HAWASSA UNIVERSITY
COLLEGE OF NATURAL AND COMPUTATIONAL SCIENCES
SCHOOL OF POST GRAGUATE STUDIES
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MSC THESIS

REMOVAL OF METHYLENE BLUE DYES FROM AQUEOS SOLUTION BY USING ACTIVATED CARBON PREPARED FROM STEM PART OF

CROTON MACROSTACHYUS (BISANA)

BY:
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OCTOBER, 2024
HAWASSA, ETHIOPIA

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A MASTER THESIS SUBMITTED TO THE SCHOOL OF GRADUATE STUDIES OF HAWASSA UNIVERSITY, COLLEGE OF NATURAL AND COMPUTATIONAL SCIENCES, DEPARTMENT OF CHEMISTRY IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTERS IN CHEMISTRY

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School of Graduate Studies
Hawassa University

Approval Sheet-1

This is to certify that the thesis entitled **“**Removal of MB dyes from aqueous solution using AC of stem part of *Croton macrostachyus* as low cost adsorbent is submitted in partial fulfillment of the requirements for the degree of Master in Chemistry of the graduate program of the Department of Chemistry, Hawassa University, and is a record of original research carried out by Hussien Mama under my supervision, and no part of the thesis has been submitted for any other degree or diploma. The assistance and help received during the course of this investigation have been accordingly acknowledged. Therefore, I recommend that it is accepted as fulfilling the thesis requirements.

Submitted by:

Hussien Mama	____________	_________
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Approved by:

Prof.Sisay Tadesse(PhD	____________	________
Name of Major Advisor	Signature	Date

School of graduate studies

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Approval sheet-2

As member of the Examining Board of the final M.Sc. open defense, we certify that we have read and evaluated the thesis prepared by Hussien Mama Midasso: “ Removal of MB dyes Using AC Prepared from Stem of *Croton macrostachyus* that it be accepted as fulfilling the thesis requirement for the degree of Masters of Science in Chemistry

Final approval and acceptance of the thesis is contingent upon the submission of the final copy of the thesis to the Council of Graduate Studies (CGS) through the school of Graduate studies (SGC), Graduate Committee (SGC) of the candidate’s major department.

I hereby certify that I have read this prepared under our direction and recommend that it be accepted as fulfilling the thesis requirements

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DECLARATION

I hereby declare that this entitled Removal of MB dyes by using AC prepared from stem part of *Croton macrostachyus* has been carried out under the guidance and supervision of my advisor ;prof. Sisay Tadesse (PhD).This thesis is original and has not been submitted for the award of any degree or diploma to any other University or institutions for a degree in any other university and that all sources or materials used for the thesis have been accordingly acknowledged.

Name: Hussien Mama

Signature: __________

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LIST OF ABBREVIATIONS AND SYMBOLS

AC	Activated carbon
ASTM	American Society for Testing Material
FTIR	Fourier Transform Infrared spectrometry
SEM	Scanning Electron Microscope
UV-VIS	Ultra Violet Visible Spectrometry
Ce	Concentration at equilibrium
k_1	pseudo first order rate constant (min^{-1})
k_2	pseudo second order rate constant (g/mgmin)
K_L	Langmuir constant related to free energy of adsorption (L/mg)
MB	Methylene blue
qe	Adsorption capacity per unit mass of adsorbent at equilibrium (mg/g)
Qm	Maximum adsorption capacity (mg/g)
qt	amount of MB dye adsorbed at time t (mg/g)
WAO	wet air oxidation
AOP	advanced oxidation process

ABSTRACT

In this study activated carbon was prepared from Stem part of Croton macrostachyus and utilized as adsorbent to study its adsorption efficiency towards removal of Methylene blue dye from aqueous solution. The AC was prepared by acid treatment and calcinated in muffle furnace at different temperature ranging from 400 ^{0}C to 700 ^{0}C. The prepared AC was characterized by using FT-IR and scanning electron microscope (SEM).FT-IR results showed that different functional groups like hydroxyl, aldehydes, and carbon-carbon double bond functional groups were observed at different wave numbers. The amount of MB dyes adsorbed was determined using UV-Vis spectrometery at its λ max of 664 nm. It was found that the adsorption of MB on adsorbent obeys the Langmuir adsorption isotherms. The Values of the equilibrium parameter 'R_L' from the Langmuir isotherm was 0.040. These results confirmed that the adsorption process of MB dye on the prepared Activated carbon is favorable.The effects of some working parameters like pH, dye initial concentration, temperature and contact time on the adsorption of MB dyes were also studied. The optimum conditions were maximum removal efficiency occur was at dose of 0.1 gram, initial concentration of 10 ppm, contact time of 90 minutes, pH of 8 and temperature of 45 ^{0}C. The dye adsorption was found to decrease with increasing initial dye concentration and the percentage removal of the dye and the amount adsorbed on the surface of the adsorbent both showed significant increase with increase in temperature up to 45 ^{o}C. The effect of contact time on the percent removal of MB dye showed increasing trend as the reaction time increase. It was observed that the pseudo-second-order kinetic model fits better with good correlation coefficient and the equilibrium data fitted well with langmuir model.

Keywords: Adsorbent, Adsorbate, Adsorption, Freundlich adsorption isotherm, Langmuir Adsorption isotherm, Methylene blue, Removal efficiency

1. INTRODUCTION

1.1. Background of the study

Dye is important as it is used to add aesthetic value in many manufacturing industries. Appeals in colored materials have been responsible for the growth of dye usage. Thousands of different dyestuffs and pigments are utilized in chemical industries, such as textile, plastic, paper, printing, pharmaceutical and food industries [1]. Dyes are released as pollutant to environment from different dyeing industrial process. Nowadays, the treatment of wastewater containing dyes is of greatest importance because it has low biodegradability and it pollutes environment [2].

Dye molecules consists of two key components: the chromophores, which are largely responsible for producing the color, and the auxochromes, which not only supplement the chromophore but also render the molecule soluble in water and enhance its affinity (to attach) toward the fibers [3] there are numerous ways to classify dye such as in term of color, chemical structure and application methods. Dyes can be classified in accordance to their solubility in water as cationic (basic dyes), anionic (acid, direct, and reactive dyes), and non-ionic (vat and disperse dyes) [4].

Various techniques have been employed to remove dyes from wastewater, including biological treatment, adsorption, chemical oxidation, coagulation, ion exchange, reverse osmosis, membrane filtration and photochemical degradation or a combination of these wastewater treatments. Most of these methods are complex treatment, complicated, imposes high cost and inefficient in large volume of wastewater. The adsorption is the method considered to viable treatment as it gives finest removal capacity as it can remove various coloring materials in wastewater. No fragments in the effluent are left as adsorption removes the dye molecule as whole. The efficiency of adsorption is significantly affected by the type of adsorbent. Activated carbon is the most commonly used as adsorbent in dye removing processes. As recent researches focused in using adsorbent from agricultural by-products, activated carbon becomes the choice.

1.2. Statement of the Problem

Waste effluent from industry can cause harm to environment especially water pollution as it is usually directed to nearby river or water source. The wastewater from industry contains elevated level of dyes, heavy metals, grease, wax and suspended solids. This can also cause harm for aquatic organisms as they can raise the COD and BOD levels of water.

Various techniques have been employed to remove dyes from wastewater, including biological treatment, adsorption, chemical oxidation, coagulation, ion exchange, reverse osmosis, membrane filtration and photochemical degradation or a combination of these wastewater treatments.

Most of these methods are complex treatment, complicated, imposes high cost and inefficient in large volume of wastewater.The adsorption is the method considered to viable treatment as it gives finest removal capacity and it can remove various coloring materials in wastewater. Adsorption processes using AC have been widely proposed and used for the removal of dye from aqueous effluents, as it has highly porous texture and large capacity to adsorb pollutants.

However, commercially available AC are expensive and, in recent years, a great deal of effort has been put into the proposal and usage of low-cost adsorbents prepared from naturally occurring materials for the removal of dyes from wastewaters.

Therefore, this research will be as one way of an important substitution of AC by producing it from locally available biomass waste. The research uses stem part of *Croton macrostachyus* locally available material for production of AC and investigate its application for adsorption of MB dyes from aqueous solutions.

1.3. Objectives

1.3.1 General objective

The main objective of this study is to remove MB dye from aqueous solution using AC prepared from stem part of *Croton macrostachyus* as the adsorbent.

1.3 2 Specific Objective

- To activate stem part of *Croton macrostachyus* by chemical activation using H_3PO_4
- To characterize the prepared activated carbon with SEM and FT-IR
- To determine the optimum experimental parameters such as pH, adsorbent dose, initial MB dyes concentration and contact time
- To fit the experimental result with various adsorption kinetics models and investigate the adsorption mechanisms using appropriate kinetic models

1.4. Scope of Study

This research is focused on the adsorption of MB dyes from aqueous solution using AC. prepared from *Croton macrostachyus* and focus on optimization of different experimental parameters.

1.5. Significance of the study

Dyes removal has become a serious environmental concern due to the nature of toxic and carcino genic various cumulative dyes life form. One of the main concerns about colored effluent is not only its toxicity, but also its undesirable aesthetic impact receiving waters.

Since many dyes have an adverse effect on human beings, the removal of color from the effluent has appeared a great importance for ensuring a healthy environment. Hence, the major significance of this study includes:

- ✓ Removal of dyes using locally available low cost materials.
- ✓ The study can also serve to produce baseline information for further studies on related areas.
- ✓ Provide better information to remove toxic and carcinogenic various commulative life form.
- ✓ It also provide a better information on how to colors from effluents.

2. REVIEW OF RELATED LITERATURE

2.1. Dye

Dyes are colored compounds, which are widely used in textiles, printing, rubber, cosmetics, plastics, leather industries to color their products results in generating a large amount of colored wastewater. Mainly dyes are classified into anionic, cationic, and non-ionic dyes.

Among all the dyes using in industries, textile industries placed in the first position in using of dyes for coloration of fiber [5]. Dyes are chemical compounds which attach themselves to fabrics or surface shells to impart color. Depolarization of waste water from textile and manufacturing industries is a major challenge for environmental managers as dyes are water soluble and produce very bright colors in water with acidic properties.

It has been projected that textile and manufacturing industries are using more than 10,000 commercially available (worldwide) dyes and the consumption of dyes in textile industry is more than 1000 tones/year and about 10-15% of these dyes are discharged into waste streams as effluents during the dyeing processes [6].

2.2. Sources of dyes and its classification

Dyes are mainly derived from natural sources without any chemical treatment [7] such as plants, insects, animals and minerals. Dyes derived from plant sources are indigo and saffron, insects are cochineal beetles and lac scale insects, animal sources are derived from some species of mollusks or shellfish, and minerals are ferrous sulfate, ochre.

Industries such as textile, printing, paper, carpet, plastic, and leather use dyes to provide color to their products.These dyes are always left in industrial waste and consequently discharged into the water body [8-11]. Dyes release into waste water from various industrial outlets, such as paper, food coloring, cosmetics, leather, pharmaceutical,dyeing, printing, carpet industries etc.The textile manufacturing and dyeing industries utilize more quantities of a large number of dyes and release these dye pollutants into environment as waste water effluents.

These dyes are highly toxic and even carcinogenic to microbial populations and mammalian animals hence these are needed to remove from the water effluents before they are released into water bodies. Dyes are stable to light and not biologically degradable; they are resistant to aerobic digestion and signify one of the difficult groups to be removed from the industrial wastewater [12].

2.3. Dye Removal Technologies

A variety of treatment processes are used in typical dye house effluent treatment technologies. These are generally classified into three types: chemical, biological, and physical processes. These technologies can be employed separately or collectively to achieve the best balance of multiple criteria including economic feasibility and process efficiency.

2.3.1. Physical process treatments

Adsorption [13] and bio sorption [14] mechanisms describe the method of attraction of dyes onto the periphery of adsorbents in the form of particulates, granules or powders by physical bonding, strong chemical affinities, van der Waal's forces, or exchange of ions with surface functional sites on the adsorbent material surfaces via chemisorption or high energy chemical affinities.

To remove pollutants and colors from wastewater, flocculation and coagulation have long been utilized. This involves adding chemicals to dirty wastewater, often with agitation, and then permitting the pollutant-laden coagulants/flocculants to settle at the vessel bottom.

Additional tertiary treatment or recycling may be applied to the refined water overflow that is dischargeinto water streams.The dyeis adsorbed on the periphery/ surface of the flocculants/coagulant without undergoing any chemical decomposition,similar to adsorption.Two typically utilized materials are ferrous sulfate and alum [15].A high settling time for cleared water, the large amount of dye-laden flocculants/coagulant produced and requiring dumping, and the economics involved with the drying of highly wet slurry preceding landfill dumping are all disadvantages.

2.3.2 Chemical process treatments

Ultraviolet light degradation has little effect on dyes. Most chemical techniques for the treatment of dye-polluted streams seek to knock down the intricate dye particles into simpler and less hazardous chemicals such as CO_2 or H_2O through a sequence of oxidative reactions. For example, chlorine, wet air oxidation (wao), ozonation, and other advanced oxidation processes (aop).

Although wao[16] is found to be efficient in the treatment of dye effluents, catalysts have been suggested as a way to improve process effectiveness [17, 18].

Ozone is commonly employed in commercial aop's for the elimination of organics and color [19]. Ozonation catalysts are being investigated [20]. Other powerful oxidizing reagent chemicals viz.

Sodium hypochlorite, chlorine, and hydrogen peroxide are being utilized commercially in the oxidation of dye-polluted streams [21, 22].

These reagents break down dyes into simpler compounds. Nonetheless, there are evidences that the benefits of utilizing chlorinated reagents may be exceeded by the production of harmful byproducts such as chloroanilines [23].

2.3.3. Biological-based treatments

Traditional aerobic techniques viz.Activated sludge has proved successful in treating polluted streams, nonetheless, they are unsuccessful at removing colors.Dye compounds are frequently hydrophilic and have a low affinity for biomass, resulting in early application [24].

Dyes are frequently resistant to microbial breakdown due to their poisonous and stable molecular structures. Dye molecules are broken down into soluble organics in the absence of oxygen, then to CH_4 and H_2S by a sequence of microbial processes. Although reasonable results for reactive, azo, and diazo dye decolorization were documented [25], the procedure had no effect on hazardous aromatic amines in the treated stream [26]

2.4. Adsorption and adsorption technologies

Adsorption may be defined as the process of accumulation of any substance giving higher concentration molecular species on the surface of another substance.

Adsorption is a popular process for purification purposes at large scales.Various contaminants in solution and in gaseous emission streams may be removed by being attracted to the surfaces of several solid phase materials, referred to as adsorbents. Adsorbents have been made from a variety of materials for a variety of uses, including water treatment, dye separation, indicators, desiccants, and catalysis.

An effective adsorption system may be capable of removing all the pollutants, releasing a contaminant-free fluid. Due to its simplicity, ease of operation, simple design, and ease of scaling up, the adsorption process is considered a better alternative in the treatment of dye from industrial effluents. It also has a high capacity and a favorable rate, and it is insensitive to harmful Chemicals [27]. It can also help to resolves removal of organics such as dyes [28, and 29]

The diffusion of dye on the surface of adsorbents is either by physical phenomena or chemical means. The dye materials bind to the adsorbent periphery by hydrogen bonding or van der Waal's forces in physisorption mechanism [30].

2.4.1 Types of Adsorption

2.4.2 Physisorption

Physical adsorption is the result of intermolecular forces of attraction between molecules of the solid adsorbent and the substance adsorbed (adsorbate). It is a readily reversible phenomenon. In industrial adsorption operation, this reversibility is used for the recovery of adsorbent for reuse, for the recovery of adsorbed substance (adsorbate).

2.4.3 Chemisorption

Chemisorption are the result of chemical interaction between the solid adsorbent and the adsorbed substance.The adhesive force and heat liberated are much greater than those found in physical adsorption.The process frequently irreversible.

2.5 Equilibrium Adsorption Isotherms

This study was done with the optimum pH of MB dyes.In order to understand the adsorbate-adsorbent interaction,optimization of adsorbent and its adsorption capacity towards a particular adsorbate is necessary for the studying the adsorption isotherms.Adsorption capacity of AC stem of *Croton macrostachyus* towards MB dyes determined by plotting the amount of MB dyes adsorbed by the biomass (qe) against equilibrium concentration (Ce) in solution .The adsorption equilibrium data were fitted to Langmuir isotherm model .

The equilibrium sorption of the MB dyes were carried out by contacting 0.1g of adsorbent derived from *Croton macrostachyus* with 250 mL of 10 mg/L, 15 mg/L, 20 mg/L, 25m g/L ,and 30m g /L in 250 mL conical flask at neutral pH and room temperature The initial pH value of each solution was adjusted with 0.1M HCl and 0.1M NaOH using pH meter.After shaking the flasks ,5 mL of samples was withdrawn at 15 min intervals from the flask, and each time the dye solution was first separated by filtration. After filtration, the concentration of MB in the supernatant solution was analyzed using UV-Visible spectrometery at λmax 664nm.

2.5.1 Adsorption Equilibrium

Adsorption is the adhesion of substance onto the surface of adsorbent solid. It can be the formation of gas, liquid or solid to the surface of solid.Adsorption occurs at solid-solid, gas-solid, liquid-liquid and liquid-gas interfaces. In adsorption equilibrium, the rate at which the material adsorbed onto surface is equal to the rate at which they desorb[32-33]. The amount of MB dyes at equilibrium is calculated from the mass balance is given by: qe = (Co - Ce) V/W .... (1).where qe is equilibrium concentration /adsorption capacity per unit mass of adsorbate -(mg/g),

Co is the initial adsorbate concentration (mg /L), Ce is equilibrium adsorbate concentration (mg/L), V

2.5.2 Langmuir adsorption isotherm

The Langmuir adsorption isotherm describes quantitatively the formation of monolayer adsorbate on the outer surface of the adsorbent and after which no adsorption takes place.Langmuir represent the equilibrium distribution between MB dyes liquid phase and adsorbent solid phase.Langmuir isotherm is valid for monolayer adsorption onto surface containing a finite number of identical sites.The model assumes uniform energy of adsorption and no transmigration of adsorbate in the plane of surface. The Langmuir linear form of expression is given as:

$$\frac{Ce}{qe} = \frac{Ce}{Qo} + \frac{1}{bQo} \text{.. .... (2).}$$

Where: Ce is the equilibrium concentration of MB dye solution (mg/L), qe is equilibrium capacity of MB dye on the adsorbent (mg/g), Qo is the monolayer adsorption capacity of the adsorbent (mg/g) and b is the Langmuir adsorption constant (L/mg) and is related to the free energy of adsorption

The shape of Langmuir isotherm is expressed in terms of separation factor, R_L

$$R_L = \frac{1}{1+K_L Co} \text{... (3).}$$

Where K_L is a constant related to the affinity of binding site and the free energy of adsorption (L /mg).

2.5.3 The Freundlich adsorption isotherm

Freundlich equation is given by: $qe = K_f Ce^* \frac{1}{n}$ .... (4).

Where K_f is a constant measuring adsorption capacity, Ce is the equilibrium concentration of adsobate in solution (mg /L), qe is the equilibrium surface coverage (amount of adsorbate adsorbed per unit mass of adsorbent (mg /g) and 1/n is the slope.The linear form of Freundlich equation is given by: $\log_{qe} = \log_{Kf} + \frac{1}{n\log Ce}$..(5).

Where K_f is adsorption capacity of adsorbent. K_f can be defined as the adsorption or distribution coefficient and represent quantity of MB dyes adsorbed onto the ACThe slope $\frac{1}{n}$ ranging between 0 and 1 was measure of adsorption intensity/ surface heterogeneity ,becoming more heterogeneous as its value more closer to zero .A value 1/n <1 indicate normal Langmuir isotherm , 1/n >1 indicative of cooperative adsorption.

A plot of $\log_q$ versus $\log_{Ce}$ gives straight line with slope = $\frac{1}{n}$ and intercept K_f

2.6 Adsorption Kinetic Study

The study of adsorption kinetics in waste water treatment is important as it not only provides valuable insight into the reaction pathways and mechanism of sorption reaction, but also describes the solute uptake rate which in turn control the residence of time sorbate uptake at the solid-solution interface [32].The kinetic data obtained from adsorption of MB dyes onto AC was studied by using common kinetic models, pseudo first kinetic model and pseudo second kinetic model.

2.6.1 Pseudo first order kinetic model

The pseudo first order kinetic model assumes that the rate of occupation site is proportional to the rate of unoccupied sites[32].The rate pseudo first order kinetic model can be given by the equation:

$$\ln(qe - qt). = k1t \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (6).$$

$$\log(qe - qt)) = \log qe - \frac{k1t}{2.303} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (7).$$

Where q_e represent the amount of MB dyes adsorbed at equilibrium (mg/ g),q_t is the amount of MB dye adsorbed at time t (mg/g),k_1 is the pseudo first order rate constant (min). A plot of $\log(q_e - q_t)$ versus t gives a straight line linear relationship from which k_1 and q_t can be obtained from the slope of the line which is = -k /2.303 and q_t obtained from the intercept

2.6.2 Pseudo second order kinetic model

The pseudo second order kinetic model assumes that the rate limiting step may be chemisorption involving the valance forces through sharing or exchange of electrons between MB dyes and adsorbent[33]. The pseudo second order kinetic model was given as:

$$\frac{1}{[qt]} - \frac{1}{[qe]} = k_2t \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (7).$$

The linearized form of pseudo second order kinetic model can be given as:

$$\frac{dq}{dt} = k_2(qe - qt)^2 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (8).$$

$$= \frac{t}{qt} = \frac{1}{K_2q^2} + \frac{t}{qe} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (9).$$

Where k_2 is the rate constant of second order adsorption(g/mgmin).The linear pilot of $\frac{t}{qt}$ versus t determine $\frac{1}{qe}$ as slop and $\frac{1}{K_2q^2}$ as intercept.

3. MATERIALS AND METHODS

3.1. Materials.

The main raw materials used for this study was stem part of *Croton macrostachyus***.**

3.1.1 Chemicals and Reagents.

The following analytical grade reagents were used without any further treatment.MB dyes($C_{16}H_{18}N_3SCl$,Unichem),phosphoric acid (H_3PO_4 (95% Merck), NaOH (Sigma-Aldrich) and 37% HCl (India) was used for activation and adjusting pH of the sample. Deionized water was used throughout the experiment for preparing solutions and washing purposes.

3.2. Apparatus and instrument

The instruments used in this study were digital electronic balance with 160 gm. loading capacity (Model JA103P,) was used to measure the activated carbon and all other chemicals. Magnetic stirrer hot plate was used for stirring and maintaining the required temperature.

pH meter (pH 211 microprocessor pH) meter used for determination of pH,) Fourier transform infrared spectrophotometer (spectrum 65 FTIR Perkin Elmer) was used for qualitative estimation of the surface functional groups and scanning electron microscopy (JEOL/EO-JCM-6000 Plus) were used for characterization of the morphologies of activated carbon.

3.3 Sample collection and Pretreatments

The stem of *Croton macrostachyus* were collected from the local area of the Hawassa. It was initially washed with the tap of water to remove dust and subsequently rinsed with distilled water multiple of times. Then, the sample was air dried at room temperature for duration of 5 days. The dried sample was then crushed into granules and sieved to achieve a particle size of 100--250 micrometers.

3.3.1 Preparation ACs

The raw material was impregnated with chemicals H_3PO_4 for 24 hours with different impregnation setups.After impregnation, the sample was carbonized at temperature of 400 -700 ^{o}C.The carbonized samples were cooled in an inert cold atmosphere to room temperature.The ACs samples were subsequently dried at 105 °C for 12 hours. Finally,AC derived from *Croton macrostachyus* stem powder was subjected to carbonization at different temperatures ranging from 400 °C to 700 °C in a muffle furnace for duration of 2 hours.

Upon completion of the carbonization process, the material was cooled in a desiccator, crushed, and sieved to a mesh size of 200 µm to ensure consistency in the study by standardizing the particle size.The activated stem of *Croton macrostachyus* samples was treated with phosphoric acid.Sample storage was carried out in enclosed containers within a desiccator to provide dry environment and prevanting contamination caused by moisture.

3.3.2 Preparation of Adsorbate

Stock solution of MB dyes ($C_{16}H_{18}N_3SCl$) containing 100mg/L prepared by dissolving 0.1g of MB dye powder in 1000 mL distilld water respectively.From the stock solution (100 ppm),a serial test solution of MB dye containing 5 mg/L, 10 mg/L, 15 mg/L, 20 mg/Land 25 mg/L were prepared and calibration curve was generated from these concentrations.

3.3.3 Adsorption Studies

The experiments on the adsorption of MB dyes on ACs were conducted out in orbital shaker at 150 rpm using 250 mL conical flasks. Aqueous solution of MB dyes in concentration of 10 mg/L, 15 mg/L, 20 mg/L, 25 mg/L and 30 mg/L onto the resulting solution,0.1g AC was added to each 250 mL conical flask at a neutral pH and room temperature.The initial pH value of each solution was adjusted with 0.1M HCl and 0.1M NaOH using a pH meter.

After shaking the flasks, 5 mL samples was withdrawn at 15 min intervals from the flasks and each time the dye solution was first separated from the adsorbent by centrifuging at 200 rpm for min at room temperature until equilibrium was reached.

After equilibration time,the adsorbents and the supernatant solution was separated byfiltration.After filtration, the concentration of MB dyes in the supernatant solution was analyzed using UV-Visible spectrophotometer by recording the absorbance changes at a wavelength of 664nm.

3.4. The Effectsof different variables on adsorption of AC

3.4.1 Dosage of Adsorbent.

The effects of various experimental parameters like contact time, pH of the solution and asorbent dosage were studied. It was found that the amount of MB dyes removal increased with the increase of contact time, solution pH and the amount of adsorbent used.The data obtained best fitted the Langmuir isotherm plot [32]. The effect of adsorbent dose was conducted using 0.025g/L, 0.05 g/L, 0.075 g/L ,0.1 g/L ,0.125 g/L and 0.15 g/L of AC of *Croton macrostachyus* was agitated with 25mL of 10ppm of MB dyes solution in each turn, at optimum contact time of 90min and pH 8.

The studies were conducted at room temperature, 25 ^{0}C with the constant shaking speed for 30min. 5 mL of the solution (sample) was withdrawn from the flask at 5min interval and the absorbance was measured using UV-vis spectrometery at λmax 664 nm.

3.4.2 Initial MB Dyes

A 0.1g of adsorbent was agitated with 250 mL of 20 ppm, 25 ppm and 30 ppm of initial dye concentration and pH of 8.The temperature was maintained at 25 ^{0}C with uniform shaking speed. The studies were carried out at optimum constant time of 90 min for maximum adsorption to realize. The results obtained were used to plot adsorption isotherms and to determine adsorption capacity UV-Visible spectrometery at $\lambda max\ \ 664nm.$

3.4.3 Contact time

The effect of contact time was tested on the potential of activate carbon by different exposure time from 15 minute to 120 min with in 15min gap with concentration of 10 ppm and 0.1g of adsorbent.Finally,the amount of MB dyes adsorbed was measured using UV-vis spectrometry at λmax 664 nm and percent of removal efficiency was calculated.

3.4.4 pH Variation

pH is an important parameter that influences the adsorption it was conducted with pH values of 2, 3,4,5,6,7,8,9 and 10. A 0.1g of adsorbent dose was agitated with 250 mL of 10mg/L of MB dyes solution at constant time 90min. 0.1MHCl and 0.1MNaOH were used to adjust the pH of the solution. The amount of MB dyes adsorbed was determined by UV-Visible spectrometery at 664nm

The plot of percentage removal for MB dyes against pH was drawn to show the effect of pH value of MB concentration.The influence of solution pH was examined to understand the adsorption mechanism.25mL of 10 ppm MB dye solution was mixed with optimum mass of AC at 200 rpm in a 250mL conical flask and agitated under mechanical shaker.5 mL of this solution (sample) was withdrawn from the flask and the absorbance was measured using UV-vis spectrometer at $\lambda max\ \ 664nm.$

3.4.5. Temperature

The effect of temperature was tested on the potential of AC by mixing 10 ppm dye solution with optimum mass of AC and the reaction was in thermostat water bath under mechanical shaker at varying temperature of 25,35,45,55 and 65 ^{0}C.

5mL of this solution (sample) was withdrawn from the flask.The amount of MB dyes, adsorbed and percent of removal efficiency for MB dyes was calculate1d and the plot of percent of removal efficiency of MB dyes,as well as the amount of MB dyes adsorbed was plotted.

3.5 Characterization of Activated carbon

3.5.1 Fourier transforms infrared spectroscopy (FT-IR)

FT-IR spectra is useful tool to identify functional groups in molecule, as each chemical bond often has a unique energy absorption band and can obtain structural and bond information on a complex to study compounds.

The pattern of adsorption of MB dyes on to adsorbent is attributed to the active group and bonds present on adsorbent.Therefore, in this study, FT-IR spectroscopy analysis was done to identify major functional group responsible for MB dyes adsorption process onto the adsorbent. The FTIR spectra of MB dyes loaded adsorbent recorded in the range of 4000 to 400 cm-^{1}.

3.5.2 Scanning electron microscope (SEM)

Scanning electron microscope is a type of microscope which is used for visualization of porous structure of a material. The sample was analyzed in a SEM to visualize the porous structure. The magnification was adjusted for getting a clear picture

4. RESULT AND DISCUSSION

4.1 Characterization of the prepared Activated carbon

4.1.1 FT-IR (Fourier Transform Infrared spectrometry)

FT-IR analysis result of AC prepared from stem part of *Croton macrostachyus* was presented in Figure 1.The spectra revealed various functional groups detected on the surface of stem of *Croto*n *macrostachyus*. *F*igure 1 shows that the FT-IR spectra of AC for the adsorption of MB dyes.The peaks at 3466cm^{-1},1720cm^{-1},1612cm^{-1}, 1245cm^{-1} correspond to hydroxyl group (O-H),carbonyl and carbon- carbon double bond(C=C) and carboxylic acid group respectively before adsorption of MB dyes onto AC.However, after adsorption of MB dyes onto AC,the peaks were shifted to 3466cm^{-1},1702cm^{-1},1639cm^{-1} and 1254cm^{-1} respectively. This shift in the absorption of peaks suggested that there were interaction of MB dye molecules with the functional groups of AC. A peak around 1720 cm^{-1} was attributed to carbonyl stretching, peak observed at 1612 cm^{-1} is assigned to the carbon to carbon double bond (C=C) After adsorption of MB dyes the peak intensity shifts this indicates adsorption process takes place on the adsorbent surface.

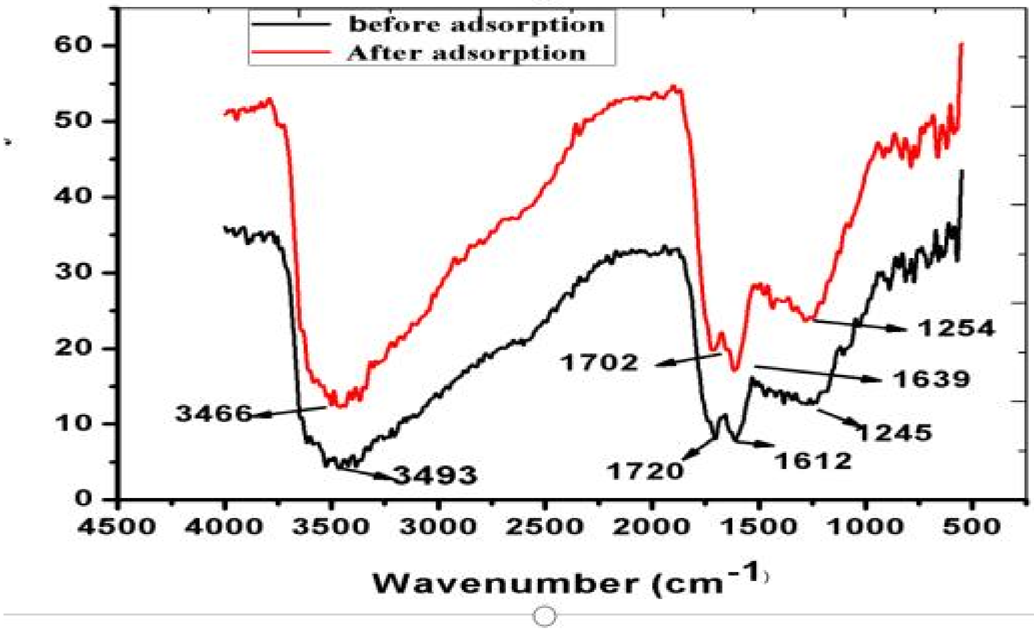

Figure 1: FTIR spectra of stem of *Croton macrostachyus* before adsorption (Black line) and after adsorption (Red Line)

4.1.2 SEM (Scanning Electron Microscope)

The AC was examined by Scanning Electron Microscope (SEM) to analyze the surface of the adsorbents. SEM of the AC before and after adsorption were presented in Figure 2.

AC before adsorption have well-developed porous surface and observed at higher magnification. The pores observed from SEM images are having diameter in micrometer (µm) range. From the Figure 2 it can also be observed that AC before adsorption has rough texture with heterogeneous surface and a variety of randomly distributed pore size.

The SEM image of AC of stem part of *Croton macrostachyus* after adsorption shows comparatively regular shape than before because the active site of AC was occupied by MB dye.Hower,the surface morphology of AC of *Croton macrostachyus* after MB dye revels a change in the topography of adsorbent, as evidenced by the appearance of reduced pore structure, holes and smooth the surface features due to the adsorption of MB in Figure 2.

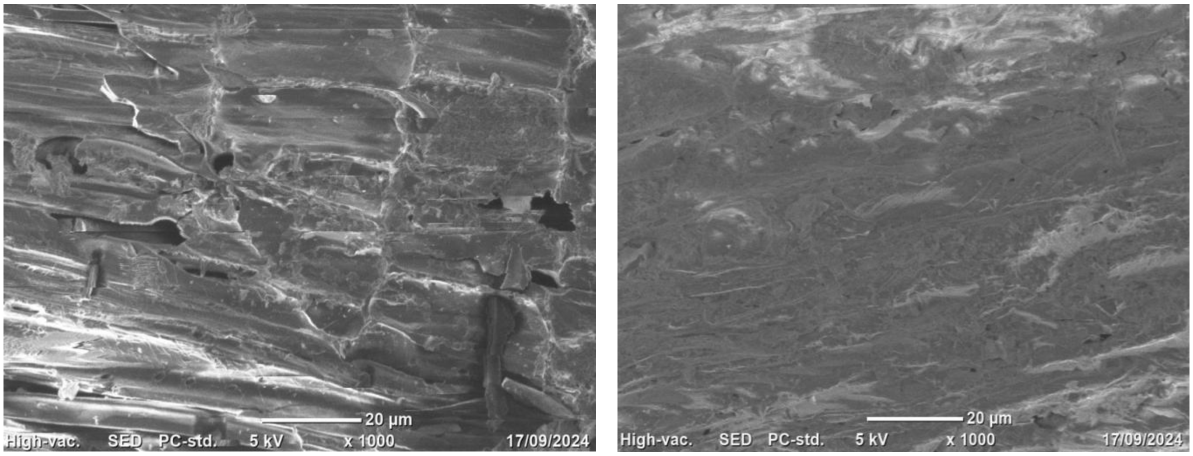

Figure 2: SEM Image of AC of *Croton macrostachyus* before adsorption (Left) after adsorption (Right)

4.2. Effect of experimental conditions

4.2.1 Effect of Adsorbent dose

The effect of adsorbent dose on adsorption capacity and adsorption efficiency of MB dyes was studied on AC of *Croton macrostachyus* adsorbent.Figure 3 illustrates that the adsorption efficiency argumented with the increase of the adsorbent amount,while the amount of adsorbed decreases with increasing mass.This may probably due to the argument surface area and number of active site available for the fixation of MB dyes.This similar to the studies reported.This was done at room temperature by varying the adsorbent amount from 0.025g to 0.1g with initial volume of solution 250 mL.For all these runs initial concentration of MB dyes, pH, contact time and temperature was constant.The result showed that the adsorption efficiency for removal of MB dyes was increased from 0.02 g to 0.1 g.This is due availability of surface site of adsorbent for relatively adsorbate species.

It shows that removal efficeincy was 52.8% when the amount was 0.025g, for 0.1g it was 95.77 % that is adsorption efficeincy was increased with increased number of adsorbtion site.

Therefore, removal efficeincy rechead in equilibrium with amount of 0.1g of AC and this was the optimum adsorbtion dose. In case of adsorption capacity, the reverse trend was observed as the dose

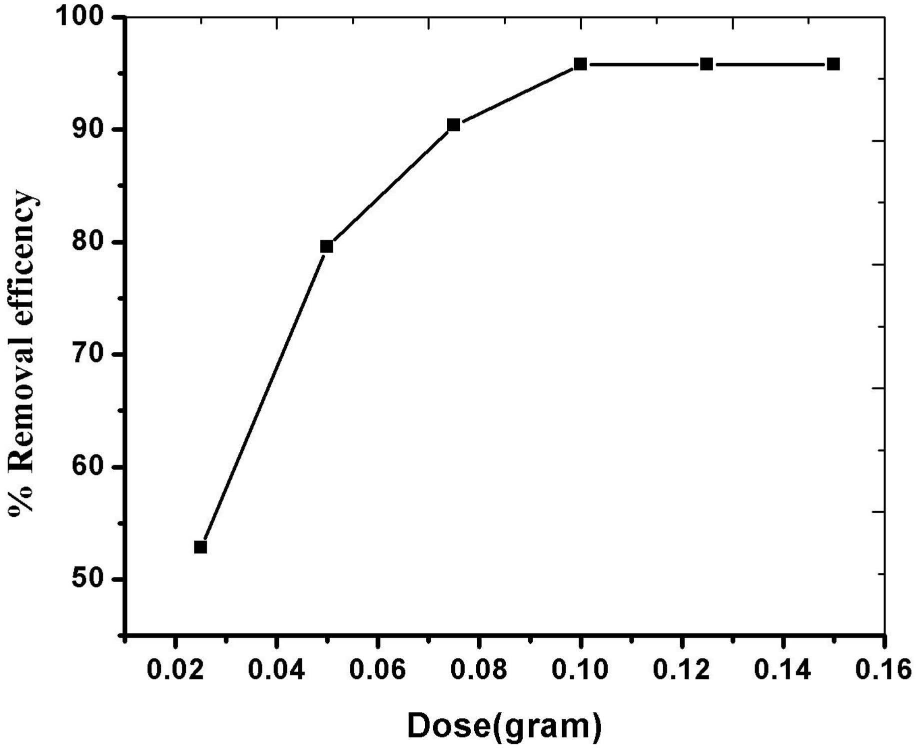

Figure 3: Effect of adsorbent dose on the removal of MB

4.2.2 Effect of initial dye concentration

Removal efficiency is greatly depended on the initial concentration of solution of adsorbate. The dye initial concentration on adsorption of MB dyes onto the AC was carried out in the concentration range of 10mg/L to 30mg/L of 250 mL of solution.Equilibrium adsorption capacity increased with increase in MB dye initial concentration from 10mg/L to 15mg/L.However, further increase in dye concentration showed no significant changes in removal efficiency of MB dye. This is due to the fact that with increased initila dye concentration, the driving force for mass transfer also increases.At low concentrations, there will be unoccupied active sites on the adsorbent surface. Above optimal MB dyes concentration, the active sites required for the adsorption of MB dyes will lack. Therefore, the removal efficiency for MB dye was 96.2% for 10mg/L,85.68% for 15mg/L and 73.13%for 20mg/L.Hence,10mg/L was the optimum concentration for MB dye removal efficiency. The results were illustrated in Figure 4 shows as removal efficiency decreased with increasing MB dye initial concentrations.

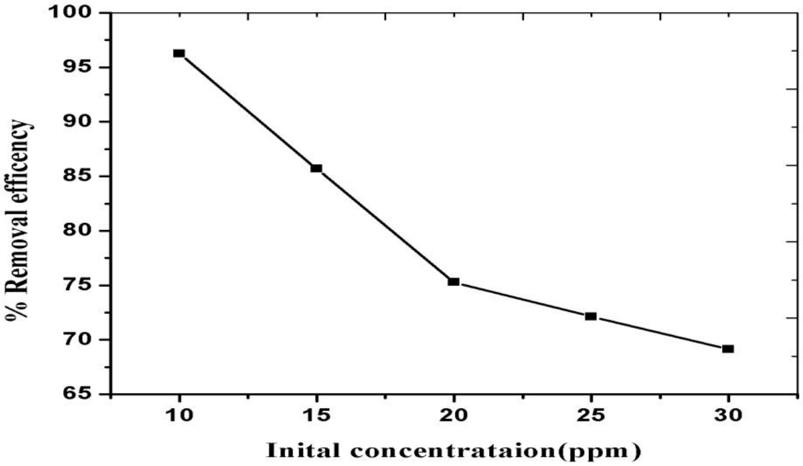

Figure 4: Effect of initial concentrations of MB dyes

4.2.3 Effect of contact time

The effect of contact time on adsorption of MB onto AC is shown in Figure 5. The MB dye removal was takes place in 90 min for AC.The equilibrium was reached after 90 min. The change in the rate of adsorption might be due to the fact that initially all the adsorbent sites are vacant and solute concentration gradient is very high. Later, the lower adsorption rate is due to a decrease in number of vacant sites of adsorbent and MB dye concentrations. This may be attributed to the lack of available active sites required for further uptake after attaining the equilibrium. The maximum removal efficiency was examined at 90 min and the percentage of removal efficiency was 96.26%. Therefore,90min is the optimum time for removal of MB dye solution.Similar results have been previouslyreportedinwrittenliterature[34].

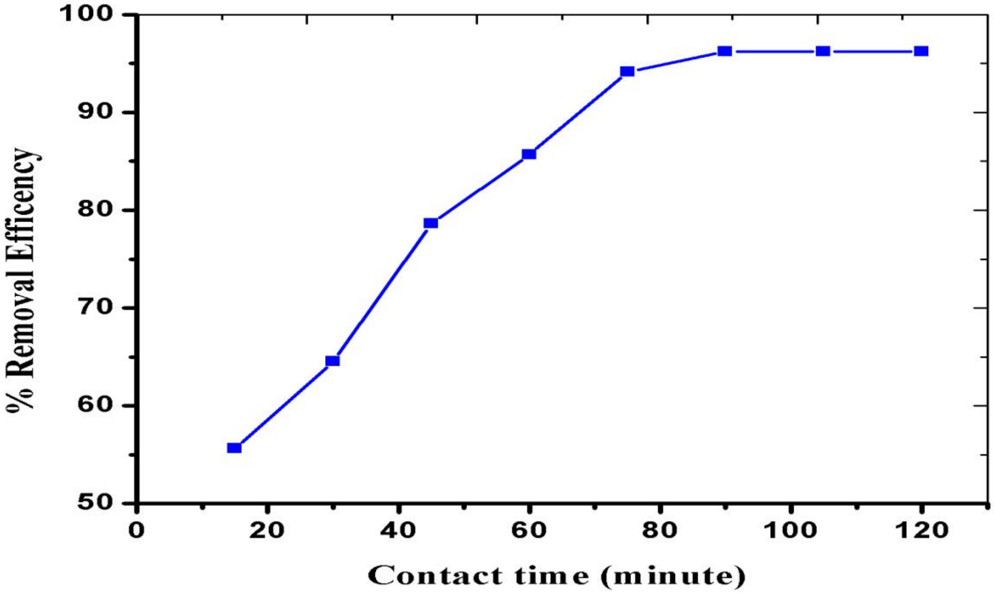

Figure 5: Effect of contact time on the removal of MB

4.2.4 Effect of pH Solution

The pH of dye solution is an important influencing factor for the adsorption of MB dye onto AC. Figure 6 shows the effect of pH adsorption on AC.The maximum removal efficiency was observed at pH 8. MB dye is cationic (basic) in nature.The basic dye gives positively charged ions when they dissolved in water.Thus, in acidic medium the positively charged surface of adsorbate tends to oppose the adsorption of cationic (basic) of adsorbate.However, when pH of solution increased, the surface acquiring a negative charge, thereby resulting in an increased adsorption of MB dye due to an increase in the electrostatic attraction between positively charged and negatively charged ions.Therefore, the percentage of removal efficiency and adsorption capacity for MB dye onto AC was increase with an increasing of pH solution. Hence, the percentage of removal efficiency was about 46% at lower pH and 95% at pH 8. Thus, pH 8 was the optimum adsorption capacity and removal efficiency of MB dye solution. This variation is quite similar to the previous reports [35].

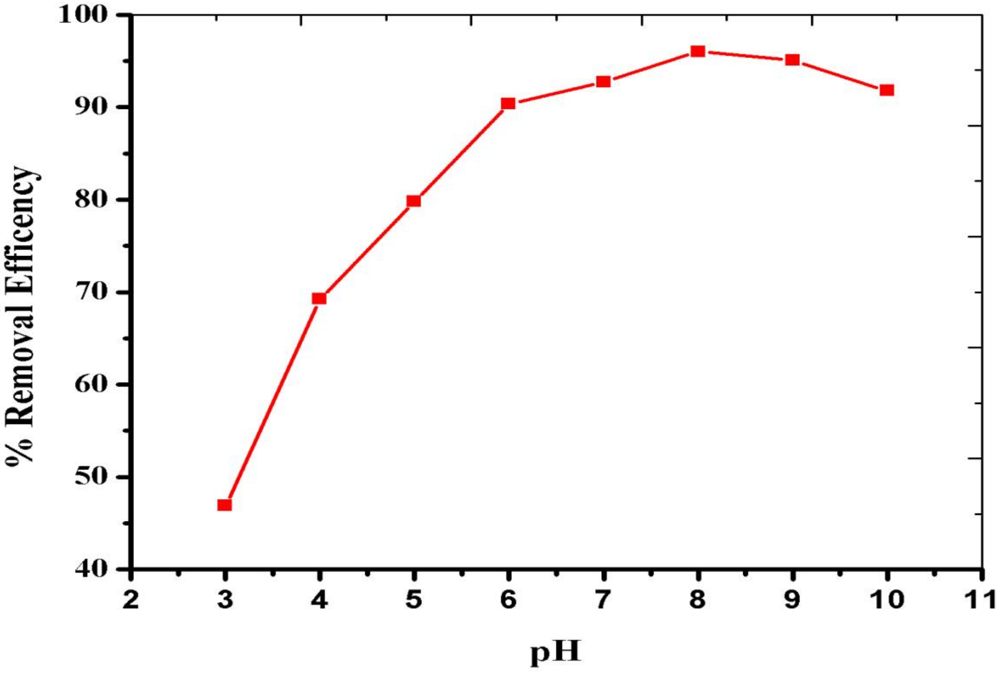

Figure 6: Effect of pH on the removal of MB

4.2.5 Effect of temperature

The effect of temperature for adsorption of MB dye molecules was studied with the temperature interval of 25 ^{0}C to 65 ^{0}C at the optimum of other parameters and the result was presented in Figure 7. The adsorption of MB dyes increases rapidly with an increase in temperature from 25 ^{0}C to 65 ^{0}C . The increase in adsorption capacity of AC was attributed to the enlargement of pore size and activation of adsorbent surface with temperature.Therefore, maximum removal efficiency for MB dye was observed when rise in temperature reaches at 45 ℃.At this temperature, the removal efficiency was about 96.5%. Hence this temperature is optimum temperature for MB dye removal. Further rise in temperature increases the mobility of the MB dye ions and reduce the swelling effect, thus enabling the large dye molecules to penetrate further.The results also indicated that adsorption of MB dye onto AC is an endothermic process.,

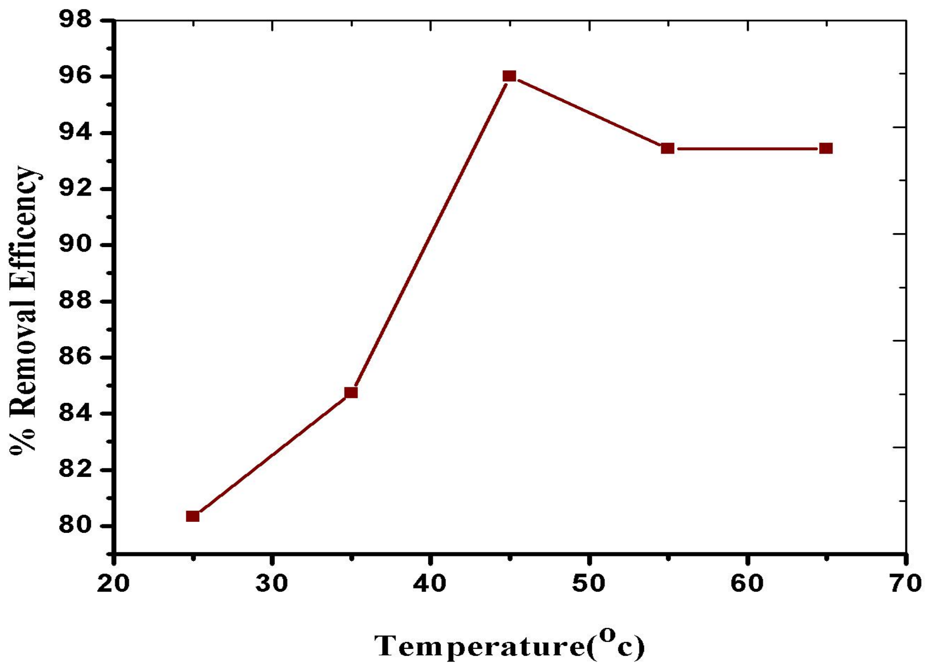

Figure 7: Effect of temperature on the removal of MB

4.3 Effect of adsorption isotherms

In this research, the data were studied using Langmuir and Freundlich models. Each of these models makes use of a parameter qe (adsorption capacity per unit mass of the adsorbent at equilibrium) in (mg/g).Table 1, show that the adsorption of MB dyes onto the AC using both Langmuir and Freundlich isotherms.The the equilibrium data were fitted to the both Langmuir and Freundlich adsorption isotherms.However,Langmuir Isotherm is more accurate because the correlation coefficient was R^2 =0.98 is greater insignificantly than R^2=0.96 for Freundlich Isotherm indicating the the posibilities of monolayer adsorption,it is noted that the slope values (1/n) are less than 1, which represents the adsorption is favorable with Langmuir Isotherm.This also suggested that the experimental data is physiorption as well as heterogeneous distribution of active site on the AC.Thefore, adsorption capacity and adsorption intensity of MB dye onto AC were well fitted with the Langmuir parameters.This also confirmed that there is uniform energy adsorption and no transmigration of adsorbate inthe plane of surface.[36].Aditionally,the values of n,(0.114) is less than 1,showing that the normal Langmuir isotherms [37].

Table 1: Langmuir and Freundlich Adsorption isotherm constant for Adsorption of AC for the removal of MB dyes

Models	constant		constant	
Langmuir	qm (mg/g)	K_L (L/mg)	R_L (L/mg)	R^2
	5.34	2.37	0.04	0.98
Freundlich	1/n (mg/g)		K_f (L/mg)	R^2
	0.114		0.012	0.96

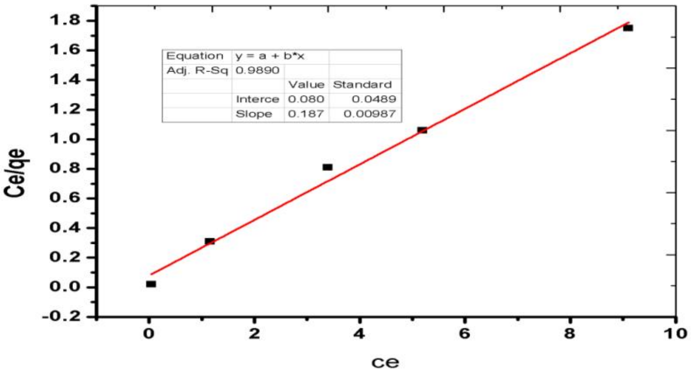

Figure8.equilibriumstudyusingLangmuirisothermforactivatedcarbon

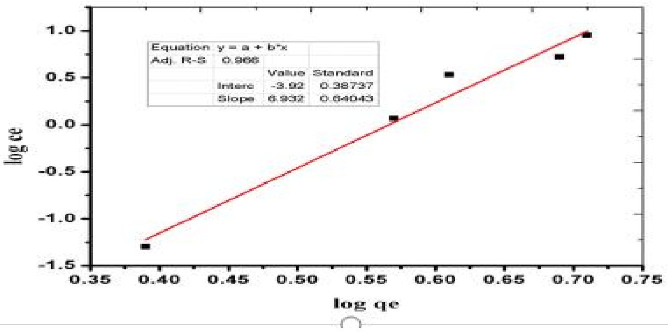

Figure 9: equilibrium study using Freundlich isotherm for activated carbon

4.4. Effect of adsorption kinetic parameters

The data for the adsorption of MB dyes onto AC were applied to both pseudo first kinetic model and pseudo second kinetic models and the results are shown in Table 1.The correlation coefficient,(R^2) for second order kinetic (0.98) insignicantly greater than that of pseudo first order kinetic model (0.895). The results appear that the model of pseudo second order was the best for describing the kinetic of MB dyes as compared to the pseudo first order kinetic model.In adition,the value of q_e calculated(qe cl.), 3.06 from pseudo second order kinetic model was approached to the experimental value (q exp), 2.48, indicating the applicability of this model of MB dyes onto AC of *Croto*n *macrostachyus*. This also suggests that the rate limiting step is chemisorption, involving the valance force through sharing or exchanges of electrons.Hence, pseudo second-order kinetics model has been successfully applied to several adsorption systems as reported by. [38].

Table 2: Kinetics parameters for the adsorption of MB at 25 ℃ onto the AC

Pseudo first order model				MB
k_1 (min^{-1})	qe exp. (mg/g)	qe cal. (mg/g)	R^2	
0.02	2.48	4.57	0.859	
Pseudo second model	qe exp. (mg/g)	qe cal.(mg/g)	R^2	
k_2 (*10^{-3}) dm^{3}mim^{-1}mol^{-1}	2.48	3.06	0.98	
0.015				

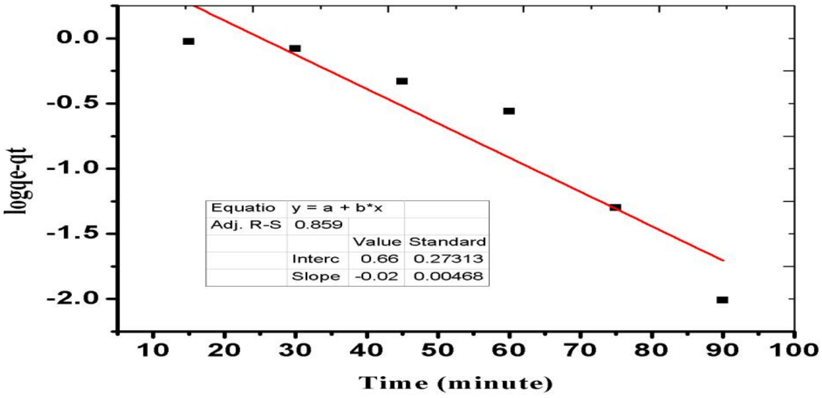

Figure 10: Pseudo first order kinetics model for MB

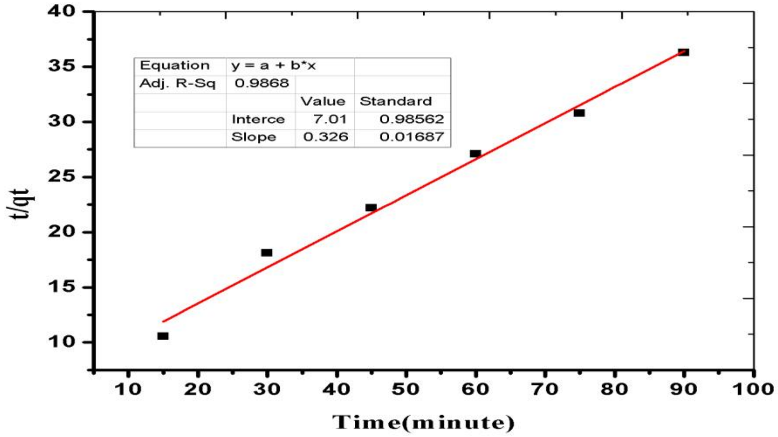

Figure 11: Pseudo second order kinetics model for MB

4.5 Thermodynamic study

The thermodynamic parameters that help us to understand the nature of the adsorption of MB on adsorbents are the standard change in Gibbs free energy (ΔG°), the standard change in entropy (ΔS°), and the standard change in enthalpy (ΔH°). These can be determined using the following equations:

$$\Delta G^\circ = -2.303RT\log K_D \ldots \ldots\ldots\ldots\ldots (9).$$

$$Kc = qe/Ce \ldots\ldots\ldots\ldots\ldots\ldots (10)$$

Where R is the gas constant (8.314 J/mol K),

T is the absolute temperature in Kelvin (K); and Kc is (L/g) is the standard

thermodynamic equilibrium constant. Similarly, the enthalpy change (ΔH°) from 298 to 318 K was computed from the following equation: $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ ... ... (11).

The thermodynamic parameters,ΔH°(kJ/mol) and ΔS° (J/mol K) for MB dye adsorption were evaluated using the above equations. The slope and intercept of the linear plot of $\ln K_D$ versus 1/T Figure12, shows that thermodynamic parameters for MB dye adsorption on AC.The positive values of enthalpy change(12645.24kJ/mol) indicates that the adsorption of MB dye onto AC is endothermic process.However, the calculated values of standard Gibbs Free energy change were negatives (-309.92 kJ/mol), indicates that the rapid and spontaneous nature of adsorption of MB dye onto the AC The negative sign of standard free energy also confirm that the adsorption of MB onto the AC was favored. The positive value of entropy, ΔS° represents an increase in the degree of freedom of the adsorbed species, (MB). The positive value of ΔS° also reflects that some changes occur in the internal structure of AC during the adsorption.

Table 3: Thermodynamic parameters for the adsorption of MB at different temperatures

Dyes	T(K)	lnKc	ΔG(kJ/mol)	ΔH(kJ/mol)	ΔS(kJ/molK)
	298	0.13	- 309.92	126.767	425.42
	308	0.54	- 1382.8		
	318	3.51	- 9279.92		

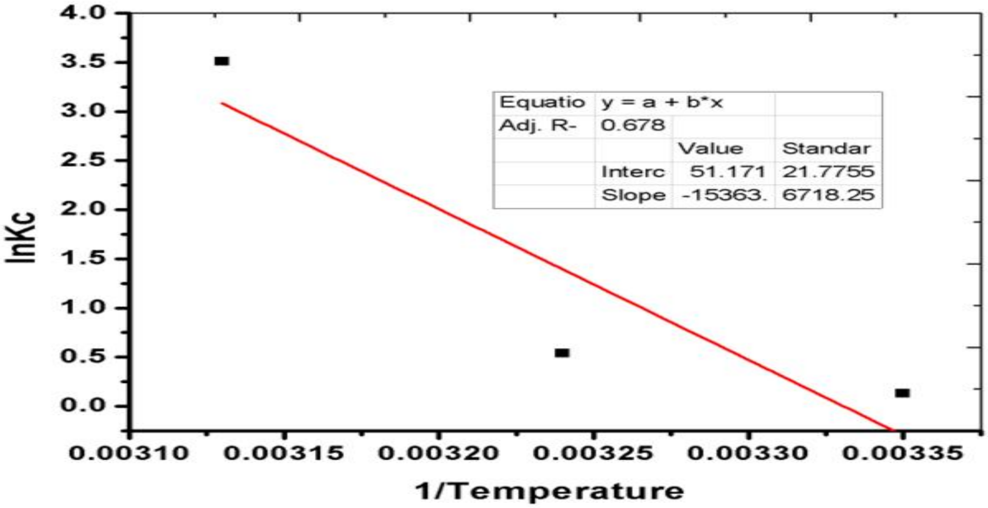

Figure 12: Van't Hoff plot for the determination of thermodynamic parameters

5. CONCLUSIONS AND RECOMMENDATION

5.1 Conclusion

Here we conducted many characterization techniques like FT-IR, SEM, pH, MB initial dye concentration, adsorbent dose, contact time and the temperature.In this study AC shows promising adsorption capacity for MB dye removal.FT-IR results showed that activated carbons of *Croton macrostachyus* have many surface active functional groups.

For MB dyes initial concentration,% removal efficience start decreasing with respect to increase in concentration of MB dyes.This happens due to fixed amount of adsorbent in increasing MB dyes concentration.For adsorbent dosage,it was seen that % removal MB dyes increases withincrease in adsorbent dosage.This trend can be attributed to because of more dosage,the surface are exposed to dyes solutions get more so that more dye can be adsorbed into the pores of adsorbent hence,more is % removal of MB dyes.

This cuold be happened at dosage of 10mg/L.For pH, % removal of MB dye is pH remains lowest in both acidic and basic medium and it occurs maximum at pH 8.This can be accounted because in acidic medium due to high H^+ concentration,there is repulsion of H^+ ion with cationic charge of dyes for which adsorption cannot takes place.

For contact time studies,it was seen that % removal efficience of MB dyes was increased between the range 20 min to 45 min and attained at steady state at 45 min.The trend can be attributed to the fact that as the contact time increases more is the adsorbate-adsorbent interaction and thus leads to more adsorption and hence % removal efficience of MB dyes gets raised with respect to increase in time.Equilibrium data were fitted to both Freundlich and Langmuir isotherm well at the studied temperature range but,Langmuir isotherm model was preferred.The SEM image after adsorption of activated carbons shows comparetively regular shape than before,reduced pore structure,holes,and smooth surface features.

The rate of adsorption was found to obey both pseudo first order kinetics and pseudo second order kinetics,but pseudo second order kinetics is preferred.The parameter R_L value=0.04 for AC of Crotonmacrostachyus which indicates the favorable adsorption of MB dyes onto AC. The negative value of standard free energy change indicated that the adsorption of MB dye onto AC was feasible and spontaneous.

The positive value of standard enthalpy change value depicted endothermic nature of adsorption at temperature of 298K, 308K and 318K. Studying through different graphs of adsorbent dose,MB dyes initial concentration,contact time,pH and temperature, I got the optimum values for each case as; 0.1g,10 ppm,90 min,pH 8 and 45 ℃ respectively.Hence,after carrying out rigorous experiments we finally came to conclusion that AC prepared from stem part of *Croton macrostachyus* can be effectively used for the removal of MB dyes effectively conducted at the optimum process condition.

5.2 Recommendation

The future studies should be intensive on applicability of the adsorbent to the real situation on where large volume of waste effluent is being discharged.

Furthermore, desorption experiments should be carried out in order to recover activated carbon from the adsorbed surface.

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