and other decorative products.

The current recycling approaches are not enough to reduce or eliminate the huge amount of disposable plastic bags produced everyday to the environment, the development of more and new techniques for recycling plastics bags is therefore of great importance in order to save the environment. The proposed study therefore seeks to synthesize mesoporous carbon (MC) from non-biodegradable plastic bags for water purification. This provides a new technique of recycling plastics bags.

## **1.2 Research Problem**

Less has been done in Tanzania particularly in urban and rural areas to reduce the production of plastic bags, and to promote their reuse and recycle. To the best of my knowledge, no attempts have been made to synthesize mesoporous carbon using plastic bags as carbon precursor.

## **1.3 Research Justification**

The need to reduce the widespread of single used plastic bags to the environment is vital, as little has been done in Tanzania to reduce, reuse and recycle disposable plastic bags. Plastic bags are non-biodegradable, thus can stay for number of years while causing adverse effects to both plants and animals (Knight, 2012).

## **1.4 Objectives**

### **1.4.1 Main Objective**

The main objective of this study was to synthesize mesoporous carbon materials from non-biodegradable plastic bags for the removal of Methylene Blue from water.

### **1.4.2 Specific Objectives**

The specific research objectives were:

- i. To synthesize and characterize mesoporous carbon material from plastic bags.
- ii. To optimize the porosity and surface area of the mesoporous carbon.
- iii. To examine the performance of mesoporous carbon for the removal of Methylene Blue.



## **1.5 Research Questions**

The research questions were:-

- i. How can mesoporous carbon be synthesized from plastic bags?
- ii. How can the porosity and surface area of mesoporous carbon be optimized?
- iii. What performance does mesoporous carbon has to remove Methylene Blue by adsorption?

## CHAPTER TWO

### SYNTHESIS AND CHARACTERIZATION OF MESOPOROUS CARBONS FROM PLASTIC BAGS USING $\alpha$ -MnO<sub>2</sub> TEMPLATE

#### Abstract

Synthesis of mesoporous carbon using plastic bags as carbon precursor by hard template technique and its characterizations had been thorough achieved. The Manganese (IV) oxide ( $\alpha$ -MnO<sub>2</sub>) acting as a template was prepared by reflux method in the laboratory.  $\alpha$ -MnO<sub>2</sub> template–polymer composite was then pyrolyzed in a tubular furnace under a nitrogen flow and optimized temperature between 400°C and 600°C and time (1hour) for each plastic scraps to  $\alpha$ -MnO<sub>2</sub> mass ratios (1:1, 1:2 and 1:3). The physical properties of carbon sample made of plastic scraps to  $\alpha$ -MnO<sub>2</sub> mass ratio (1:1) at a temperature of 600°C was carbon black and characterized. Results from powder X-ray diffraction (XRD) showed that a sample made was amorphous carbon materials. The Brunauer, Emmett, and Teller (BET) identified the average pore diameter of 14.2 nm and calculated specific surface area of 15.18 m<sup>2</sup> g<sup>-1</sup>. The N<sub>2</sub> adsorption-desorption isotherm studies at 77K showed a type IV isotherm provided evidence that mesoporous carbon was successfully developed. The BJH (Barret–Joyner–Halenda) plot showed the mesopore size distributions of the carbon material to be within a range between 8.19 nm - 14 nm expressing mesoporous carbon characteristic.

**Keywords:** Plastic bags, Mesoporous carbon, Characterization

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#### 2.0 Introduction

Mesoporous carbon materials were synthesized from disposable plastic bags used as carbon precursor through hard template method with alpha manganese (IV) oxide ( $\alpha$ -MnO<sub>2</sub>) adopted as a template.

Mesoporous carbon materials have pore diameter of 2 to 50 nm (Dustin *et al.*, 2015). This pore size is good for a number of applications including water purification, gas separation, catalyst supports, and electrodes for batteries and fuel cells (Rodriguez-Reinoso, 1997).

Different methods have been achieved to synthesize mesoporous carbon materials; these include the catalytic activation of carbon precursors in the presence of metals and organometallic compounds (Tamai *et al.*, 1996), carbonization of polymer blends with thermally unstable components (Patel *et al.*, 2002; Ozaki *et al.*, 1997), and carbonization of polymer aerogels such as resorcinol–formaldehyde resins (Al-Muhtaseb and Ritter, 2003; Tamon *et al.*, 1998) among others. However, most of the mesoporous carbons synthesized using the above-mentioned methods have broad pore size distributions (Lee *et al.*, 2004). In order to synthesize mesoporous carbons with uniform and interconnected pores for practical applications; template synthesis has been extensively applied in recent years (Lee *et al.*, 2004). It has been reported that manganese oxide octahedral molecular sieves- OMS-2 can be used as a template due to its high specific surface area, high porosity, and average oxidation state (Sriskandakumar *et al.*, 2009). Thus,  $\alpha$ -MnO<sub>2</sub> was used as a template to make mesoporous carbon using plastic bags as carbon precursor.

## **2.1 Experiment**

### **2.1.1 Materials and Methods**

Plastic bags as carbon precursor, potassium permanganate (KMnO<sub>4</sub>), manganese sulphate monohydrate (MnSO<sub>4</sub>.H<sub>2</sub>O) and conc. nitric acid (HNO<sub>3</sub>) were used to make manganese (IV) oxide (MnO<sub>2</sub>) as a template, oxalic acid and distilled water used in etching- a process to remove  $\alpha$ -MnO<sub>2</sub> from mesoporous carbon and washing respectively to obtain mesoporous carbon.

Melting of plastic scraps together with ( $\alpha$ -MnO<sub>2</sub>) was made in a box furnace (Lindberg/Blue M, Model: BF51731) at 250°C and carbonization process made in tubular furnace (Carbolite, Model: MC16-GB-C-1.04) at a temperature between 400°C and 600°C under inert N<sub>2</sub> (99.99% purity) for varied plastic bag scraps to  $\alpha$ -MnO<sub>2</sub> mass ratios (1:1, 1:2 and 1:3).

### **2.1.2 Synthesis**

#### **(i) Synthesis of Mesoporous $\alpha$ -MnO<sub>2</sub> Templates**

Regular octahedral molecular sieves (OMS-2), having the cryptomelane structure, were prepared followed the literature by refluxing mixtures of KMnO<sub>4</sub>, MnSO<sub>4</sub>, concentrated HNO<sub>3</sub> and in aqueous solution for 24 h (Sriskandakumar *et al.*, 2009).

OMS-2 was adopted in this study as it has very good oxidation catalyst for organic species i.e. Polymers in plastic bags due to high specific surface area, high porosity, and average oxidation state (Sriskandakumar *et al.*, 2009).

## (ii) Mesoporous Carbon Synthesis using $\alpha$ -MnO<sub>2</sub> Templates

The plastic bags were made in scraps using a scissor, measured using digital balance with varied mass ratio of plastic bag scraps to Manganese oxide (1:1, 1:2, and 1:3) and then melted together with  $\alpha$ -MnO<sub>2</sub> forming a uniform powdered mixture of  $\alpha$ -MnO<sub>2</sub> template–polymer composite after cooling. Then, the mixture from plastic bag scraps to  $\alpha$ -MnO<sub>2</sub> mass ratio (1:1, 1:2, and 1:3) i.e. template–polymer composite was then pyrolyzed in a tubular furnace (Carbolite, Model: MC16-GB-C-1.04) under a nitrogen flow at a temperature range of 400 and 600°C for each mass ratio at a heating rate of 10 °C min<sup>-1</sup> for 1 h to carbonize the polymer. Finally, finished by  $\alpha$ -MnO<sub>2</sub> removal from the template–polymer composite using oxalic acid solution at room temperature under filtration with distilled water to obtain mesoporous carbon which dried at 100°C and characterized.

### 2.1.3 Characterization

The properties of the synthesized mesoporous carbon were investigated by using powder X-ray diffraction (XRD), Brunauer, Emmett, and Teller (BET) was used to determine surface area. The BJH (Barret–Joyner–Halenda) method was applied to analyze the mesopore size distributions using the adsorption branch.

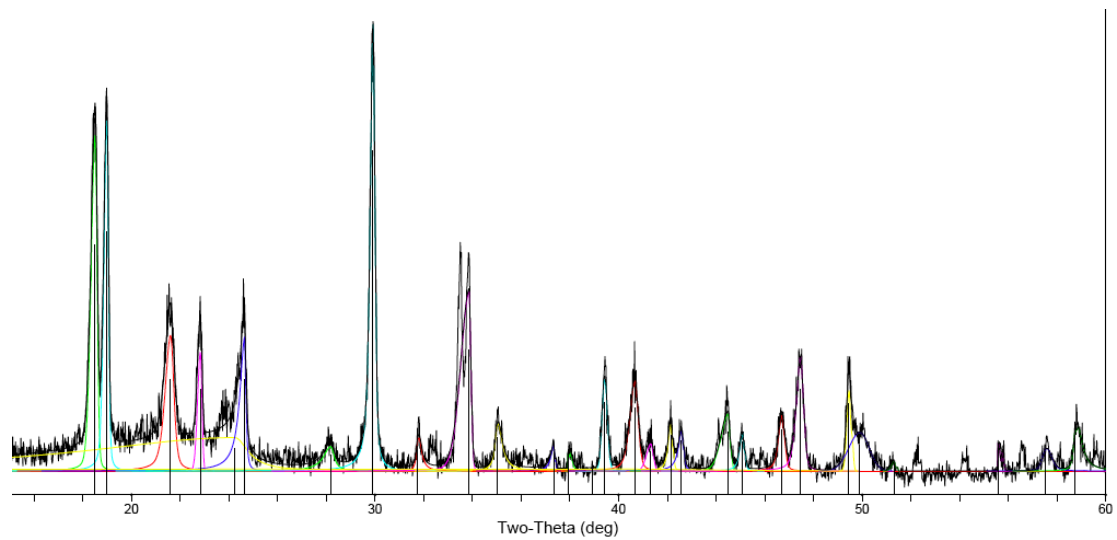
## 2.2 Results and discussion

XRD results showed that the crystalline nature of mesoporous carbon was amorphous according to Table 1 and Fig. 1.

**Table 1:** XRD summary report

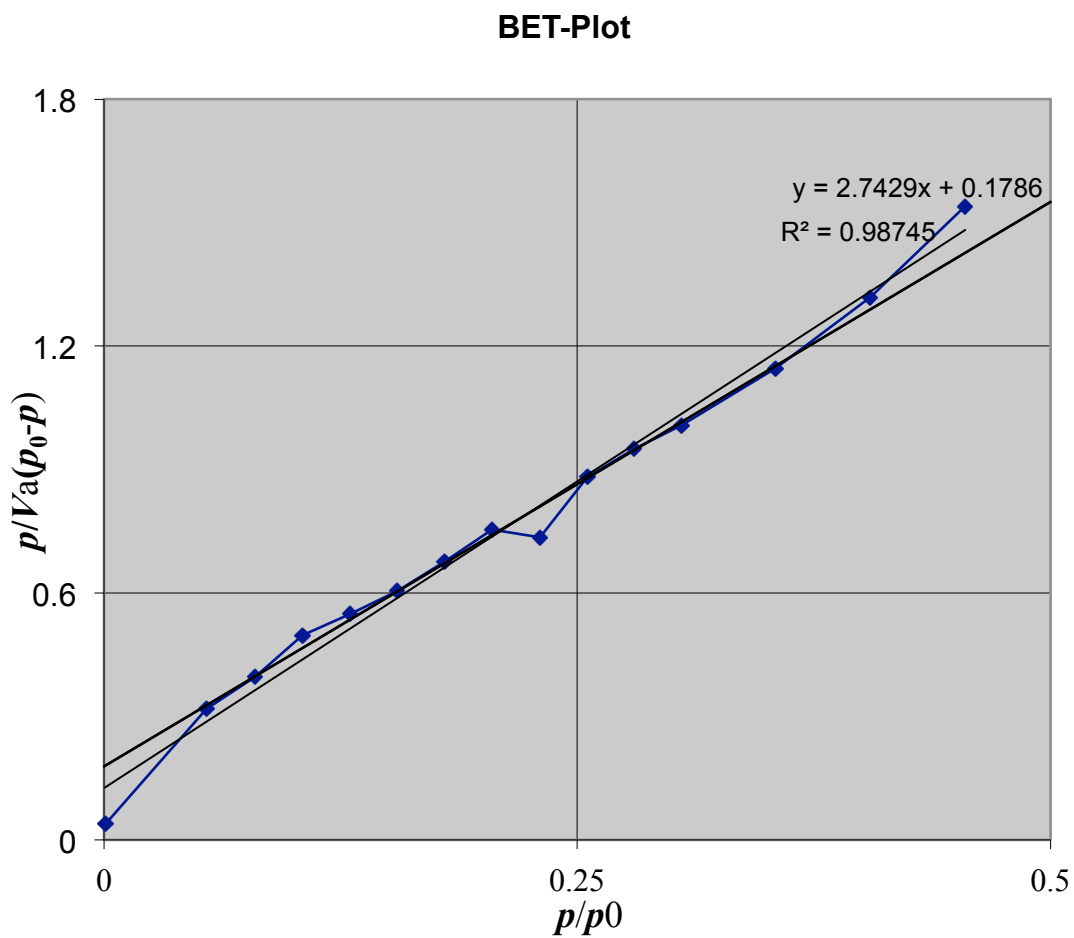
2-Theta (deg)	d (Å)	Height	Area (a1)	Area%
24.229 (0.899)	3.6705 (0.2682)	59 (10)	22 824 (6185)	100
38.926 (?)	2.3118 (?)	4 (?)	5183 (?)	22.7

Amorphous Peak, Total Area = 116 458 (6560), Crystallinity = 75.95% (17.31%), FWHM-Threshold = 5.0



**Figure 1:** XRD patterns of mesoporous carbon.

The results from Fig. 1 shows a peak at 24.229 degree which correspond to 59 (10) reflection as amorphous peak for mesoporous carbon and other crystalline peak for other impurities.



**Figure 2:** BET plot for mesoporous carbon.

BET plot for mesoporous carbon in Fig. 2 has been summarized on BET report in Table 2, whereby the values have been used to calculate the specific surface area of mesoporous carbon.

**Table 2:** BET Summary Report

Sample weight	9.82E-02	[g]	
Standard volume	9.097	[cm <sup>3</sup> ]	
Dead volume	14.571	[cm <sup>3</sup> ]	
Equilibrium time	0	[sec]	
Adsorptive	N2		
Apparatus temperature	0	[C]	
Adsorption temperature	77	[K]	
Adsorption cross section area	0.162	[nm <sup>2</sup> ]	
Starting point			2
End point			14
Slope			2.7429
Intercept			0.1786
Correlation coefficient			0.9961
V <sub>m</sub>			0.3423 [cm <sup>3</sup> (STP) g <sup>-1</sup> ]
a <sub>s,BET</sub>			1.4898 [m <sup>2</sup> g <sup>-1</sup> ]
C			16.361
Total pore volume ( <i>p/p</i> <sub>0</sub> =0.990)			0.0053 [cm <sup>3</sup> g <sup>-1</sup> ]
Average pore diameter			14.2 [nm]

BET results in Table 2 revealed that mesoporous carbon synthesized (i.e. plastic scraps to  $\alpha$ -MnO<sub>2</sub> mass ratio 1:1 at 600°C) showed a pore diameter of 14.2 nm.

The total and specific surface area of a mesoporous carbon was calculated using equation (1) and (2) respectively (Brunauer *et al.*, 1938) and specific information from Table 2.

$$\text{Total Surface Area} = \frac{V_m \cdot N_{av} \cdot A_{cs}}{\text{Weight of adsorbate gas}} \quad (1)$$

where, V<sub>m</sub> is molar gas volume for a monolayer adsorbed gas molecules in [cm<sup>3</sup>(STP) g<sup>-1</sup>], N<sub>av</sub> is Avogadro's number = 6.022 x 10<sup>23</sup> mol<sup>-1</sup>, A<sub>cs</sub> is for adsorption cross section of the adsorbing species.

$$\text{Specific surface area} = \frac{\text{Total surface area}}{\text{Mass of test solid sample in gram (m)}} \quad (2)$$

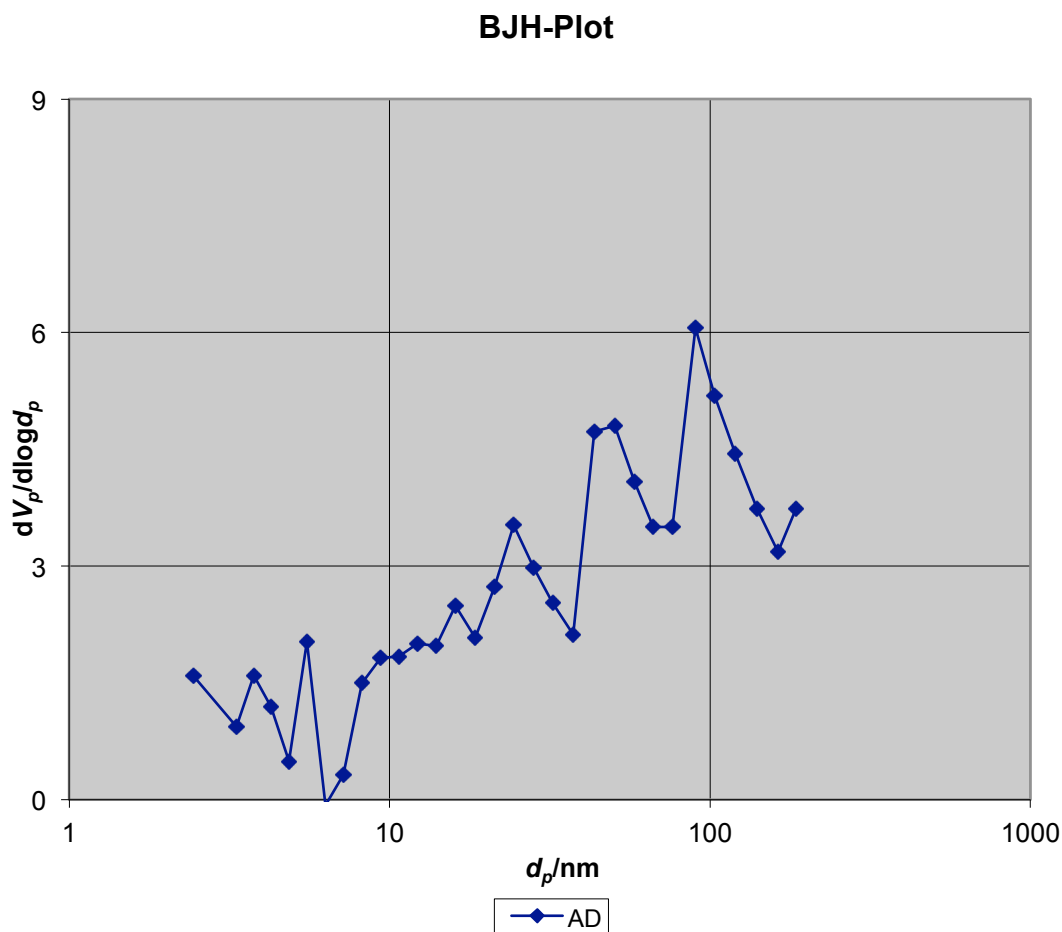
Thus, 
$$\text{Specific Surface Area} = \frac{V_m \cdot N_{av} \cdot A_{cs}}{m (g) \times 22400 (\text{cm}^3 \text{mol}^{-1})} \quad (3)$$

By using equation (1) and (2) to make equation (3) using data from Table 2, the specific surface area (SSA) of mesoporous carbon is given as;

$$SSA = \frac{0.3423 [\text{cm}^3(\text{STP}) \text{g}^{-1}] \times 6.022 \times 10^{23} \text{mol}^{-1} \times 16.2 \times 10^{-20} \text{m}^2}{9.82 \times 10^{-2} \text{g} \times 22400 \text{cm}^3 \text{mol}^{-1}}$$

$$= 15.18 \text{ m}^2 \text{g}^{-1}$$

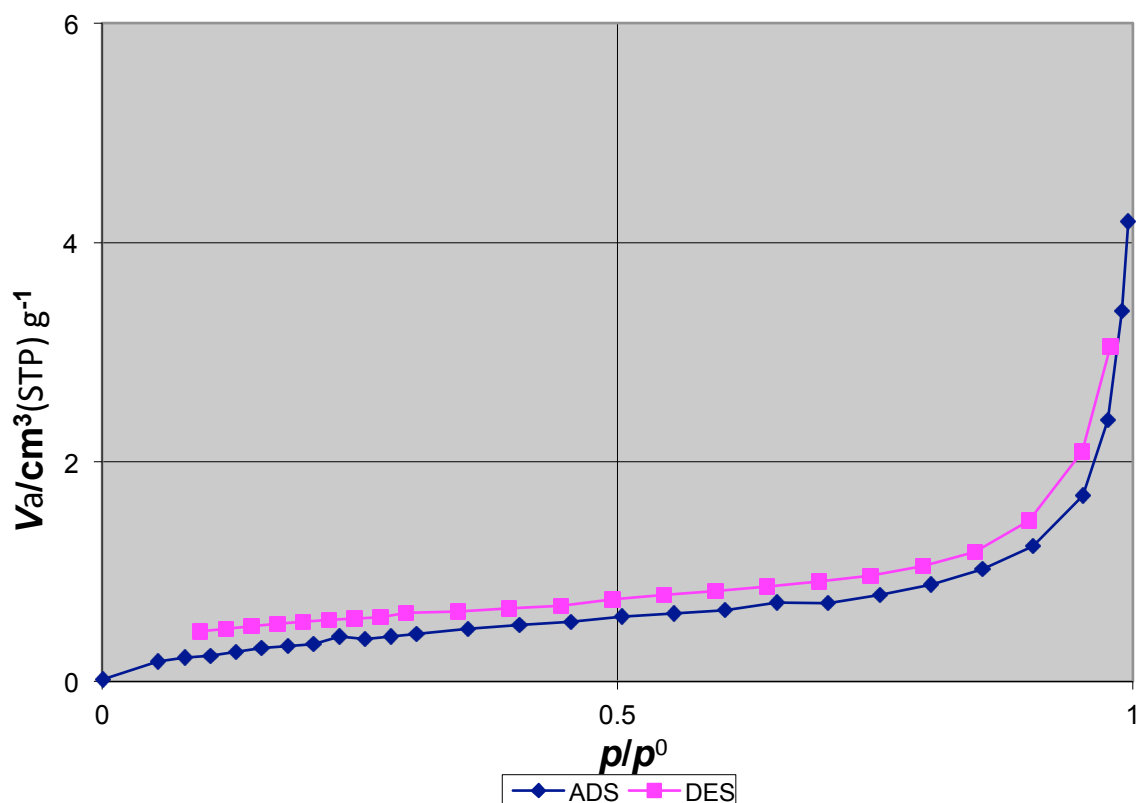
The specific surface area of  $15.18 \text{ m}^2 \text{g}^{-1}$  for mesoporous carbon material was obtained without any improvement of surface area after synthesis to save the purpose of this study. Though, could be improved by activation method.



**Figure 3:** BJH plot for pore size distribution of mesoporous carbon.

Fig. 3 showed the pore size distributed between 8.19 nm – 14 nm expressing mesoporosity of carbon material. Whereby the average pore diameter of mesoporous carbon according to BET results in Table 2 is 14.2 nm.

### Adsorption / desorption isotherm



**Figure 4:** N<sub>2</sub> adsorption-desorption isotherm of mesoporous carbon at 77K.

The isotherm of the adsorption of nitrogen on the mesoporous carbon sample at 77 K is given in Fig. 4 which showed a class IV isothermal type; the only valid for porous materials exhibiting a feature of mesoporous solid (Lowell *et al.*, 2004 ; Fagerlund, 1983).

### 2.3 Conclusion

In this work, mesoporous carbon was prepared from plastic bags used as carbon precursor together with  $\alpha\text{-MnO}_2$  adopted as a template. The structural order and textural properties of all the materials have also been studied by Powder X-ray diffraction (XRD) results identified the crystal structure of mesoporous carbon as amorphous structure. Brunauer, Emmett, and Teller (BET) identified the surface area. The BJH (Barret–Joyner–Halenda) plot showed that mesopore size distributions within a range of 8.19 nm to 14 nm. The isotherm studies with N<sub>2</sub> adsorption-desorption of a sample at 77K was type IV isotherm, expressed mesoporous carbon characteristic thus provided an assurance that synthesized carbon material from plastic bags precursor using a hard template  $\alpha\text{-MnO}_2$  under optimized temperature of 600°C was mesoporous carbon.



## CHAPTER THREE

### REMOVAL OF METHYLENE BLUE USING MESOPOROUS CARBON PREPARED FROM DISPOSABLE PLASTIC BAGS<sup>1</sup>

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#### **Abstract**

Adsorption of Methylene Blue dye from aqueous solution using mesoporous carbon synthesized from non-biodegradable plastic bags as carbon precursor was studied. Batch experimental results revealed that adsorption process was highly dependent on, initial dye concentration, contact time, temperature, pH and adsorbent dosage. The dye adsorption equilibrium was rapidly attained in the first 30 min of contact time. Removal of dye in acidic solutions was better than in basic solutions. The adsorption of dye decreased with increasing initial dye concentration. The mesoporous carbon material adsorbed 80% of the Methylene Blue dye in less than 35 min with test solutions of concentration 0.2 –1 mg/L, whereby maximum removal efficiency of mesoporous carbon observed at minimum concentration. Absorbance decreased for an increase in adsorbent mass, where as percentage color removal increased from 80 to 87% with an increase in adsorbent mass from 50 to 300 milligrams. The results showed that mesoporous carbon was effective to remove Methylene Blue dye from aqueous dye solutions and can be applied to deal with industrial effluents.

The experimental equilibrium data were analyzed by the Langmuir and Freundlich models, which revealed that Langmuir model was more suitable to describe the Methylene Blue adsorption than Freundlich model. The isotherm data fitted Langmuir model with maximum dye adsorption capacity of 1.644 mg/g at 80°C.

**Keywords:** Methylene Blue, Wastewater, Mesoporous carbon, Non-biodegradable plastic bags, Adsorption isotherms

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### 3.0 Introduction

In developing countries, textile wastewater is an important water pollution source, which often contains high levels of un-fixed dyes (about 20%) (Wang *et al.*, 2010). Textile wastewater has been reported to contain dyes and pigments from leather, paper, plastic, and other industries effluents (Öden and Özdemir, 2013; Álvarez-Torrellas *et al.*, 2015). Dyes are of great concern because of their extensive use, bio-recalcitrant properties, and toxic aromatic intermediates (Oh *et al.*, 1997). Many dyes and pigments have toxic as well as carcinogenic, mutagenic and teratogenic effects on aquatic life and also possibly on humans, specifically those containing benzidine group in their structure (Álvarez-Torrellas *et al.*, 2015). The discharge of industrial effluents with dyes and pigments into streams cause water pollution, as the color produced contains amounts of organic dyes in water, which are considered of high concern due to its possible harmful effects.

Research studies have identified various uses of industrial dye. Among other industrial dyes; Methylene Blue- a cationic dye, is used as a model compound for the adsorption of organic dyes from aqueous solution (Álvarez-Torrellas *et al.*, 2015). Also, Methylene Blue is used as dye for leather and cellulosic fibres, redox indicator and ISO test pollutant in semiconductor photo catalysis (Álvarez-Torrellas *et al.*, 2015) and used as a material for dyeing cotton, wood and silk (Rao *et al.*, 2013). Apart from the potential uses, Methylene Blue can have several harmful effects on aquatic ecosystems and it can be considered as potentially carcinogenic (Álvarez-Torrellas *et al.*, 2015).

Therefore, development of effective and economic techniques for dye removal is necessary (Wang *et al.*, 2010), also it is an important aspects of wastewater treatment before discharge as it is difficult to remove the dyes from the effluent, because dyes are not easily degradable and are generally not removed from wastewater by conventional wastewater treatment systems (Sarioglu and Atay, 2006).

Treatment technologies that have been recommended to meet color removal requirements are physico-chemical treatment operations, including adsorption-electro-chemical adsorption, oxidation, chemical precipitation, coagulation, ultra-filtration, and photo-oxidation (Öden and Özdemir, 2013; Kannan *et al.*, 2001; Bhattacharyya, 2005). Each with its merits and limitations in application (Öden and Özdemir, 2013).

Among the identified methods, adsorption is a widely used and has been shown to be an efficient, and economical alternative for the removal of dyes from aqueous solutions and in wastewaters (Madrakian *et al.*, 2012; Bhattacharyya *et al.*, 2005; Walker, 1998). Activated carbon i.e. granulated activated carbon (GAC) or powdered activated carbon (PAC) as adsorbent is commonly used for dye removal. However, it has certain shortcomings that include limited availability, low adsorption capacity, they are expensive and difficult to regenerate or disposal of it has several problems. (Jin-Gang Yu *et al.*, 2014; Sarioglu and Atay, 2006) . Recently, a great deal of attention has been focused on the application of nano-structured materials as adsorbents to remove toxic and harmful organic substances from wastewater (Aditya *et al.*, 2011; Mohmood *et al.*, 2013). Thus, the use of several low cost adsorbents has been studied by many researches using waste orange peel, banana bith, cotton waste, rice husk, betonite clay, Neem leaf powder, powdered activated sludge, perlite, bamboo dust, coconut shell and groundnut shell, rice husk, and straw, duck weed, and sewage sludge, as adsorbents for removal of various dyes from wastewaters (Sarioglu and Atay, 2006). The adsorption capacities (% adsorption) of different type of adsorbent (carbon samples) on Methylene Blue by comparison have been studied (Rao *et al.*, 2013) and summarized in Table 3.

**Table 3:** Comparison of adsorption capacities (% adsorption) of different adsorbents carbon samples on Methylene Blue (Rao *et al.*, 2013).

Types of adsorbent	% Adsorption
Activated carbon (coconut shell)	75
Activated carbon (fruit peel)	73
Activated Carbon (palm kernel shell)	71
Saw dust	70
Pistachio shell	44
Zeolite material	40

The intention of this study was to adopt adsorption method in order to investigate the effects of initial dye concentration, contact time, temperature, pH and adsorbent dosage on the sorption capacity by using Methylene Blue dye on mesoporous carbon synthesized from waste non-biodegradable plastic bags. Furthermore, the isotherms and kinetics data were evaluated.

### 3.1 Materials and Methods

Methylene Blue (MB, M61320-7E; chemical formula,  $C_{16}H_{18}ClN_3S \cdot 3H_2O$  from UNI-CHEM, Chemical Reagents) was used as the adsorbate in without further purification while mesoporous carbon was used as adsorbent in this study. The distilled water was used to make a stock solution of Methylene Blue. The concentration of dye solution remaining (residual) was determined using calibration curve in Fig. 6 obtained from the corresponding maximum wavelength ( $A_{max} = 600 \text{ nm}$ ) using UV-Visible Spectrophotometer.

The amount of dye adsorbed at equilibrium onto mesoporous carbon,  $q_e$  (mg/g), was calculated by the following mass balance relationship:

$$q_e = V(C_o - C_e)/M \quad (1)$$

Where  $C_o$  and  $C_e$  are the initial and the equilibrium dye concentrations (mg/L),

$V$  is the volume of solution (L) and  $M$  is the amount of mesoporous carbon used (g). The percentage dye removal (%) was calculated using the following equation;

$$\text{Dye Removal (R\%)} = (C_o - C_e)/C_o \times 100 \quad (2)$$

The effect of contact time was investigated using 50 mg (0.05g) of mesoporous carbon synthesized at 400°C and 600°C for each sample mixture of mesoporous carbon to  $\alpha\text{-MnO}_2$  mass ratios (i.e. 1:1, 1:2, and 1:3). 1 mL (10 mg/L) from stock solution (1000 mg/L) was used to make 100 mL MB solution measured in 100 mL volumetric flask then mixed using magnetic stirrer in 250 mL conical flask placed on stirrer at room temperature. Sample mixtures were collected from the flask at various time intervals (5, 10, 15, 20, 25, and 30 min), centrifuged and analyzed for residual MB (filtrate) concentration using UV-VIS spectrophotometer.

#### 3.1.1 Adsorbent (Mesoporous Carbon) Preparation

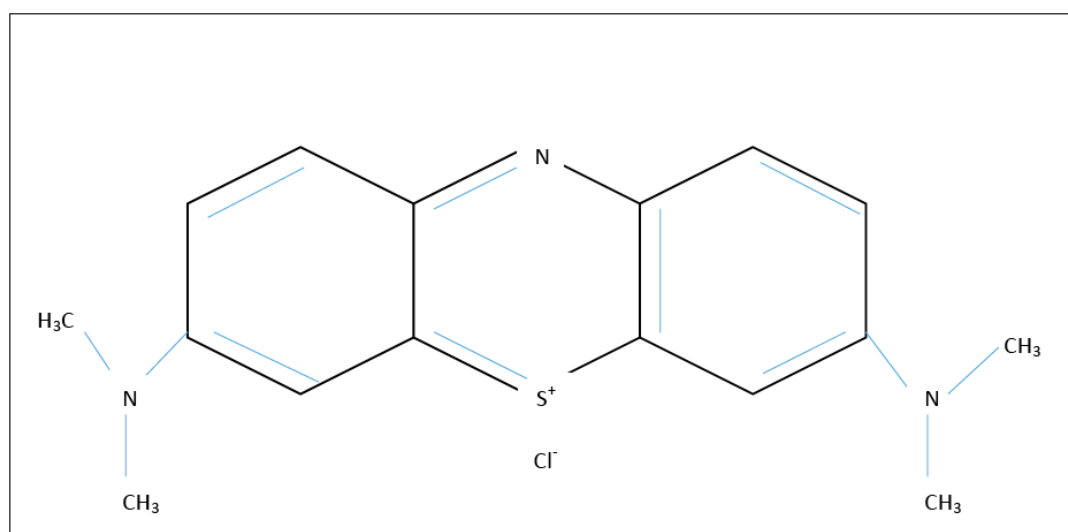
In this study, mesoporous carbon materials as adsorbents were synthesized from plastic bags as carbon precursor using hard template method with alpha-Manganese oxide ( $\alpha\text{-MnO}_2$ ). Manganese oxides were synthesized by reflux method using  $KMnO_4$ ,  $MnSO_4 \cdot H_2O$ , concentrated  $HNO_3$  and corresponding metal nitrates or oxides in aqueous solution for 24 h (Sriskandakumar *et al.*, 2009).

MnO<sub>2</sub> as one of the largest families of porous materials with various structures such as, tunnel structure octahedral molecular sieves (OMS), octahedral layered structure (OL-1), and amorphous manganese oxide (AMO) materials have been extensively studied (Sriskandakumar *et al.*, 2009).

Octahedral molecular sieves (OMS), Doped and undoped OMS-2, having the cryptomelane structure, were prepared by refluxing mixtures of KMnO<sub>4</sub>, MnSO<sub>4</sub>.H<sub>2</sub>O, concentrated HNO<sub>3</sub> and corresponding metal nitrates or oxides in aqueous solution for 24 h (Sriskandakumar *et al.*, 2009). Whereby, OMS-2 was adopted in this study as it has very good oxidation catalyst for organic species due to high specific surface area and high porosity (Sriskandakumar *et al.*, 2009).

### 3.1.2 Adsorbate (Methylene Blue) Preparation

The structural formula of Methylene Blue is shown in the Fig. 5. It has a maximum visible absorbance ( $A_{\max}$ ) at a wavelength ranging from 661-665 nm and is dark blue in color (Öden and Özdemir 2013) and (Sriskandakumar *et al.*, 2009). The Methylene Blue was chosen in this study because of its known strong adsorption onto solids (Shahryari *et al.*, 2010).



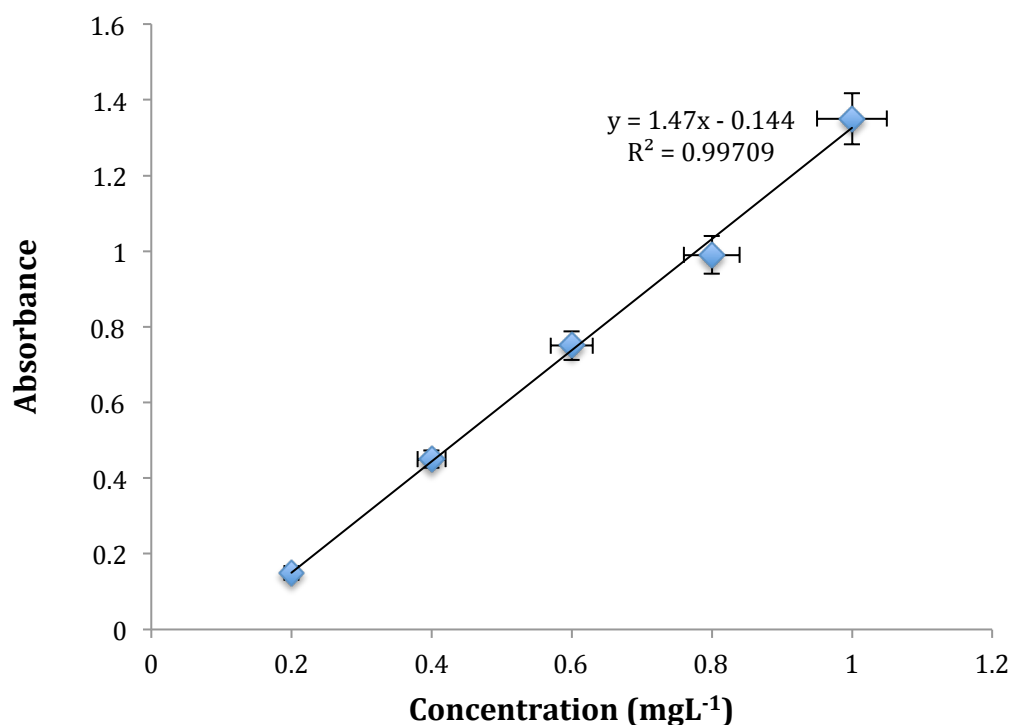
**Figure 5:** Methylene Blue chemical structure

A stock solution of Methylene Blue concentration 1000 mgL<sup>-1</sup> was prepared by diluting 1 g of Methylene Blue powder in a 1000 L of distilled water, whereby 1 mL (10 mgL<sup>-1</sup>) from stock solution was diluted with distilled water using 100 mL conical flask to make test solutions with a concentration of 0.2 to 1 mgL<sup>-1</sup>.

### 3.1.3 Calibration Curve

**Table 4:** Standard samples and absorbance for Methylene Blue dye.

Concentration (mgL <sup>-1</sup> )	Absorbance
0.2	0.15
0.4	0.45
0.6	0.75
0.8	0.99
1.0	1.35



**Figure 6:** The calibration curve of UV-Vis Spectrophotometer at ( $A_{\max} = 600 \text{ nm}$ ).

### 3.1.4 Adsorption Studies (Batch Experiments)

In adsorption studies, effect of contact time plays vital role irrespective of other experimental parameters effecting adsorption kinetics (Jirekar *et al.*, 2014). The sample of Methylene Blue was taken in separate flasks and adsorption studies were carried out at different contact time, same pH and constant initial concentration of dyes with fixed amount of adsorbents i.e. mesoporous carbon synthesized at 1:1, 1:2 and 1:3 plastic scraps to  $\alpha\text{-MnO}_2$  mass ratios in a temperature of 400 and 600°C for each mass ratio.

Standard technique (Vogel, 1970) was followed to determine the dye concentration using UV-VIS Spectrophotometer. The same technique was used to screen out the mesoporous carbon materials to identify the most efficient in adsorption of Methylene Blue.

**Table 5:** Screening of carbon materials i.e. mesoporous carbon (50 mg) at pH = 6.8, 29.8°C, with initial Methylene Blue concentration of 1 mgL<sup>-1</sup>.

<b>Synthesized carbon materials: Activation temperature and Mesoporous carbon to <math>\alpha</math>-MnO<sub>2</sub> mass ratio</b>	<b>Absorbance of solution after Filtration</b>
400°C 1:1	0.37
<b>600°C 1:1</b>	<b>0.143</b>
400°C 1:2	0.43
600°C 1:2	0.31
400°C 1:3	0.483
600°C 1:3	0.633
Plastic black 600°C	0.196

Mesoporous carbon synthesized from 600°C and 1:1 (mass of plastic bag scraps: mass of  $\alpha$ -MnO<sub>2</sub>) with lower absorbance of 0.143 implied that, more Methylene Blue dye has been adsorbed on mesoporous carbon (600°C 1:1) as compared to the other mesoporous carbon materials on the same concentration of Methylene Blue dye i.e. Table 5.

Adsorption experiments were carried out using mesoporous carbon with lower absorbance (i.e. 600°C 1:1 with 0.143 absorbance) at room temperature (29 ± 1 °C) in batch technique whereby a stock solution of Methylene Blue of concentration 1000 mg/L was used. The effect of initial concentration (0.8, 0.6, 0.4, and 0.2 mgL<sup>-1</sup>), the effect of contact time (30, 40, 50, 60, 70, 80, and 90 min) on sorption of Methylene Blue on mesoporous carbon materials, the effect of temperature (30, 40, 50, 60, 70, and 80°C), effect of pH in acidic (HCl) and alkaline (NaOH) medium and effect of adsorbent doze (mg) were studied.

### **3.1.5 Effect of Initial Concentration**

To study the effect of Methylene Blue concentration, 50 mg of adsorbent was added to 1.0 mgL<sup>-1</sup> from a stock solution of Methylene Blue with concentration of 1000 mg/L and was stirred for optimum time. Then, the procedure was repeated at pH 6.8 with 100 mL of solution with different initial concentrations 0.8, 0.6, 0.4, and 0.2 mgL<sup>-1</sup> with the agitation speed and room temperature was kept constant. The samples was filtered and analyzed for Methylene Blue concentration.

### **3.1.6 Effect of Contact Time on Methylene Blue Sorption.**

To study the effect of contact time on Methylene Blue sorption, 50 mg of mesoporous carbon material (600°C, 1:1) was taken to 1 mL of aqueous solution of initial Methylene Blue concentration 1000 mg/L stock solution to make 100 mg/L at known pH 6.99 and room temperature of (29±01 °C) and the steering was provided for 30 min. The experiment was repeated for different time intervals like 30, 40, 60, 70, 80, and 90 min at constant agitation speed. After each interval of time the sample was filtered and analyzed using UV-VIS spectrophotometer to determine optimum contact time.

### **3.1.7 Effect of Temperature**

Effect of temperature was another significant physico-chemical process parameter to be studied because temperature will change the adsorption capacity of the adsorbent and plays an important role in the sorption process (Aksu *et al.*, 2008) of the textile dyes and pigments. The sorption of Methylene Blue on mesoporous carbon materials was investigated in the range of 30–80°C.

### **3.1.8 Effect of pH**

The pH of the aqueous solution is an important controlling parameter in the sorption process of textile dyes, especially on the adsorption capacity. It influences not only the surface charge, and the degree of ionization of the functional groups of the adsorbent, but also the dye chemistry. (Crini *et al.*, 2007; Salisu *et al.*, 2015).

A mass of 50 mg of mesoporous carbon material (i.e.1:1 at 600°C) was added to an aqueous solution of Methylene Blue 1 mg/L in 100 mL with hydrochloric acid (0.5N) and sodium hydroxide (0.5N), respectively. The two solution, each allowed to undergo shaking for optimum time and temperature 29.8°C. Then, each sample was analyzed for the percentage absorption.



### 3.1.9 Effect of Adsorbent Dose

The effect of adsorbent dose on Methylene Blue dye removal was determined from varied amount of 50 mg - 300 mg of mesoporous carbon (600°C, 1:1) at of pH 6.8,  $C_o=1$  mg/L,  $V = 100$  mL at a temperature of 26.8°C and stirrer for 30 minute. Each test sample was centrifuge and the filtrate observed for absorbance using UV-VIS Spectrophotometer.

### 3.2 Adsorption Isotherms

Adsorption isotherms are used to illustrate the distribution of adsorbate between solid and solution phase at equilibrium. An optimized data of adsorption process design can be achieved with the help of isotherm studies (Malekbala *et al.*, 2014). Adsorption isotherm was basically applied to describe how solute interacts with adsorbents. The application of isotherm equations (3 and 4) can be compared and judge the correlation coefficients  $R^2$  (Rao *et al.*, 2013). These isotherms are useful in predicting removal efficiency or estimating the total amount of adsorbent needed to adsorb a required amount of Adsorbate and the from solution (Chung *et al.*, 2015).

$$\text{Langmuir Isotherm: } (C_{eq}/q_{eq}) = (1/bq_{max}) + (1/q_{max})C_{eq} \quad (3)$$

$$\text{Freundlich Isotherm: } \log q_{eq} = \log K_f + n \log C_{eq} \quad (4)$$

Where,  $q_{eq}$  is the amount adsorbed per unit weight of adsorbents at equilibrium.  $C_{eq}$  is the equilibrium concentration of the Adsorbate (mg/L).  $q_{max}$  is equal to  $q_{eq}$  for a complete mono layer. While  $b$  is the Langmuir constant and  $K_f$  is the Freundlich constant related to the adsorption capacity.

Adsorption isotherms of Methylene Blue were determined at various temperatures 30, 40, 50, 60, 70, and 80°C to decide whether the adsorption process is exothermic or endothermic.

In all cases, the adsorptive capacity ( $q_e$ ) was calculated according to equation (1) and results presented in Table 7.

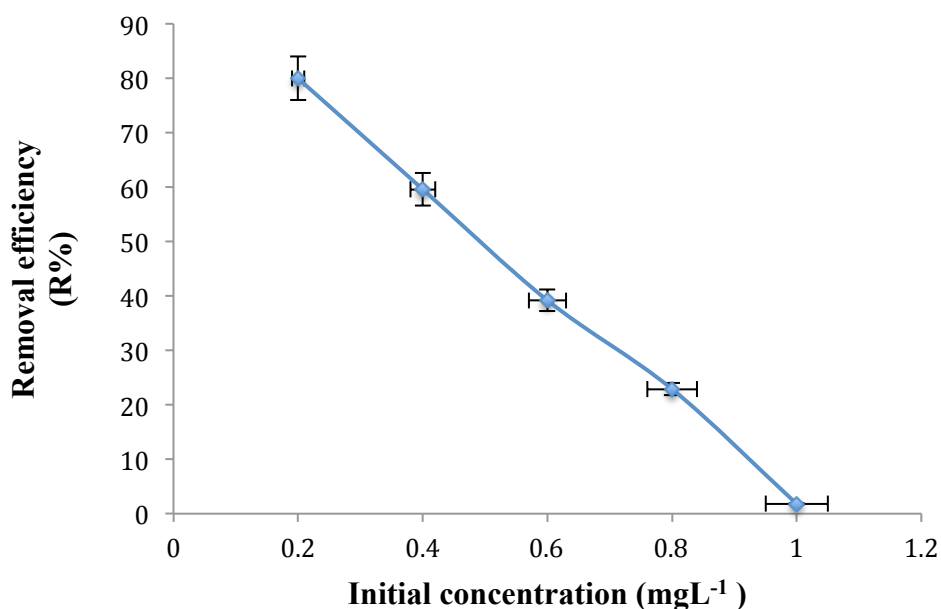
### 3.3 Results and Discussion

#### 3.3.1 Effect of Initial Concentration

The effect of initial concentration is shown in Fig.7 whereby the study has shown that the percentage of dye removal by mesoporous carbon (50 mg) was 80% high at initial concentration  $0.2 \text{ mgL}^{-1}$  at a time of 30 min. The lowest dye removal 1.8% was observed for concentration of  $1 \text{ mgL}^{-1}$ . This indicates that an increase in the dye concentration had caused the decrease in the percentage of dye removal, even though the amount of dye being adsorbed is increased.

**Table 6:** Effect of initial dye concentration: 50 mg of mesoporous carbon ( $600^\circ\text{C}$ , 1:1), pH 6.8,  $C_o = 1 \text{ mgL}^{-1}$ ,  $V = 100 \text{ mL}$  and  $26.8^\circ\text{C}$ .

Methylene Blue concentration ( $\text{mgL}^{-1}$ )	Absorbance	$C_e$ ( $\text{mgL}^{-1}$ )	% Dye Removal: $(R\%) = (C_o - C_e)/C_o \times 100$
0.2	0.15	0.2	80
0.4	0.45	0.404	59.6
0.6	0.75	0.608	39.2
0.8	0.99	0.771	22.9
1.0	1.3	0.982	1.8

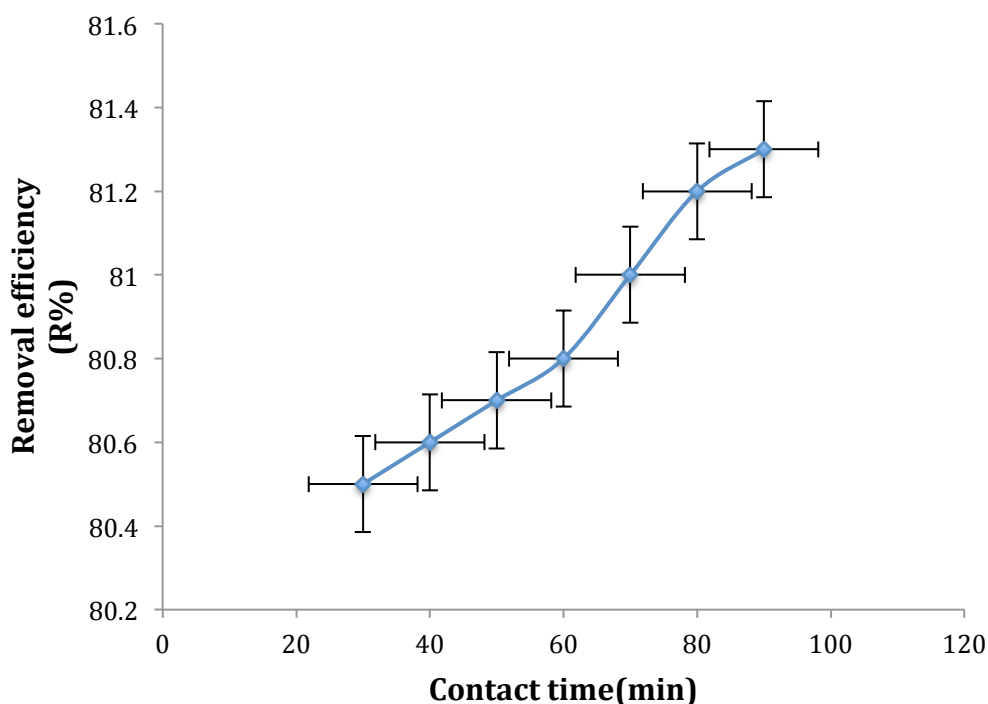


**Figure 7:** Effect of concentration of Methylene Blue onto mesoporous carbon.

At lower concentrations almost all the adsorbate present in the solution could interact with the binding sites and thus % adsorption higher than those higher at initial concentrations. At higher concentrations and lower adsorption sites yield is due to the saturation of adsorption of sites.

### 3.3.2 Effect of Contact Time

The study had shown that for the mesoporous carbon the percentage of dye removal was high. The adsorption data for the uptake of Methylene Blue versus contact time at initial concentration 1mg/L was shown in Fig.8. It indicated that the adsorption of Methylene Blue increases with increase in contact time. The amount of dye uptake was found to occur in the first rapid phase (35 min) and there after the sorption rate was found to be constant. This is due to an increased number of vacant sites available at the initial stage and after a lapse of time, the remaining vacant surface sites are difficult to be occupied due to repulsive forces between the solute molecules on the solid and bulk phases.



**Figure 8:** Effect of contact time of mesoporous carbon (600°C and 1:1).

Effect of contact time on % adsorption of Methylene Blue on to mesoporous carbon was studied at a time of 30 min using 50 mg of mesoporous carbon 1 mL of 1000 mg/L to form 100 mL solution of individual Methylene Blue solution concentration at pH 6.8, temperature 30°C.

The data obtained from the adsorption of Methylene Blue on to mesoporous carbon, showed that a constant time of 30 min was sufficient to achieve equilibrium and adsorption did not change significantly with further increase of time.

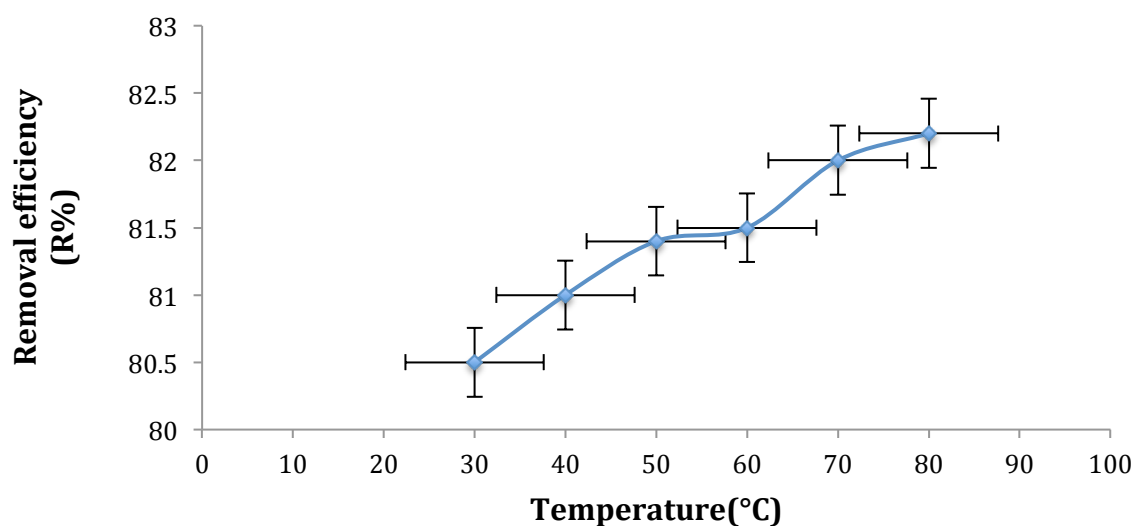
### 3.3.3 Effect of Temperature

Effect of temperature on the adsorption of Methylene Blue at 0.1 g in 1000 mL adsorbent concentration, 35 min of contact time, pH 6.8 and initial dye concentration of  $1 \text{ mgL}^{-1}$  was shown in Fig. 9.

**Table 7:** Effect of temperature: 30 - 80°C, M= 50 mg (0.05 g) of mesoporous carbon

(600°C, 1:1), pH 6.8,  $C_0=1 \text{ mgL}^{-1}$  and  $V = 100 \text{ mL}$ .

Effect of Temp. (°C)	Absorbance	Ce(mg/L)	% Dye Removal (R%)	qe(mg/g)	Ce/qe
30	0.143	0.195	80.5	1.61	0.121
40	0.135	0.19	81	1.62	0.117
50	0.13	0.186	81.4	1.628	0.114
60	0.128	0.185	81.5	1.63	0.113
70	0.12	0.18	82	1.64	0.11
80	0.118	0.178	82.2	1.644	0.108



**Figure 9:** Effect of temperature on removal of Methylene Blue.

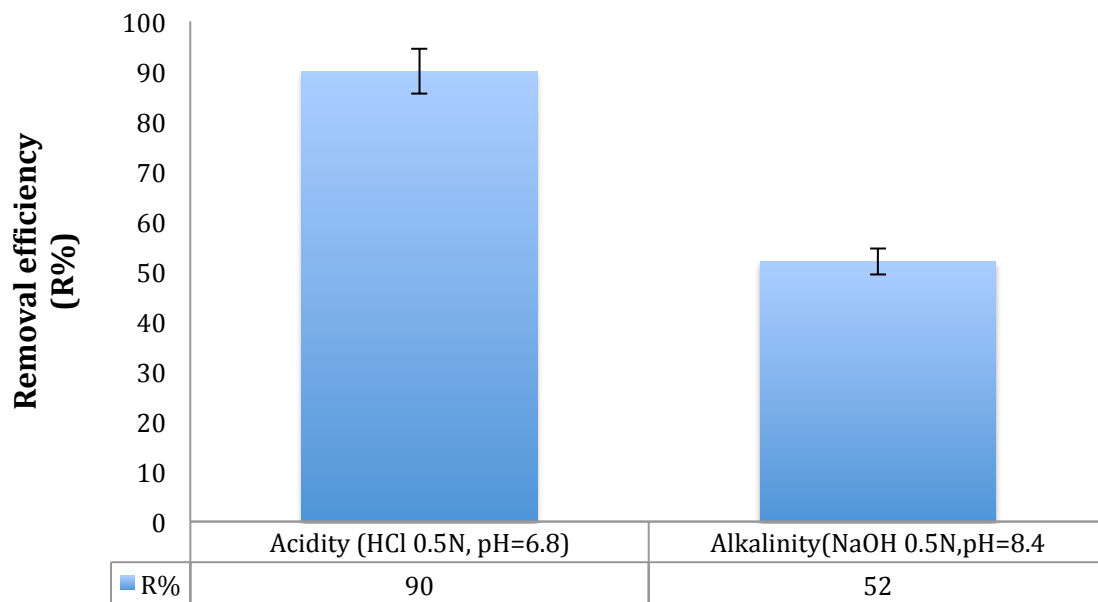
As the temperature increased from 30 to 50°C, the removal of dye percentage also increased with no further increased in removal of dye percentage when temperature increased to 60°C. Increased further temperature to 70°C increased the removal of dye percentage; no further increase in the removal of dye percentage with further increase in temperature from 70°C.

The adsorption capacity increases with temperature due to the increase of the rate of diffusion of the adsorbate molecules across the external boundary layer and the internal pores of the adsorbent particle, which decreases in case viscosity of the solution for highly concentrated suspensions. In addition, changing the temperature will change the equilibrium capacity of the adsorbent for a particular adsorbate (Alkan *et al.*, 2008; Abd El-Latif *et al.*, 2009). The maximum removal dye percentage at 80°C is found to be 82%. The increased amount of adsorption with increasing temperature signifies that the adsorption process is an endothermic process.

### 3.3.4 Effect of pH

The effect of pH on the percentage removal of Methylene Blue is shown in Fig.10 under various other fixed operating conditions. The initial pH of adsorption medium is one of the most important parameters affecting the adsorption process. It can be seen here that the percentage of dye removal increased from 87 to 90 % in acidic medium of pH value 6.8, but there was a decrease in dye removal from 87 to 52 % in alkaline medium of pH value 8.4.

Methylene Blue being an anionic dye, adsorbed onto the adsorbent surface effectually at lower pH values since the adsorbent surface attained at lower pH. As a result adsorption of Methylene Blue onto mesoporous carbon was better in acidic medium.



**Figure 10:** Effect of pH on % removal of Methylene Blue

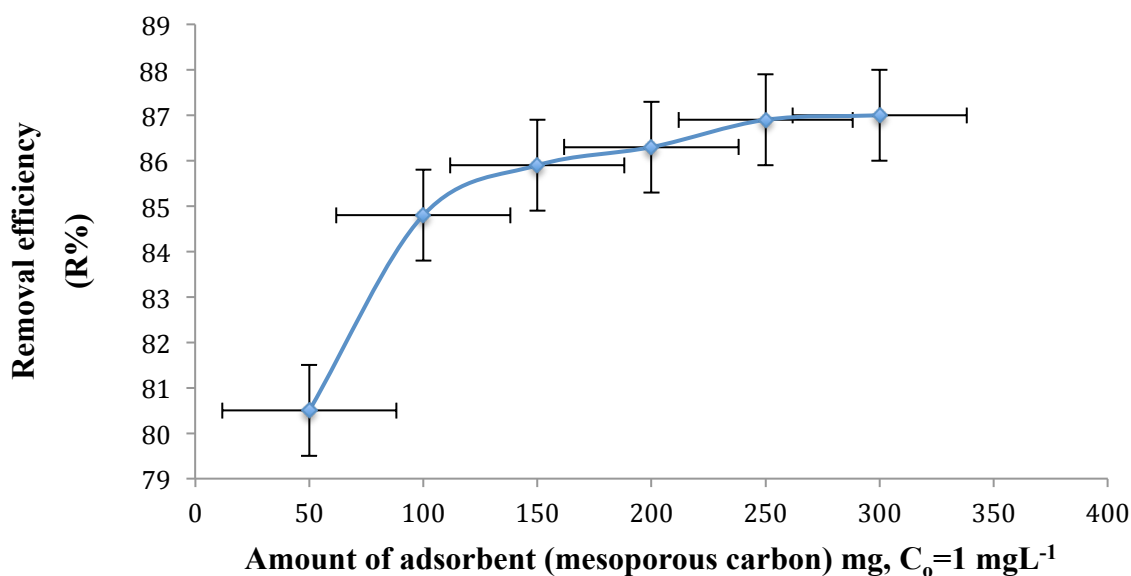
### 3.3.5 Effect of Adsorbent Dosage

**Table 8:** Effect of adsorbent dose: 50 mg - 300 mg of mesoporous carbon (600°C, 1:1) ,  
pH 6.8,  $C_0=1 \text{ mg}^{-1}$ ,  $V = 100 \text{ mL}$  and  $26.8^\circ\text{C}$ .

Weight of mesoporous carbon (mg)	Absorbance	$C_e$ (mg/L)	$q_e$ (mg/g)	% Dye Removal (R%)
50	0.143	0.195	1.61	80.5
100	0.08	0.152	1.696	84.8
150	0.063	0.141	1.718	85.9
200	0.057	0.137	1.726	86.3
250	0.048	0.131	1.738	86.9
300	0.047	0.13	1.74	87

From Fig.11 with results from Table 8, it was observed that, the amount of the dye adsorbed varied with varying adsorbent mass. Absorbance decreased for an increase in Adsorbent mass from 50 to 300 milligrams, where as percentage color removal increased from 80 to 87% with an increase in adsorbent mass. The decrease in Absorbance with increasing adsorbent mass is due to the concentration gradient between Methylene Blue concentration in the solution and the Methylene Blue concentration in the surface of the adsorbent.

The increase in the percentage of dye removal is due to increase in the surface area and availability of Adsorption site with increase in the Adsorbent dosage.



**Figure 11:** Effect of adsorbent amount on the removal of Methylene Blue by adsorption on mesoporous carbon.

Adsorption efficiency in Fig. 11 increased due to the increased number of adsorption sites. Therefore, removal efficiency reached in equilibrium with the amount of 250 mg of mesoporous carbon.

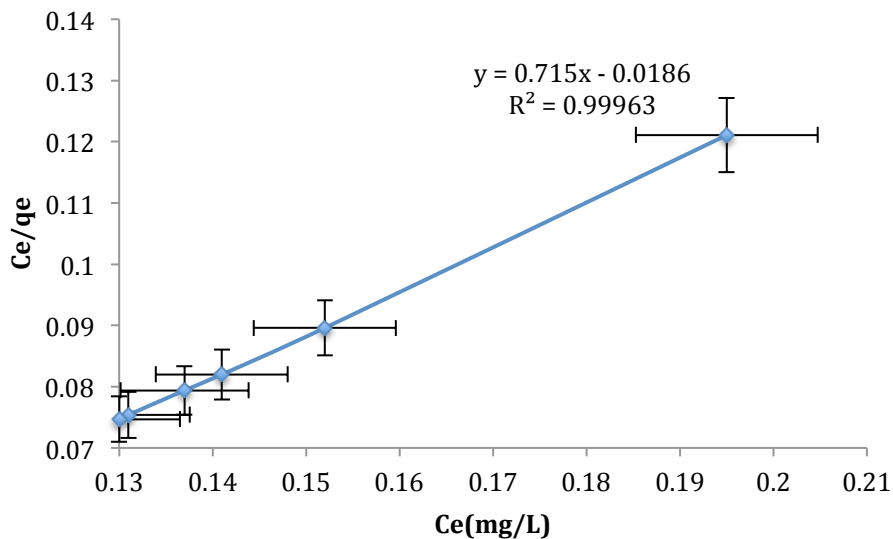
### 3.3.6 Adsorption Isotherms of Methylene Blue

The Langmuir, Freundlich, and the equilibrium adsorption isotherms of Methylene Blue adsorption onto synthetic mesoporous carbon with average pore diameter (14.2 nm) was conducted at 30°C and pH = 6.8, results are shown in Fig. 12 and Fig. 13, respectively. The parameters for each model were obtained and presented in Table 9.

### 3.3.7 Langmuir Isotherm

Isotherms assume monolayer Adsorption onto a surface containing finite number of Adsorption sites of uniform strategies of adsorption with no transmigration of Adsorbate in the plane of surface (Rao *et al.*, 2013). The linear form of Langmuir Isotherm equation is given following Equation (3). The Langmuir constants  $b = 38.46$  and  $q_{max} = 1.3986$  are obtained from the graph. A plot of  $C_{eq}/q_{eq}$  versus  $C_{eq}$  from Equation (3) and results of Table 9 for Methylene Blue to adsorption onto mesoporous carbon is presented in the Fig.12.

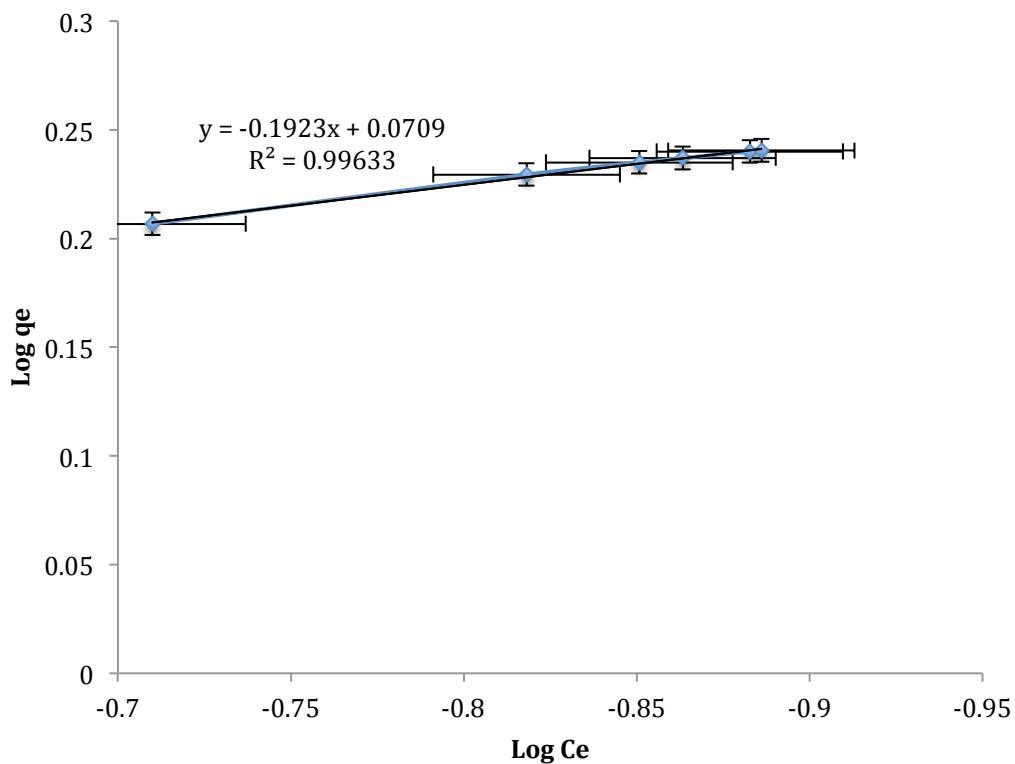
The  $R^2$  value of 0.9996 indicated that the adsorption data of Methylene Blue onto mesoporous carbon best fitted the Langmuir isotherm model.



**Figure 12:** Langmuir Adsorption isotherm at 50 mg /100 mL of adsorbate concentration.

### 3.3.8 Freundlich Isotherm

Unlike Langmuir Isotherm, Freundlich isotherm assumes heterogeneous surface energies, in which the energy term in Langmuir equation varies as a function of the surface coverage, the linearized form of Freundlich isotherm is according to equation (4) (Rao *et al.*, 2013). The slope  $n$  ranging between 0 and 1 is a measure of adsorption intensity or surface heterogeneity becoming more heterogeneous as its value coming closer to zero. From Fig. 13, we obtain the slope  $n = -0.1923$  and intercept  $K_f = 0.0709$  and  $R^2 = 0.9963$ .



**Figure 13:** Freundlich adsorption isotherm of adsorbate concentration at 50 mg /100 mL.



**Table 9:** Equilibrium constants for adsorption of Methylene Blue onto mesoporous carbon.

Isotherm	Constants
Langmuir: (Equation 3 and Figure 12)	$b = 38.46$
	$q_{\max} = 1.3986$
	$R^2 = 0.9996$
Freundlich: (Equation 4 and Figure 13)	$K_f = 0.0709$
	$n = -0.1923$
	$R^2 = 0.9963$

In order to assess different isotherms and their ability to correlate with experimental results, the coefficient of determination ( $R^2$ ) was employed to ascertain the fit of each isotherm with experimental data.

From Table 9, the coefficients of determination values were higher for Langmuir than for Freundlich. This indicates that the Langmuir isotherm is clearly the better fitting isotherm for the experimental data.

The essential feature of Langmuir isotherm can be expressed by separation factor ( $R_L$ ), a dimensionless constant, can be represented as:

$$R_L = 1 / (1 + bC_0) \quad (5)$$

where,  $C_0$  is the initial MB concentration (mg/L) (Malekbala *et al.*, 2014) and  $b$  the Langmuir isotherm constants  $b$  (L/mg), where  $R_L$  can be calculated from Table 9. In general, an isotherm can be irreversible ( $R_L = 0$ ), favourable ( $0 < R_L < 1$ ), linear ( $R_L = 1$ ), or unfavourable ( $R_L > 1$ ) (Mall *et al.*, 2006).

The value of ( $R_L$ ) was found to be 0.026. Thus, for Methylene Blue adsorption on mesoporous carbon (600°C, 1:1),  $R_L$  falls in the range of favourable adsorption process (i.e.  $0 < R_L < 1$ ).

### **3.4 Conclusion**

Adsorption of Methylene Blue over mesoporous carbon as an adsorbent has been studied. The adsorption behavior of Methylene Blue on mesoporous carbon from aqueous solution has been investigated. Adsorption isotherms fitted well with the Langmuir model. Using the Langmuir isotherm the adsorption capacity of Methylene Blue on mesoporous carbon was calculated to be 1.3986 mg/g. Whereby the finding shows that the mesoporous carbon material applied in adsorption performed better with Methylene Blue dye removal efficiency of 80% in less than 35 min higher than those identified carbon materials (adsorbents) (Rao *et al.*, 2013).

## CHAPTER FOUR

### GENERAL DISCUSSION, CONCLUSION AND RECOMMENDATION

#### 4.1 General Discussion

In this study, we have presented a recycling technique for the non-biodegradable plastic bags. The main objective of the study was to synthesize mesoporous carbon materials from non-biodegradable plastic bags for water purification-Methylene Blue removal in aqueous solution by adsorption.

Mesoporous carbon from plastic bags synthesized using a hard template technique with  $\alpha$ -MnO<sub>2</sub> followed optimization process of temperature between 400-600°C and plastic scraps to  $\alpha$ -MnO<sub>2</sub> mass ratios (1:1, 1:2 and 1:3), whereby, plastic scraps to  $\alpha$ -MnO<sub>2</sub> mass ratio of 1:1 at a temperature of 600°C provided carbon black desired for characterization.

XRD summary report showed that the carbon sample was amorphous in nature expressing amorphous peak for mesoporous carbon at 24.229 degree corresponding to 59 (10) reflection. BET results showed that synthesized mesoporous carbon from plastic bags using  $\alpha$ -MnO<sub>2</sub> as template has an average pore diameter of 14.2 nm which expressing a mesoporosity of carbon and specific surface area of 15.18 m<sup>2</sup> g<sup>-1</sup> which was useful to scope of the study.

Mesoporous carbon (1:1, 1:2 and 1:3 plastic scraps to  $\alpha$ -MnO<sub>2</sub> mass ratio) synthesized at a temperature between 400-600°C were all tested for efficiency in Methylene Blue removal in aqueous solution by adsorption. Following the screening procedures; it's only mesoporous carbon (1:1, 600°C) that expressed removal efficiency of 80% with test solutions of concentrations 0.2 to 1 mg/L as compared to 75% removal efficiency of Activated carbon (coconut shell) on Methylene Blue with test solutions of concentrations 0.02 to 0.1 g/L (Rao *et al.*, 2013).

## 4.2 Conclusion

We have seen that in order to have desired features of mesoporous carbon from plastic bags it is vital to undergo melting process of plastic bags together with  $\alpha$ -MnO<sub>2</sub> template before carbonization in a tubular furnace under N<sub>2</sub> at a temperature of 600°C. Another interesting observations from the study were; it's essential to use  $\alpha$ -MnO<sub>2</sub> as a template for a good results otherwise no mesoporous carbon can be made from plastic bags used as carbon precursor in 1:1 plastic scraps to  $\alpha$ -MnO<sub>2</sub> mass ratio. Also, it was observed that;  $\alpha$ -MnO<sub>2</sub> played a double role i.e. enhancing breaking down of polymer chain in plastic bags and acting as a template to form mesoporous carbon.

Using plastic bags waste as carbon precursor to prepare mesoporous carbon under  $\alpha$ -MnO<sub>2</sub> used as a template provided another recycling technique of plastic bags. The finding of this study can be available to share insight and build awareness in addressing solid waste management challenges i.e. plastic bags in particular.

The finding showed that the Methylene Blue dye removal efficiency of mesoporous carbon of 80% in 30 minutes provided another contribution to curb industrial wastewater containing Methylene Blue dye before discharged to the environment.

## 4.3 Recommendations

In Tanzania, scattering of solid wastes in the environment - plastic bags in particular remains a big challenge. Thus, from this work, it is recommended that:

- (i) More awareness campaigns should be conducted in the community to think alternative ways of utilizing the plastic bags and seek for reusable bags when they go for shopping.
- (ii) Business owners in the market should charge the customers for any plastic bags other than free offering. Also, reward the customers with reusable bags. This should be taken as a punishment but reducing spread of plastic bags to environment.
- (iii) This work is a call to industries in Tanzania to adopt industrial ecology (i.e. waste from one industry to be a raw material in another industry) for environmental conservation. Plastic bags as waste from domestic and industries have been used in this work to synthesize mesoporous carbon for industrial water purification.

Specifically, based on the findings of this study, it is proposed that future work should consider the following;

- (i) Plastic bags with multi-colors affect the formation of mesoporous carbon. Thus, not all plastic bags of HDPE can be recycled with technique in this study.
- (ii) The regulatory authorities should think of adopting one form of plastic bags which can easily be recycled by chemical means i.e. plastic bags of HDPE below 30-60  $\mu\text{m}$  with one colour. This alternative is valid in case they have failed to ban the importation of varieties of plastic bags in the market and wish to invest more in related research.
- (iii) Any researcher can take over this work to the next level if possible can synthesize and activate the mesoporous carbon and compare the efficient of both (i.e. mesoporous carbon from this study and activated mesoporous carbon) in adsorption of Methylene Blue in aqueous solution.
- (iv) The specific surface area of  $15.18 \text{ m}^2 \text{ g}^{-1}$  for mesoporous carbon as identified by BET can be improved with activation technique for further application.
- (v) The synthesized mesoporous carbon can be tested further for efficient in water purification with reference to fluoride removal, desalination and removal of other forms of dyes.
- (vi) Carry out cost –effectiveness process in synthesis of mesoporous carbon from plastic bags. Carbonization of the precursor required a temperature of not less  $600^\circ\text{C}$  to make mesoporous carbon, which is energy consuming process.
- (vii) The amount of template used i.e.  $\alpha\text{-MnO}_2$  and that of amount of plastic scraps should be in a mass ratio of 1:1 to have a black carbon (mesoporous carbon).
- (viii) Safe and environment friendly technique in Melting of plastic scraps before carbonization was tricky; plastic scraps must thorough be mixed and carbonized together with the template  $\alpha\text{-MnO}_2$ . Thinking about another procedure is recommended to simplify the process.
- (ix) Another template apart from  $\alpha\text{-MnO}_2$  can be used to synthesize mesoporous carbon from non-biodegradable plastic bags.

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